

EIS

*Electrochemical
Impedance
Spectroscopy*

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1. Introduction

The measurement program *EIS* (Electrochemical Impedance Spectroscopy) offers all tools for the investigation of impedance in surface engineering, electrochemical power generation, corrosion research, catalysis or even in basic electrochemical research. At the same time, *EIS* provides some global setting pages useful also for other measuring methods.

As you may have already noticed, the ZAHNER electrochemical workstation hardware (ZENNIUM X, ZENNIUM pro, ZENNIUM, ZENNIUM E/E4/EC, IM6 and others) has got only a few switches (mainly for emergency purpose). The entire system is controlled by software. This makes working with the ZENNIUM systems very easy and comfortable. No confusing switches, no manual switch settings, etc. In addition, software controlled functions (in contrast to hardware switches) can be automated. E.g. ranging, calibration and measurements will be carried out automatically. All this contributes to the high accuracy, the reliability and the easy handling of the ZENNIUM systems.

The *Series Measurement* feature of *EIS* lets you record impedance spectra, depending on one additional quantity measured by the system through extra analogue or digital inputs (via optional hardware plug-ins or via network virtual instruments). Also inherent and internal quantities like time, potential or controlled current can be taken to control recording.

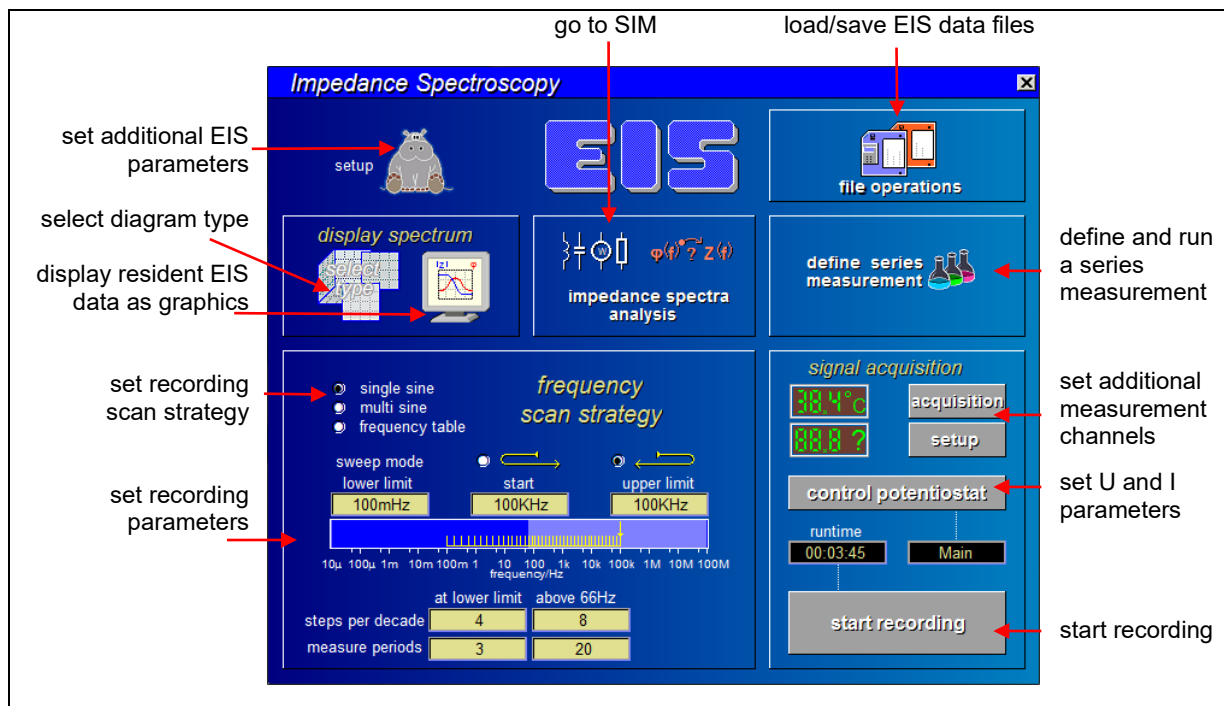
Due to its graphical user interface, *EIS* is easy to handle. All settings are guided by dialogues, control routines will check inputs for range violations. During measurement, *EIS* provides you with an online display with a selectable graph (Bode, Nyquist, etc.), time domain displays for voltage (U) and current (I) as well as FFT spectrum displays for U and I. With these items you have a complete visual control of the measurement and you are able to detect disturbances immediately.

After completion of a measurement, *EIS* offers a variety of ways to store, export, process and treat the data in a very flexible manner. Spectra may be stored together with their complete history as binary data, allowing a reliable way to reproduce measurements: simply opening a former measurement file reconfigures the instrument according to the prior measurement conditions. For an immediate analysis, the measured spectra may be transferred directly to the simulation & fitting program *SIM*, in parallel to the storage.

Data may be exported as plain ASCII text lists, as high-quality vector graphics (Windows®-EMF), or as screenshot-bitmap. The export path may be chosen via the Windows®-clipboard, via data file storage, redirected for printer output or paste into the internal processing software *ZEdit* and *CAD* for further text- and/or graphical editing purposes.

2. EIS Main Page

Click on the  icon on the **Main Menu** page to open the EIS main page.



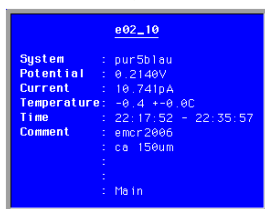
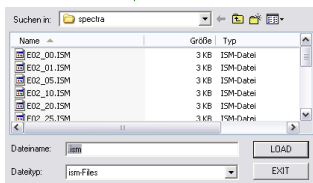
The *EIS* main page is the central page for measuring *Electrochemical Impedance Spectra*. Here you also set the recording parameters such as *Sweep Mode*, *Frequency Range*, *Steps per Decade*, *Measure Periods* and from here you have access to different submenus such as *Series Measurement*, *Control Potentiostat* or *Display Spectrum*.

When preparing an EIS measurement proceed in the following order:

- **connect the cell**
- **check the cell connections**
- **check the object**
- **set up a measurement**
- **record and save an EIS spectrum**
- **check and document the results**

2.1 File Operations

2.1.1 Open



This function allows you to load/save EIS data from/to the hard disk of your PC. Click on the icon and select in the submenu, whether you want to open previously stored EIS data or save actual EIS data.

If there are no data in memory, this submenu is skipped.

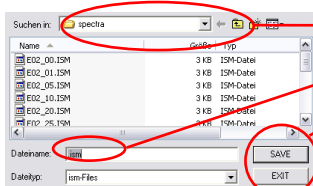
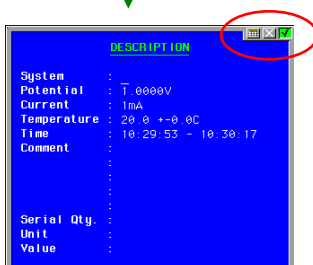
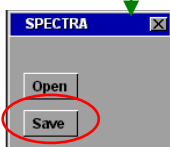
After you have selected **Open**, a file browser displays only EIS data files (file extension **.ism**) for opening.

Select a path and a file and click on the **LOAD** button to load the file into the **THALES** software. Click on the **Display Spectrum** icon on the EIS main page to display the data in a graphical form.

The next box shows the measurement parameters of the loaded data. Click on it if you want to close it.

NOTE: Opening a file will switch off the potentiostat and configures the potentiostat according to the loaded measurement settings automatically. Therefore, loading a measurement file is an easy way to perform a new measurement with previously used settings.

2.1.2 Save



If there are data in memory, usually after an EIS spectrum measurement, you may want for **Save** them on hard disk for storage.

A **description** box opens where you may input your measurement parameters and comments. Some lines will be filled automatically by the software (e.g. potential, current and measuring time) others are free for the user to fill and are not used for any calculation. The last three lines are reserved for series recording information. In a series EIS run they will be filled automatically. You may use these lines to define spectra for series analysis even if they were created as single measurements.

Accept the inputs by clicking on the button in the upper right corner or reject the inputs by clicking on the button. Click on the button to call the calculator.

In the following browser navigate to the desired path, Input a file name and

Click on the **SAVE** button to save the data.

Click on the **EXIT** button to cancel the saving.

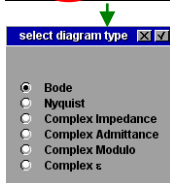
2.2 Display Spectrum



Click on this icon to display the spectrum resident in memory. This may be measured or loaded data. The functions available in the Display Spectrum page are described later in this chapter.



Click on this icon if you want to change the type of the diagram.



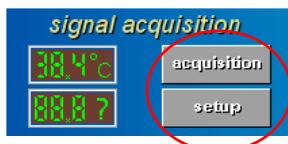
Select the type of the diagram type to be displayed here. The diagram types are described in detail later in this chapter.

2.3 Impedance Spectra Analysis



Clicking on this icon will lead you directly to the **SIM** page where you can create equivalent circuits and fit the model to the measured data. The impedance data resident in the EIS memory have to be stored as data file before it can be read within the **SIM** software partition. For more information about **SIM** refer to the chapter **SIM** of this manual.

2.4 Signal Acquisition



The **Signal Acquisition** pages **Setup** and **Acquisition** let you configure and activate additional channels to be recorded or output along with the EIS spectrum. To do this, optional hardware (TEMP/U, DIO, DA-4, FE-42, etc.) or software drivers for virtual **NET** instruments are needed. The same pages are accessible from the **THALES** main menu. The **Signal Acquisition** pages are described in detail in a separate chapter of this manual.

3. Cell Connections

The first thing to do is connecting the electrochemical cell and/or the measuring object to the front terminals of the electrochemical workstation.

For **standard impedance object** (1 Ohm to 100 MΩ) use one of the **BNC cable sets** shipped with the system. Keep in mind: the shorter the cables the better the quality of the measurement.

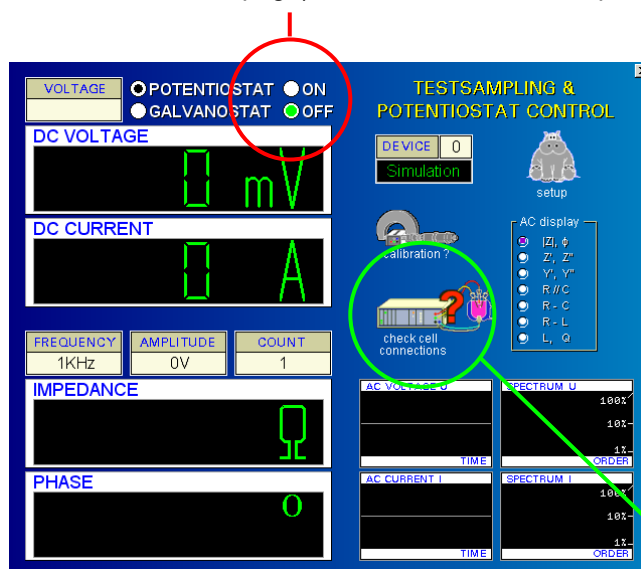
For **high impedance objects** (100 MΩ and higher) we recommend to use the optional **HiZ probe**. Its use can make sense also in lower impedance ranges if the artefacts caused by non-perfect reference electrodes are too prominent. In addition, you should use a **Faraday Cage** for shielding your cell and the cell cables when measuring high impedances. The Faraday Cage has to be grounded at the **Ground** connector to the backside of the electrochemical workstation.

For **low impedance objects** (less than 1 Ω) we recommend to use the optional **LoZ-cable set**. These are twisted-pair cables which reduce the mutual inductance which is prominent in low-impedance measurements noticeably.

The shields of the BNC-connectors and the Lemos plugs of any ZAHNER-elektrik electrochemical workstation are *actively driven*! This minimizes the influence of the stray capacity of the cables.

! Do not connect the shield of the electrochemical workstation to ground or to the cell!
Do not short-cut the shields!

Before connecting your cell to the front terminals, go to the **Control Potentiostat** page (click on the button with the same name in the *EIS Main* page) and make sure that the potentiostat is off.



Then go to the page **Check Cell Connections** (click on the button with the same name in the *Control Potentiostat* page). Here you are able to select your connection scheme. You are guided step-by step through the connection sequence now.

Check Cell Connections

2 electrodes

ZenniumPro

Connected Probe:

- Main Pot
- U-Buffer
- HiZ-Probe
- CVB120
- IF-Probe
- FRA-Probe

Controlled Voltage:

- 5 V
- 15 V

Compliance Voltage:

- 14 V
- 28 V

Connection Scheme:

- no ref. electrode
- with ref. electrode

Exit **Check Cell Connections**.

Shows the selected device. Change device on **Control Potentiostat** page.

Choose plugged probe set (FRA-Probe is only available with **FRA** software module).

Set controlled voltage, if a buffer or an external potentiostat is selected or **ZENNIUM pro/X** is used.

Select compliance voltage (only **ZENNIUM pro/X**).

Select reference electrode.

!

Connect all the four terminals to the cell.
Connect each of the four cell cables to the terminal with the same color, only.
Connect always in the sequences:

1. Test electrode power (black)
2. Test electrode sense (blue)
3. Reference electrode (green)
4. Counter electrode (red)

If you do not, the system and/or your object may get damaged.

The **U-buffer** shipped with the electrochemical workstations Zennium /E can be used to extend the voltage range of the system up to ± 10 V. Another important function of the **U-buffer** is to decouple the cable load of the connection lines from potentially high impedance reference electrodes. Use the **U-buffer**, if your reference electrode system impedance exceeds some $K\Omega$. The **U-buffer** is connected to the Lemos terminal **Probe E**. Then, connect the **Reference Electrode** and the **Test Electrode Sense** to the **U-buffer** instead of to the BNC terminals.

For **Zennium Pro** and **Zennium X** the controlled voltage range can be selected between ± 5 and ± 15 volts in the check cell connection menu directly.

Check Cell Connections

2 electrodes

Main Potentiostat with U-Buffer

Connected Probe:

- Main Pot
- U-Buffer
- HiZ-Probe
- CVB120
- IF-Probe
- FRA-Probe

Voltage Range:

- 4 V
- 10 V

Connection Scheme:

- 2 electrodes
- 3 electrodes
- 4 electrodes

Check Cell Connections

2 electrodes

ZenniumPro

Connected Probe:

- Main Pot
- U-Buffer
- HiZ-Probe
- CVB120
- IF-Probe
- FRA-Probe

Controlled Voltage:

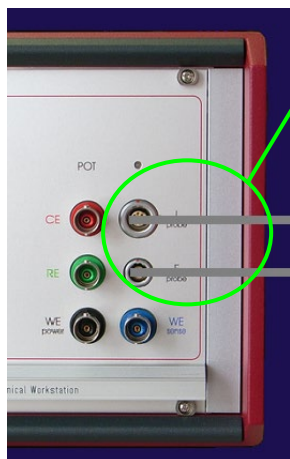
- 5 V
- 15 V

Compliance Voltage:

- 14 V
- 28 V

Connection Scheme:

- no ref. electrode
- with ref. electrode



Both, *HiZ* probe or the *LoZ*-cable set are to be plugged to the Lemosa terminals (**Probe I** and **Probe E**) on the *IM* front panel. All the four electrodes are connected to the *HiZ* probe and the *LoZ*-cable set, respectively.

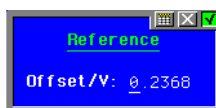
! When using the Lemosa terminals the BNC terminals must be left unconnected!

After you made your choice, click the middle mouse button or press the **[Esc]** key to return to the *Control Potentiostat* page.

If you did select an electrode setup with a reference electrode (three- or four-electrodes) you are now asked for the reference electrode potential. The most common electrode types are listed and the correct potential is automatically used when selecting one of these types.

reference electrode potential	
electrode	V at RT
<input type="radio"/> user defined reference :	0.2368
<input checked="" type="radio"/> Ag/AgCl/1nKCl :	0.2368
<input type="radio"/> Ag/AgCl/sat.KCl :	0.1976
<input type="radio"/> Calomel/1nKCl :	0.2807
<input type="radio"/> Calomel/sat.KCl :	0.2415
<input type="radio"/> Hg/HgSO ₄ /1nH ₂ SO ₄ :	0.682
<input type="radio"/> Hg/HgSO ₄ /sat.H ₂ SO ₄ :	0.65
<input type="radio"/> Hg/HgO/1nNaOH :	0.14
<input type="radio"/> Hg ₂ Cl ₂ /Hg/0.1nKCl :	0.336
<input type="radio"/> Hg ₂ Cl ₂ /Hg/1nKCl :	0.283
<input type="radio"/> Hg ₂ Cl ₂ /Hg/sat.KCl :	0.244

If your type of reference electrode is not listed, or if you prefer to refer your data to the physical potential, you may use the entry *User Defined Reference*. In that case you have to enter the individual reference electrode potential (in V) after clicking on ☒. Enter zero, if you refer to the physical potential reference.



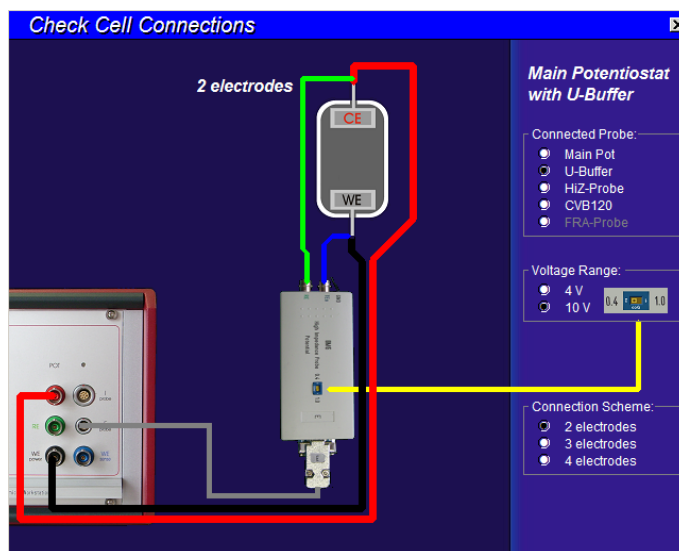
Clicking on ☒ will lead you back to the *Control Potentiostat* page.

! Always connect all the four terminals to the cell, even if you use a 2-electrode set-up. The potentiostat will be switched off automatically as soon as you change any *Check Cell Connection* setting.

! Before switching on the potentiostat make sure that cell and potentiostat are wired correctly. A missing sense connection - either reference electrode or working electrode sense - may result in uncontrolled currents and floating potentials. Thus the cell or the potentiostat may be damaged.

3.1 Connected Probes

3.1.1 U-Buffer (ZENNIUM and ZENNIUM E)



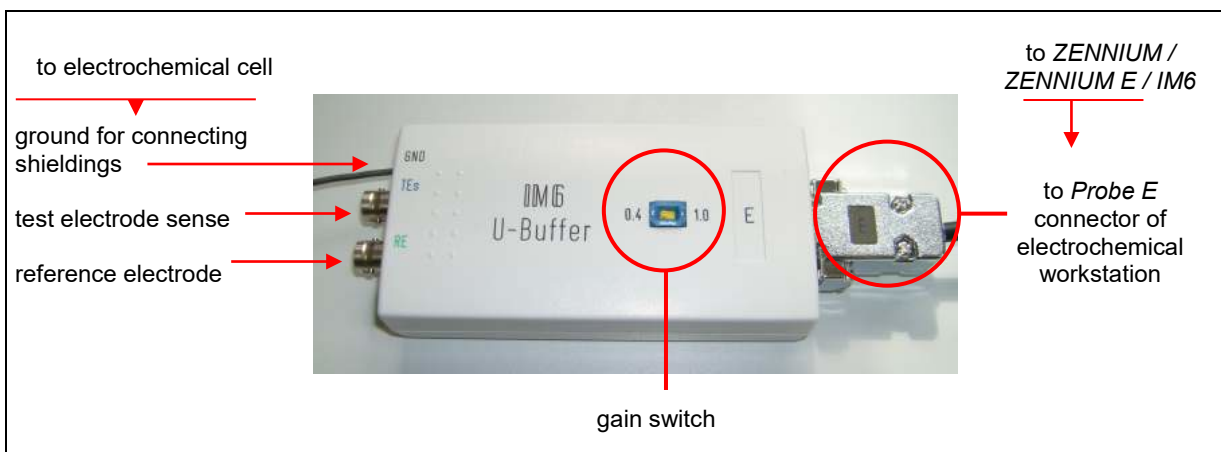
The *U-Buffer* is shipped with the *ZENNIUM* and *ZENNIUM E* systems by standard. It is used to decouple high source resistance reference electrodes from the cable load, or when an extended voltage range of up to +10 V is needed. If you are dealing with high-impedance objects, do not use the *U-Buffer*. It is not calibrated to the older ZAHNER-elektrik *IM*-system individually. For those applications use the optional *HiZ-Probe* set instead. It is calibrated to each *electrochemical workstation* individually and is therefore able to provide optimal accuracy.

! RE and WE sense BNC connectors on the front panel of the ZAHNER-elektrik electrochemical workstation have to be left unconnected.

With *U-Buffer* the *ZENNIUM* / *ZENNIUM E* has the following input specifications:

Input resistance : > 100 GΩ

input capacitance : < 30 pF (compensated to 0 ± 5pF due to software calibration)



The *U-Buffer* amplifier may be used in the two-, three- and four-electrode arrangements if the voltage range of the potentiostat has to be increased to up to $\pm 10V$. The *U-Buffer* has to be connected to the *Probe E* Lemos connector on the front panel of the electrochemical workstation.

Don't connect the *U-Buffer* to the *Probe E* Lemos connector of an external potentiostat (*PP*, *XPOT*, *EL*). These devices are equipped with an internal buffer available by setting the buffer gain factor in the *Check Cell Connections* page.

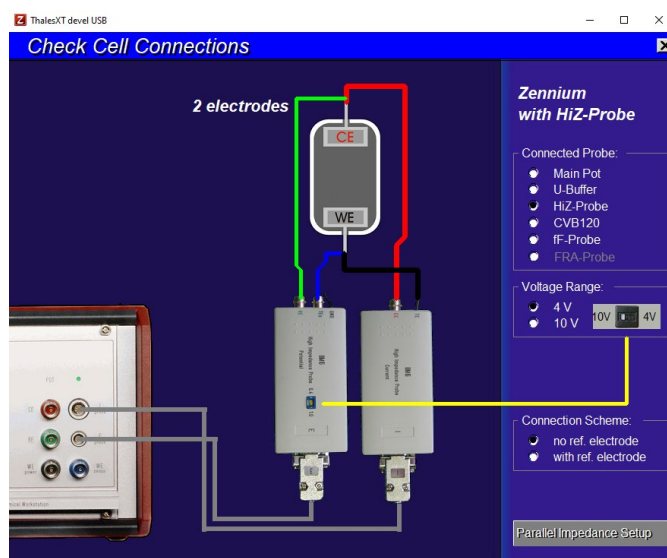


The setting of the gain switch of the *U-Buffer* cannot be detected automatically by the **THALES** software. Make sure that the correct gain factor (1 or 0.4) is set corresponding to the controlled voltage menu of the *Check Cell Connections* page.

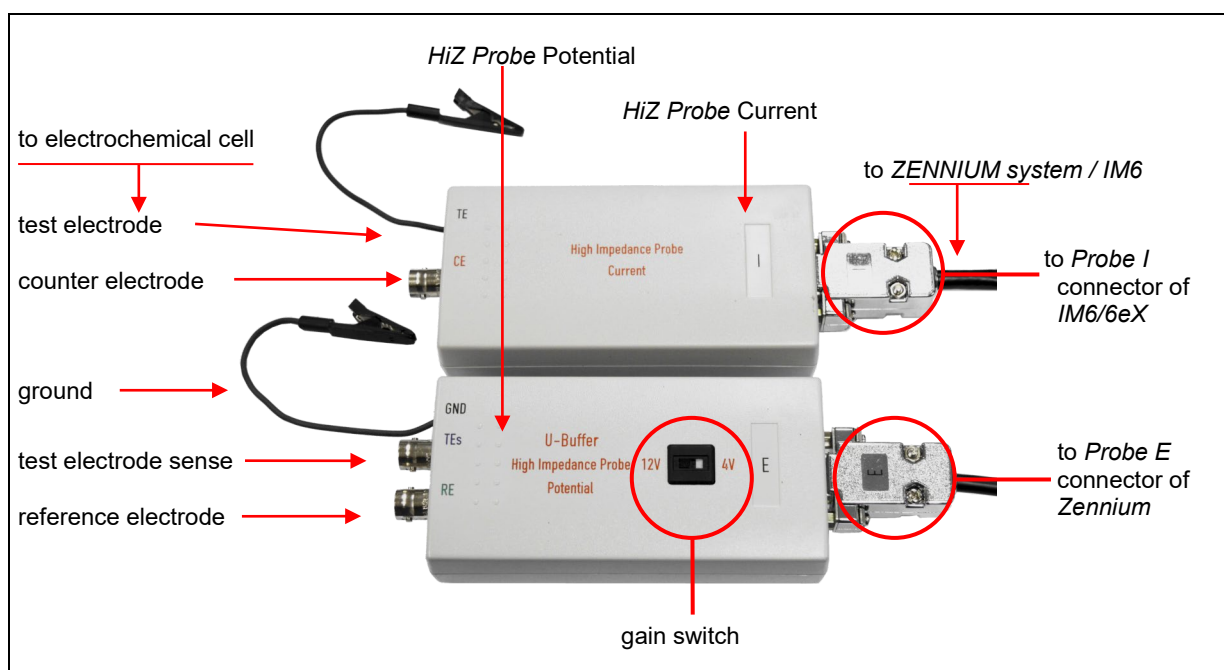
For **ZENNIUM pro/X** the *U-buffer* can be used as an option to reduce noise level on high ohmic objects (inside shielded cases and near by the object).

[For details of the buffer function please refer to the appendix.](#)

3.1.2 HiZ-Probe (Option)

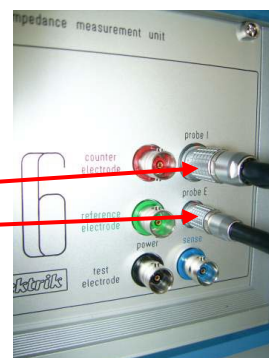


The *HiZ Probe Set* is an option which should be used when measuring on objects with an impedance $>100 \text{ M}\Omega$ or if you encounter disturbances with high impedance objects. The *HiZ Probe Set* is calibrated together with the electrochemical workstation, which it is used with. Therefore, it is not recommended to change *HiZ* probes, to mix the two amplifier boxes or to use a *HiZ* probe with a system it is not calibrated for. To reach the high accuracy the *HiZ* probe provides, you have to copy the *HiZ* calibration data (*calfacj.bin*) to the hard drive as described in the [HiZ probe manual](#) appendix.



The *HiZ Probe Set* is to be connected to the Lemosa terminals *Probe I* and *Probe E* on the front panel of the electrochemical workstation.

High Impedance Probe Current → *Probe I*
High Impedance Probe Potential → *Probe E*



For detailed information about installation and handling of the *HiZ Probe Set* please refer to the [HiZ Probe manual](#) appendix shipped with the *HiZ Probe*.

The *HiZ-U-Buffer* has to be connected to the *Probe E* Lemosa connector on the front panel of the electrochemical workstation and the *HiZ I Probe* has to be connected to the *Probe I* Lemosa connector. It is calibrated to each *IM*-system individually and therefore can provide optimal accuracy.



All BNC connectors on the front panel of the electrochemical workstation have to be left unconnected.

With *HiZ-Probe* the electrochemical workstation has the following input specifications:

Input resistance : > 1000 TΩ typical

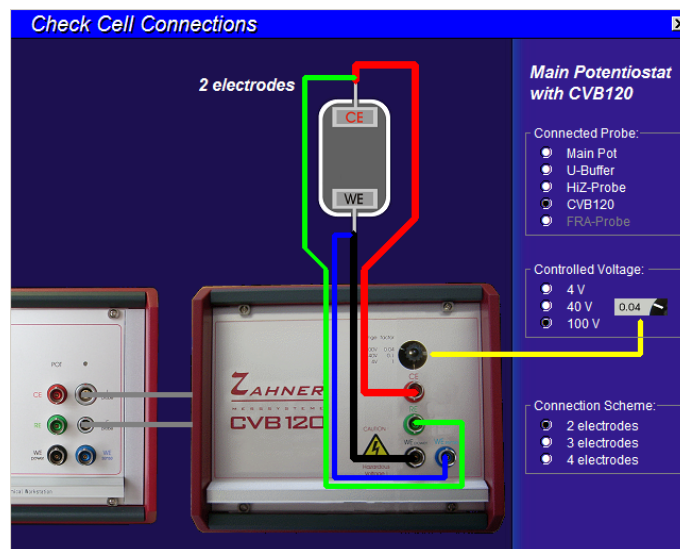
input capacitance : < 5 pF (compensated to 0 ± 1pF due to software calibration)



Before switching on the potentiostat make sure that cell and potentiostat are wired correctly. A missing sense connection - either reference electrode or test electrode sense - may result in uncontrolled currents and floating potentials. Thus, the cell or the potentiostat may be damaged.

[For details please refer to the appendix.](#)

3.1.3 CVB120 (Option)



The [CVB120 compliance voltage booster](#) is used to extend the controlled voltage of the *Zennium* up to 100V and the compliance voltage up to 120V. The *CVB120* has to be connected to the *Probe E* and *Probe I* Lemos connector on the front panel of the ZAHNER-elektrik electrochemical workstation.

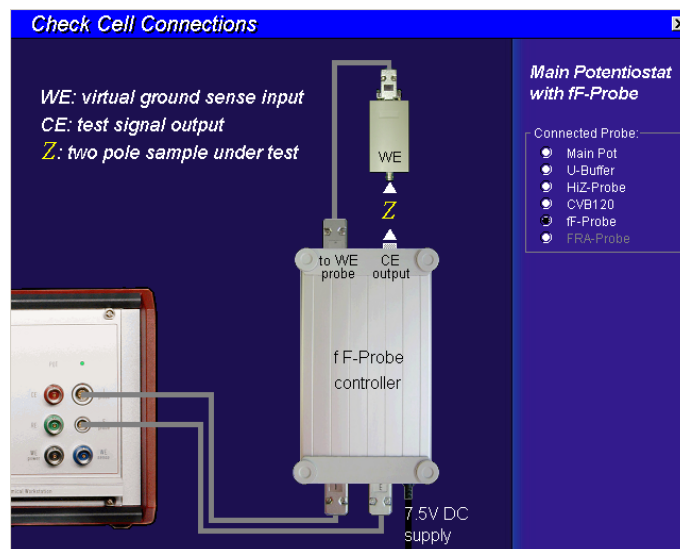


All BNC connectors on the *ZENNIUM* front panel have to be left unconnected.



Before switching on the potentiostat make sure that cell and potentiostat are wired correctly. A missing sense connection - either reference electrode or test electrode sense - may result in uncontrolled currents and floating potentials. Thus, the cell or the potentiostat may be damaged.

3.1.4 fF-Probe (Option)



The *femto-Farad Probe* works as a front-end to the electrochemical workstation. Apart from its limited current capability, all basic functionalities of the *THALES* software are supported. In particular impedance spectroscopy can be applied. Due to the fact, that the primary measurement magnitude is the complex impedance, besides the sample capacity, resistive and DC contributions can be determined as well.

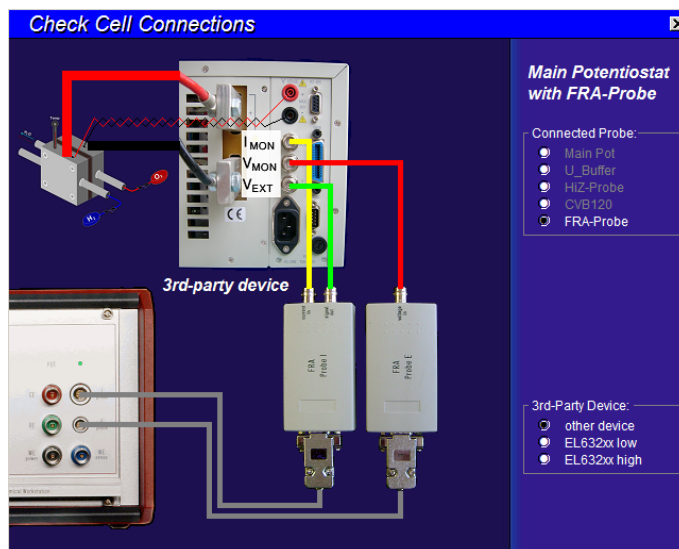
The *femto-Farad Probe* has to be connected to the *Probe E* and *Probe I* Lemos connector on the front panel of the electrochemical workstation.

For further information please refer to the [femto-Farad Probe manual](#).



All BNC connectors on the front of the electrochemical workstation panel have to be left unconnected.

3.1.5 FRA-Probe (Option)



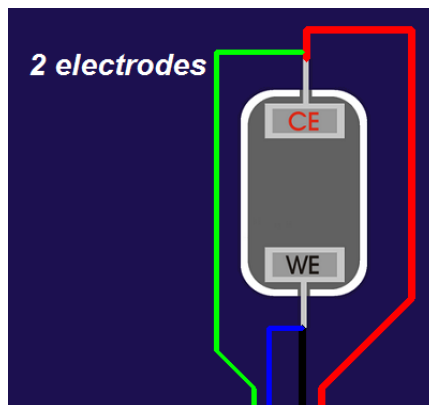
3rd party devices (electronic loads) can be interfaced from *THALES* with the *FRA-Probe*. The *FRA-Probe* is not available for the **EIS** software package. Therefore the radio button is deactivated. To use the *FRA-Probe* start **FRA** software package from the *THALES* main menu. For further information please refer to the [FRA-Probe manual](#).



All BNC connectors on the front of the electrochemical workstation panel have to be left unconnected.

3.2 Electrode Schemes

3.2.1 Two Electrodes



The two pole scheme may be understood as the standard Kelvin arrangement known from precision current measurements. The current lines as the potential sensing lines will be connected to the corresponding electrodes of the cell. In electrochemistry the two pole scheme allows the measurement of the full cell's impedance.

Connect the electrodes as follows:

	Electrochemical Workstation		CELL
1.	working electrode power HIZ-I-buffer test electrode	→	working electrode
2.	working electrode sense U-Buffer - TEs	→	working electrode
3.	reference electrode U-Buffer - RE	→	counter electrode
4.	counter electrode HIZ-I-buffer counter electrode	→	counter electrode

In the two-electrode arrangement the electrochemical workstation has the following input specifications:

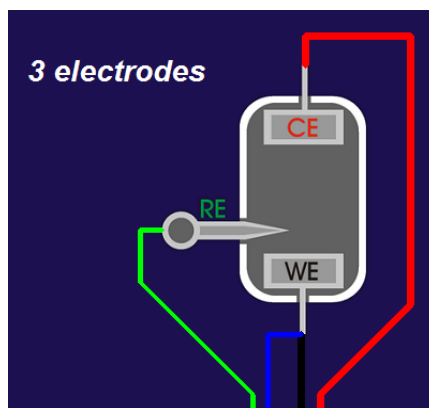
Input resistance : > 50 GΩ

input capacitance : < 50 pF (compensated to 0 ± 5pF due to software calibration)



Before switching on the potentiostat make sure that cell and potentiostat are wired correctly. A missing sense connection - either reference electrode or test electrode sense - may result in uncontrolled currents and floating potentials. Thus the cell or the potentiostat may be damaged.

3.2.2 Three Electrodes



The three electrode scheme will be used in the traditional potentiostatic arrangement of a half cell. In order to obtain a high-accuracy measurement of the absolute potential a reference electrode must be used. This electrode is to be connected to the reference electrode input of the potentiostat. The stray-capacitance of the cable has to be as small as possible. Use the IM cable set for best results. Try to avoid a twisting of the wires of the reference electrode and the counter electrode. If possible keep a large distance between these two cables.

Connect the electrodes in the following sequence:

	Electrochemical workstation		CELL
1.	working electrode power HIZ-I-buffer test electrode	→	working electrode
2.	working electrode sense U-Buffer - TEs	→	working electrode
3.	reference electrode U-Buffer - RE	→	reference electrode
4.	counter electrode HIZ-I-buffer counter electrode	→	counter electrode

In the three-electrode arrangement the electrochemical workstation has the following input specifications:

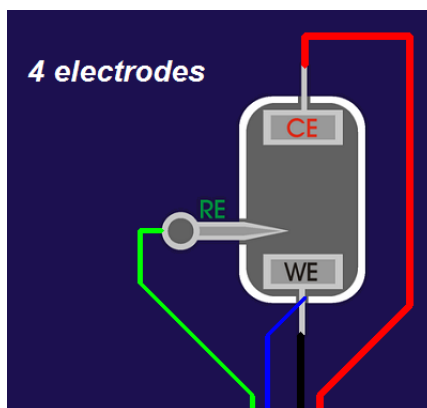
Input resistance : > 50 GΩ

input capacitance : < 30 pF (compensated to 0 ± 5pF due to software calibration)



Before switching on the potentiostat make sure that cell and potentiostat are wired correctly. A missing sense connection - either reference electrode or test electrode sense - may result in uncontrolled currents and floating potentials. Thus the cell or the potentiostat may be damaged.

3.2.3 Four Electrodes



The four electrode arrangement must be chosen when using a second reference electrode as *test electrode sense*. An application of the four electrode arrangement are measurements on symmetric cells. e.g. for arrangements with diaphragms. Both reference electrodes should be connected to the corresponding input of the potentiostat with cables of as little stray capacitance as possible. Use the *IM* cable set for best results. Try to avoid a twisting of the wires of the reference electrodes and the cables of the working/counter electrodes. If possible keep a large distance between these cables.

Connect the electrodes in the following sequence:

Electrochemical workstation		CELL
1.	working electrode power HIZ-I-buffer test electrode	→ working electrode
2.	working electrode sense U-Buffer - TEs	→ working electrode sense
3.	reference electrode U-Buffer - RE	→ reference electrode
4.	counter electrode HIZ-I-buffer counter electrode	→ counter electrode

In the four-electrode arrangement the electrochemical workstation has the following input specifications:

Input resistance : > 100 GΩ

input capacitance : < 50 pF (compensated to 0 ± 5pF due to software calibration)



Before switching on the potentiostat make sure that cell and potentiostat are wired correctly. A missing sense connection - either reference electrode or test electrode sense - may result in uncontrolled currents and floating potentials. Thus, the cell or the potentiostat may be damaged.

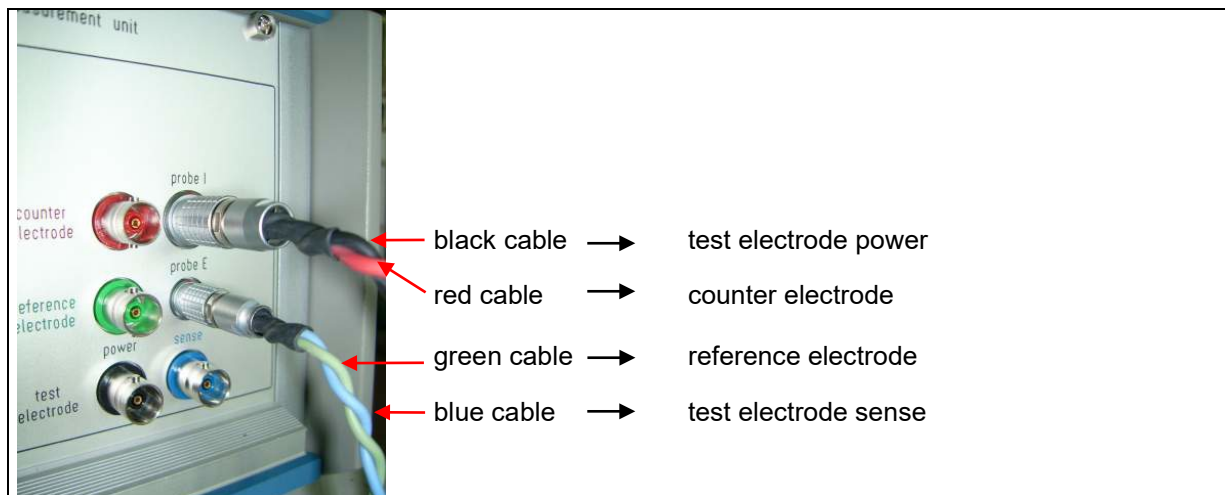


Shielded cables will increase the parasitic capacitance but decrease the coupling capacitance. The best way to suppress both types of disturbances is to maximize the distances especially to the counter electrode and to shield the whole measuring arrangement, e.g. with a Faraday cage.

[For details please refer to the appendix.](#)

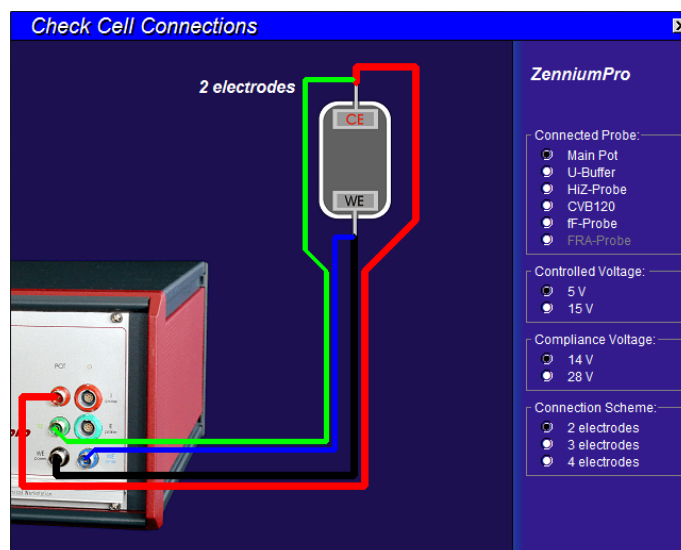
3.3 LoZ Cable Set (Option)

For **low impedance objects** ($<1 \Omega$) we recommend to use the optional **LoZ-cable set**. These are twisted-pair cables which reduce the mutual inductance prominent in low-impedance measurements. For twisted-pair cables the probe connectors are used instead of the BNC-connectors (*Probe I* and *Probe E*) because twisting of the cables can start directly at the output jacks. Each straight (untwisted) piece of wire of some centimetres in length is long enough to produce a strong magnetic field interfering with the sense signals. Furthermore, the internal circuits of the *Probe I* and *Probe E* outlets are optimised for that purpose.



[For the pin-out of the *Probe I* and *Probe E* connectors please refer to the appendix.](#)

3.4 High Compliance Voltage (ZENNIUM X / pro)



ZENNIUM X and ZENNIUM pro provide two compliance voltage ranges.

	normal mode	high compliance mode
ZENNIUM X	$\pm 14 \text{ V}$	$\pm 28 \text{ V}$
ZENNIUM pro	$\pm 16 \text{ V}$	$\pm 32 \text{ V}$

The switching can be done on the 'Check Cell Connections' page. There, the user can adjust the ZENNIUM X / pro electrochemical workstation accordingly to the requirements of the planned experiments.

The low compliance mode is set by default and grants the highest accuracy of the electrochemical workstation.



Using high compliance mode for experiments with a required compliance voltage below 16 V (X) or 14 V (pro) will reduce the maximum output current and add unnecessary noise to the measurement.

4. Control Potentiostat

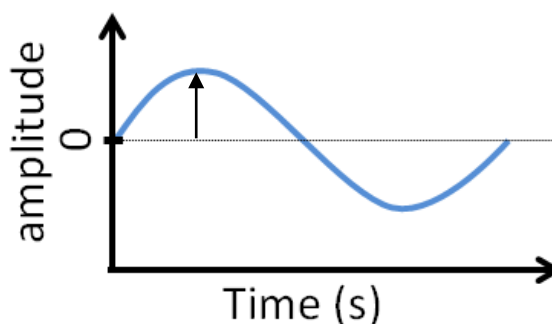
Back to the **Control Potentiostat** page you may notice a particular DC potential in the **DC Voltage** display. This is the **rest potential** of your test object. If characters like ' $\pm \#.###$ ' are displayed, the potential exceeds the limits of the potentiostat which may arise from an improper connection of your test object.

The **Control Potentiostat** page is very useful for testing your external measurement setup, such as cabling, cell, electrodes, connections to the object, etc. Here you may apply different combinations of AC and DC voltages and currents at frequencies of interest. You may have a (first) look at the measurement values and signals at the selected frequency. Furthermore, the AC- and DC-parameters **DC voltage/current**, **AC amplitude** and potentiostat mode (potentiostatic or galvanostatic) are to be defined here for an EIS measurement to follow. And – very important – the potentiostat is switched on and off here. Please note, that the potentiostat is switched off automatically, when the potentiostat mode is changed.

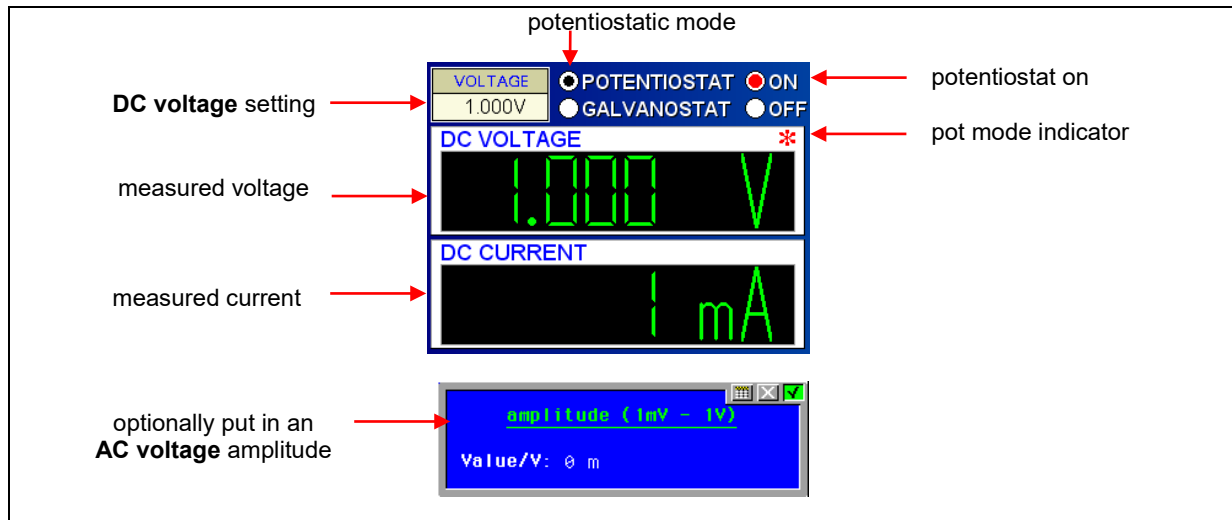
The screenshot shows the 'Control Potentiostat' interface with the following labeled components:

- set DC voltage or DC current:** Points to the 'VOLTAGE' field showing '1.250V'.
- DC voltage display:** Points to the 'DC VOLTAGE' display showing '1.250 V'.
- DC current display:** Points to the 'DC CURRENT' display showing '1.36 mA'.
- set frequency:** Points to the 'FREQUENCY' field showing '1kHz'.
- set AC amplitude:** Points to the 'AMPLITUDE' field showing '100mV'.
- set average count:** Points to the 'COUNT' field showing '5'.
- AC display 1:** Points to the 'IMPEDANCE' display showing '19 Ω '.
- AC display 2:** Points to the 'PHASE' display showing '-57.0°'.
- POT switch:** Points to the 'POTENTIOSTAT' and 'GALVANOSTAT' mode selectors.
- select POT device:** Points to the 'DEVICE' field showing '0'.
- close button:** Points to the 'X' button in the top right corner.
- global measuring settings:** Points to the 'TESTSAMPLING & POTENTIOSTAT CONTROL' window.
- go to Calibration page:** Points to the 'calibration?' button.
- set AC display type:** Points to the 'AC display' list with options like '|Z|, ϕ ', 'Z', 'Z'', 'Y', 'Y'', 'R//C', 'R-C', 'R-L', 'L, Q'.
- go to Check Cell Connections:** Points to the 'check cell connections' button.
- AC voltage display:** Points to the 'AC VOLTAGE U' waveform display.
- voltage spectrum:** Points to the 'SPECTRUM U' frequency spectrum display.
- AC current display:** Points to the 'AC CURRENT I' waveform display.
- current spectrum:** Points to the 'SPECTRUM I' frequency spectrum display.

The AC amplitude in EIS is the amplitude from the zero point to the peak.



4.1 Potentiostatic Mode



The operation mode of the potentiostat/galvanostat of the ZAHNER-elektrokemische Arbeitsstation and of external potentiostats is selected in the *Control Potentiostat* page. Click on the POTENTIOSTAT dot to select potentiostatic mode. An asterisk at the DC VOLTAGE instrument indicates the potentiostatic mode setting in ON state. In potentiostatic mode the DC-voltage is set in the VOLTAGE input box. It is the controlled and stabilized quantity. In consequence, the measured signal is the current.

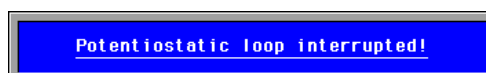
The potentiostatic mode of operation is recommended for most AC-impedance measurements, due to its extreme wide dynamic range and un-problematic perturbation amplitude control.

Switching on the potentiostat in potentiostatic mode will cause the software doing the following:

- The defined DC-voltage is applied to the measured object (within the limits of the POT)
- DC-voltage and DC-current are measured and displayed
- The DC-voltage is regulated and fixed, the DC-current depends on the test object
- If an AC-amplitude is defined it is superimposed to the DC-voltage, and
 - o The AC data are calculated from the AC-voltage and AC-current and displayed.
 - o The AC-signals are displayed in the scopes (time domain and frequency domain (FFT)).

NOTE 1:

Active measurements rely on the principle, that a measuring instrument is able to vary certain physical conditions at an object under test in a well defined manner. In case of EIS, a certain test AC modulation (sinus perturbation) is superimposed to the stationary DC conditions. A hardware feedback loop (potentiostatic or galvanostatic feedback) shall ensure, that the test signal is correctly established. In order to judge the reliability of the results, the system checks, if the set value of the test signal really matches the measured amplitude within certain limits. If the tolerance band is violated, the system assumes an error condition present in the environment of the external setup. In any such case you will obtain an error message during your impedance measurement: **'Potentiostatic loop interrupted'**.



In practice, a lot of situations may occur, where the instrument is unable to establish a test signal of sufficient magnitude. Here is the list of the most probable reasons:

- The cables (power as well as reference and/or test electrode sense) are not connected properly to your test object.
- The DC current is exceeding the specified current limit of the workstation.
- The DC voltage at the object is exceeding the specified voltage limit of the workstation.
- The inner resistance of the counter electrode(s) in a three or four electrode cell is too high.
- The Haber-Luggin capillary in a three or four electrode cell is too close to the working electrode (shading effect).
- The reference electrode or the Haber-Luggin capillary in a three or four electrode cell has a too high inner resistance (mostly caused by an electrolyte column interruption due to gas bubbles).
- The cables are too long for a low impedance test object.
- Each three or four electrode cell arrangement has a characteristic maximum frequency limit, due to parasitic properties of cables, shields and, most important, reference electrodes. An attempt to measure EIS at a frequency beyond this limit will prompt this message, too.
- Generally in any measurement technique, 'wanted' measurement signals have to compete with 'unwanted' signals (noise) present in the set-up under test. If noise pick-up from the environment exceeds the useful signals to a certain degree they may overload the signal acquisition paths and again the above error message may occur.

Most of the above mentioned error conditions can be easily avoided by carefully designed cell set-up, wiring and shielding precautions. Please refer to the corresponding hints in the article attached in the manual folder of the *THALES* installation c:\thales\manuals\Introduction to Electrochemical Instrumentation.

It is an extract from:

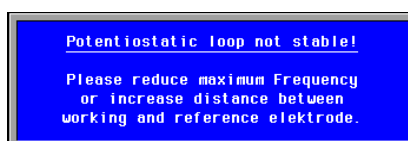
Analytical Methods in CORROSION SCIENCE AND ENGINEERING, Edited by Phillippe Marcuse, Florian Mansfeld, CRC Press, Taylor & Francis Group, 2006.

ISBN-13: 978-0-8247-5952-0

ISBN-10: 0-8247-5952-4

NOTE 2:

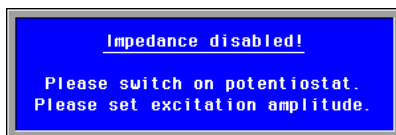
The hardware feedback loop mentioned in note 1 implies the principle possibility for parasitic oscillations eventually occurring between the potentiostat (which acts as a power operational amplifier) and the cell (which acts as an external feedback path). The system tests the stability of the loop. If oscillations are detected, the loop bandwidth is automatically reduced, until stability is achieved. If the operator attempts to measure EIS at frequencies significantly beyond this bandwidth, the error message '**Potentiostatic loop not stable**' will be displayed.



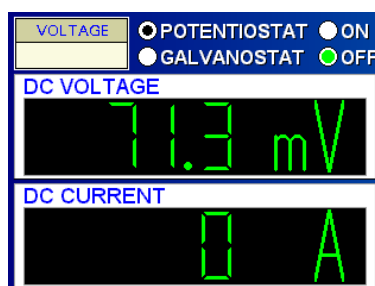
Mostly, a cell set-up not appropriate to dynamic measurement requirements is the reason for this error condition. In the above mentioned article you will also find hints how to design an optimal cell set-up and how to avoid such problems.

NOTE 3:

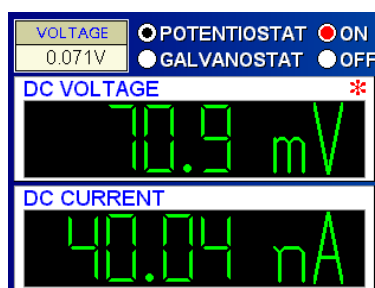
The system tries to assist the operator in many situations. If settings are incomplete or insufficient to perform an action wanted, depending on security considerations, in some cases the user may be informed by messages. In other cases the action may be continued by an automatic introduction of missing settings. Generally, settings done manually by the operator in the **Control Potentiostat** page are taken as obligatory. Missing settings may cause error messages, for instance a missing AC amplitude setting will lead to the message



or initiate a default routine. The state of the potentiostat (on/off) prior to a measurement routine is of particular interest for this behavior. The EIS routines of *THALES* generally apply: The state prior to an EIS spectrum will be kept or established again after the spectrum run. (The same philosophy is taken by *THALES* for all the other measurement methods which use the potentiostat definitely in the on-state to be performed, like in **CV** or **I/E**. It makes no sense to meet this strategy in all cases, for instance in measurement tasks which may use mixed modes (on or off) like done in **POL** or **PVI**). As an example for the strategy of assisting through default values consider the following: if an operator connects a cell for the first time after starting the instrument, no setting for the potentiostat set voltage is present and the corresponding input field is empty:



At the moment the operator switches on the potentiostat without filling in the set-value field, for security reasons the actually measured OCP is taken as set-value and then the potentiostat is switched on:

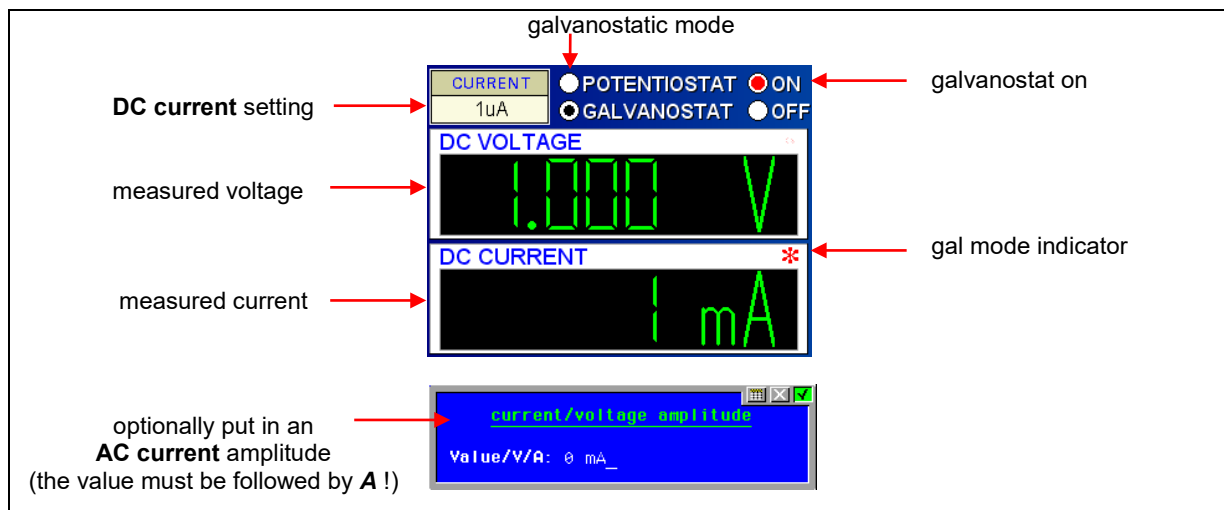


Note, that from the moment, a set-value is present, this value is taken as obligatory when switching off or on again *manually*, even, if the OCP changes during an off-state.

This situation differs from the following sequence, where the instrument has to switch on the potentiostat *automatically*. Consider, you leave the **control-potentiostat** page with AC set value established, but the potentiostat is still switched off. Then *THALES* will overwrite an eventually present DC-voltage set-value by the actually measured OCP, switch on and perform the spectrum. *After* the spectrum is completed, the potentiostat is switched off again. This implies, if you want to perform a spectrum at a dedicated DC-set-voltage different from the OCP, you have to switch on the potentiostat prior to the measurement. In this case, the state of the potentiostat will be on also after the spectrum is completed.

The strategy to handle the on/off-state is continued in the more complex procedures: if you want to perform for instance an impedance spectra series vs. DC-set-voltage, the individual spectra have to be recorded at certain DC-set-voltages. Depending on the starting state, the system will keep the on-state between the spectra and after completion of the whole series, or it will switch off after each spectrum and after completion of the whole series. In the latter case before each spectrum a ramp is automatically introduced, starting from the actually OPC and ending at the dedicated DC-set-voltage. This strategy is also used for **CV** and **I/E** scans.

4.2 Galvanostatic Mode



Click on the GALVANOSTAT dot to select galvanostatic mode. An asterisk at the DC CURRENT instrument indicates the galvanostatic mode setting. In galvanostatic mode the DC-current is set in the CURRENT input box. It is the controlled and stabilized quantity. In consequence, the measured signal is the voltage.

While for most research objects potentiostatic mode for EIS should be preferred, galvanostatic mode may have certain advantages for batteries and fuel cells for instance. They are better characterised by a steady state current than by a potential, because the corresponding voltage may change significantly during charging/discharging or changes in the support process control. In this case galvanostatic mode of operation should be preferred.

Switching on the potentiostat in galvanostatic mode will cause the software doing the following:

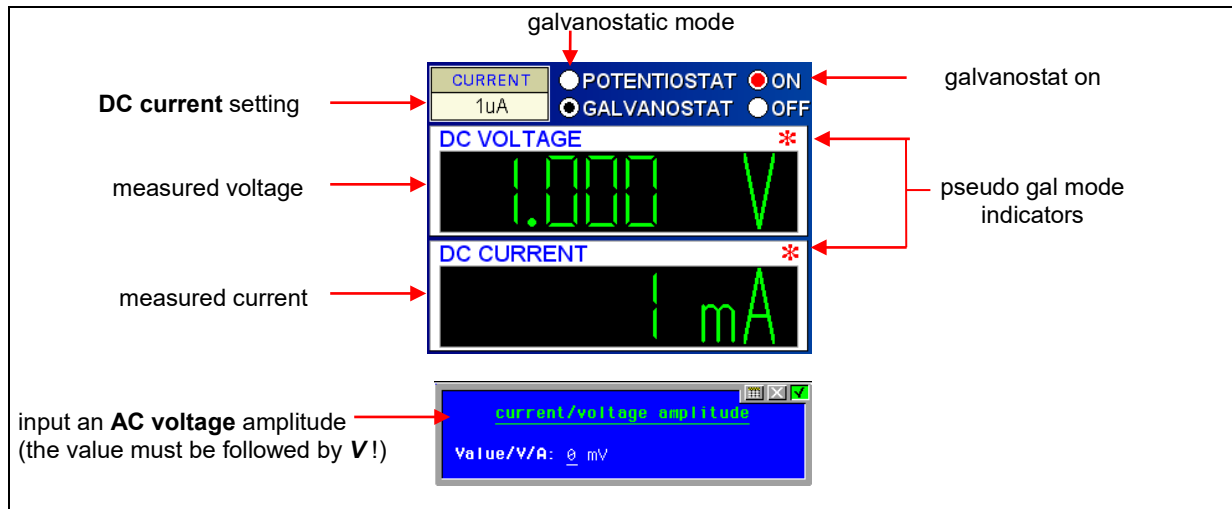
- The defined DC-current is applied to the measured object (within the limits of the POT)
- DC-voltage and DC-current are measured and displayed
- The DC-current is controlled and fixed, the DC-voltage depends on the test object
- If an AC-amplitude is defined it is superimposed to the DC-current, and
 - o The AC data are calculated from the AC-voltage and AC-current
 - o The AC-signals are displayed in the scopes (time domain and frequency domain (FFT)).

NOTE:

For the galvanostatic mode similar considerations regarding possible error conditions are valid as for the potentiostatic mode. Besides this, galvanostatic mode does not exhibit the excessive wide dynamic range for the measured impedance available in potentiostatic mode with up to 12 orders of magnitude in current sensitivity ranging. In galvanostatic mode the current range is fixed by the sum of the DC set current and the current amplitude. Galvanostatic mode is only appropriate for systems with a relative small impedance change over frequency.

The fixed current amplitude may also cause problems regarding the violation of the linearity rule valid for all impedance technique: often electrochemical systems exhibit much higher impedance at lower frequencies. In this case the resulting AC-voltage amplitude may overload the system under test.

4.3 Pseudo-Galvanostatic Mode



In pseudo-galvanostatic mode the **DC current** and the **AC voltage amplitude** are set. DC current control is recommended in investigations of drifting systems, similar to the considerations for true galvanostatic mode. Consider a fuel cell in a test stand. Test measurements of fuel cells will be done by the variation of many parameters like temperature, gas-pressure, etc. The variation of those parameters may cause a significant drift of the potential at a characteristic current. This will cause a dramatic drift of the flowing DC-current due to the steep I/E-characteristic of the system if true potentiostatic mode is used. By feedback on other parameters of the system the equilibrium may be distorted significantly. Therefore, a controlled DC current is better suited for those measurements.

In pseudo-galvanostatic mode the DC loop is controlled by software while the hardware is kept in potentiostatic mode. Set point value is the defined DC-current, which is regulated by controlling the DC-potential. During the measurement of an impedance sample the DC-potential is fixed to the last measured value and then the AC potential is superimposed. When the sample is finished, control is returned to the software current control loop. One of the following situations is found:

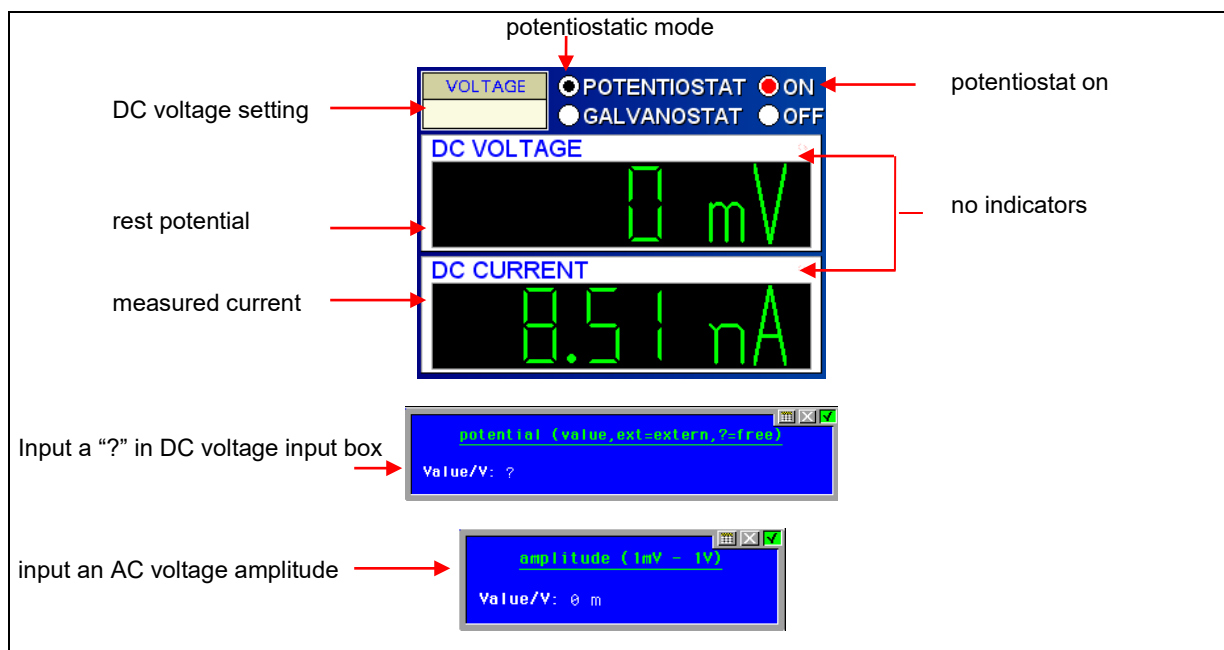
1. The measured current lies within the stability criteria. In this case the program immediately continues with the EIS measurement.
2. The measured current is out of the tolerance band. The potential will be regulated by the software to meet the current set point again. The EIS measurement will be continued as soon as the steady state is reached again or the maximum delay time has run down.
3. The measured current runs out of a tolerance band being defined by the limits

$$I_{upper} = 2 \cdot I_{set} \quad \text{and} \quad I_{lower} = \frac{I_{set}}{2}.$$

The controller will change to hardware galvanostatic mode of operation and by applying the DC potential measure found as DC-set-voltage a new starting potential for the stabilizing loop will be obtained. This shall ensure fast regulation response in the case of higher deviations.

The set DC-current will be regulated by control of the DC-potential due to the defined current range and criteria of stability being defined in the global measurement presets submenu.

4.4 Rest Potential Mode



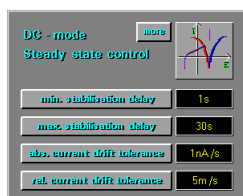
The 'rest potential' mode is used for measurements in which no DC-current must flow, even if the measured system is not very stable. To select the rest potential mode switch to the position POTENTIOSTAT, and input a question mark "?" in the DC VOLTAGE input box while the potentiostat is already in the on state. These settings will activate the rest potential measuring routine.

Please note the difference between the rest potential mode and setting the DC voltage to zero:

Rest potential mode -> potentiostat applies the measured rest potential, no current is flowing
DC potential = 0 V -> DC potential is fixed to 0 V by the potentiostat, excessive current may flow in active systems like batteries.

The rest potential mode is mostly recommended for the investigations of systems of slowly changing state. Consider a corroding electrode, where the system's DC-parameters are changing slightly. Impedance measurements at the rest potential will be done by the following strategy: The potentiostat will be switched on applying the last rest potential having been measured.

If the DC-current is within the limits defined in the *EIS Setup* page the AC-measurement will start. After each measured frequency the DC-current will be measured. If the DC-current is within the limits the measurement will be continued. If the DC-current is out of range the AC-measurement is stopped and the rest potential is measured anew. The new rest potential is applied and the measurement is continued. The stability as the controlled range of the zero current is defined in the



DC-mode Stability criteria in the EIS Setup (see chapter EIS Setup).

NOTE:

Pseudo-galvanostatic as well as pseudo-rest-potential mode have certain limitations due to the fact, that software control relies on a minimum stability of the systems under test. Rapidly changing systems cannot be evaluated successfully by this techniques. On the other hand, the same prerequisites are necessary for all kinds on impedance measurements.

4.5 DC/AC Settings

Graph Box	Parameter	Unit	Range ZENNIUM X/pro	Range ZENNIUM	Range ZENNIUM E
VOLTAGE 1.250V	DC voltage (potentiostatic mode)	V	± 5 V (standard) ±15 V (extended) ? = free ext = external source	± 4 V (standard) ±10 V (extended) ? = free ext = external source	± 4 V (standard) ±10 V (extended) ? = free ext = external source
CURRENT 1uA	DC current (galvanostatic & pseudo-galvanostatic mode)	A	±4 A ZENNIUM X ±3 A ZENNIUM pro	±2.5 A	±2 A
FREQUENCY 1KHz	Frequency used for test measurement	Hz	ZENNIUM X: 10 mHz – 12 MHz ZENNIUM pro: 10 mHz – 8 MHz	10 mHz – 4 MHz	10 mHz – 2 MHz
AMPLITUDE 100mV	AC amplitude: Voltage in potentiostatic & pseudo-galvanostatic mode, Current in galvanostatic mode	V A	standard: 1 mV – 2 V (pot, pgal) extended: 1 mV – 6 V (pot, pgal) 1 pA – 3 A (gal) – Pro 1 pA – 4 A (gal) – X 0 = AC amplitude off	1 mV – 1 V (pot, pgal) 1 pA – 2 A (gal) 0 = AC amplitude off	1 mV – 1 V (pot, pgal) 1 pA – 2 A (gal) 0 = AC amplitude off
COUNT 5	Count of averaging cycles used for each frequency sample in Testsampling and C/E. This value is overwritten in EIS spectra	#	1 - 1000	1 - 1000	1 - 1000
DEVICE 0 Simulation	POT-device to be active for test measurement	#	Depending on the # of devices connected	Depending on the # of devices connected	Depending on the # of devices connected

For the DC-voltage setting you may use one of the following inputs:

value	Set a fixed DC-potential. For all measurements this DC-potential will be applied.
?	With the ? character you activate the free running mode. The DC-potential will be regulated so that the DC-current is zero. In this mode the DC-voltage displays shows the OCP (open circuit potential).

Like usual in the *THALES* environment, all input-boxes accept not only pure values but also the following technical **multiplier prefixes (engineer's units)**:

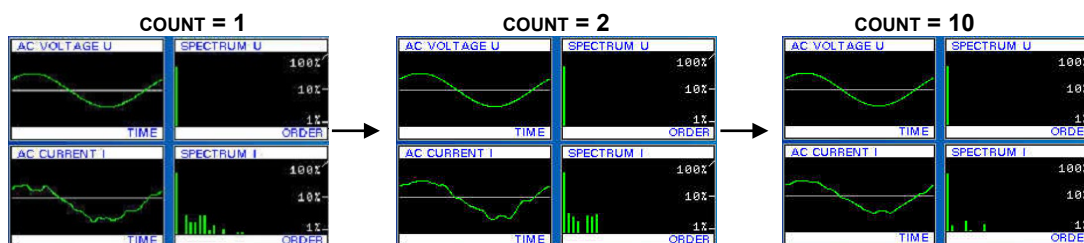
prefix	meaning	multiplier
a	atto	10 ⁻¹⁸
f	femto	10 ⁻¹⁵
p	pico	10 ⁻¹²
n	nano	10 ⁻⁹
u	mikro	1/1000000
m	milli	1/1000
k, K	Kilo	1.000
M	Mega	1.000.000
G	Giga	10 ⁹
T	Tera	10 ¹²
P	Peta	10 ¹⁵
E	Exa	10 ¹⁸

You need not input the unit (V, Hz, A, etc.). This is done by the software automatically (exception: amplitude in pseudo-galvanostatic (V) and galvanostatic (A) mode).

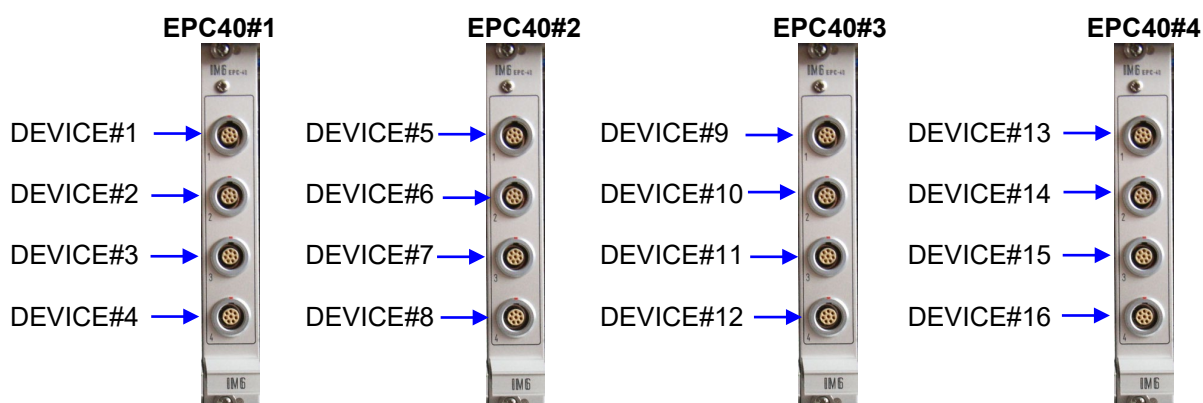
Examples:

0.1 = 100m = 1e-1
1000 = 1k = 1K = 1e3
1000u = 1m = 0.001 = 1e-3

For the determination of the impedance it is generally recommended to average a certain number of sinus signal periods for each frequency sample. Basically, a single sine corresponds with a “dirty” (non-monochromatic) spectrum of the test signal. The test signal spectrum gets the cleaner, the more sinus periods are averaged. Besides this, the signal-to-noise ratio increases with the average count. The **COUNT** parameter defines the number of cycles to be integrated in each measurement point. The higher the count the smoother the signals in the time-domain display and the higher the measuring time and accuracy. A good indicator of the signal being close to a sine wave is the SPECTRUM display. A pure sine wave shows only one line. Additional lines indicate noise and harmonics and with this a distortion of the sine wave signal. Please refer again to the article in *c:\thales\manuals\Introduction to Electrochemical Instrumentation.pdf* for detailed information.



In case you are working with one or more **external potentiostats** or with a **RMux** card select the **DEVICE** number (channel number of EPC40 or of the **RMux**) you would like to be active (0 = internal IM POT). After the input the **IM** is detecting the type of the device. The device name (**PP200**, **PP210**, **PP240**, **EL300**, **EL101**, **NProbe**, etc.) will be displayed in the **DEVICE** box, then.



After all parameters are set you may switch on the potentiostat by clicking on the **ON** button:

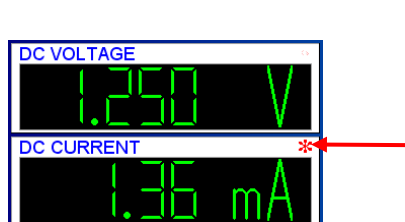


4.6 Instrument Displays

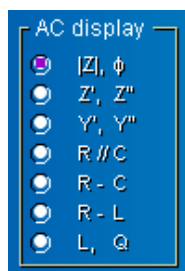
Now the **DC instrument displays** are showing the measured values for DC voltage and DC current. The **DC voltage** is measured between *reference electrode* and *test electrode sense*. In electrochemical diction, the reference potential is virtually zero.

The **DC current** displayed is the current flowing from the *counter electrode* to the *test electrode power*. In electrochemical diction "positive" means anodic, "negative" means cathodic with respect to the *test electrode*.

A **red asterisk** indicates which of the two quantities (voltage or current) is controlled by the potentiostat/galvanostat (example: galvanostatic mode). The other quantity is measured.



The **AC instrument displays** can only work if an **AC Amplitude** is set. They may be configured for displaying the quantities needed with the **AC Display Selector**.

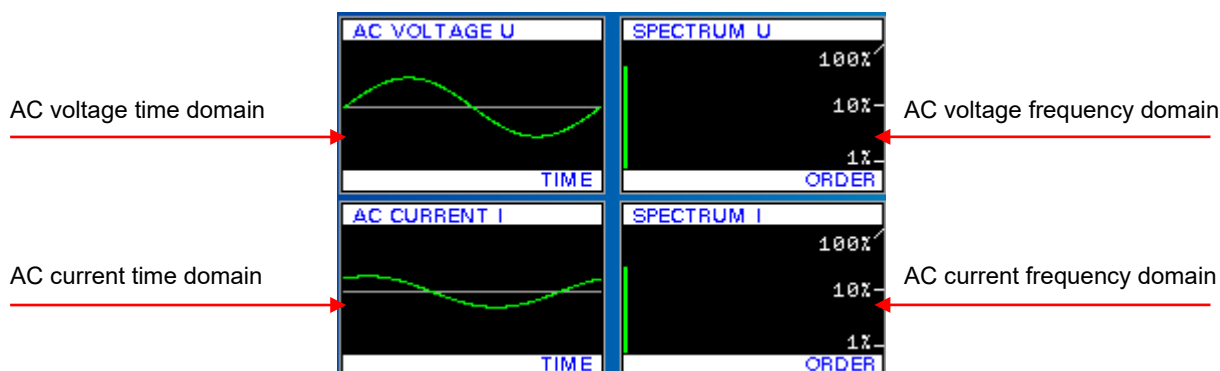


The following display types are available:

Setting	Display 1	Unit	Instrument displays
 Z , Φ	Impedance modulus value	Ω	IMPEDANCE 19.2 Ω
	Phase angle between AC voltage and AC current	$^{\circ}$	PHASE -55.8 $^{\circ}$
Z', Z''	Real part of the impedance	Ω	REAL PART Z' 10.8 Ω
	Imaginary part of the impedance	Ω	IMAGINARY PART Z'' -15.9 Ω
Y', Y''	Real part of the admittance	Ω^{-1}	REAL PART Y' 29.3 m Ω^{-1}
	Imaginary part of the admittance	Ω^{-1}	IMAGINARY PART Y'' 43.2 m Ω^{-1}
R // C	Resistance (in parallel to capacitance)	Ω	RESISTANCE 34.1 Ω
	Capacitance (in parallel to resistance)	Farad	CAPACITY 6.87 μF
R - C	Resistance (in series to capacitance)	Ω	RESISTANCE 10.8 Ω
	Capacitance (in series to resistance)	Farad	CAPACITY 10 μF
R - L	Resistance (in series to inductance)	Ω	RESISTANCE 10.8 Ω
	Inductivity (in series to resistance)	Henry	INDUCTIVITY -2.52 mH
L, Q	Inductivity, Quality factor	Henry	INDUCTIVITY -2.52 mH
			QUALITY -1.47

4.7 Graphic Realtime AC Displays

Besides the four instruments, four graphic realtime displays are showing the AC voltage and the AC current signals in the time domain (waveform) and in the frequency domain (spectrum).




These displays are very useful for detecting disturbances of the measurement signals very easily. The AC voltage at the output of the electrochemical workstation (*test electrode* and *counter electrode*) is a pure single-frequency sine signal. This should be shown in the *AC Voltage Time Domain* display. This single frequency should also dominate in the *AC Voltage Frequency Domain* display. There may be small side lines, but best is when there is only one line of the frequency selected. Accordingly, the AC current should be as close as possible to a single-frequency sine form and the frequency display should show only one line or only small side lines.

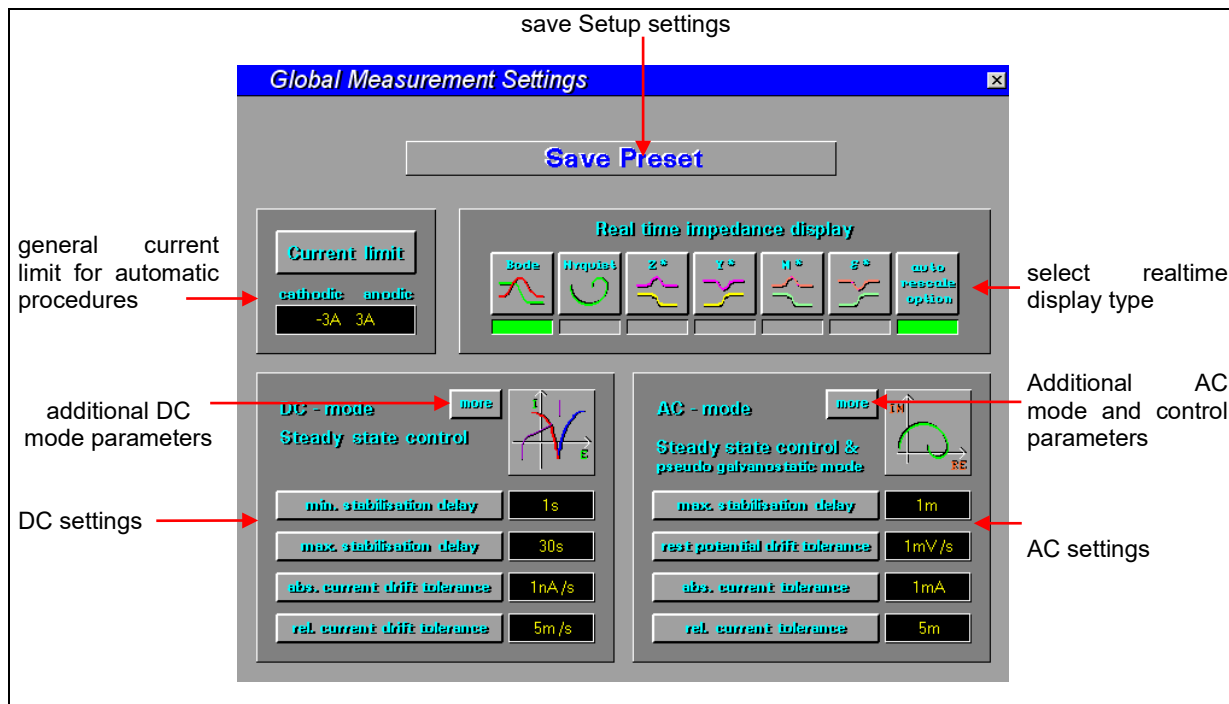
If you encounter disturbances in these signals, make sure that for high-impedance measurements you have a good shielding of your object/cell. The shielding has to be grounded at the GND banana connector at the backside of the Zennium device. Remember that the shield of the cell cables must not be connected to GND! For very high impedances use the optional *HiZ Probe Set* which you position as close as possible to the object/cell. For low-impedance measurements use cables as short as possible. For very low impedances use the *LoZ Cable Set* (option) which also should be as short as possible.



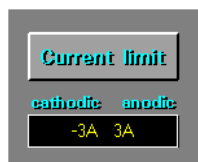
The electrochemical workstation is working on the basis of the most accurate strategy: A monochromatic excitation in combination with a multispectral response analysis. This enables outstanding features like realtime drift correction and a realtime estimation of the accuracy. All these features are described in detail in the chapter 7.10 [Advanced Features](#).

5. EIS Setup

Clicking on the Hippo icon  in the *Control Potentiostat* page leads you to the *EIS Setup* page where more specific setting for the impedance measurement can be edited. You can reach this page also from the *EIS Main* page by clicking on the same Hippo icon.



5.1 Global Current Limit



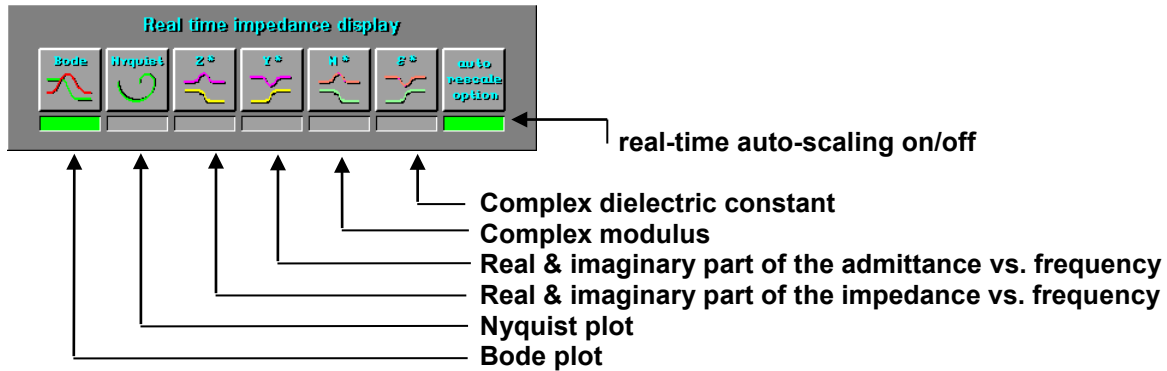
Click on the "current limit" button in order to set a current limit for the electrochemical workstation [A], valid in DC- and combined AC-DC techniques. If these limits are violated, the measurement may be stopped and an error message is displayed. Depending on the method running, the current limit event may also cause inverting of scanning procedures or a procedure restart. Set the current limit to a value lower than the "damaging" current. The software will not allow to trespass this current in automatic DC- and combined AC-DC procedures. Cathodic and anodic current can be defined separately.

Please note that the current limit control is NOT ACTIVE in **Control Potentiostat** and pure AC measurements.

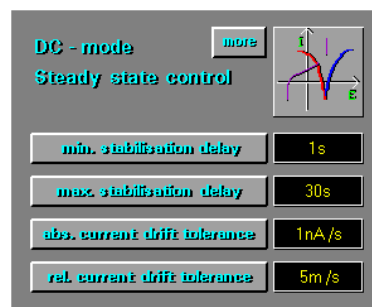
For the *ZENNIUM X* the maximum current is ± 4 A, for the *ZENNIUM pro* it is ± 3 A, for the *ZENNIUM* it is ± 2.5 A and for the *ZENNIUM E* it is ± 2 A.

5.2 Default on-line display

Click on one of these icons in order to select the curve type you like to be displayed by default in the EIS *Measurement Page*.



5.3 DC-Mode Parameters



min. stabilisation delay 1s

Defines the minimum time (s) the system has to wait for steady state conditions before starting a measurement. The minimum delay time will be held, even if other stability criteria have already been fulfilled.

max. stabilisation delay 30s

Defines the maximum time (s) the system has to wait for steady state conditions. After the maximum delay time the program will continue to measure, even if other criteria of stability have not yet been met. If you encounter stability problems this value has to be set to appropriate conditions.

abs. current drift tolerance 1nA/s

Defines the absolute current drift tolerated for steady state conditions

$$dI_{\text{absolute}} = \frac{I(t) - I(t - dt)}{dt}$$

The absolute drift tolerance is given in units of A/sec, useful in the regime of small currents with potentially changing sign.

rel. current drift tolerance 5m/s

Defines the relative current drift (difference of two successive current points) tolerated for steady state conditions.

$$dI_{\text{absolute}} = \frac{I(t) - I(t - dt)}{I(t - dt)} \cdot \frac{1}{dt}$$

The relative current drift tolerance is given in units of 1/sec. It is useful in the regime of higher currents, when the absolute drift tolerance is no adequate measure for stability.

Steady state control

Changing the applied potential or current to a system, mostly causes a distortion of the equilibrium. Before taking the next sample the system should become stationary again. Stationarity must especially be considered for the following measurement methods:

a) Steady state current density over potential measurements (I/E)


Steady state current potential curves are measured with respect to user-defined criteria of stability. Changing the potential at a conducting system will usually disturb the stationarity of the flowing current. Due to the system's properties the current response to a dE-pulse may be dramatic - e.g. charging or discharging processes may be initiated. Thus, current stationarity should be ensured before a new I(E) sample will be measured.

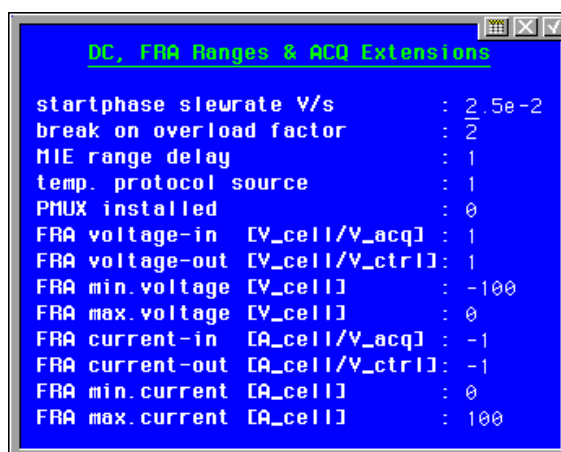
b) Capacity Recording (C/E)

Measuring the capacity over the potential demands special care on the stationarity of the studied system. Stationarity will be controlled automatically by the program as changes of the potential will disturb the current equilibrium. Depending on the selected potential resolution the applied voltage may be changed in intervals. Due to the dE/dt the system will respond by current response signals. Before measuring a new C(E) sample, current stationarity should be ensured.

c) Impedance Spectra Series Measurements

Impedance series measurements demand some settling time after the new regulation variable has been applied. Changes of the control parameter will generally cause some kind of perturbation of the system's steady state. Defining the stabilisation delay sufficiently high will offer new stability of the system before measuring the next impedance spectrum. Depending on the regulating variable steady state parameters of both - DC-mode and AC-mode - may become relevant. The delay for series measurements are defined in the **Series Measurement** page.

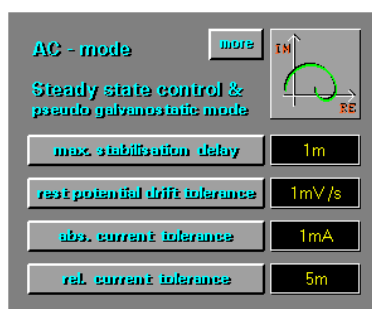
More DC-mode settings can be found by clicking on the  button. An input box will open allowing you to define the following parameters:



Parameter	Range	Default	Description
Start phase slew rate V/s	1m-1	1e-2	Starting ramp phases are introduced automatically, if a method needs potentiostatic control, but the initial state of the potentiostat was off. The start phase slew rate defines the ramp speed. Note: The ramp phase is subject of the global current limit !.
break on overload factor	1 - 10	2	In I/E-DC scans (and also in starting ramp phases) the global current limit may be overdriven within the settling time in a defined way: <i>the break on overload factor</i> defines, how much overload beyond the global current limit is tolerated during settling.
MIE range delay (s)	0 - 10	1	In Multicell-I/E an auto-range triggering may be

			delayed intentionally to prevent excessive ranging events when testing noisy systems.
temp. protocol source	0, 1	1	In procedures under temperature control (for instance EIS spectra series vs. set temperature) there are two choices for the automatic entry of the temperature into the protocol box: 0 means, that the temperature claimed by the controller (usually close to the set-value) is recorded. 1 means, that the temperature from another sensor (usually the real temperature), provided in the signal acquisition VI #0, is recorded.
PMUX installed	0; 1	0	When a RMUX relay scanner is installed, the global current limit is bound to max. $\pm 0.5A$ due to the smaller current capability of the RMUX card channels. When the RMUX is back-upped by the external PMUX, this limitation can be skipped.
FRA voltage-in [V_cell/V_acq]	-1000 - 1000	1	If a FRA module (option) for interfacing an external third-party load is connected, you must set the factor for cell voltage corresponding to a signal input of 1V.
FRA voltage-out [V_cell/V_ctrl]	-1000 - 1000	1	If a FRA module (option) for interfacing an external third-party load is connected, you must set the factor for cell voltage corresponding to a signal output of 1V. (potentiostatic mode)
FRA min.voltage [V_cell]	-1000 - 0	-100	If a FRA module (option) for interfacing an external third-party load is connected, you must set the minimum voltage of the external device.
FRA max.voltage [V_cell]	0 - 1000	0	If a FRA module (option) for interfacing an external third-party load is connected, you must set the maximum voltage of the external device.
FRA current-in [A_cell/V_acq]	-1000 - 1000	-1	If a FRA module (option) for interfacing an external third-party load is connected, you must set the factor for cell current corresponding to a signal input of 1V.
FRA current-out [A_cell/V_ctrl]	-1000 - 1000	-1	If a FRA module (option) for interfacing an external third-party load is connected, you must set the factor for cell current corresponding to a signal output of 1V. (galvanostatic mode)
FRA min-current [A_cell]	-1000 - 0	0	If a FRA module (option) for interfacing an external third-party load is connected, you must set the minimum current of the external device.
FRA max-current [A_cell]	0 - 1000	100	If a FRA module (option) for interfacing an external third-party load is connected, you must set the maximum current of the external device.

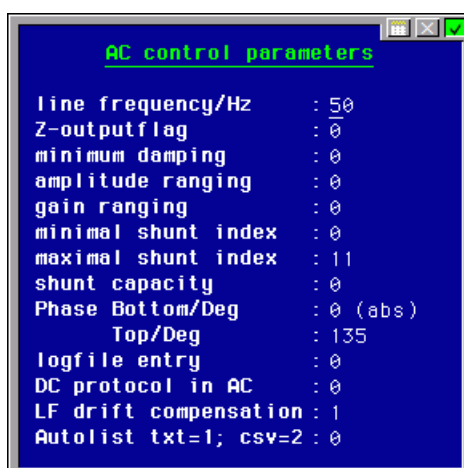
5.4 AC-Mode Parameters



AC-mode steady state control is used for C/E-measurement and for impedance spectra series measurements if the control parameter is the DC-current. Further on, the stability of the rest potential and in the pseudo galvanostatic mode AC stability control will be used. The control parameters are:

max. stabilisation delay 1m	Defines the maximum time (s) the system has to wait for steady state conditions. After the maximum delay time has expired the program continues with the measurement, even if other criteria of stability have not yet been reached. This delay time should be increased for more stringent steady state control.
rest potential drift tolerance 1mV/s	Maximum drift of the rest potential to be considered as sufficient steady state. This parameter is used if a measurement will be performed under control of the rest potential. This tolerance is defined by $dE_{drift} = \frac{E(t) - E(t - dt)}{dt}$ The rest potential drift tolerance is given in units of V/sec.
abs. current tolerance 1mA	Defines the absolute current drift tolerated band for sufficient steady state conditions. $I_{min} = I_{set} - I_{tol}$; $I_{max} = I_{set} + I_{tol}$ The absolute tolerance is given in units of A.
rel. current tolerance 5m	Defines the relative current drift (deviation between current measurements in a time interval of 1s) tolerated for sufficient steady state conditions. $dI_{relative} = \frac{I(t) - I(t - dt)}{I(t - dt)}$

More AC-mode settings can be found by clicking on the **more** button. An input box will open allowing you to define the following parameters:



Parameter	Range	Def.	Description
line frequency/Hz	50; 60 [Hz]	50	Mains line frequency (country-specific). This parameter is used to set a notch filter against mains line interference.
Z-output flag	0; 1	0	If set to "1" this parameter disables the breaking of a measurement after detecting noise in the measurement signal. If set to "0" (default) in case of noise the error message Potentiostatic Loop Interrupted is displayed and the measurement is stopped.
minimum damping	0 - 4	0	Reduce bandwidth of potentiostat. 0 is maximal, 4 is minimal bandwidth.
amplitude ranging	0; 1	0	If enabled the AC amplitude is automatically increased if too less perturbation response signal is detected.
gain ranging	0; 1	0	The automatic gain ranging can be enabled (1) or disabled (0).
minimal shunt index	0 - 11	0	Allows to select a minimum shunt resistance for current measurement and with this a maximum current (low impedance) measurement range. The shunt resistance tables are listed in the appendix. This will encounter also a hardware current limit.
maximal shunt index	0 - 11	11	Allows to select a maximum shunt resistance for current measurement and with this a maximum current sensitivity (high impedance) range. The shunt resistance tables are listed in the appendix.
shunt capacity	0 - +2n	0	Software compensation of the shunt (counter electrode) input capacitance [F] of the potentiostat. It must be set to approximately 50pF/m, if a shielded counter electrode cable is used. It is strongly recommended to avoid shielded counter electrode cables. Instead, a common Faraday cage for instrument and cell should be preferred.
Phase Bottom / Deg		0	Phase Scaling start for Bode representation of EIS spectra
Top / Deg		90	Phase Scaling end for Bode representation of EIS spectra
logfile entry	0 – 7	0	If <i>logfile entry</i> is set, impedance measurements are

	0 1 2 3 4; 6 5; 7		<p>accompanied by automatic logging of additional information in a log-file for diagnostic purposes, optionally visualized in the Z-Trace window.</p> <p>Logging option deactivated</p> <p>Impedance ranges and intermediate results are logged for diagnostic purposes</p> <p>Harmonic content of harmonics 2 to 10 of the actual impedance sample response are stored together with frequency and date time information (amplitudes are normalized to the fundamental), see the format below.</p> <p>Combination of 1 and 2</p> <p>Enhanced THD information consists of harmonic content (2), excitation harmonics and response harmonics. The corresponding noise distortions are only calculated for frequency points below 66 Hz! (see the ASCII data format below)</p> <p>Visualized in the Z-Trace window and appended as THD tables to the ASCII formatted EIS data file. This files can be created automatically with the Autolist function (see bottom of this table).</p> <p>Combination of 1 and 4</p>
DC protocol in AC	0; 1	0	If <i>DC protocol in AC</i> is enabled (1), DC parameters are measured at each frequency point and logged as additional data rows to the measurement file.
LF drift compensation	0; 1	1	<i>LF drift compensation</i> is enabled (1) by default to use automatic drift compensation in the low frequency range (<2 Hz). Disable <i>LF drift compensation</i> only for demonstration (not recommended)
Autolist txt=1; csv=2	0-2 0 1 2	0	<p>Select Autolist to save binary and ASCII data files automatically (same folder and filename).</p> <p>EIS data is only saved in binary format *.ism</p> <p>EIS data is saved in binary format *.ism and ASCII formatted text file *.txt</p> <p>EIS data is saved in binary format *.ism and ASCII character separated value file *.csv</p>

Please refer to the appendix for a list of the shunt resistors used in the electrochemical workstation and in the external potentiostats.

The harmonic content data protocol is created, when **logfile entry** is set to the value 2, see above. The harmonics are pre-processed in a way, that they can be used directly for second harmonic analysis or for harmonic distortion analysis. One line is created for every impedance sample, starting with a time stamp of the format YYMMDDHHMMSS (Year, Month, Day, Hour, Minute, Second) and followed by the measuring frequency in Hz. Then a list of nine harmonics in ascending order follows. The order one (fundamental) could be omitted, because the harmonic amplitudes are already normalized to a value of one for the fundamental. The data set is always calculated from the response function. This means, that in potentiostatic mode the list of current harmonics is created, in galvanostatic mode it is the list of voltage harmonics. The harmonic content, eventually present already in the force function (usually close to zero) is already compensated in the response function. If the absolute value of the response fundamental is needed, one can calculate it from the force amplitude and the actual impedance modulus by:

$$A_{r1} = \frac{A_f}{|Z|} \text{ in potentiostatic mode, } A_{r1} = A_f \cdot |Z| \text{ in galvanostatic mode.}$$

Example: Autosave ASCII EIS data with enhanced THD information (logfile entry = 4-7; Autolist = 1)

File.....: - JUN,25,2015
System.....
Potential...: 0.000V
Current.....: -1.7438mA
Temperature: -0.8+-0.0C
Time.....: 14:05:26 - 14:06:42
Comment.....

(area/cm²):

Impedance samples

Lines: 18
Columns: 5

Number	Frequency/Hz	impedance/Ohm	Phase/deg	Significance	Time/s
1	1.0000e+02	1.3580e-04	13.31	0.992	0.0
2	7.9621e+01	1.3637e-04	11.71	0.995	2.5
3	6.3246e+01	1.3432e-04	9.32	0.994	4.2
4	5.0238e+01	1.3308e-04	7.27	0.999	6.0
5	3.9905e+01	1.3358e-04	5.09	0.998	7.9
6	3.1698e+01	1.3390e-04	4.14	0.994	9.9
7	2.5179e+01	1.3524e-04	4.09	0.998	12.1
8	2.0000e+01	1.3231e-04	2.90	0.997	14.4
9	1.5887e+01	1.3193e-04	1.83	0.999	17.0
10	1.2619e+01	1.3331e-04	2.10	0.998	19.9
11	1.0024e+01	1.3229e-04	1.31	0.999	23.1
12	7.9621e+00	1.3345e-04	0.96	0.996	26.8
13	6.3246e+00	1.3161e-04	0.45	0.999	31.5
14	5.0238e+00	1.3187e-04	1.02	0.999	36.4
15	3.9905e+00	1.3142e-04	0.20	0.995	42.1
16	3.1698e+00	1.3347e-04	0.81	0.996	48.8
17	2.5179e+00	1.3261e-04	-0.05	0.994	56.6
18	2.0000e+00	1.3265e-04	0.90	0.999	65.9

EIS data

THD-data:

data:	normalized	frq:	1.0e+2	harm:	1.56e-2	1.12e-2	5.82e-3	7.57e-3	9.78e-4	4.86e-3	1.52e-3	3.9e-3	3.49e-3	noise:	1.07e-1
data:	normalized	frq:	7.96e+1	harm:	8.58e-3	9.73e-3	8.68e-3	5.58e-3	3.33e-3	8.73e-4	4.6e-3	4.48e-3	2.58e-3	noise:	1.2e-1
data:	normalized	frq:	6.32e+1	harm:	1.23e-2	6.09e-3	4.19e-3	1.16e-3	6.66e-3	2.77e-3	8.92e-4	1.27e-3	1.76e-3	noise:	1.09e-1
data:	normalized	frq:	5.02e+1	harm:	9.6e-4	1.9e-3	5.37e-3	2.4e-3	1.29e-3	8.08e-4	7.18e-4	3.14e-3	3.01e-3	noise:	1.37e-1
data:	normalized	frq:	3.99e+1	harm:	4.94e-3	2.86e-3	3.1e-3	2.05e-3	2.64e-3	2.27e-3	6.24e-3	3.0e-3	3.74e-3	noise:	1.14e-1
data:	normalized	frq:	3.17e+1	harm:	1.5e-2	3.16e-3	9.96e-3	3.92e-3	4.04e-3	3.78e-3	2.55e-3	6.75e-4	3.03e-3	noise:	1.86e-1
data:	normalized	frq:	2.52e+1	harm:	3.94e-3	4.32e-3	3.66e-3	7.25e-3	4.23e-3	2.54e-3	1.64e-3	3.18e-3	4.51e-4	noise:	1.08e-1
data:	normalized	frq:	2.0e+1	harm:	5.87e-3	2.18e-3	2.27e-3	1.02e-3	3.66e-3	3.03e-3	3.25e-3	1.24e-3	3.24e-3	noise:	4.15e-2
data:	normalized	frq:	1.59e+1	harm:	1.48e-3	1.06e-3	7.16e-3	4.22e-3	2.09e-3	4.11e-3	1.34e-3	3.36e-3	4.69e-3	noise:	1.37e-3
data:	normalized	frq:	1.26e+1	harm:	2.99e-3	5.2e-3	7.46e-3	2.2e-3	5.28e-3	1.88e-3	4.17e-3	3.08e-3	1.82e-3	noise:	2.07e-2
data:	normalized	frq:	1.0e+1	harm:	8.76e-4	6.08e-3	7.01e-4	4.24e-3	1.21e-3	2.78e-3	2.3e-3	2.56e-3	5.06e-3	noise:	8.31e-4
data:	normalized	frq:	7.96e+0	harm:	5.19e-3	1.04e-2	6.38e-3	8.05e-3	4.56e-3	5.55e-3	1.68e-3	2.61e-3	2.75e-3	noise:	5.98e-4
data:	normalized	frq:	6.32e+0	harm:	1.36e-3	2.5e-3	2.27e-3	5.66e-3	3.63e-3	2.93e-3	7.18e-4	4.86e-3	1.85e-3	noise:	1.5e-3
data:	normalized	frq:	5.02e+0	harm:	4.25e-4	2.1e-3	2.19e-3	2.06e-3	3.07e-3	7.24e-4	2.92e-3	2.62e-3	3.14e-3	noise:	6.75e-4
data:	normalized	frq:	3.99e+0	harm:	9.58e-3	7.1e-3	5.04e-3	2.85e-3	2.59e-3	2.1e-3	2.34e-3	2.97e-3	1.42e-3	noise:	6.51e-4
data:	normalized	frq:	3.17e+0	harm:	7.01e-3	9.75e-3	1.72e-3	3.66e-3	6.22e-3	3.15e-3	1.25e-3	1.13e-3	6.34e-4	noise:	2.32e-1
data:	normalized	frq:	2.52e+0	harm:	1.34e-2	5.12e-3	3.54e-3	1.57e-3	4.42e-3	2.43e-3	6.8e-4	2.3e-3	2.21e-3	noise:	2.89e-2
data:	normalized	frq:	2.0e+0	harm:	1.48e-3	1.87e-3	6.9e-3	1.62e-3	5.08e-3	1.7e-3	4.89e-3	3.33e-3	1.5e-3	noise:	6.82e-4

Pre-processed harmonics
(logfile entry = 2)

data:	excit	frq:	1.0e+2	harm:	1.56e-3	5.22e-4	2.62e-5	2.94e-4	3.34e-5	5.55e-5	2.29e-5	2.44e-5	7.35e-6	noise:	3.99e-5
data:	excit	frq:	7.96e+1	harm:	1.54e-3	6.89e-4	3.75e-5	3.26e-4	2.54e-5	7.86e-5	3.05e-5	1.94e-5	2.76e-5	noise:	3.68e-5
data:	excit	frq:	6.32e+1	harm:	1.64e-3	7.47e-4	4.36e-5	3.81e-4	3.37e-5	1.31e-4	2.19e-5	3.36e-5	2.48e-5	noise:	3.37e-5
data:	excit	frq:	5.02e+1	harm:	1.67e-3	7.88e-4	5.61e-5	3.79e-4	4.25e-5	1.12e-4	1.77e-5	3.63e-5	2.4e-5	noise:	2.48e-5
data:	excit	frq:	3.99e+1	harm:	1.65e-3	8.48e-4	8.26e-5	4.44e-4	8.62e-6	1.42e-4	2.63e-5	3.58e-5	4.84e-5	noise:	3.51e-5
data:	excit	frq:	3.17e+1	harm:	1.68e-3	9.11e-4	5.16e-5	4.98e-4	2.51e-5	1.86e-4	4.37e-5	5.27e-5	2.87e-5	noise:	2.18e-5
data:	excit	frq:	2.52e+1	harm:	1.65e-3	5.93e-4	6.51e-5	2.37e-4	3.48e-5	7.22e-5	1.05e-5	2.68e-5	1.53e-5	noise:	2.5e-5
data:	excit	frq:	2.0e+1	harm:	1.59e-3	7.24e-4	4.29e-5	3.51e-4	2.87e-5	9.32e-5	3.63e-5	3.27e-5	7.37e-6	noise:	1.12e-5
data:	excit	frq:	1.59e+1	harm:	1.61e-3	8.32e-4	6.39e-5	3.84e-4	3.31e-5	9.89e-5	1.88e-5	2.8e-5	5.15e-5	noise:	5.5e-5
data:	excit	frq:	1.26e+1	harm:	1.63e-3	7.98e-4	3.77e-5	3.46e-4	3.28e-5	1.11e-4	2.17e-5	2.47e-5	1.78e-5	noise:	3.4e-6
data:	excit	frq:	1.0e+1	harm:	1.63e-3	8.7e-4	4.54e-5	4.33e-4	3.84e-6	1.25e-4	2.16e-5	5.11e-5	8.12e-5	noise:	2.06e-6
data:	excit	frq:	7.96e+0	harm:	1.69e-3	9.4e-4	2.97e-5	4.56e-4	3.08e-5	1.63e-4	3.43e-5	5.04e-5	4.92e-5	noise:	2.41e-6
data:	excit	frq:	6.32e+0	harm:	1.02e-3	1.62e-3	2.15e-4	6.53e-4	5.68e-5	2.63e-4	2.61e-5	1.15e-4	1.62e-5	noise:	4.21e-6
data:	excit	frq:	5.02e+0	harm:	1.22e-3	1.44e-3	2.14e-4	5.45e-4	4.65e-5	2.27e-4	3.14e-5	1.26e-4	2.86e-5	noise:	1.67e-6
data:	excit	frq:	3.99e+0	harm:	1.31e-3	1.3e-3	1.83e-4	4.1e-4	4.03e-5	1.96e-4	2.13e-5	1.21e-4	3.96e-5	noise:	1.43e-6
data:	excit	frq:	3.17e+0	harm:	1.35e-3	1.12e-3	1.51e-4	2.31e-4	1.35e-5	1.02e-4	7.45e-6	5.61e-5	2.33e-5	noise:	2.01e-6
data:	excit	frq:	2.52e+0	harm:	1.4e-3	1.13e-3	1.31e-4	2.18e-4	1.83e-5	9.5e-5	1.82e-5	5.82e-5	3.28e-5	noise:	1.99e-6
data:	excit	frq:	2.0e+0	harm:	1.49e-3	1.14e-3	1.21e-4	2.34e-4	2.7e-5	1.01e-4	1.77e-5	5.27e-5	4.07e-5	noise:	1.4e-6

Raw excitation harmonics
(normalized to fundamental)

data:	response	frq:	1.0e+2	harm:	1.71e-2	1.17e-2	5.85e-3	7.87e-3	1.01e-3	4.92e-3	1.54e-3	3.92e-3	3.49e-3	noise:	1.07e-1
data:	response	frq:	7.96e+1	harm:	1.01e-2	1.04e-2	8.71e-3	5.91e-3	3.36e-3	9.52e-4	4.63e-3	4.5e-3	2.61e-3	noise:	1.2e-1
data:	response	frq:	6.32e+1	harm:	1.39e-2	6.83e-3	4.23e-3	1.54e-3	6.69e-3	2.9e-3	9.14e-4	1.31e-3	1.78e-3	noise:	1.09e-1
data:	response	frq:	5.02e+1	harm:	2.63e-3	2.69e-3	5.43e-3	2.78e-3	1.33e-3	9.2e-4	7.36e-4	3.18e-3	3.03e-3	noise:	1.37e-1
data:	response	frq:	3.99e+1	harm:	6.58e-3	3.71e-3	3.18e-3	2.49e-3	2.65e-3	1.19e-4	6.27e-3	3.04e-3	3.79e-3	noise:	1.14e-1
data:	response	frq:	3.17e+1	harm:	1.66e-2	4.07e-3	1.0e-2	4.42e-3	4.07e-3	3.96e-3	2.59e-3	7.28e-4	3.05e-3	noise:	1.86e-1
data:	response	frq:	2.52e+1	harm:	5.59e-3	4.92e-3	3.72e-3	7.48e-3	4.26e-3	2.61e-3	1.66e-3	3.2e-3	4.66e-4	noise:	1.08e-1
data:	response	frq:	2.0e+1	harm:	7.46e-3	2.9e-3	2.32e-3	1.05e-2	3.69e-3	3.13e-3	3.28e-3	1.28e-3	3.25e-3	noise:	4.15e-2
data:	response	frq:	1.59e+1	harm:	3.09e-3	1.9e-3	7.22e-3	4.61e-3	2.13e-3	4.21e-3	1.36e-3	3.39e-3	4.74e-3	noise:	1.37e-3
data:	response	frq:	1.26e+1	harm:	4.62e-3	6.0e-3	7.49e-3	2.55e-3	5.32e-3	1.99e-3	4.19e-3	3.11e-3	1.83e-3	noise:	2.07e-2
data:	response	frq:	1.0e+1	harm:	2.5e-3	6.95e-3	7.47e-4	4.68e-3	1.22e-3	2.9e-3	2.32e-3	2.61e-3	5.14e-3	noise:	8.31e-4
data:	response	frq:	7.96e+0	harm:	6.88e-3	1.14e-2	6.41e-3	8.51e-3	4.59e-3	5.71e-3	1.72e-3	2.66e-3	2.8e-3	noise:	5.98e-4
data:	response	frq:	6.32e+0	harm:	2.39e-3	4.12e-3	2.48e-3	6.32e-3	3.69e-3	3.19e-3	7.44e-4	4.97e-3	1.87e-3	noise:	1.5e-3
data:	response	frq:	5.02e+0	harm:	7.92e-4	3.54e-3	2.4e-3	2.61e-3	3.12e-3	9.51e-4	2.95e-3	2.75e-3	3.17e-3	noise:	6.75e-4
data:	response	frq:	3.99e+0	harm:	1.09e-2	8.41e-3	5.23e-3	3.26e-3	2.63e-3	2.29e-3	2.36e-3	3.09e-3	1.46e-3	noise:	6.51e-4
data:	response	frq:	3.17e+0	harm:	8.36e-3	1.09e-2	1.87e-3	3.89e-3	6.24e-3	3.25e-3	1.26e-3	1.18e-3	6.57e-4	noise:	2.32e-1
data:	response	frq:	2.52e+0	harm:	1.48e-2	6.25e-3	3.67e-3	1.78e-3	4.43e-3	2.53e-3	6.98e-4	2.36e-3	2.24e-3	noise:	2.89e-2
data:	response	frq:	2.0e+0	harm:	2.97e-3	3.01e-3	7.02e-3	1.86e-3	5.11e-3	1.8e-3	4.91e-3	3.38e-3	1.54e-3	noise:	6.82e-4

Raw response harmonics
(normalized to fundamental)



Noise distortion is only calculated for frequency points below 66 Hz.
For higher frequencies the noise values are not applicable.

6. Calibration

The basic calibration of the electrochemical workstations can only be done at ZAHNER-elektrik company because high-precision resistors, high-precision instruments and a special software are needed. The result of this basic calibration are the calibration files shipped with the instruments on a separate disk. For a maximum accuracy of the system it is needed to copy the calibration data to the hard drive of your computer as described in chapter [Installation & Getting Started](#) of this manual.

6.1 Automatic Calibration

Always after a cold-start of an electrochemical workstation, a single calibration cycle is performed automatically as soon as you enter a measurement module of the *THALES* software. You can realize this procedure by the clicking of relays on start up. This type of calibration is done using internal precision resistors. The cell is disconnected from the electronics during this procedure. It is needed for re-adjusting the offset and the gain factors of the AD-converters, amplifiers i.e. and it is accompanied by a system hardware self-test.

The automatic and the manual calibration routines are able to detect hardware failures if the calibration parameters trespass a defined tolerance range. If a hardware failure is observed you are asked to enter the Text Editor **Zedit**. There you find a list of the most important calibration parameters. Copy the list and send it to the ZAHNER service centre in Kronach, Germany, directly (email: support@zahner.de). More detailed information can be found in the chapter "diagnostics and trouble shooting".

6.2 Manual Calibration



In addition, different types of calibration can be performed also manually by the user by clicking on the "Calibration" icon. In the simplest case the initial start up calibration is repeated.

6.2.1 IM6 / Zennium / Zennium E

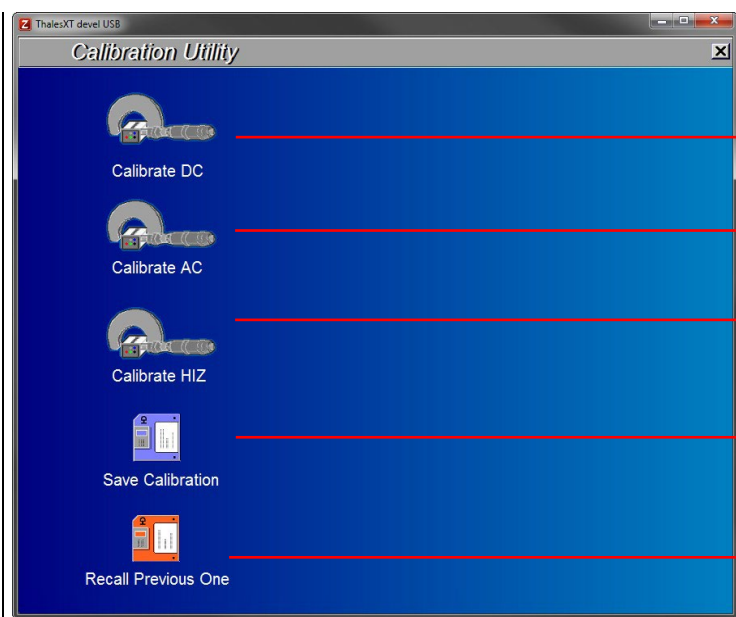
Pressing the **[p]**-key on the keyboard at the beginning of the calibration causes the software to enter additional diagnostics and copy the diagnostic- and calibration results to the internal Text Editor **ZEdit**.

Pressing the **[s]**-key on the keyboard at the beginning of the calibration causes the software to enter a more time consuming routine (several minutes) which covers also AC calibration. The new calibration data will be saved after the calibration is finished. Please keep in mind that the old calibration data are overwritten in this case. This calibration is also performed if the system cannot find a valid set of calibration data in the PC storage.

A manual recalibration of the spectrometer should be done under one of the following circumstances:

1. The machine has been started at a very low ambient temperature of the laboratory. In this case some of the potentiostat's and of the amplifier's components might show some kind of temperature drift. Wait for about a quarter of an hour and recalibrate the spectrometer.
2. The machine will be run continuously over days and weeks. Under these circumstances time dependent drifts may occur. Thus, before starting a new series of measurements or at the beginning of a new laboratory day execute a recalibration.

6.2.2 Zennium pro / Zennium X



The screenshot shows the 'Calibration Utility' window with a blue background and five icons. Red arrows point from each icon to a descriptive text block on the right.

- Calibrate DC**: Calibrates DC offsets and gains (takes about 100 seconds)
- Calibrate AC**: Calibrates AC signal paths (takes about 8 minutes)
- Calibrate HIZ**: Calibrates DC input for high ohmic measurements (takes about 2 minutes)
- Save Calibration**: Saves DC and AC calibration values to `C:\Thales\hardware\im6\sernum\calidatx.bin`
- Recall Previous One**: Load calibration values from selected file

! When performing HIZ calibration set device to grounded mode, connect inputs as short as possible (CE to RE and WE to WEsense) and shield potentiostat frontend wires.



7. EIS Measurement

Doing EIS measurements means to do a set of single impedance measurements at different **AC** frequencies. The *THALES* software sweeps through a frequency range in defined steps and in a defined direction (from high to low frequencies and/or vice versa). The impedance data at each step are recorded. Usually, during the measurement sweep, the **DC voltage** or the **DC current** are held constant at a defined level by the potentiostat/galvanostat. Differing from that, measurements done in the “pseudo open circuit mode” the **DC voltage** set value depends on the actual **OCP** of the sample under test.

A basic prerequisite of EIS is that the sample is sufficiently stable during the recording time of the spectrum. Otherwise, the frequency sample points of a measurement scan will not fit to each other, because they belong to different states of the tested system. How to detect and treat time drift and other instabilities is described later. In the single sine mode at least one full period of the actual frequency will be applied without recording. This “pre-wave” is used to control the auto-ranging and helps to get the system settled before the impedance point is recorded by the following cycles. It is recommended to use more than one **measure periods**. Following the pre-wave, this number of periods is measured and averaged. The result is displayed, then stored in the RAM memory of the instrument and the software goes to the next point. Because period-time increases with decreasing frequency, the time required for measuring one point increases in the same way. E.g. one period of a 1 mHz sine wave takes 1000 s = 16.7 minutes. Together with the pre-wave, a 1mHz sample runs for at least half an hour.

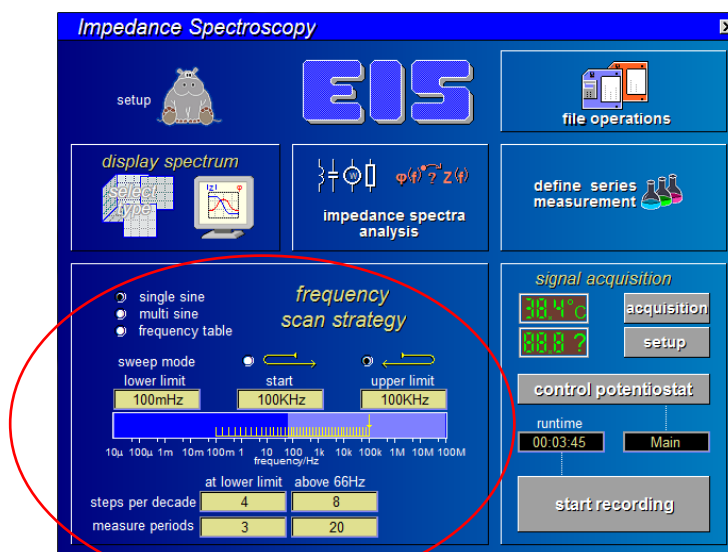
The user should be aware, that from physics there is a close relationship between information density on the one hand and invested measurement time on the other hand – simply spoken: the shorter the measurement time the less is the measurement accuracy.

One should consider this, when setting frequency scan parameters or when deciding for a certain frequency scan strategy.

A couple of the recording parameters effective as well for an EIS spectrum are set on the **Control Potentiostat page**. These are:

- DC set voltage/current
- Potentiostat feedback control mode
- Potentiostat on/off state on start
- AC perturbation amplitude
- Active potentiostat device #

All these parameters were already discussed earlier.



The spectra recording parameters are set on **EIS main page**.

7.1 Frequency Scan Strategy

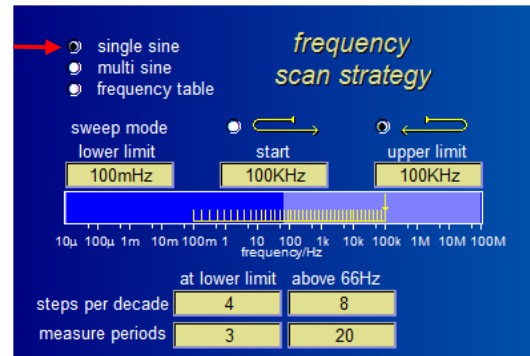
The frequency scan strategy decides, which measurement accuracy can be achieved for which expenditure of time:

7.1.1 Single Sine

In the single sine mode, the maximum accuracy of the impedance data is achieved. The single sine mode is therefore the recommended scan strategy for high quality impedance spectra. The Zahner measurement principle of “monochromatic excitation combined with polychromatic analysis” uses the fundamental wave for the impedance analysis, while using the harmonic content for an accurate error estimation.

When selecting the single sine scan strategy, all frequency scan parameters can be adjusted freely, what is explained in detail in the following chapters.

It is recommended to set the minimum periods count to 2 or higher at the low frequency limit. This enables the outstanding proprietary features of *THALES* like real time drift correction and real time measurement accuracy estimation covering the complete frequency scan. These features are described in detail in the chapter 7.10 [Advanced Features](#).

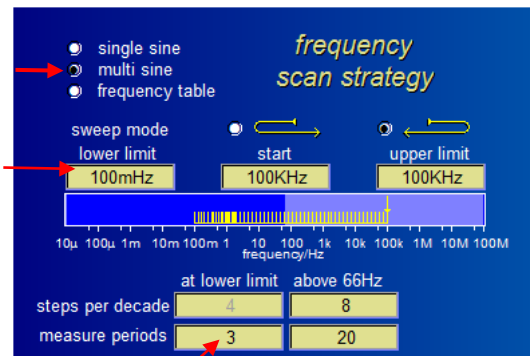


7.1.2 Intelligent Multi Sine (*iMS*)

The *iMS* (intelligent multi sine) feature applies an optimized excitation signal combining a set of sine waves with different frequencies, thus minimizing the accuracy disadvantages of this method significantly. Depending of the settings, *iMS* can reduce the measurement time by a factor of about two to three.

iMS is available from a frequency limit of 100mHz and below. The affected frequency range is from lower limit to a 20 times higher frequency.

Due to optimized amplitude processing and oversampling Zahners unique features like real-time drift compensation and error calculation are available in a restricted version also for *iMS* providing an excellent quality compared to standard multisine. These features are described in detail in the chapter 7.10 [Advanced Features](#).



Measure period count effect on the quality of *iMS*:

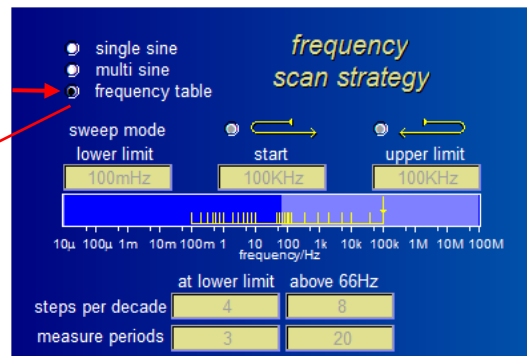
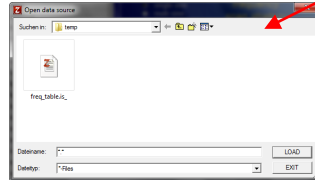
measure period	≥ 3	2	1
available from lower frequency limit [Hz]	≤ 100m	≤ 66m	≤ 33m
real-time drift compensation	fully	fully	fully
error calculation	fully	partially	partially

7.1.3 Frequency Table

Special measurement tasks may require direct control of the measurement frequencies and periods. For this you can simply load a user defined set of frequency/periods values (separated by white spaces).

for example:

2500	100
5.76e+2	20
74.5	5
13	2
1.15e-2	1



7.2 Sweep Mode

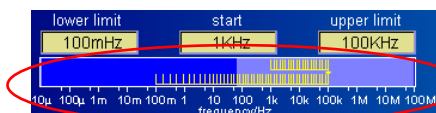
A recommended method is to start at a middle frequency (i.e. 1 kHz), sweep up to the highest frequency and turn around to sweep down to the lowest frequency of the defined range. Consequently, time-drift effects and noise can be easily identified if the samples from the scanning downwards do not match with the samples from scanning upwards. In this case, the spectrum can be stopped manually, before too much time is lost for a non-significant measurement.

Generally, the software averages the data recorded upward and downward at the same frequency. This offers the possibility to compensate the influence of time-drift to a certain degree, as long as the drift is not too excessive. Therefore, an also useful method to compensate a moderate time-drift is, to start at the highest frequency, sweep down to the lowest frequency, turn around and sweep to the highest frequency again. This way the complete scan is averaged.

Starting at low frequencies is not recommended in general, because this proceeding is in-efficient regarding settling time minimization.



Here you decide whether first the sweep runs upwards and then downwards or vice versa.



start sets the frequency where the sweep will start.
upper limit sets the highest frequency of the sweep.
lower limit sets the lowest frequency of the sweep.

The frequency sweep and the measurement points are displayed graphically for an overview.

Frequency ranges:

upper limit \geq start \geq lower limit

upper system limit (ZENNIUM X: 12 MHz, ZENNIUM pro: 8 MHz, ZENNIUM: 4 MHz, ZENNIUM E: 2 MHz) \geq upper limit $>$ lower limit

upper limit $>$ lower limit \geq 10 μ Hz

If you do not want a part of the frequency region to be covered twice, set the **start** frequency equal to the **upper limit** and select the second **sweep mode**. Then the system sweeps from the **upper limit** to the **lower limit**. If you really want to sweep from the **lower limit** to the **upper limit**, set the **start** frequency equal to the **lower limit** and select the first **sweep mode**.

7.3 Steps per Decade

	at lower limit	above 66Hz
steps per decade	4	10
measure periods	4	20

This parameter defines how much measurement points are to be recorded in each decade of the frequency range. You may set a different number of points per decade for the frequency region below 66 Hz (**at lower limit**) and **above 66 Hz**. The default setting is 4 points per decade below and 10 points per decade above 66 Hz.

What is the reason for the splitting at 66Hz? Below 66Hz the measuring time will become dominant, while it is nearly constant within a decade above 66Hz where the time for data treatment is dominant. Thus, splitting into two regions offers the possibility to optimise the two factors resolution over measuring time and accuracy over measuring time.

7.4 Measure Periods

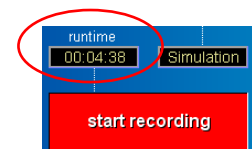
	at lower limit	above 66Hz
steps per decade	4	10
measure periods	4	20

This parameter defines how many sine cycles are to be averaged for one measurement point. The function is identical to the parameter **Count** in the **Control Potentiostat** page and overwrites it in the case of an EIS measurement. Like with the **Steps per Decade** you are free to set the values independently for frequencies below and above 66 Hz.



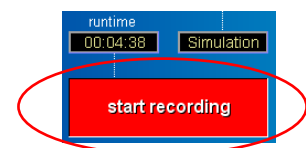
It is recommended to set the minimum periods count to 2 or higher at the low frequency limit. This enables the outstanding proprietary features of **THALES** like real time drift correction and real time measurement accuracy estimation covering the complete frequency scan. These features are described in detail in the chapter 7.10 [Advanced Features](#).

7.5 Runtime



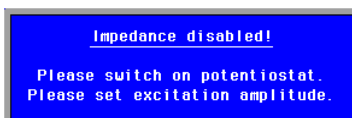
The **runtime** box gives you an estimation of the time the measurement will take. Depending on the measurement object deviations of the real runtime may occur.

7.6 Start Recording



Now you may start the measurement by click on the **start recording** button.

If you forgot to set an AC amplitude, it is not possible to carry out an EIS measurement. The system will display the following message box ...



... and will jump to the **Control Potentiostat** page where you can enter these settings.

7.7 Quick Guide

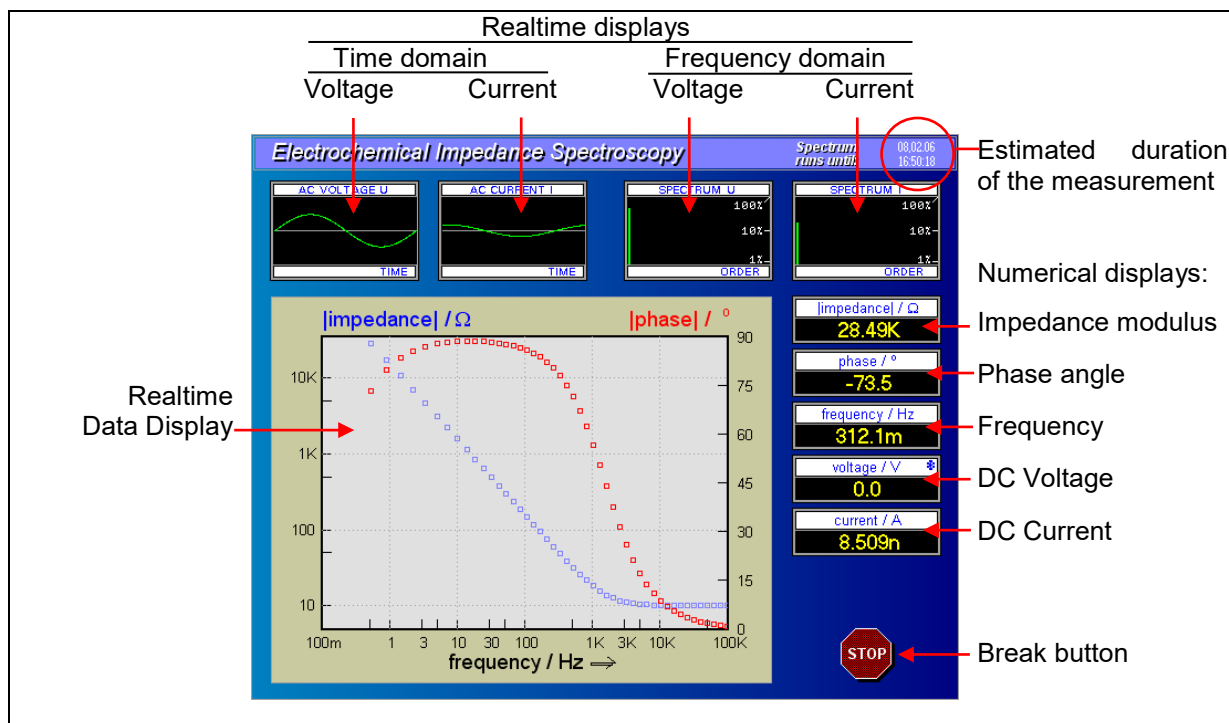
Here again in a short form the recommended **steps for setting up an EIS spectrum**. Follow this scheme, if you deal with a new object for the first time:

step	function	page
1.	Be sure, the potentiostat is switched off.	Control Potentiostat
2.	Switch off the AC amplitude.	Control Potentiostat
3.	Select the connection scheme you are working with.	Check Connections
4.	Connect your cell / sample to the instrument.	Cell
5.	Check whether the OCP is in the range you suggested.	Control Potentiostat
	If the <i>DC Set Voltage</i> field is still empty, proceed.	
5.	Otherwise use the OCP read out as set voltage. Be careful regarding the OCP sign and magnitude!	Control Potentiostat
7.	Switch on the potentiostat and check whether the current is in the expected range minimal.	Control Potentiostat
8.	Set the DC potential, if you intend to leave the <i>OCP</i> conditions.	Control Potentiostat
9.	Set the AC amplitude.	Control Potentiostat
10.	Check by the values displayed if the EIS measurement is o.k.	Control Potentiostat
	If you want to change the spectral default values:	
11.	Change the sweep mode.	EIS main page
12.	Change the start frequency and the upper and lower limit.	EIS main page
13.	Change the steps per decade for below and above 66 Hz.	EIS main page
14.	Change the measure periods for below and above 66 Hz.	EIS main page
15.	Check the duration of the EIS recording.	EIS main page
16.	Start the recording.	EIS main page


Because of all control parameters adjusted differently can be stored as default, in the case of repetitive measurements or measurements on well known objects, you may start with step 1 and directly go to step 16.

7.8 Recording Page

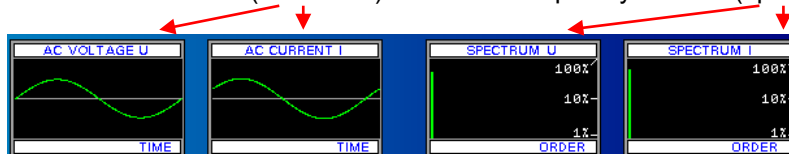
During recording, the **EIS Recording** page will be displayed:



During an EIS spectrum is being recorded you have a lot of real-time displays which provide a perfect overview of all important measurement parameters and data. Graphical and numerical displays let you decide any time whether the measurement is o.k. or whether it is bad (e.g. disturbed or not stable).

You may break the measurement any time by clicking on the  button. The software will complete the recent measurement point and then **break** the measurement. In that case the measurement cannot be continued. If you only want to **pause** the measurement, simply place the cursor on top of the STOP icon. You may continue by removing the cursor to a different area.

Same as in the **Control Potentiostat** page, four real-time displays are showing the AC voltage and the current signals in the time domain (waveform) and in the frequency domain (spectrum).



These displays are very useful for detecting disturbances of the measurement signals very easily. The AC voltage at the output of the instrument (*test electrode* and *counter electrode*) is a pure single-frequency sine signal. This should be shown in the AC VOLTAGE TIME DOMAIN display. This single frequency should also be dominating in the **AC Voltage Frequency Domain** display. There may be small side lines, but best is having only one line at the frequency selected. Accordingly, the AC current should be as close as possible to a single-frequency sine form and the frequency display should show only one line or only small side lines.

If you encounter disturbances in the signals, make sure that for high-impedance measurements you have a good shielding of your object/cell. The shielding has to be grounded at the **GND** banana connector at the backside of the electrochemical workstation. For very high impedances use the

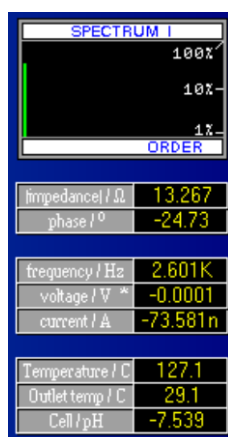
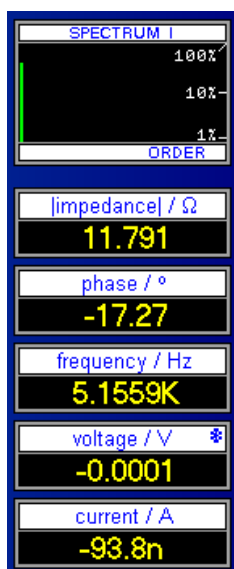
optional *HiZ Probe Set* which you position as close to the object/cell as possible. For low-impedance measurements use cables as short as possible. For very low impedances use the *LoZ Cable Set* (option) which also should be as short as possible.



The real time EIS display is used also in applications, where the object of the transfer function is not a two-pole impedance, i.e. in CIMPS or MPTF measurement (discussed in individual manuals). In that cases the meaning as well as the labelling of the displays are different and will be adapted concerning the different method.



The ZAHNER-elektrik electrochemical workstations are working on the base of the most accurate strategy: A monochromatic excitation is used in combination with a multi-spectral response analysis. This enables outstanding features like real-time drift correction and a real-time estimation of the accuracy. All these features are described in detail in the chapter 7.10 [Advanced Features](#).

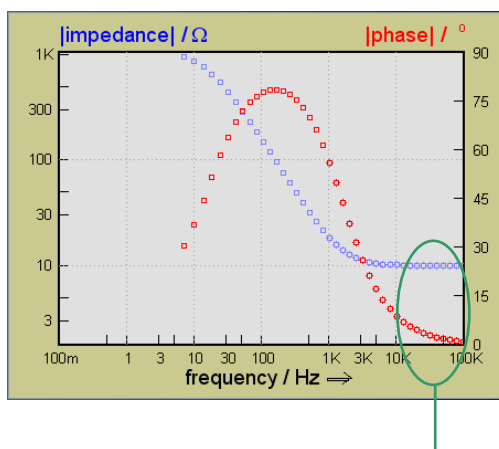


Besides, you have an overview of the recent measurement data in numerical displays:

Impedance modulus, phase angle, frequency, DC voltage and DC current of the recent measurement point are displayed.

Please note, that the display is supplemented by the additional channels defined for recording in the **data acquisition** page, if the *logging option* is active. In this case, the shape of the displays is changed to smaller characters. For details please refer to the **Data Acquisition & Control** manual.

In the real-time graph the measured data are displayed in the form you defined in the **EIS-Setup** page with **Default on-line Display**. Our example shows a Bode-Plot.



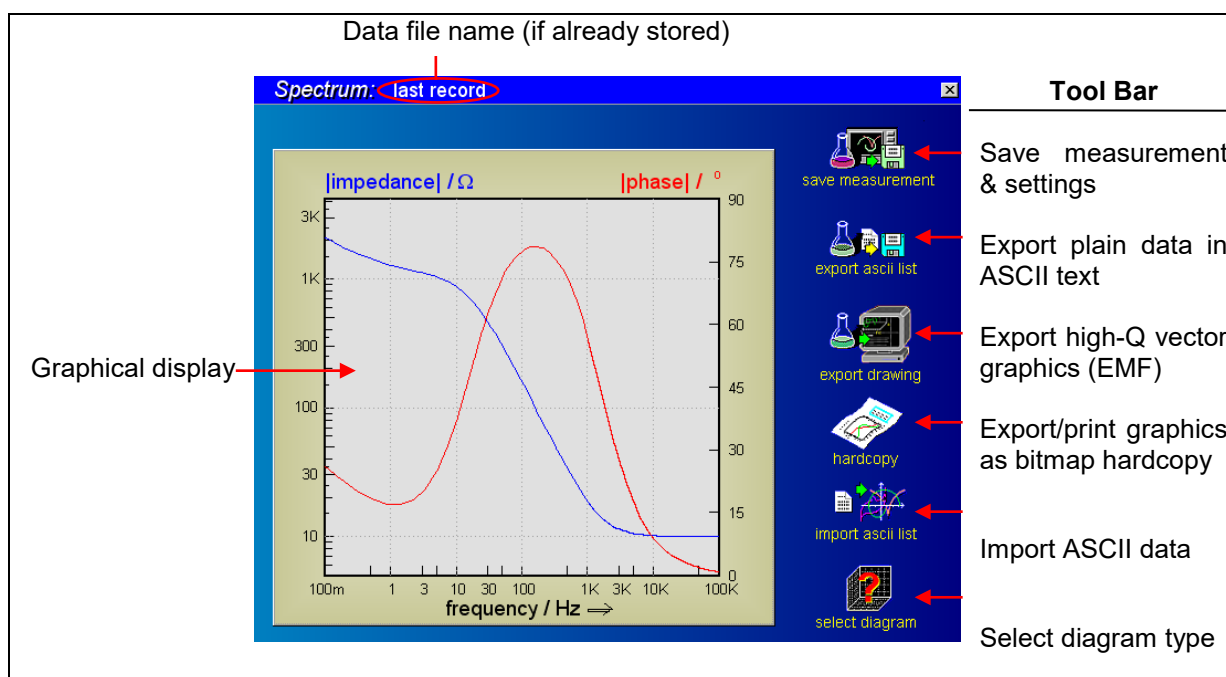
If you selected the start frequency not equal to the lower or upper limit, a part of the EIS spectrum is measured twice. If the upward and the downward curves in this area match you did not have a time effect (sample stable). If both curves differ, the sample is not stable over time.

Please keep in mind that the lower the frequency the longer the measurement time. Measuring e.g. one point at 1 mHz with a count of 4 periods per point takes more than one hour. So, it is advisable to measure only down to the frequencies you really need.

Prior to an impedance measurement the impedance range to be covered is estimated by the software. During the measurement, however, measured data may leave the estimated range. If the **auto rescale** option is enabled the graph scaling is updated each time the data are running out of the limits.

7.9 Display Spectrum

As soon as the recording of the EIS spectrum is completed, the display will change to the following screen:

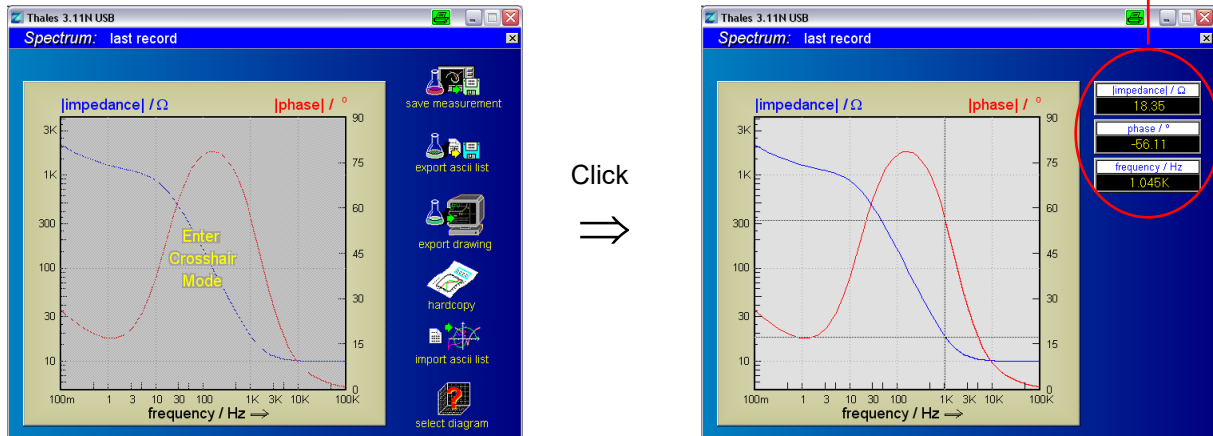


Here you may

- analyse the curve using a pair of cursors
- save the measurement data
- export the data as an ASCII list
- transfer the graph to the **THALES CAD** software
- export or send the graphics to a printer
- select a different diagram type
- import a list of ASCII data.

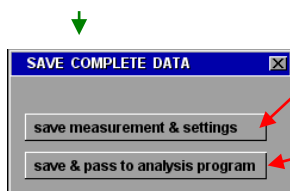
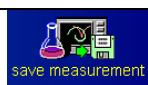
7.9.1 Crosshair Mode

For analysing the curves with a crosshair simply click on the graph. Two cursors will appear, each following the course of one curve (e.g. impedance and phase). The crosshair values are displayed at the right hand side of the spectrum window (e.g. impedance, phase, frequency).



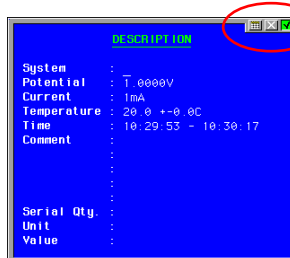
The cursors will follow the movements of the mouse and the cursor left/right buttons of the keyboard. To leave the crosshair mode click the **middle mouse button** or press the **ESC** key on the keyboard.

7.9.2 Save Measurement



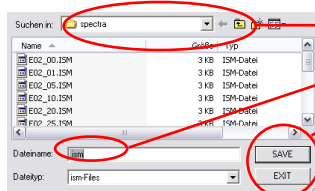
Save the recorded data + the measurement parameters + the comments to the hard disk and return to the *EIS* page.

Save the recorded data + the measurement parameters + the comments to hard disk and pass them directly to the *SIM* software for analysis. You will end up in the *SIM* page.



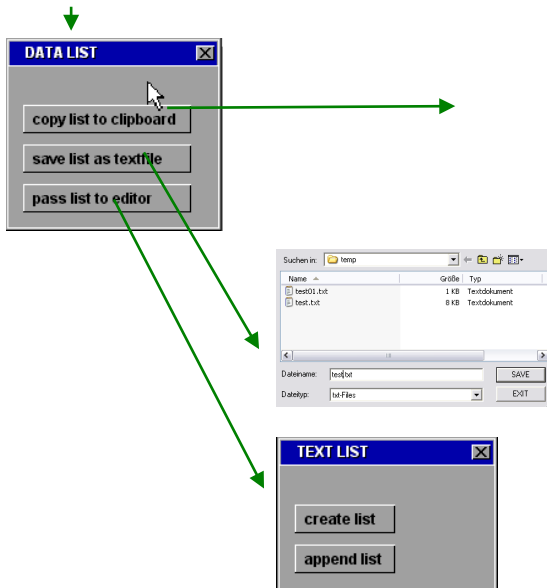
When clicking on either of the buttons a **description** box opens where you may input your measurement parameters and comments. Some lines will be filled automatically by the software (e.g. potential, current and measuring time) others are free for the user to fill. User parameters are not used by the software for any calculation. They are for the user's information only.

Accept the inputs by clicking on the ☒ button in the upper right corner or reject the inputs by clicking on the ☐ button. Click on the button to call the calculator.



In the following browser navigate to the desired path, input a file name and click on the **SAVE** button to save the data or click on the **EXIT** button to cancel the saving.

7.9.3 Export ASCII List

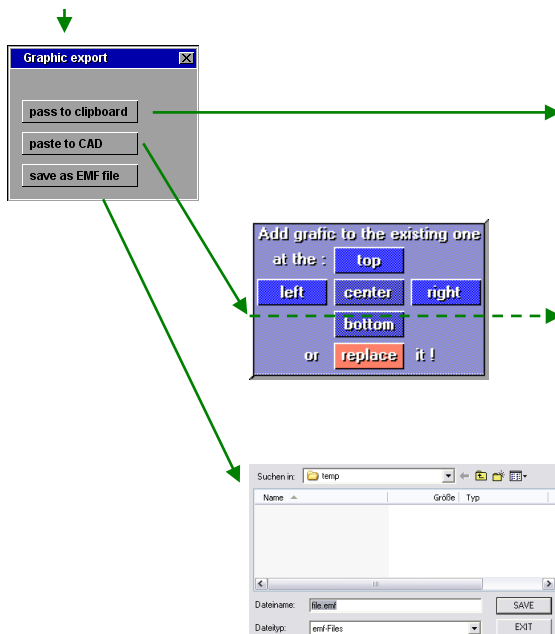


Copies the content of the measurement data of the recorded impedance spectrum as an ASCII text into the *Windows*® clipboard.

Saves the measurement data of the recorded impedance spectrum as an ASCII text file. Select a path and a file name in the browser window. Exported ASCII lists have the file-extension **.txt** !

Passes the ASCII list to the *THALES* text editor **ZEdit** e.g. for editing the data. You will end up in the text editor main menu. If you already have some text in ZEdit, you may want to append the ASCII list to the existing text. Chose **append list** in that case.

7.9.4 Export Drawing

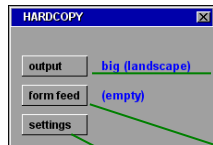
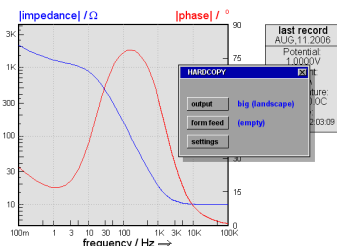


Copies the graphics to the *Windows*® clipboard. From there you may paste it to any Windows program which is able to paste graphics from the clipboard (Word, PowerPoint, Draw, etc.).

Copies the graph to the *THALES* CAD software directly. If the CAD graphic board is empty the graph is positioned in the middle of the board. If there already is a graphic loaded, you are asked where to place the new graphics relative to the resident one. Only in that case the box shown to the left will appear.

Saves the graphics to the hard drive in the EMF format. Select a path and a file name in the browser window. You may load the graphics from there to any Windows software which is able to handle EMF files. Click on the **save** button to save the graphics. Click on the **exit** button to cancel the operation.

7.9.5 Hardcopy



Clicking on the hardcopy icon creates the hardcopy version of the graph on the screen and gives you the following options:

output : sends the graphics to the device selected under **settings**.

form feed : sends a form feed to the printer

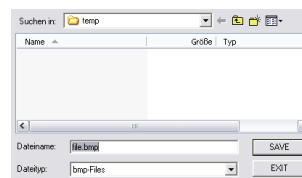
settings : toggles through the following options

— **big (landscape)**: sends a A4 format graphics to the printer

— **small (portrait)**: sends an A5 format graphics to the printer

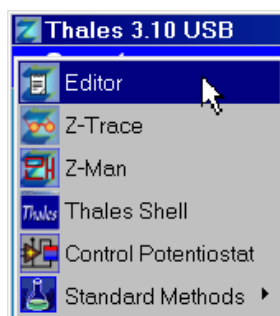
— **to clipboard** : sends the graphics to the Windows clipboard

— **save as file** : allows you to save the graphics to the hard disk as an EMF file



Select a path and a file name in the browser box and click on the save button to **save** the data. Click on the **exit** button to cancel the operation.

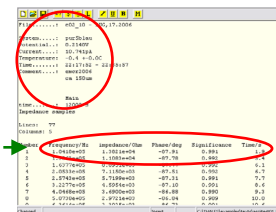
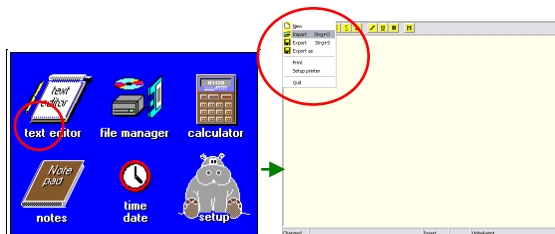
7.9.6 Import ASCII List



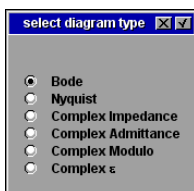
This option imports a list of ASCII data from **ZEdit**. Before you can use this function you have to open an ASCII list of the data to be converted into **ZEdit**, then you can import it to the **EIS** program for analysis by a click on this button. You may enter **ZEdit** either by using the pull-down-menu on the left side of the task bar or from the **THALES Shell** -> **UTIL** -> **text editor**. The import function is able to convert other formats (i.e. of EG&G and Solartron) to the **Zahner** EIS format. Some formats (of course the Zahner-format) are detected and translated automatically by special key-words of the file header. So, do not remove or modify the header prior to the conversion. Other data file formats can be imported by setting a header line according to the columns on top of the data list, containing the keywords **frequency**, **impedance**, **admittance**, **phase**, **-phase**, **real_part**, **imaginary_part**, **significance**, **time** or by using the **ALEX** module of the **THALES** software.

You also may wish to modify your measurement data (e.g. eliminate distorted points around 50 Hz) manually. Do this by exporting, editing (in **ZEdit**) and re-importing the data.

A quick guide for loading an ASCII data file to **ZEdit** (for more detailed information please refer to the chapter **ZEdit** in this manual):



7.9.7 Select Diagram

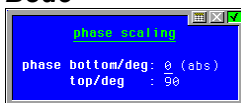


Select from this selector box one of the curve types to be displayed:

- Bode** : Bode-Plot (impedance modulus & phase angle)
- Nyquist** : Nyquist-Plot
- Complex Impedance** : real & imaginary part of impedance
- Complex Admittance** : real & imaginary part of admittance
- Complex Modulo** : complex modulo
- Complex ϵ** : complex dielectric constant

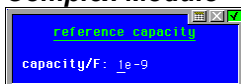
Click on the ☒ button to accept your choice. Click on the ☐ button to cancel the operation.

Bode



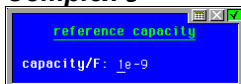
If you selected **Bode** you have to input the phase scaling.
phase bottom/deg : lower end of the phase scale. Add the keyword (abs) in brackets to force absolute value display of the phase angle.
top/deg : upper end of the phase scale

Complex Modulo



If you selected **Complex modulo** you have to input the **reference capacity** in **Farad**.

Complex ϵ



If you selected **Complex ϵ** you have to input the **reference capacity** in **Farad**.

7.10 Advanced Features

It is a serious intention of Zahner to provide the user with the best quality measurement data and the best analysis tools ever possible. In the four decades history of Zahner's experience in EIS many outstanding features were developed. The user is encouraged to compare carefully the measurement quality of the data acquired with Zahner instruments with the results from competitors and the features of for instance the EIS simulation and fitting program regarding robustness, speed, significance and versatility.

Here a short discussion will follow about some features affecting the EIS measurement data quality.

7.10.1 Online Error Determination

The primary intention for the application of EIS is to find out the precise numerical values of some magnitudes of interest, like the physical and kinetic parameters of the system under test. Therefore, the entire process of measurement, interpretation and analysis of EIS data usually aims towards the achievement of a set of those characteristic parameters.

The principle error structure of EIS data is thoroughly treated in the literature. However, a consistent error treatment, beginning with the experimental data and rating the error propagation through the typical simulation and fitting procedure in order to find out the individual uncertainty of an evaluated parameter, has an important prerequisite: a reasonable uncertainty estimation of the initial EIS measurement data must be available.

The simple strategy to measure the data at certain frequencies for several times and calculate the uncertainty from the scatter has severe disadvantages: a latter error reduction by calculating the mean values scales only with the square root of the time invested, while a continuous coherent data acquisition would have reduced the error proportionally with time. Besides, coherent data acquisition often can suppress deviations perfectly, even if the individual time slot samples would exhibit large scatter – a too pessimistic error estimation from this simple procedure is the consequence.

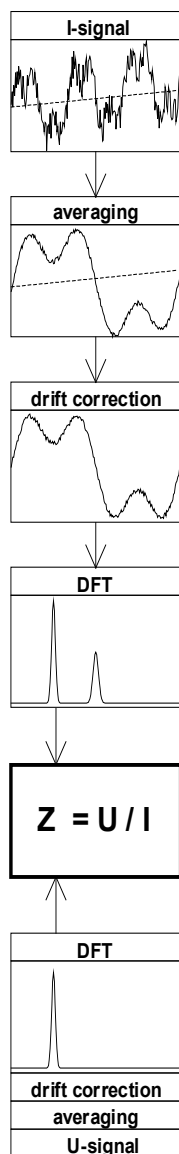
Zahner developed an alternative way based on FFT harmonic analysis, which is able to provide uncertainty estimation for every individual frequency sample. The procedure uses the fact, that under monochromatic (sinusoidal) excitation of a system, the harmonic distortion of the response signal can be used as a measure for the uncertainty. A special weighting function, which takes into account the inter-correlation of the harmonics, delivers very realistic error estimation. In the reference the principle of this “weighted harmonics autocorrelation WHA” algorithm as well as the results of EIS control experiments is discussed. It is shown, that the consideration of the measurement data uncertainty predicted by the WHA within the data processing of the CNLS fitting procedure leads to reasonable results for an error estimation of the final parameters of interest enables the impedance user to perform a Consistent Uncertainty Estimation of his physical parameters evaluated by EIS. Online Error Determination records automatically reasonable uncertainty estimation of the initial EIS measurement data based on weighted harmonics autocorrelation. Due to this a complete and consistent error treatment from the measurement to the final analysis can be performed.

Refer to:

Impedance Contributions Online 6 (2008) P4-1 – P4-13

7.10.2 Automatic Drift Compensation

Let us lead our attention to the problem of measuring time. Strictly speaking, electrical impedance is only defined for stationary systems. Nevertheless, EIS has also to be applied to systems that are not perfectly stable.



Depending on the grade of non-stationarity, during the recording time of a complete spectrum significant changes of the system under test may occur. In consequence, the spectrum belongs to different states of the system and is therefore addressed as "non-causal". How to treat such spectra is discussed closer in the next chapter. At sufficient non-stationarity it is even possible for the drift to be large enough for a noticeable change in the stationary component during the determination of one sample in the lower frequency range.

Assuming that periodic methods are being used, this drift can be determined during the spectral measurement, and to be compensated for through calculation. This procedure is addressed here as "online drift compensation" and sketched in the figure on the left. On top of the diagram an EIS response signal, interfered by noise, harmonic distortion and drift is symbolized ("I-signal"). By means of the Zahner high over-sampling averaging technique, noise is reduced by consecutive acquisition of several periods, shown in the next part of the diagram ("averaging"). From the mean DC value of the consecutive cycles a drift function, leading to a non-periodic share can be determined and subtracted from the averaged data ("drift correction"). Finally, the Discrete Fourier Transformation ("DFT") can isolate the "wanted" system response (the fundamental) from the "unwanted" (the harmonic content).

The Zahner Drift Compensation reduces the impact of steady state violations already during the measurement in the high precision single sine mode. It will be applied automatically at frequencies below 1 Hz. In the *ims* mode the Automatic Drift Compensation cannot be calculated from consecutive periods due to the "one shot principle", but in a Zahner proprietary way from the response of the fundamental. Due to that, the fundamental should not be excited, if compensation is wanted. This limits *ims* including drift compensation to a lowest frequency of the double of the inverse of the shot time.

Refer to:

Validation and Evaluation of Electrochemical Impedance Spectra of Systems with States that Change with Time

C. A. Schiller, F. Richter, E. Gülzow 3, N. Wagner
J. Phys. Chem. Chem. Phys. 3 (2001) 374

Relaxation Impedance as a Model for the Deactivation Mechanism of Fuel Cells due to Carbon Monoxide Poisoning

C. A. Schiller, F. Richter, E. Gülzow, N. Wagner
J. Phys. Chem. Chem. Phys. 3 (2001) 2113

7.10.3 Z-HIT

Impedance spectra from changing systems are difficult to interpret. Time effects can, however, very easily be detected in EIS data. A normal electrochemical impedance spectrum corresponds, as a rule, to the spectrum of an ideal two-pole, and does not have any discontinuities, strong resonances or jumps. For the Bode diagram of such spectra, the logarithmic Hilbert transformation for impedance two-poles, Z-HIT, predicts that the impedance modulus course, H , can be determined to a good approximation from the course of the phase angle, φ (Eq. "ZHIT").

$$\ln|H(\omega_o)| \approx \text{const.} + \frac{2}{\pi} \int_{\omega_s}^{\omega_o} \varphi(\omega) d \ln \omega + \gamma \cdot \frac{d\varphi(\omega_o)}{d \ln \omega} \quad (\text{Z-HIT})$$

The integral of φ over the logarithm of the frequency, ω , is formed for this purpose. The additional correction provided by a fraction, γ , of the derivative of φ provides a high precision in the approximation.

If the impedance modulus course calculated in this way does not agree well with the impedance curve determined experimentally, differences in the low frequency region of the spectrum suggest temporal drift, whereas those in the high-frequency regions indicate interference resulting from mutual inductance.

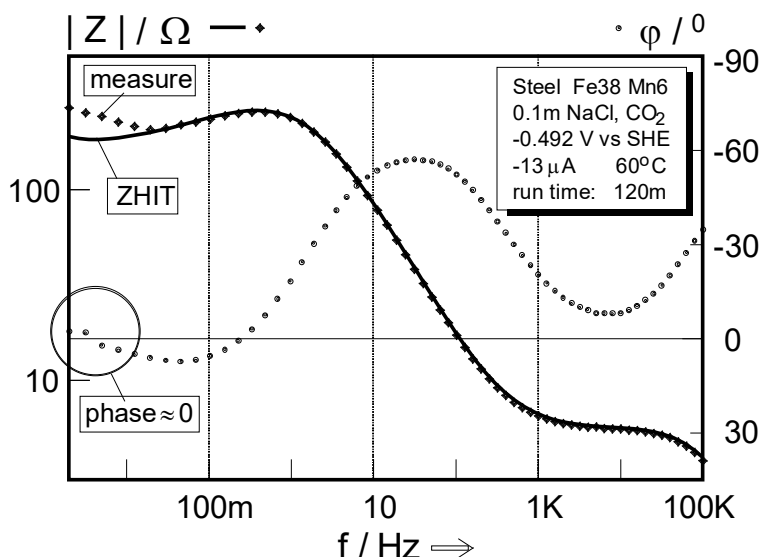


Figure: Impedance spectrum of a non-stationary, corroding electrode in the Bode representation. The visual inspection unveils a violation of the ZHIT-rule moving to low frequencies: Impedance- and phase-course should depend approximately like a mathematical function and its first derivative, but the measured impedance modulus rises significantly, while the phase angle tends to zero. The result of a precise calculation of the expected impedance course from the phase course after Eq. "ZHIT" is displayed as a solid curve.

There is a whole family of methods based on the so called Kramers-Kronig relations with the intention to detect distortions in EIS data. Z-HIT is distinguished by simplicity: even without any mathematical treatment – simply by taking a close look at the Bode diagram – one is able to detect distortions of the proper shape of an impedance spectrum by comparing sign and magnitude of the phase angle with the gradient of the impedance modulus course. Looking on a correctly measured Bode-diagram in one observes, that a phase-angle, tending to zero, corresponds to an impedance modulus gradient, tending to zero at this frequencies. The negative maximum of the phase angle in turn corresponds to the negative maximum gradient of the

impedance at the inflection point – very close to the relationship between a mathematical function and its first derivative.

Differing from that, the impedance modulus course of a non-stationary (corroding) electrode in the figure on top exhibits a divergence at low frequencies: while the average phase angle is near zero, the gradient of the measured impedance (rhomb symbols) is clearly negative. The solid line in the diagram, calculated from the phase angle after Eq. "ZHIT", indicates the (correct) impedance course to be expected in the absence of any interference.

EIS measurements should be examined for signs of time effects – most easily by visually inspection based on the THALES Z-HIT. These effects, along with parasitic effects associated with the cell being measured and the cables are the main causes of incorrect measurements. Our intelligent software can minimise the coarsest effects of drift during the measurement and it supports subsequent correction by means of the interpolation of spectral series vs. time.

Refer to:

The Evaluation of Electrochemical Impedance Spectra Using a Modified Logarithmic Hilbert Transform

W. Ehm, H. Göhr, R. Kaus, B. Röseler, C.A.Schiller
Acta Chim. Hung. 137 (2000) 145

Z-HIT – a Simple Relation Between Impedance Modulus and Phase Angle, Providing a New Way to the Validation of Electrochemical Impedance Spectra

W. Ehm, R. Kaus, C. A. Schiller, W. Strunz, *New Trends in Electrochemical Impedance Spectroscopy and Electrochemical Noise Analysis*, ed. F. Mansfeld, F. Huet, O. R. Mattos, Electrochemical Society Inc., Pennington, NJ, 2001, vol. 2000-24, 1

Validation and Evaluation of Electrochemical Impedance Spectra of Systems with States that Change with Time

C. A. Schiller, F. Richter, E. Gülzow 3, N. Wagner
J. Phys. Chem. Chem. Phys. 3 (2001) 374

Relaxation Impedance as a Model for the Deactivation Mechanism of Fuel Cells due to Carbon Monoxide Poisoning

C. A. Schiller, F. Richter, E. Gülzow, N. Wagner
J. Phys. Chem. Chem. Phys. 3 (2001) 2113

Electrochemical power sources – Fuel cell

N. Wagner, in *Impedance Spectroscopy: Theory, Experiment, and Applications*, 2nd Edition, Edited by Evgenij Barsoukov and J. Ross Macdonald, John Wiley & Sons, Inc., ISBN: 0-471-64749-7 (2005) pp.497-537

Handbook of PEM Fuel Cell Durability

N. Wagner, Volume 2: PEM Fuel Cell Diagnostic Tools, Chapter 3: *Electrochemical Impedance Spectroscopy (EIS)*, Eds. H. Wang, X.-Z. Yuan and H. Li, CRC Press, Taylor & Francis Group, London, UK, ISBN: 078-1-4398-3919-5 (2011) pp. 37-70.

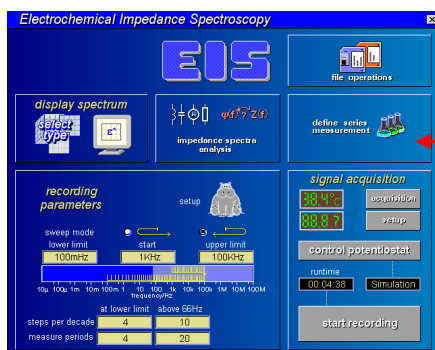
Minimal Measurement Time in Electrochemical Impedance Identification

R. H. Milocco,
Electrochim. Acta 39, 10 (1994) 1433-1439.

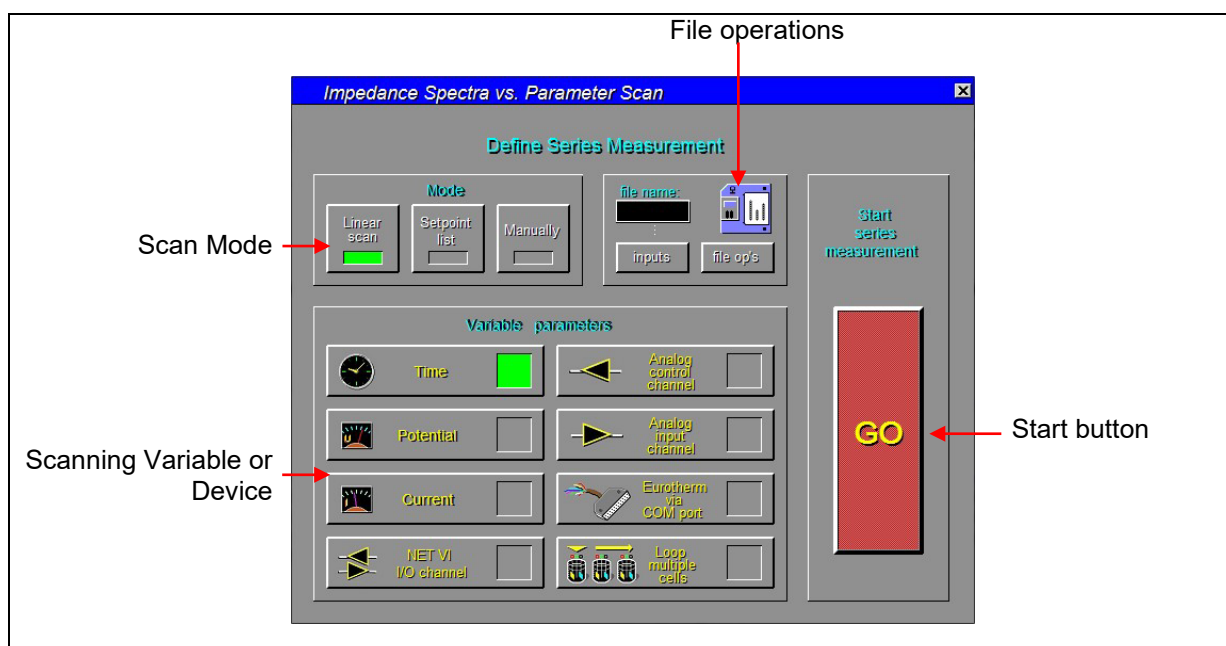
8. Series Measurement

The Series Measurement feature allows you to record up to 100 impedance spectra in dependence of an additional quantity, such as time, temperature, potential, current, etc. In addition, you may scan through a number of cells. All spectra of one series have the same EIS recording parameters (frequency range, resolution, AC amplitude, etc.) which are set in the same way a single spectrum is recorded (see chapters above). They are saved automatically to hard disk using the defined file name which is extended by the number of the spectrum in the series (e.g. *series00*, *series01* ... *series99*). The spectra may be analysed individually or in the *series analysis* mode of the SIM.

Series EIS measurements allow to investigate an object under changing conditions. The conditions must change slowly, so that a steady state is established to a certain degree within an impedance spectrum. An example for an application is the recording of spectra over time during charging or discharging a battery. Another example is the investigation of capacitor diodes over the potential or annealing studies by measurements over the temperature. Control parameter may be an internally available value (time, potential, current) or an external value (temperature, pH-value, pressure, etc.). For recording some of these parameters you need optional hardware and/or software drivers for *THALES* Network Virtual Instruments. E.g. for series measurements dependent on temperature you need a **TEMP/U** card plug-in or an **Eurotherm 2404** temperature controller connected via network. To be able to scan through a number of cells you need an **RMux** card or a **PMux** module or your electrochemical workstation must be extended to a cluster through an EPC42 card by additional slave potentiostats (PP-series, XPot, NProbe...).



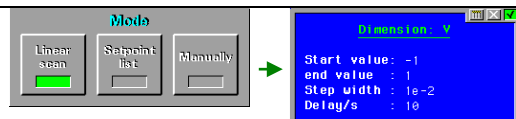
By clicking on this icon you get to the **Series Measurement** page.



8.1 Scan Mode

The **Scan Mode** settings define how to scan through the quantity selected in the **Variable Parameters** box (time, potential, current, external quantities). **Linear Scan** lets you go through a range of the quantity in equidistant steps. **Setpoint List** lets you input a list of up to 100 points of measurement. In the setting **Manually** you may change the conditions and start each measurement manually. If the **Variable potential** is selected each step is reached by a ramp protecting the sample from steep voltage transitions. The ramp speed and current limits are set in the **global measurement set-up** page.

8.1.1 Linear Scan



In **Linear Scan** Mode you scan through a range of the defined quantity in equidistant steps (linear).

Start value : Value where the scan has to start
End value : Value where the scan is finished
Step width : Interval in which the measurements have to be carried out
Delay / s : Delay between reaching a scan-point and starting the measurement (settling time)

8.1.2 Linear scan over time

start time	Absolute time of the computer clock. The start time is set in units of hours, minutes and seconds. During definition of the time parameters the actual time is displayed in the input box.
duration	Starting at the start time the program will start impedance measurements until the total measurement time of <i>duration</i> has expired. The <i>duration</i> is set in units of hours, minutes and seconds.
delay	Delay time defines the time difference of the starting times of two successive impedance measurements.



Set the delay time higher than the estimated measurement time shown on the Recording Parameters page. If measurements take longer than the delay time the equidistance of the spectra can not be guaranteed or less spectra will be measured.

8.1.3 Linear scan over potential/current

start value	Sets the potential or current at which the series measurement has to start. Potential and current will be given in units of V and A, respectively.
end value	Destination potential or current at which the series measurement is stopped.
step width	Step width of potential or current between two successive measurements. Setting the start value higher than the end value will require the input of a negative step width.
delay	After the new value of potential or current is reached the program waits for this number of seconds to ensure steady state conditions at the object.



The delay time should not been defined too short because changes in potential and current may cause distortions of equilibrium. Allow the system to settle before continuing with measurements.

The effect of the series control by DC-set-voltage or DC-set-current is related to the actual working mode of the potentiostat:

Use DC-voltage only in potentiostatic mode.

Use DC-current only in galvanostatic- or pseudo-galvanostatic mode.

8.1.4 Linear scans controlled by analogue I/O-channels

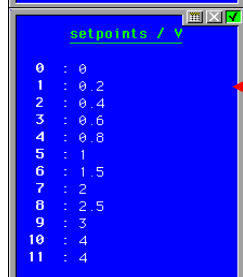
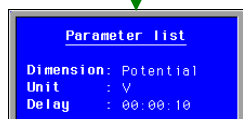
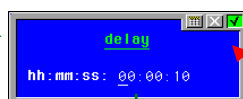
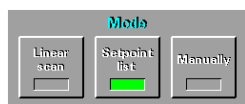
Linear scans using additional analogue i/o-channels are working in a similar way as linear scans over potential or current do. The range parameters and the step width are given in the physical units defined for the corresponding channel on the **Data Acquisition Setup** page. The physical unit set there is displayed at the top of the appearing input box.

start value	Sets the value at which the series measurement has to start. Potential and current will be given in units of V and A, respectively.
end value	Destination value at which the series measurement is stopped.
step width	Step width between two successive measurements. Setting the start value higher than the end value will require the input of a negative step width.
delay	After the new value is reached the program waits for this number of seconds to ensure steady state conditions at the object.



The delay time should be defined sufficiently high to offer the system some time to get settled.

8.1.5 Setpoint List



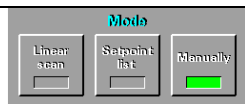
This mode lets you define a list of points at which the system has to measure. The list has not to be linear or steady.

In the first input box you define a delay time valid between the individual spectra for settling. After reaching a set point, the software waits for the duration of the delay time before the measurement is started.

In the second box you may input the set points in the quality of the scan parameter set in the **Variable Parameters** box.

Up to 99 set points can be defined but only 12 points are displayed in the box. You can scroll through the list using the cursor keys or the RETURN key of your keyboard. The transition between two points always is a linear ramp.

8.1.6 Manually



This mode lets you trigger the measurements of the scan manually. This brings the advantage to have a look at the last spectrum measured before starting the recording of the next spectrum. The example shows *time* as the scanning parameter. You now may input the next time a measurement should be started. Similar to *time* you also may use other control variables for manual triggering (e.g. *potential*, *current*, *temperature*, etc.)









You may convert a series of single measurements into a series measurement by renaming the last two characters of the file names into a series of numbers. To ensure the advanced series analysis features of SIM, you should edit the last three lines of an individual EIS spectrum's comment page in a way, that a consistent description of the series quantity name, dimension and value appears.





8.2 Scan Variable or Device

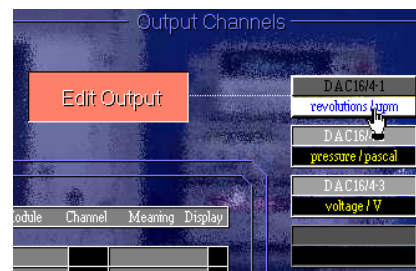
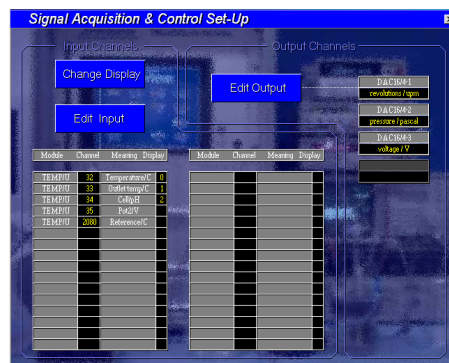
In this section you set the parameters of the scan variable. This may be an internal signal (time, potential, current), an external signal (analog input, analog output, interface control channel) or a number of **RMux/PMux** channels. For using external signals you may need an optional hardware such as **TEMP/U**, **FE42**, **DA4**, etc or **NET-VIs**. **THALES** is able to communicate via TCP/IP with external measurement and control units (NET-VIs) connected to any computer in the network. Zahner can support Net VI technology to the instrument you apply. The only requirement is a RS232 interface able instrument. Refer to [Signal Acquisition Manual](#) for configuring NET-VIs.

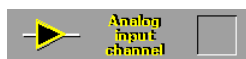
8.2.1 Internal signals

 Time 	A series of spectra will be recorded over a certain interval of time, allowing studies of time dependent processes.
 Potential 	A series of spectra will be recorded in dependence of the DC potential, allowing studies of potential dependent processes.
 Current 	A series of spectra will be recorded in dependence of the DC current, allowing studies of processes dependent on the current density.

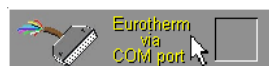
8.2.2 External signals

 NET VI I/O channel 	<div data-bbox="478 907 710 1030"> <p>Select a NET-IO registered:</p> <p><input checked="" type="radio"/> EUROTHERM <input type="radio"/> HP34401A</p> </div> <div data-bbox="478 1064 861 1176"> <p>configure EUROTHERM outputs</p> <p>temperature tolerance/C : 1 settling time/s : 5</p> </div>	Select the NET-VI (with I/O ability) of variable parameter (only if more than one NET-VI is registered to the THALESsoftware).
 Analog control channel 	Four analogue outputs are provided by an optional DA4 DA-converter module and NET-VIs with input channel. These channels can be calibrated and correlated to any quantity to be controlled in the <i>Signal Acquisition Setup</i> page:	Set trigger conditions: tolerance window for parameter settling time to determine overshoots or ensure steady state





Additional analogue input channels are provided by the optional modules FE42, TEMP/U and NET-VIs with output channels. In the *Signal Acquisition Setup* page the inputs can be calibrated and linked to one of the 'digital instrument displays' of the *Signal Acquisition & Output Control* page:

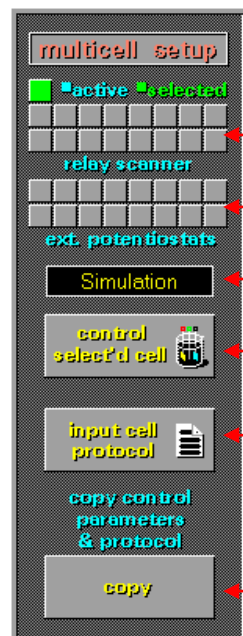


Generally, *THALES* is able to communicate via TCP/IP with external measurement and control units (NET-VIs) connected to any computer in the network. Besides this, an **Eurotherm 2404CG**, which is able to control the temperature of an oven, may be connected directly to the COM port of the PC controlling the IM instrument. This opens a cheap way to perform series measurements over controlled temperature.

8.2.3 Channels



Using an optional **RMux** card, an optional **PMux-S** device or a number of external potentiostats of the PP- or EL-series you may perform series measurements scanning through a number of cells (channels). Clicking on the **Loop Multiple Cells** icon opens the **Multicell Setup** box on the right hand side of the page.



The **Multicell Setup** lets you define:

The cannels of a **RMux** or a **PMux-S** to be selected and recorded

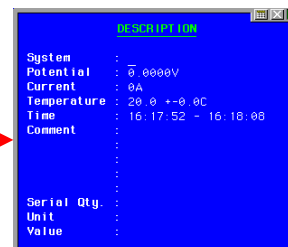
The external potentiostats (PP or EL) to be selected and recorded

The selected channel (device) is displayed

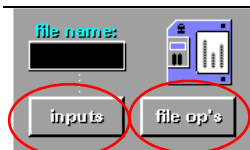
Click here to call the **Control Potentiostat** page in order to set up the selected channel / device

Click here to input the description of the selected cell.

Click here if you want to copy the control and protocol parameters of the selected cell to all active cells.



8.2.4 File name



To select a folder click on **File Ops**. The file manager opens and lets you navigate through the drives.

To input a file name click on the button **Inputs**. Enter the file name you want to be used for the complete series of spectra. Each single spectrum is saved individually so that you may analyse it individually or in the context of the complete series.

The file name of each spectrum is complemented by a two-digit number which specifies the number of the spectrum in the series. If any of the file names to be created already exist, an error message will be displayed and you have to put in a different file name.



In the **Description** box you may input a complete description of your experiment in 13 lines. The most important parameters are already named, the rest you may input under **Comment**.

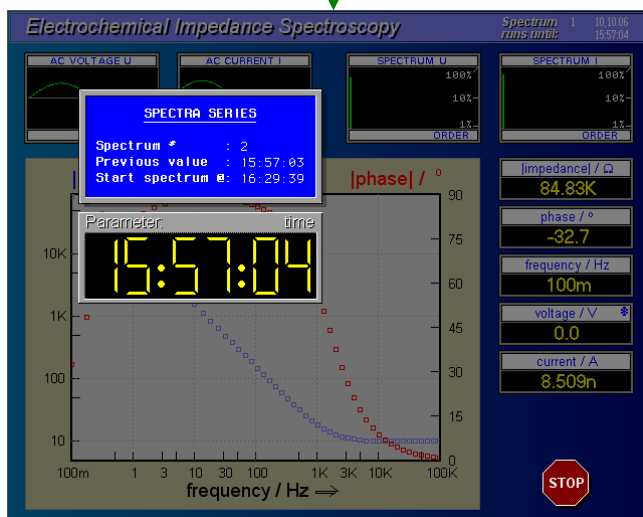
Some of the parameters are entered by the software automatically (potential, current, etc.). Please note, that the last three lines are reserved for the entries generated by the series run.

8.2.5 Start series measurement



Click on the **GO** button to start the series measurement.

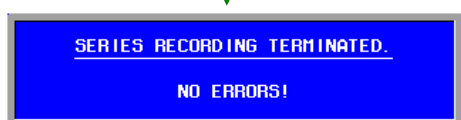
An AC-excitation amplitude should have been set. If this setting is missing, the program will jump to the **Potentiostatic Control Page** to let you do this setting. After correction and leaving the **Potentiostatic Control Page** the series will be started.



You will be informed during the series measurement prior to each single measurement of the following parameters:

- number of the next spectrum
- starting value of previous spectrum
- starting value of next spectrum
- actual series parameter value

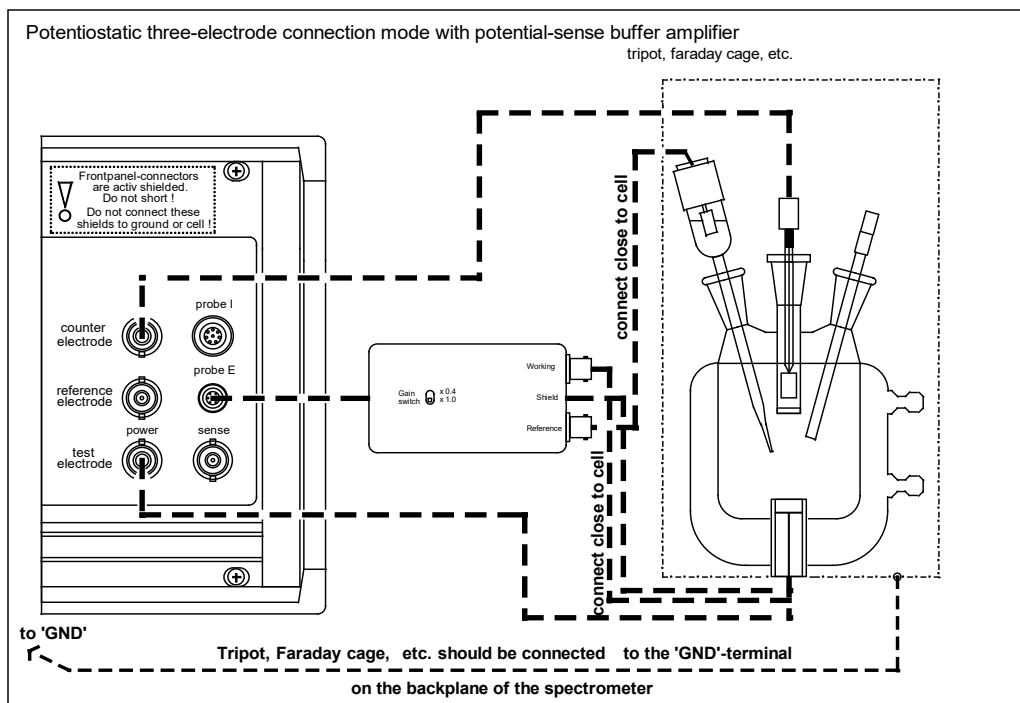
In the example time is taken as control variable.



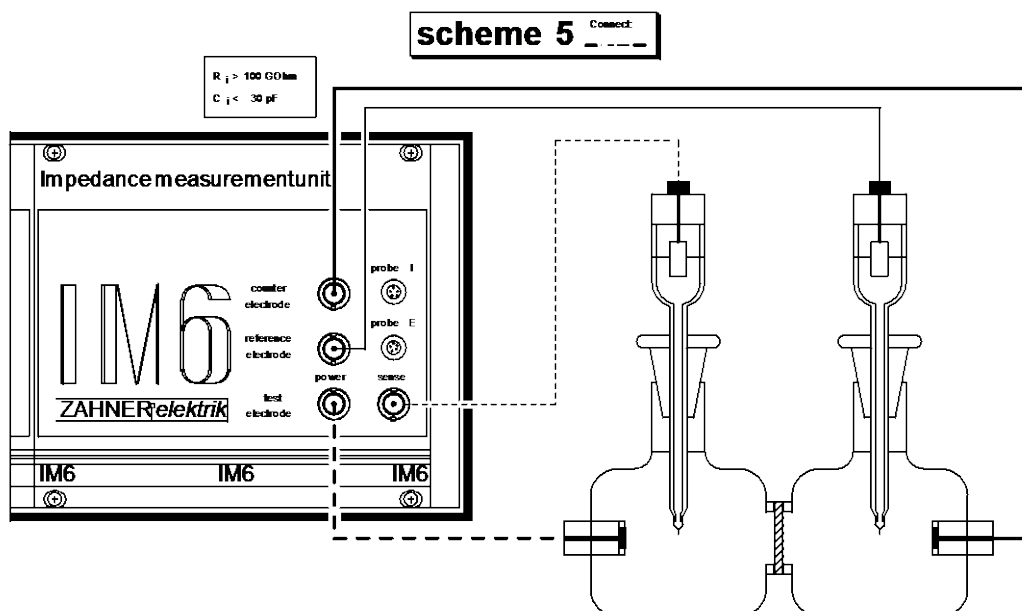
By this info box you are informed about the ending of the series measurements and whether any error occurred during the measurements.

9. Appendix

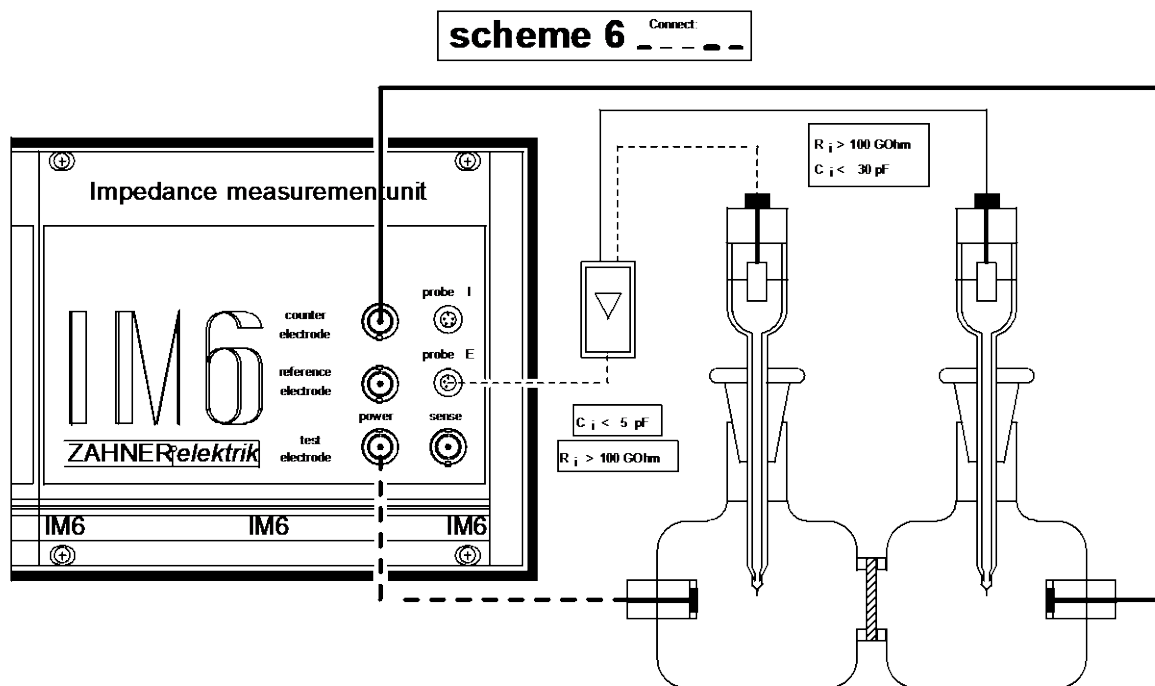
Typical cell connection ⚠ Attention ! Frontpanel-connectors are active shielded !
Do not short ! Do not connect these shields to ground or cell !



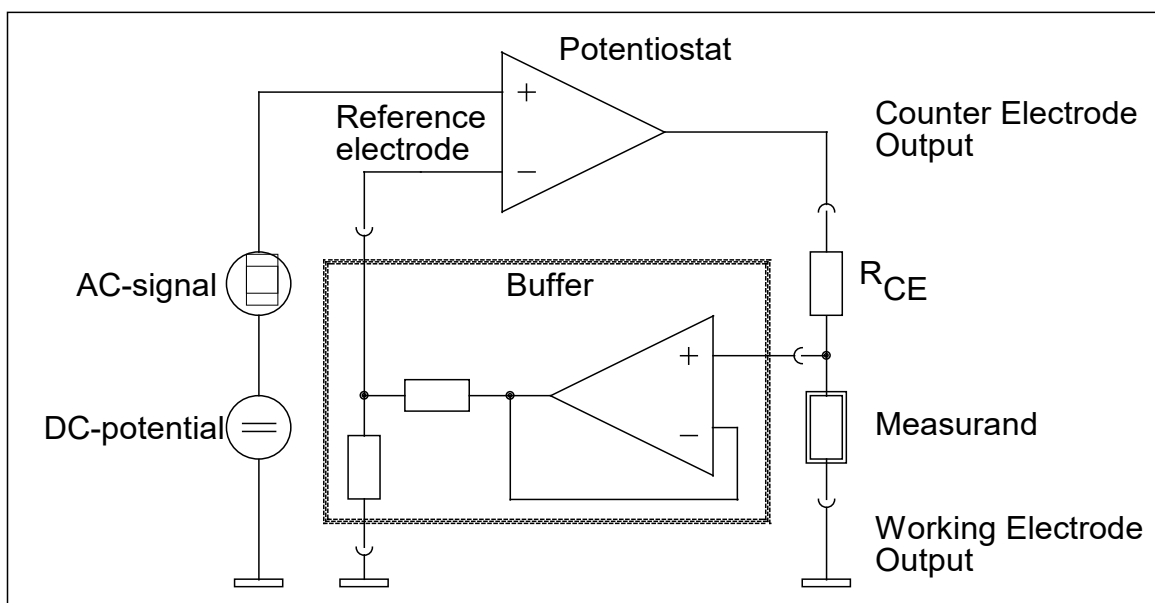
Appendix 1: Detailed connection scheme for 3 electrodes with buffer



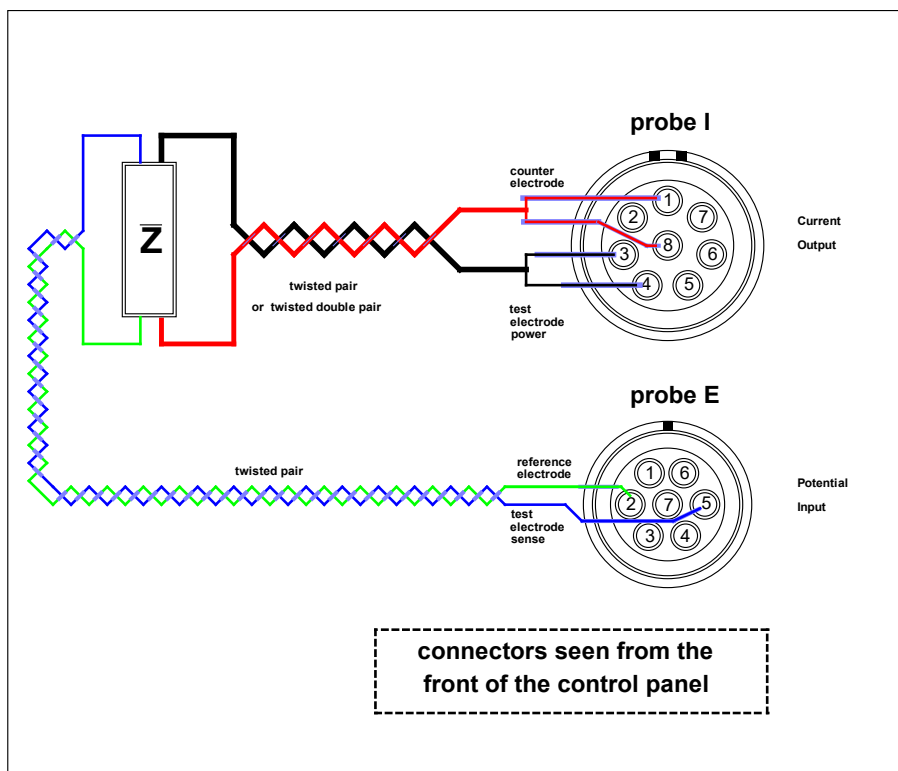
Appendix 2: Detailed connection scheme for 4 electrodes without buffer



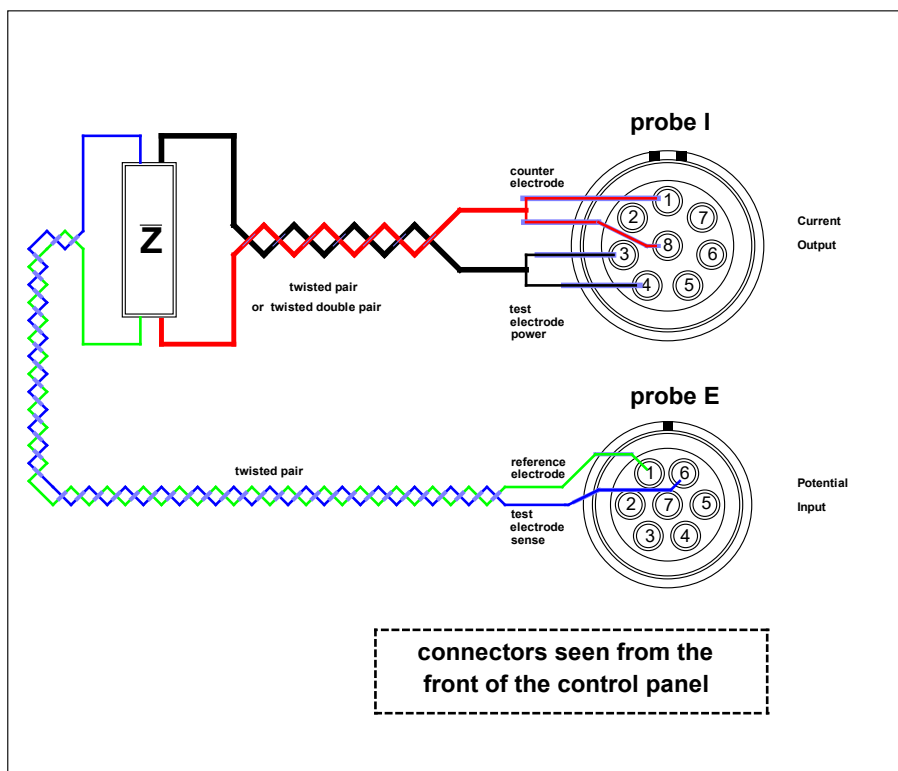
Appendix 3: Detailed connection scheme for 4 electrodes with buffer



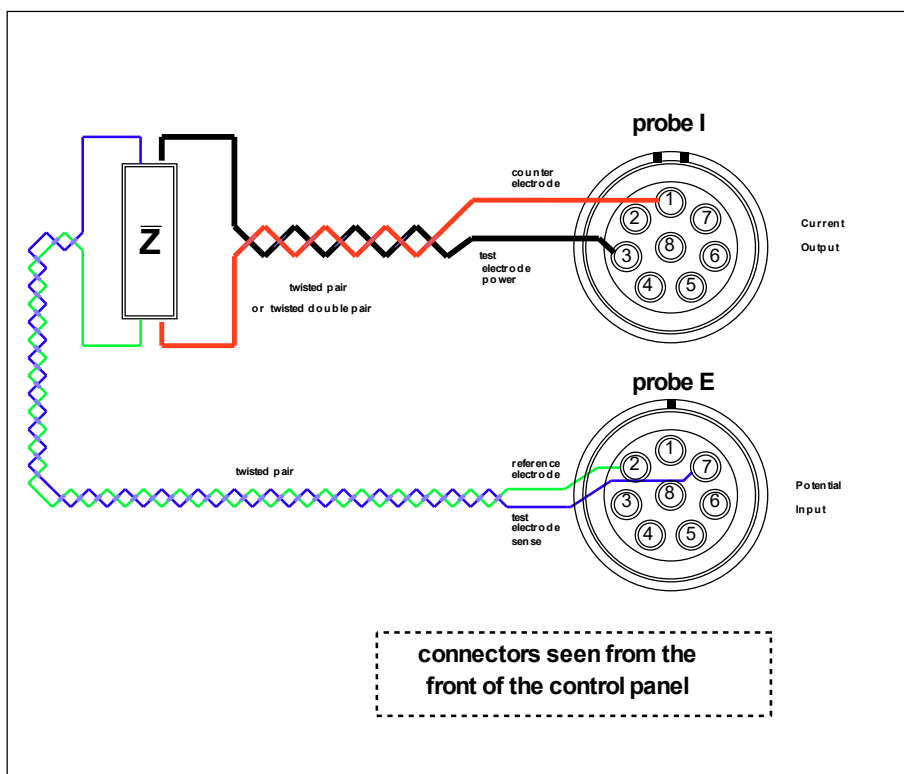
Appendix 4: Buffer block diagram



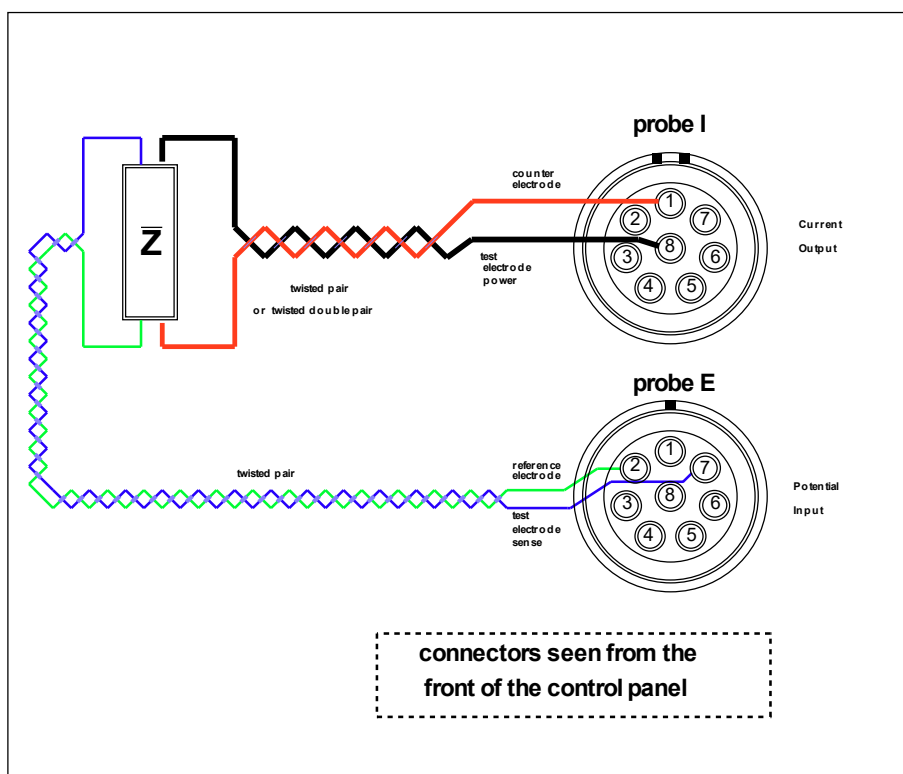
Appendix 5: Pin-out of the *Probe I* and *Probe E* connectors
NOTE! Only IM6 / 6ex



Appendix 6: Pin-out of the *Probe I* and *Probe E* connectors
NOTE! Only ZENNIUM



Appendix 7: Pin-out of the *Probe I* and *Probe E* connectors
NOTE! Only Zennium E / E4



Appendix 6: Pin-out of the *Probe I* and *Probe E* connectors
NOTE! Only ZENNIUM pro / X / XC