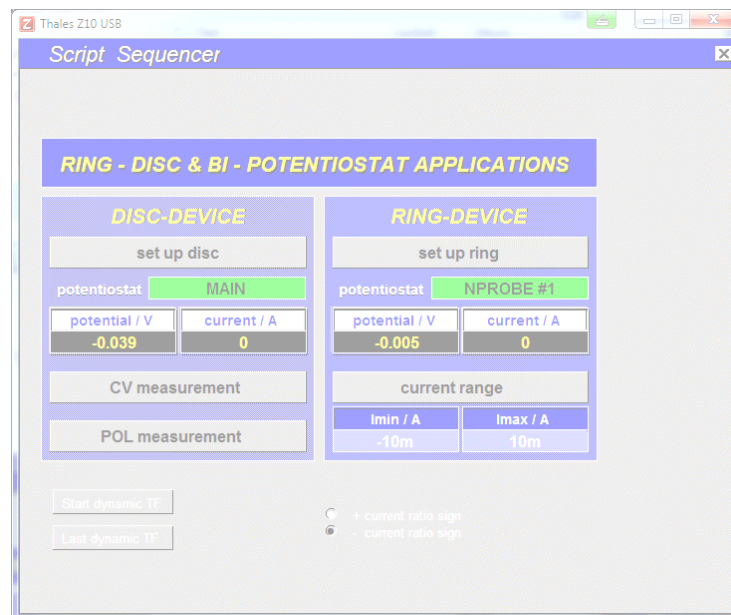# Ring-Disc & Bi-Potentiostat

Ring-Disc and Bi-Potentiostat Applications

The „ring-disk" and "bi-potentiostat" software – in the following addressed shortly as "RD" – was designed to support the investigation of electrochemical set-ups consisting of two electrochemical cells which are partly electrically separated, but electrochemically coupled. A typical application is the evaluation of (usually rotating) ring-disk electrodes. A ring-disk electrode is represented by two electrically separated working electrodes – the inner "disk" and the concentric outer "ring". The electrochemically coupling is supported by a common electrolyte vessel, enabling the transport of active species from the disk to the ring by rotation controlled diffusion.

For a ring-disk experiment the arrangement from principle consists of a common counter-, a common reference- and two separated working electrodes in a common electrolyte vessel (Fig. 1).
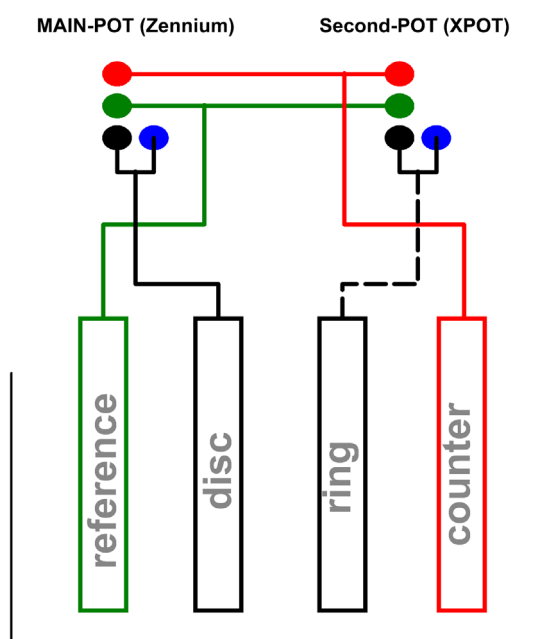

Figure 1: Connection scheme of a bipotentiostatic set-up, e. g. ring-disc setup using Zennium (master) and XPOT(slave).

A second example is the investigation of membrane transfer reactions for instance by means of a Devanathan's cell. Here the primary cell creates an electrochemical active species (for instance hydrogen) which may migrate through the membrane working electrode into the secondary cell side.

The arrangement from principle consists of individual counter- and reference electrodes in the electrolytically separated cell parts but with a common membrane working electrode in between (Fig. 2).
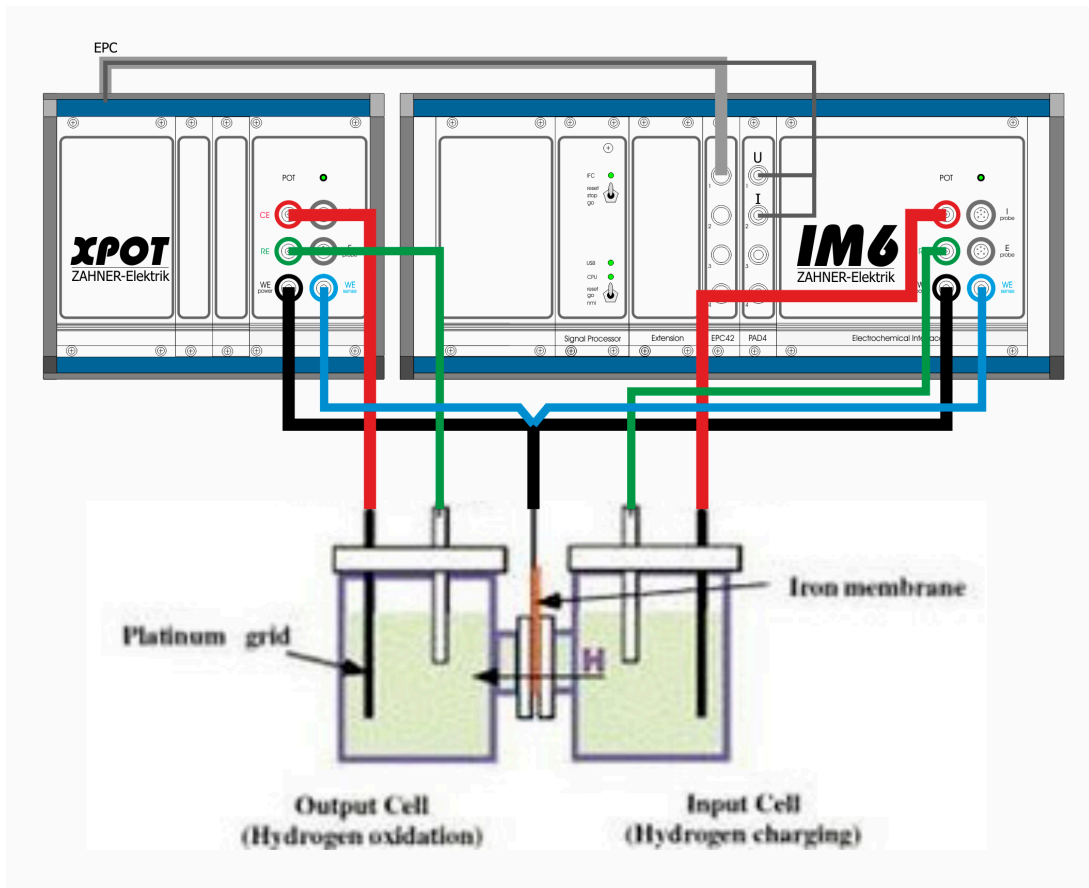
Figure 2: Connection scheme of a bipotentiostatic set-up for the investigation of membrane transfer functions in a Devanathan's cell.

The RD-software panel is opened by means of the pull-down menu through "optional methods" → "Ring Disk Bi-Potentiostat"

Figure 3: The RD software panel is opened by means of the pull down menu.

The RD panel normally appears like shown in Fig. 4 with the focus on ring-disk experiments.
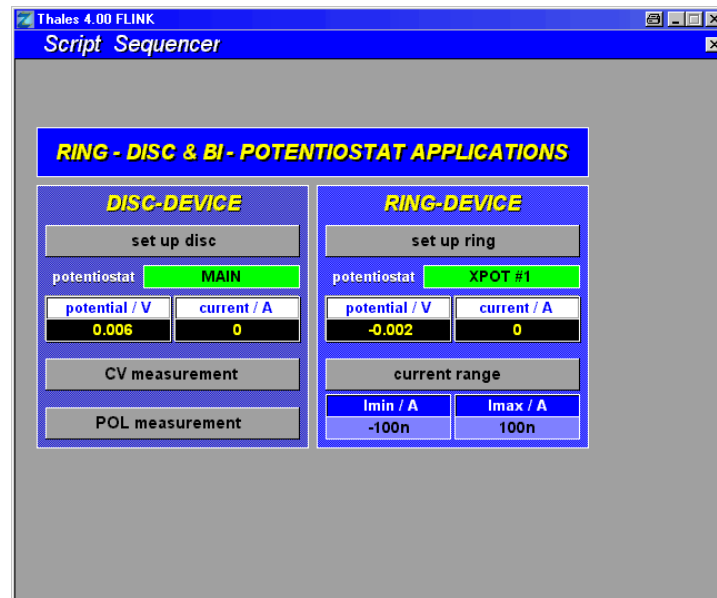

Figure 4: Standard appearence of the Bipotentiostat software menu.

If the software detects the presence of the "PAD4" four channel parallel impedance extension together with the corresponding calibration file, in addition the sub-menu for parallel dynamic transfer functions appears. Here the standard RD panel can be used to configure for instance the DC conditions of a Devanathan's cell and the dynamic transfer function submenu may start an EIS measurement at the primary cell, while synchronously recording the dynamic transfer current ratio between the primary and the secondary cell side.
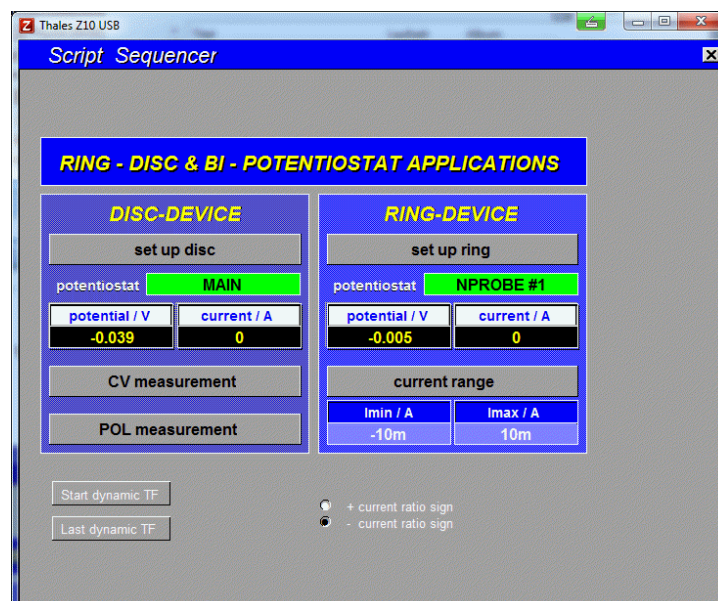

Figure 5: The appeerence of the Bipotentiostat software menu, if the PAD4 extension is detected

Hardware settings:

The RD software expects the following hardware set up:

- Master (= Disc)   Main potentiostat IM/Zennium
- Slave   (= Ring)   Slave (EPOT/XPOT/PP) on EPC-Channel 1

The measurement can only be started when the Slave has been connected to EPC channel 1 and after the slave has been booted!

The ring electrode current acquisition by the slave will be operated in the fixed-range-mode. The user has to define an appripriate current range.

Software set up:

The analog channels for voltage and current of the Slave are automatically assigned as signal acquisition inputs as soon as the ringdisk software is started. The correct definition can be seen in the „Signal Acquisition set up". The corresponding parameters may be checked as being described in the following:
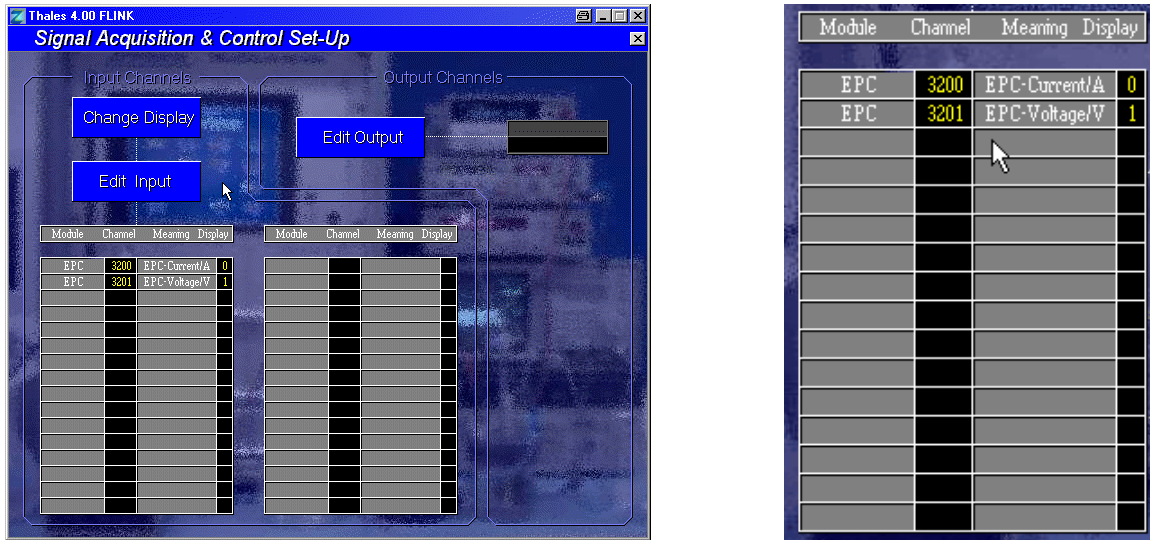
- From THALES main menu
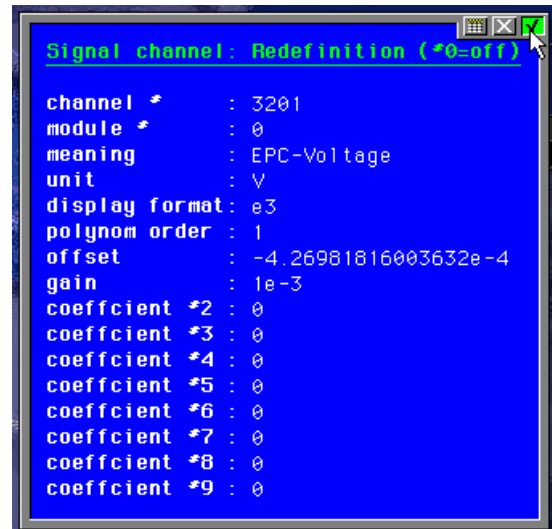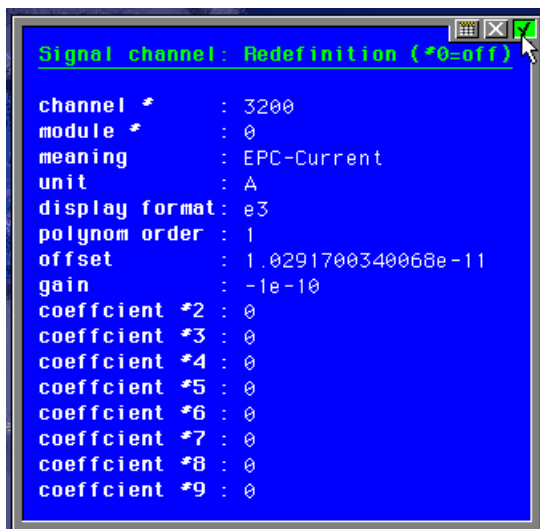

- From EIS main menu

Example:

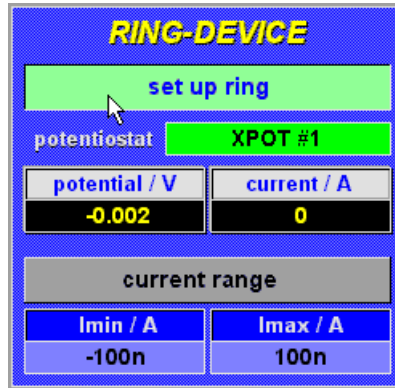Changing parameters (usually unnecessary):

The basic functions of the RD software:

From the main menu the following subroutines will be called to set up and start selective methods:

set up ring
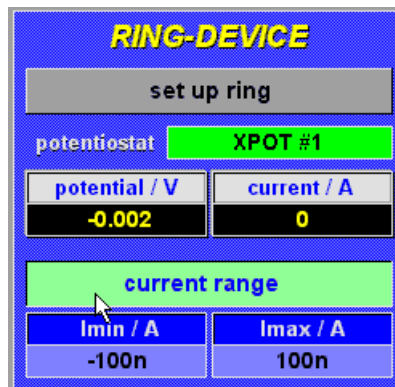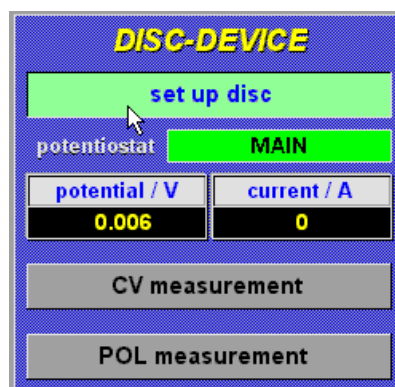
set up Slave potentiostat

current range

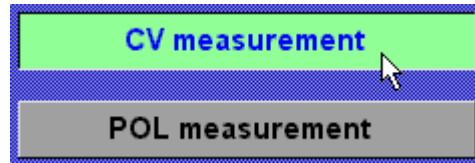fixed current range of slave

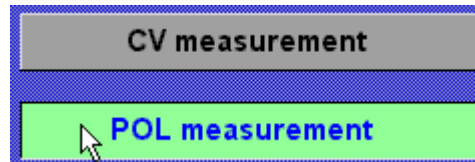### set up disc

set up main potentiostat

Supported standard methods:

- **CV**

- **POL**

When one of the standard methods is called RD jumpes to the main menu of either CV or POL. From the corresponding menu the measuremant can be started and the measured data may be stored

The ring current (and voltage) measured by the slave will be recorded as acquisition channels.

- the data will be displayed online numerically
- using the online display function, the ring data can be displayed graphically
- the recorded data will be put out in additional columns of the text data list:
-
- File............:   - JUN,03.2009
-
- System..........:
- Control.........:
- Temperature.....: -2.02n +-10.4mA
- Time............: JUN,03.2009
- Comment.........: 10:56:32 - 10:57:08
-
-
-
-
- Electr.area/sqcm:
-
- polarization data
-
- Lines: 32
- Columns: 5
-

Number	Time/s	Potential/V	Current/A	XCurrent/A	XVoltage/V
1	0.0	1.0000e+00	9.9770e-09	-2.001e-08	-2.000e+00
2	1.0	1.0000e+00	9.9762e-09	-2.001e-08	-2.000e+00
3	2.0	1.0000e+00	9.9767e-09	-2.001e-08	-2.000e+00
4	3.0	1.0000e+00	9.9765e-09	-2.001e-08	-2.000e+00
5	4.0	1.0000e+00	9.9757e-09	-2.001e-08	-2.000e+00
6	5.0	1.0000e+00	9.9756e-09	-2.001e-08	-2.000e+00
7	6.0	1.0000e+00	9.9756e-09	-2.001e-08	-2.000e+00
8	7.0	1.0000e+00	9.9762e-09	-2.001e-08	-2.000e+00
9	8.0	1.0000e+00	9.9765e-09	-2.001e-08	-2.000e+00
10	9.1	1.0000e+00	9.9769e-09	-2.001e-08	-2.000e+00
11	10.1	1.0000e+00	9.9758e-09	-2.001e-08	-2.000e+00

How to Set-Up a Ring-Disc Experiment

In the following example a bipotentiostat (ring-disc arrangement) is described assuming that a Zennium workstation (Zennium, ZenniumE, ...) serves as main potentiostat and an XPOT works as slave.

The first procedure you have to perform is to disconnect the jumper at the rear panel of the XPot (4 mm black- and bare banana connectors must be opened).

This makes the XPOT measuring in floating mode (disconnects the XPOT working electrode from ground=housing of the XPOT).
If this jumper is closed, the working electrodes of Zennium and XPOT are connected (short circuit). Thus, the jumper must be disconnected for ring-disk experiments. As a result, the potential of the working electrode of the XPOT can be set independently (from the potential of the Zennium).

Please note, if Zennium AND XPot are connected at the same time to the cell (like in bipotentiostat arrangement), the cell is grounded due to the connection of the working electrode (Zennium) to ground (metal chasis of the Zennium housing).

In the next step, the cell must be connected to both potentiostats. In Figure 6, the cabling scheme of main- (Zennium) and slave (XPOT) potentiostat is plotted schematically.
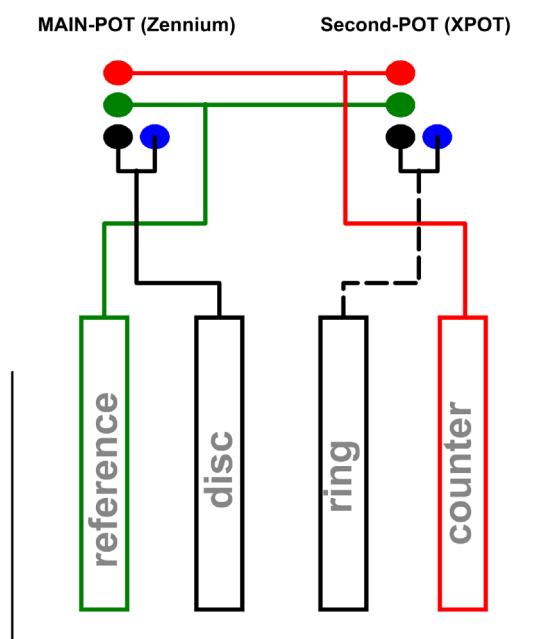

Figure 6: Connection scheme of a bipotentiostatic set-up, e. g. ring-disc setup using Zennium (master) and XPOT (slave).

Next, one can switch to the ring disc script. At the beginning, both potentiostats display approximately the same potential values and the notation of master and slave - Zennium as well as XPOT- are highlighted in a green color (Fig. 7).
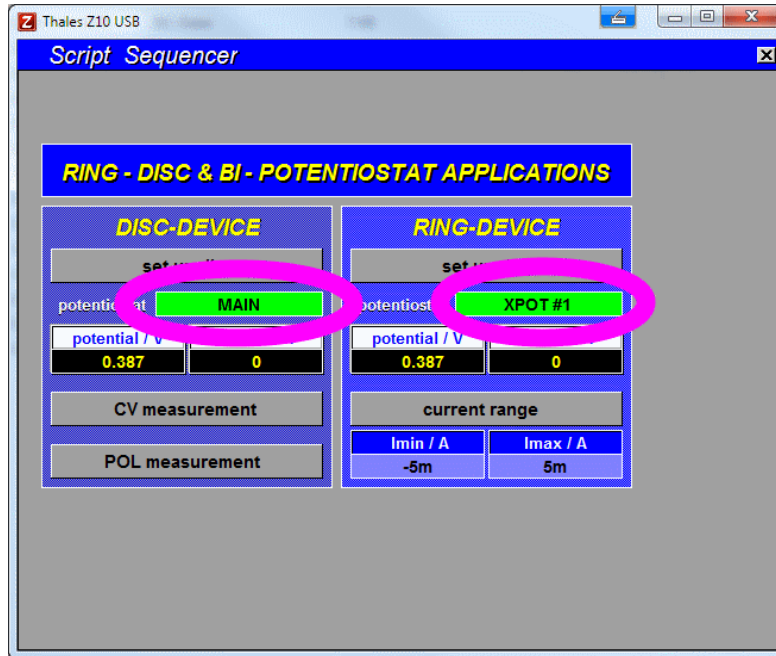

Figure 7: RD software panel after start

Next open the slave potentiostat panel by clicking "set up ring", set the desired potential value for the ring-electrode and switch "ON" (Fig. 8).
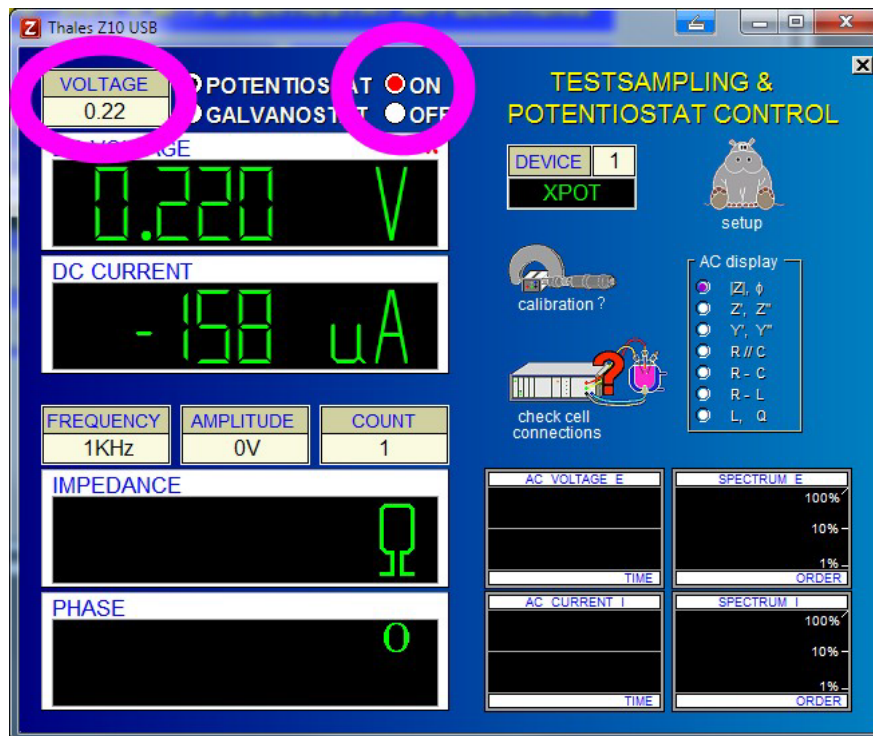

Figure 8: Setting up the slave potentiostat (ring electrode); first setting the desired potential and switching ON afterwards

When you return to the main menu of the RD panel (clicking *escape* or middle mouse button), the RD screen appears as follows (Fig. 9). Please note that the notation of the slave (XPOT) is now highlighted in red color, indicating that the slave potentiostat is switched ON now.
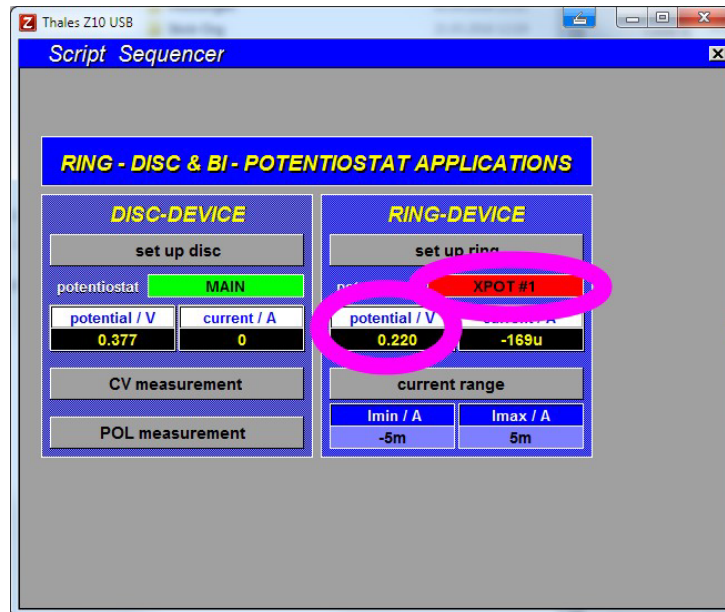
Figure 9: Main window after setting the state of the slave potentiostat

Next you can set-up the main potentiostat (responsible for the disc-electrode) similary to the configuration of the slave potentiostat.

If you like to perform a CV experiment click on the "CV measurement" button. Then you can set-up the CV parameters for the disk electrode connected to the main potentiostat like depicted in Fig. 10.

Figure 10: Setting up the main potentiostat (disc) for a CV experiment

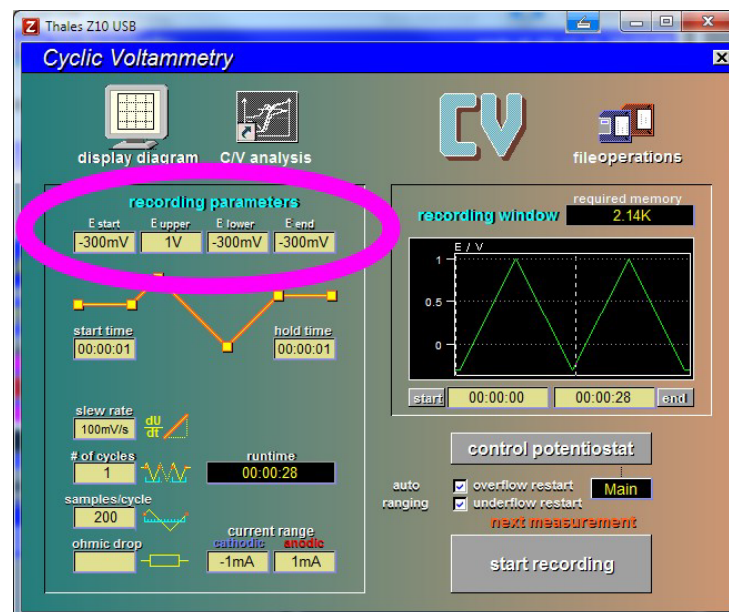After starting the experiment, the values of current and potential of the slave potentiostat (ring electrode) are displayed as acquisition channels (Fig. 11).
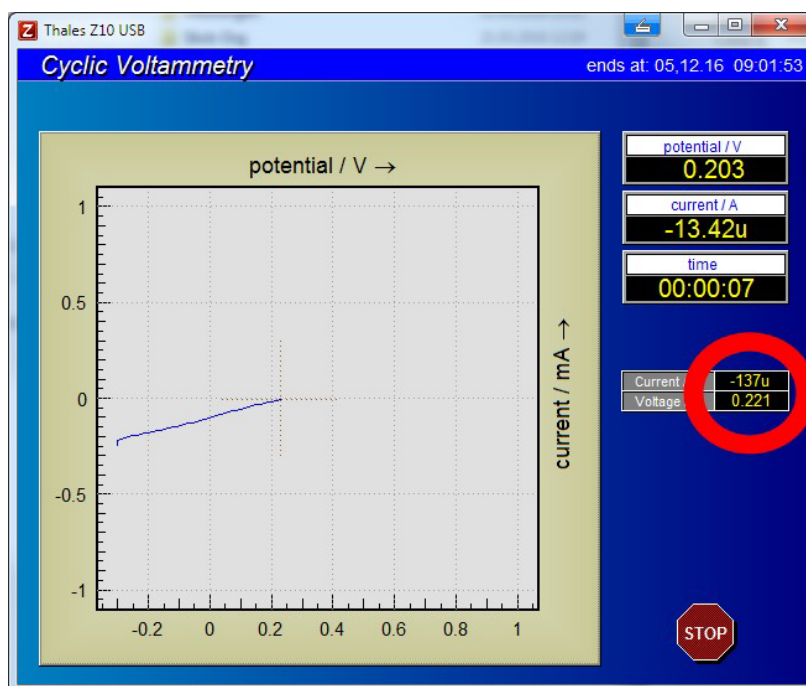
Figure 11: Display of potential- and current values of the slave potentiostat (ring electrode) during the experiment performed with the main potentiostat.

The real-time plot of both measurements, i.e. disc-current vs. potential as well as ring-current vs. potential can be achieved, activating the online display feature:
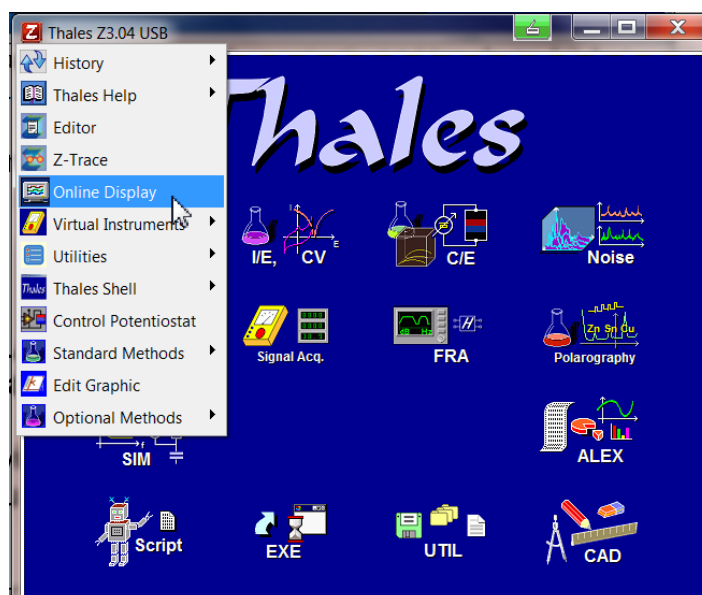
Activate the Online Display using the pulldown menu entry (clicking on the "Z"-icon on the top-left of the Thales window).

In the Online Display window you can activate a "Slave Window" in order to display both diagrams simultaneously – see Fig. 12.

Figure 12: Current/potential plots; left hand side: Graph in the Thales window; middle: plot of disc current vs. scan potential (main potentiostat/Zennium); right: plot of the ring-current (slave/XPOT) vs. the scan potential.
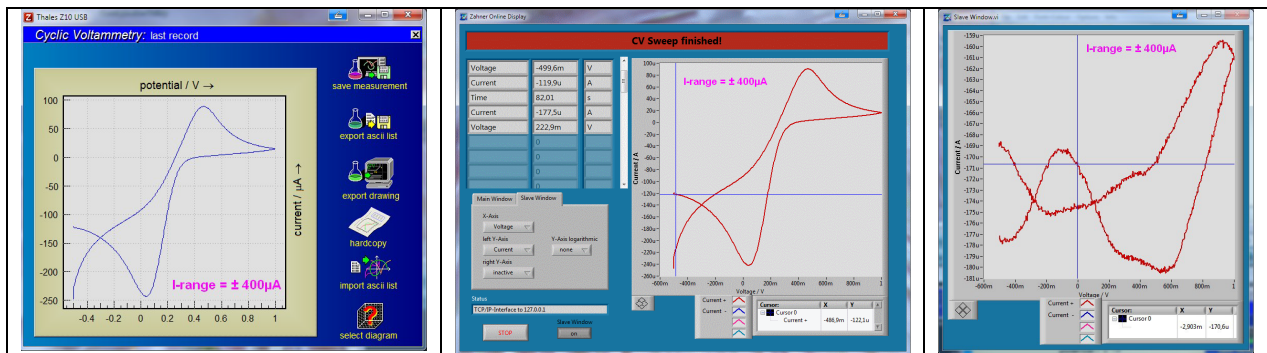
Transfer currents to the ring electrode may be small. Please follow the hints below in order to achieve a sufficient signal to noise ratio:

1.) For the experiment, the optimum current range for the ring electrode at the slave potentiostat must be selected in the RD panel. For the disk electrode select the current range in the corresponding program CV or POL. Please plan for both conditions some reserve in order to avoid a current overflow interrupt. For instance, if the maxium current expected is within +/- 200 µA, the current range must be set to at least -250µA/+250µA.
2.) Select a location for the experiment with small disturbance by environmental noise ("electro-smog").
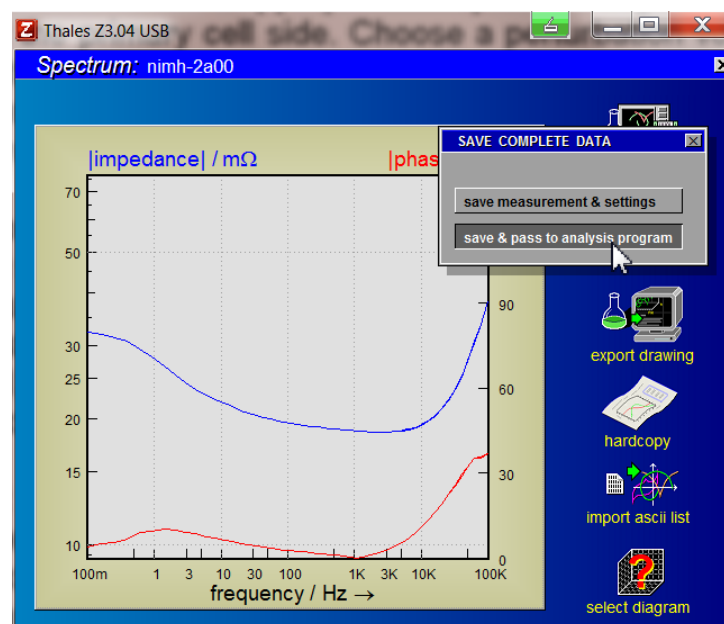3.) The noise level can be further reduced by setting up the experiment within a Faraday cage.

Figure 13: Save EIS data after recording and pass to SIM analysis program.

How to Set-Up a Membrane Dynamic Transfer Function Experiment

Please refer to the previous section describing the set-up for a ring-disk experiment - most of the considerations are valid also for the membrane transfer experiment, with one important exception: Perform the cell connection like described in Figure 2.

Use the manual access to the primary (disk device) and the secondary cell (ring device) and the CV- or POL function in order to get an impression upon the order of magnitude of the currents appearing and the time scale of the membrane transfer. This will help you to find out a relevant frequency range for the key dynamic transfer function experiment.

Then use the EIS set-up panel to set an appropriate frequency range for the EIS spectrum to be measured at the primary cell side. Choose a perturbation voltage via the "disk device" access for the primary cell – due to the relatively small current ratio to be expected you should be generous in order to increase the signal to noise ratio – but keep the lineary condition in mind.

If the primary cell is set up potentiostatic on, an appropriate excitation amplitude and frequency range is set, the secondary cell is also set up potentiostatic on and an appropriate current range is selected, you can start the EIS experiment.

Use the "Start dynamic TF" button. An EIS experiment will take place performed at the primary cell, while the PAD4 will acquire synchronously voltage and current from the secondary cell side via the extra connectors from the slave to the PAD4.

After completion you will get back to the RD panel, where you can enter the storage and analysis functions via the "Last dynamic TF" button. This sequence is necessary in order to enable the RD software to reconstruct the correct spectra types "transfer impedance" and "dynamic current ratio" from the data delivered by the PAD4.

Be aware, that after a correct set-up in the RD environment you can immediately perform an EIS spectrum by means of the standard way nevertheless – but then the result for the additional spectra acquired is erroneously interpreted as cell spectra from a stack measurement as standard.

After storage of the data (Fig. 13), you can open the three created spectra as a series by the SIM program. Three different transfer function types will be available:

1. Channel: primary EIS: $Z^* = \dfrac{\widetilde{U}_{primary}}{\widetilde{I}_{primary}} [\Omega]$

2. Channel: transfer impedance: $Z_{transfer}{}^* = \dfrac{\widetilde{U}_{primary}}{\widetilde{I}_{secondary}} [\Omega]$

3. Channel: dynamic current ratio: $Ratio_{transfer}{}^* = \dfrac{\widetilde{I}_{secondary}}{\widetilde{I}_{primary}} [A/A]$

Usually a species generated at one side of the membrane will shift the activity for this species at the secondary side in a way, that is consumed, if the potential at the secondary side is kept constant. The sign of the transfer current ratio is therefore usually negative. In order to get a more convenient graph for the dynamic transfer functions, the user has the possibility to invert the sign by means of the toggle switch "+/- current ratio sign".