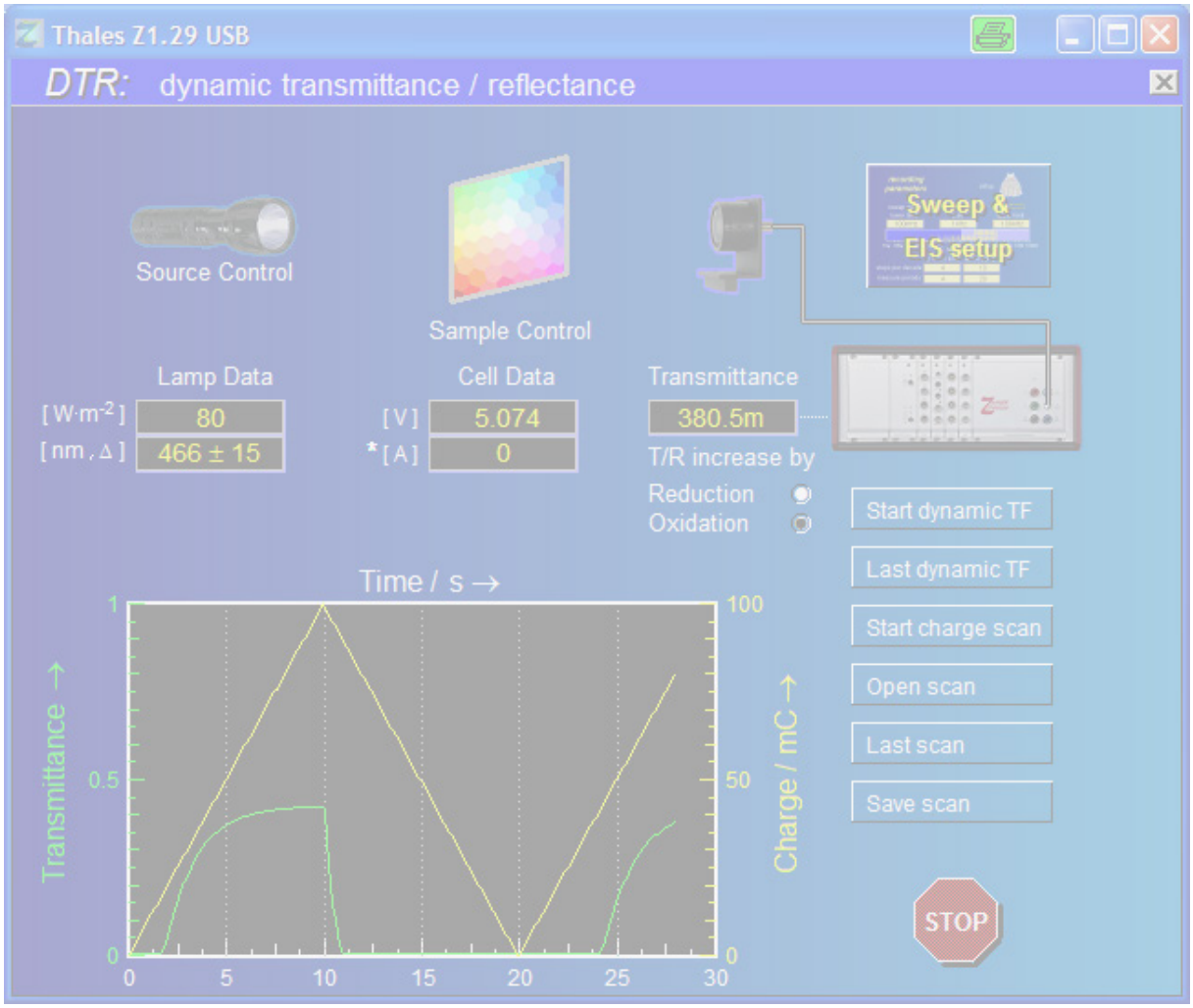
CIMPS-dtr

Dynamic Transmittance / Reflectance Measurements



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1. Introduction

Some physical systems change their optical properties under the influence of an electrical voltage or current applied. Such behavior is of high scientific interest and reached already great economic importance in the fields of electronic displays, smart windows and electronic newspapers, acting as electro-chromic devices.
The electric control of their absorbance may have influence on the spectral properties of such systems. Dependent on the state, color or tone may change, what can be investigated quantitatively by means of CIMPS-abs. For many applications, besides color aspects, the dynamic properties are of high importance as well. The switching time, very important for instance for displays and modulators or the reaction time of smart windows is determined by the kinetic processes of transport- and Redox-reactions or structural re-organization which cause the optical changes.
Dynamic Transmittance Reflectance DTR transfer function analysis follows the ideas popular for instance in Electrochemical Impedance Spectroscopy. The basic transfer function in EIS is given between voltage and current. Like for EIS, in DTR a bias control voltage (or current) applied to the sample is modulated by a small test signal amplitude. Differing from EIS, the sample is illuminated using a certain calibrated static intensity P, and the transmitted or reflected light P^* is recorded and treated as response signal in dependence of the electrical excitation.
The dynamic transfer function DTR is calculated as the quotient between the response modulation signal (the relative intensity change in time $P^*/P = TR^*$) and the excitation signal (Voltage U^* or current I^*, dependent on the selected mode, potentiostatic or galvanostatic).
In the frequency domain, the time dependency of both signals can be cancelled out in the quotient, apart from a characteristic phase shift φ which may depend on the frequency ω.

$$U^* = \hat{U} \cdot e^{j\omega t}, \quad I^* = \hat{I} \cdot e^{j\omega t}$$ (force signals, amplitudes $\hat{U}, \hat{I}$, j = imaginary unit)

$$\frac{P^*}{P} = TR^* = \hat{TR} \cdot e^{j\omega t + \varphi}$$ (response signal, amplitude $\hat{TR}$)

$$DTR_{pot} = \frac{TR^*}{U^*} = \frac{\hat{TR} \cdot e^{j\omega t+\varphi}}{\hat{U} \cdot e^{j\omega t}} = \frac{\hat{TR}}{\hat{U}} \cdot e^{j\varphi}, \quad \left[DTR_{pot}\right] = V^{-1}$$ (potentiostatic DTR)

$$DTR_{gal} = \frac{TR^*}{I^*} = \frac{\hat{TR} \cdot e^{j\omega t+\varphi}}{\hat{I} \cdot e^{j\omega t}} = \frac{\hat{TR}}{\hat{I}} \cdot e^{j\varphi}, \quad \left[DTR_{gal}\right] = A^{-1}$$ (galvanostatic DTR)

DTR spectra can be understood in principle like EIS. Time constants can be extracted and assigned to certain charge transfer, relaxation and transport processes. Their characteristic phase angle helps to distinguish between them.
It is known, that EIS suffers from the ambiguity of the spectra: different mechanisms may lead to identical dynamic transfer functions. It is an exceptional property of DTR, that the response function can be assigned unequivocally to an occurring colored species. In combination with EIS, DTR may help to cancel out further ambiguities, like it can be done also in combination with IMPS/IMVS data.
DTR can be performed with most calibrated light sources of different spectral properties from the Zahner portfolio. By changing the wavelength, DTR may be extended selectively to the case, when more than one colored species is present.
DTR is a brand-new field. Unlike in EIS or CIMPS, immediate modeling support is not available from Zahner at the moment. The user may profit nevertheless from the stringent treatment of DTR data in Thales, which is orthogonal to the treatment of EIS and CIMPS data. The user is invited to define his own mathematical models via the USR function in SIM for simulation and fitting purposes.
DTR gives valuable dynamic information which belongs to a certain bias within the systems steady state characteristic. Besides, CIMPS-dtr supports slow, quasi-static scan features determining the steady state characteristics. In order to characterize the static transmittance reflectance behavior in

dependence of the applied voltage, the sample voltage can be swept linearly between two limiting voltages under potentiostatic control. It is save to assume, that mostly not the direct current, but the accumulated charge is more characteristic for the description of an actual quasi-static TR-state of an electro-chromic system under galvanostatic control. Therefore the TR-characteristic in galvanostatic mode is supported in form of a charge scan.

2. Hardware and Installation

CIMPS-dtr consists of the following components:

- Standard CIMPS system
- SEL 033 calibrated photosensor with cable set fitting to the main potentiostat probe E/I
- Additional slave potentiostat for sample control

Connect the standard CIMPS components LDA, light source potentiostat and feedback photodiode in the way described for standard CIMPS and route the EPC Channel 1 to the light source potentiostat.

Connect the photo-electrochemical cell PECC respectively the sample under test to the additional slave potentiostat (sample control potentiostat) and route the EPC Channel 2 to the Cell potentiostat.

Connect the SEL 033 calibrated photosensor to the main potentiostat.

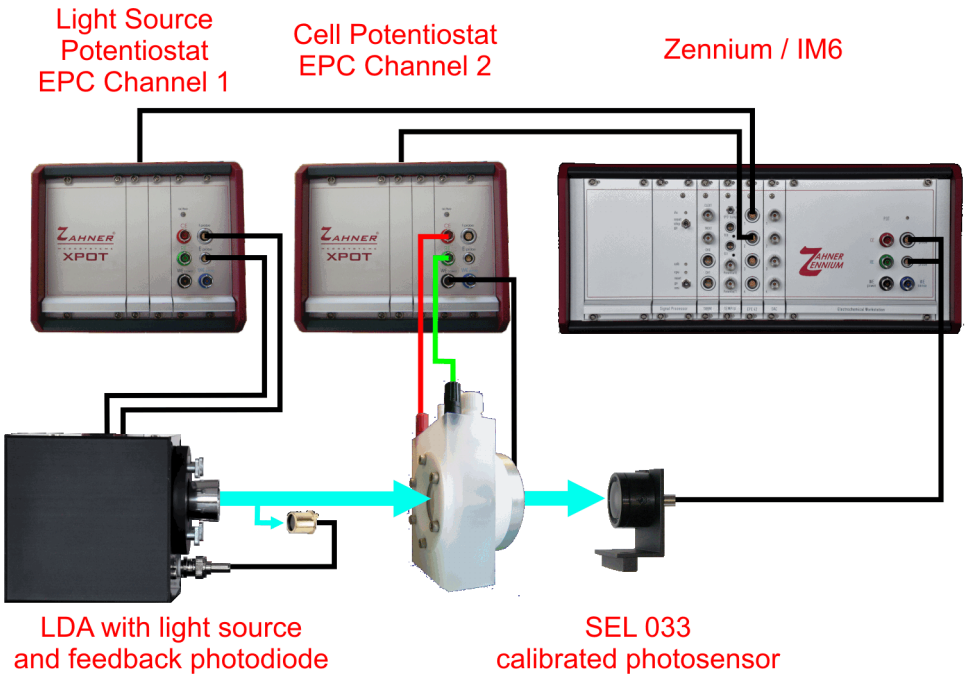


Fig. 1 Connection scheme of CIMPS-dtr. The probe E/I connectors of the light source are connected to the slave potentiostat (PP211 or XPOT) using the cable supplied with CIMPS-dtr. The photo sensor located in front of the cell is connected to the BNC socket of the LDA.

!	An enclosure covering the complete optical bench is necessary to avoid detrimental effects caused by ambient light during the whole measurement time.

3. CIMPS-dtr Software

3.1. Startup

CIMPS-dtr is easily activated by using the pull down menu as shown in Fig. 2. To open the pull down menu click onto the Z-icon in the title bar of the Thales window.



Fig. 2 Start of CIMPS-dtr using the pull down menu

After initialization of the three potentiostats, the main window of CIMPS-dtr is displayed (see Fig. 3).

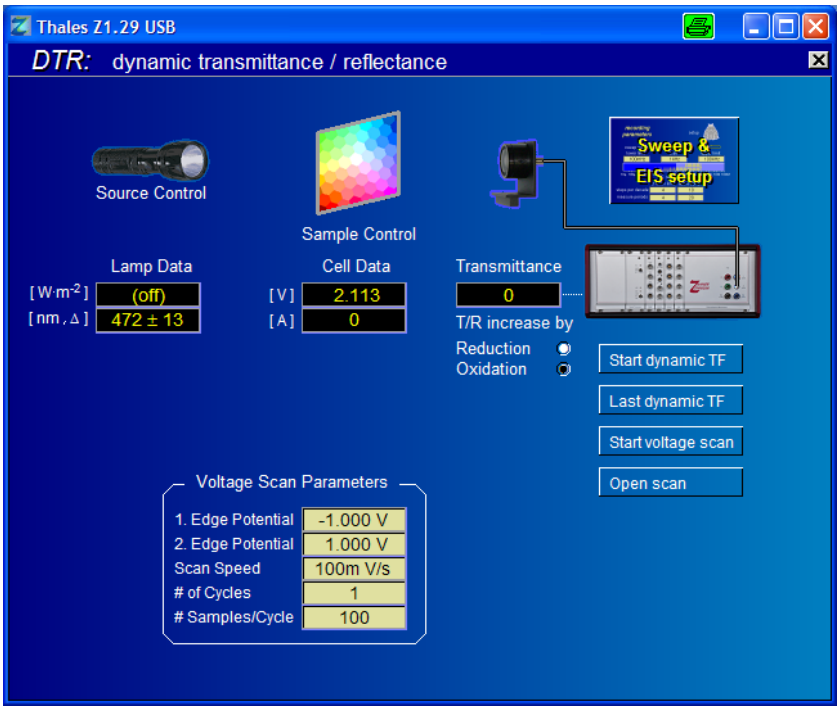


Fig. 3 Main window of CIMPS-dtr after startup

3.2. Light Source Control

All functions necessary for controlling the light source are easily accessible by the light source control icon. Differing from standard CIMPS, access is established through an intermediate dialog menu.



Fig. 4 Icon of the light source control in default (left hand side) and active state (right hand side).

3.2.1. Light Source Calibration

Light sources delivered by Zahner are calibrated allowing the direct input of light intensity in W/m². Therefore the calibration file of the light source has to be loaded before use.

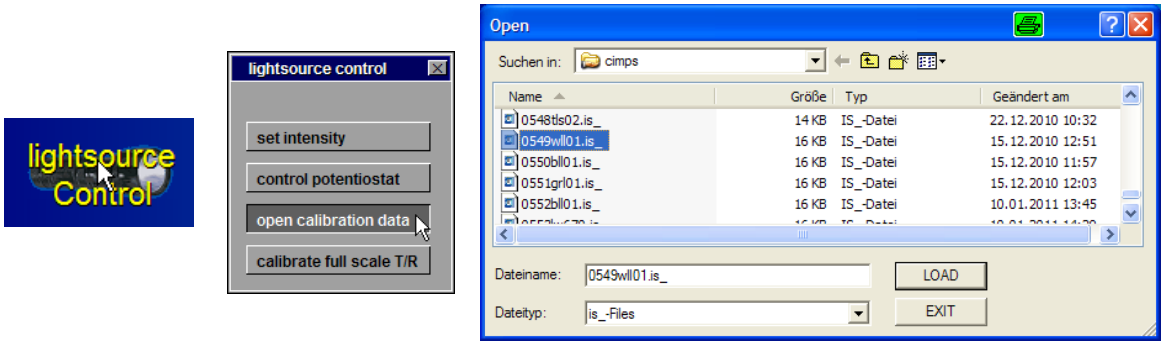


Fig. 5 Loading light source calibration data.

Click the light source control icon (Fig. 5, left hand side) to open the light source control dialog. In the light source control dialog (Fig. 5, middle) select open calibration data. Now the file dialog for choosing the light source calibration file opens (Fig. 5, right hand side). In the file dialog select the file corresponding to the light source. After installation of the calibration data CD, light source calibration files are located in c:\thales\cimps. The name of the calibration file consists of the serial number and the ordering code of the light source, e.g. 0549wlr01 for the white light source with serial number 549.

3.2.2. Intensity Control

The intensity of the light source is set by clicking the light source control icon (Fig. 6, left hand side). In the light source control dialog (Fig. 6, middle) select “set intensity” to open the intensity dialog (Fig. 6, right hand side). Enter the desired intensity here and confirm by either hitting the enter key or clicking the green button top right.



Fig. 6 Setting the intensity of the light source

By setting an intensity of 0 W/m² the light source is switched off. Here the confirmation dialog (Fig. 7) offers two options. In case of “yes” the light source potentiostat is switched off so the current-carrying leads are floating. In case of “no” the light source potentiostat stays on but is set to 0V.

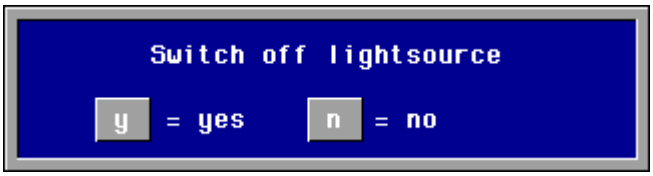


Fig. 7 Options for switching off the light source

3.2.3. Control Potentiostat

The test sampling screen of the light source potentiostat can easily be reached by selecting “control potentiostat” (Fig. 8). The potential displayed here is not the voltage applied to the LED but has a special meaning. It is the response signal of the feedback sensor at the cell site. Control voltages are automatically calculated by the set intensity function (refer to chapter 3.2.2) so setting a voltage here is not necessary.

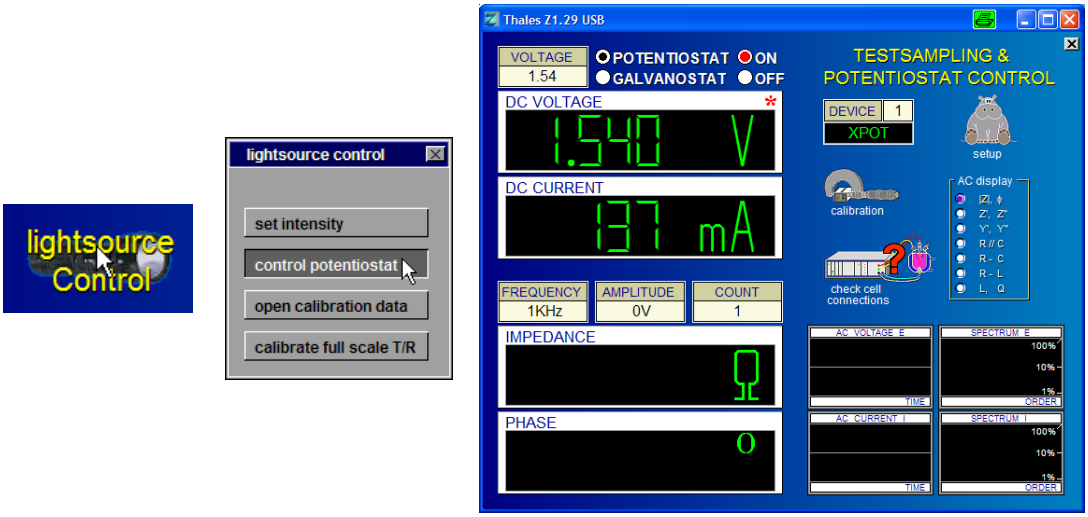


Fig. 8 Entering test sampling of the light source potentiostat

3.2.4. Full Scale Transmittance / Reflection Calibration

The absolute intensity measured by the SEL 033 calibrated photo diode depends on the preset intensity of the light source, the optical aperture of the experimental setup and the state of the sample investigated. Therefore a reference measurement considered as maximum transmittance has to be done. This is accomplished by selecting “calibrate full scale T/R” in the light source control (Fig. 9 left hand side and middle). Now adjust the experimental setup for maximum transmittance and acknowledge the dialog of Fig. 9 right hand side by clicking it.

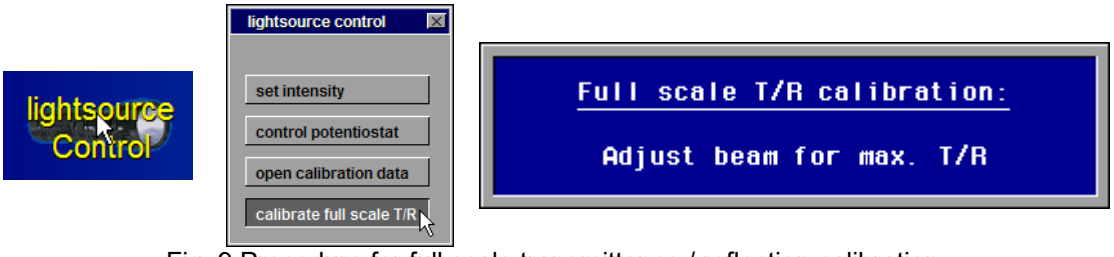


Fig. 9 Procedure for full scale transmittance / reflection calibration

In case the SEL 033 calibrated photodiode was not connected to the Zennium/IM6 potentiostat an error message is displayed. Check the connection of the SEL 033 and repeat the full scale calibration. The same error is displayed in case ambient light disturbs the reference measurement. In this case reduce ambient light e.g. by using an enclosure around the optical bench.

3.3. Dynamic Transfer Functions

After the light source has been activated and a transmittance full scale calibration has been performed (refer to chapter 3.2) dynamic transmittance measurements can be done.

3.3.1. Sample Control

In order to record dynamic transfer functions the state of the sample and the excitation signal have to be set. Therefore click the sample control icon (Fig. 10 left hand side and middle) to enter testsampling and potentiostat control (Fig. 10 right hand side). Here choose either potentiostatic or galvanostatic mode, set a DC bias and amplitude. Now return to the CIMPS-dtr main screen by pressing the middle mouse button or by clicking the x button at the top right.

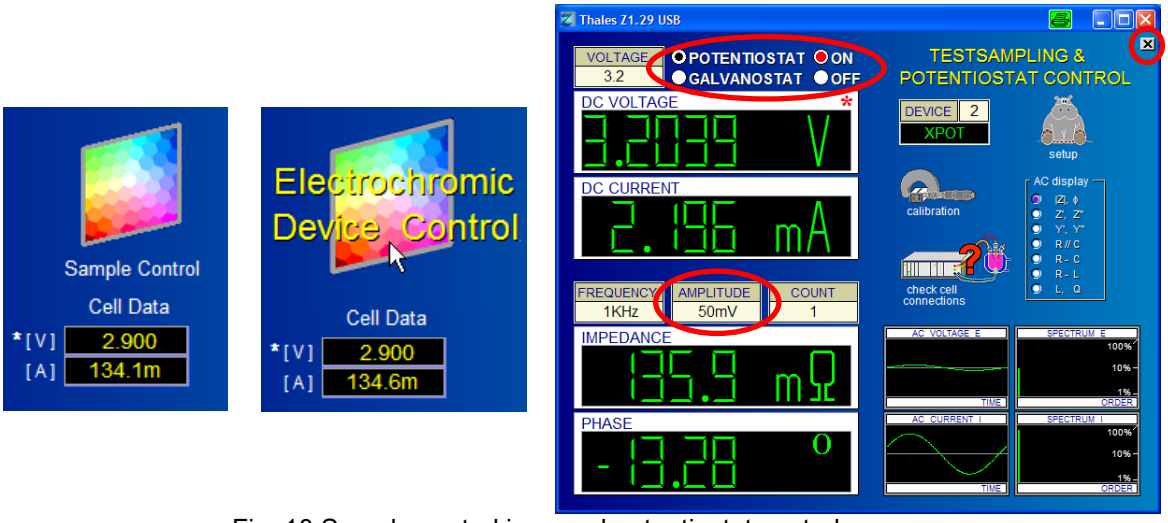


Fig. 10 Sample control icon and potentiostat control screen

The actual potential and current of the sample are displayed in the CIMPS-dtr main screen. The controlled quantity (potential for potentiostatic mode and current for galvanostatic mode) is marked with an asterisk (see Fig. 10 left hand side and middle).

3.3.2. Sweep and EIS-Setup

The frequency range and the parameters of the dynamic measurement are set in the sweep and EIS setup. Pease consider, that electro-chromic processes often appear at slow timescales. Using high test frequencies under this circumstances will only reflect artifacts due to the break-down of the response signal to zero.

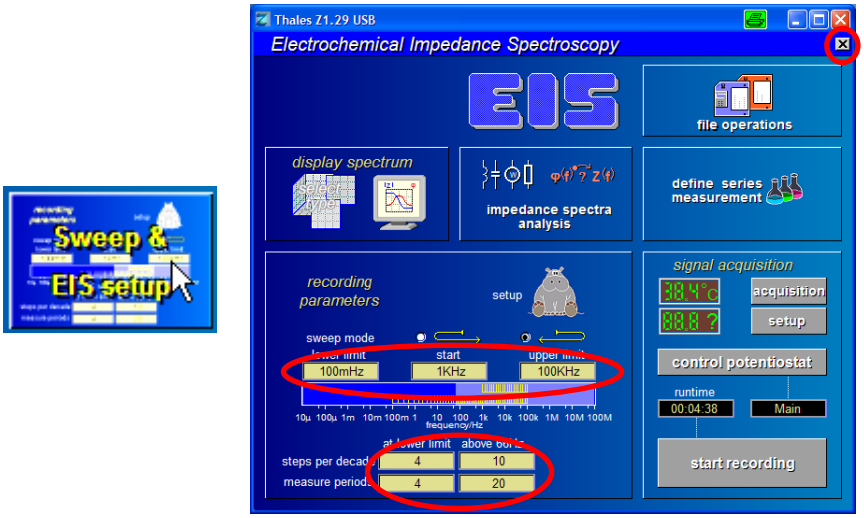


Fig. 11 Setting up frequency range and parameters for dynamic measurements

For details regarding the function of the recording parameters refer to the EIS manual. When finished return to the CIMPS-dtr main screen with the middle mouse button or by clicking the x button at the top right.

3.3.3. Sign of response

The response of a sample to an excitation can be divided into two general cases. Either transmittance can increase with oxidation at the working electrode, i.e. when driving potential more positive. Or transmittance can increase with reduction at the working electrode, i.e. when driving potential more negative. These two cases differ in a phase shift of 180° in the force response relationship. In order to get minimum phase spectra the type of sample can be set by the radio buttons shown in Fig. 12.

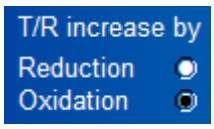


Fig. 12 Setting the sign of response

In case the sign of response is set to the wrong direction phase will be shifted by 180°.

3.3.4. Recording Dynamic Transmittance Spectra

After all settings are done, the measurement can be started by clicking the “Start dynamic TF” button (Fig. 13 left hand side). During measurement the spectrum and most recent data are displayed online (Fig. 13 right hand side). Concerning details of this screen also refer to the EIS manual.

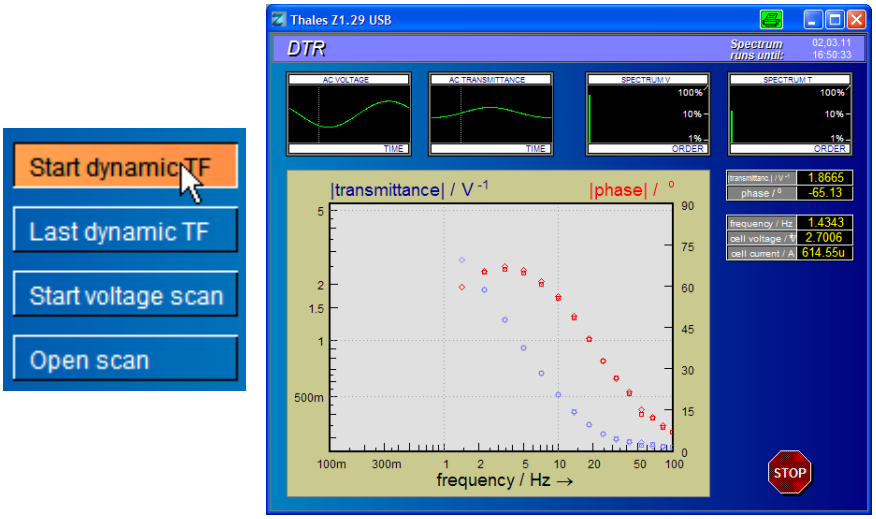


Fig. 13 Starting and recording dynamic measurements

After measurement has finished, the spectrum is displayed for review and saving in different formats (Fig. 14 left hand side). For a first quick investigation of the spectrum click the graph to activate the crosshair mode (Fig. 14 right hand side).

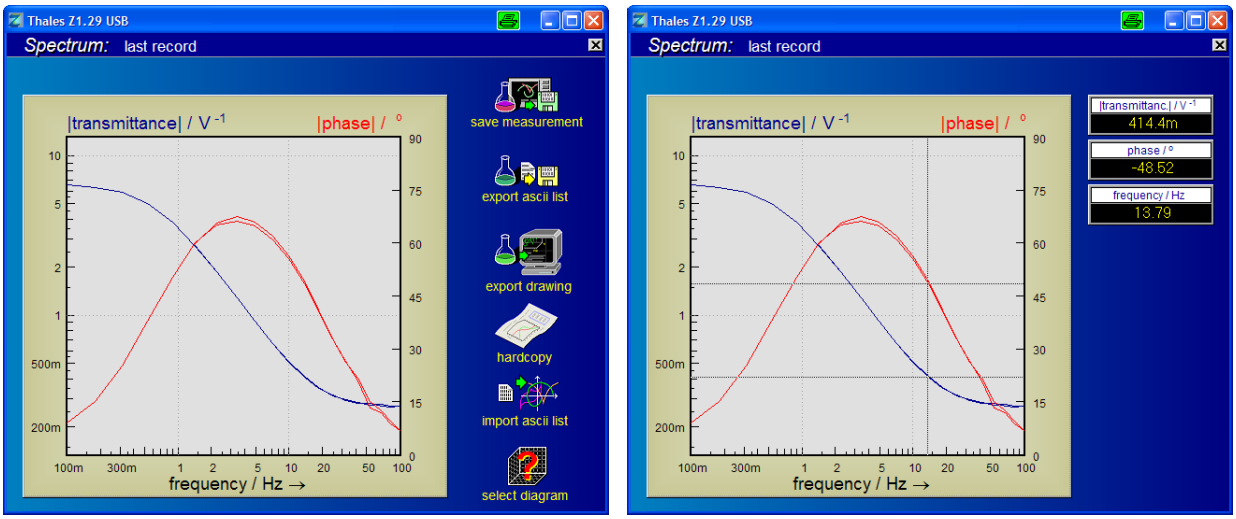


Fig. 14 Display of spectrum after measurement and crosshair mode

You can return to this screen from the CIMPS-dtr main screen using the “Last dynamic TF” button until a new measurement is started.

3.3.5. Saving Dynamic Transmittance Spectra

In the display spectrum screen (Fig. 14 see left hand side) click “save measurement” in order to save the spectrum. Now two options are available (Fig. 15 right hand side). “Save measurement & settings” returns to the display spectrum screen (see Fig. 14) after the file is saved. “Save & pass to analysis program” saves the file to disk and automatically opens it in SIM, the simulation and fitting program of Thales.

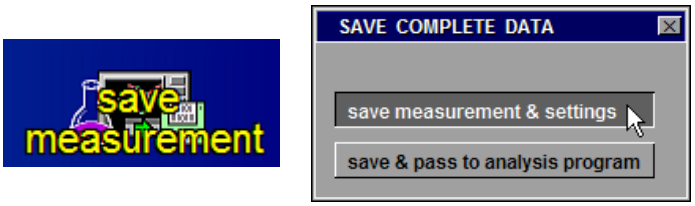


Fig. 15 Saving transmittance spectra

In both cases a dialog for entering additional information about the experiment is opened (Fig. 16 left hand side). The data entered here will be saved in the header of the file and can be retrieved when opening or exporting the spectrum later. When finished click the green button on the upper right corner. In the file dialog (Fig. 16 right hand side) select a path and filename for saving the spectrum.

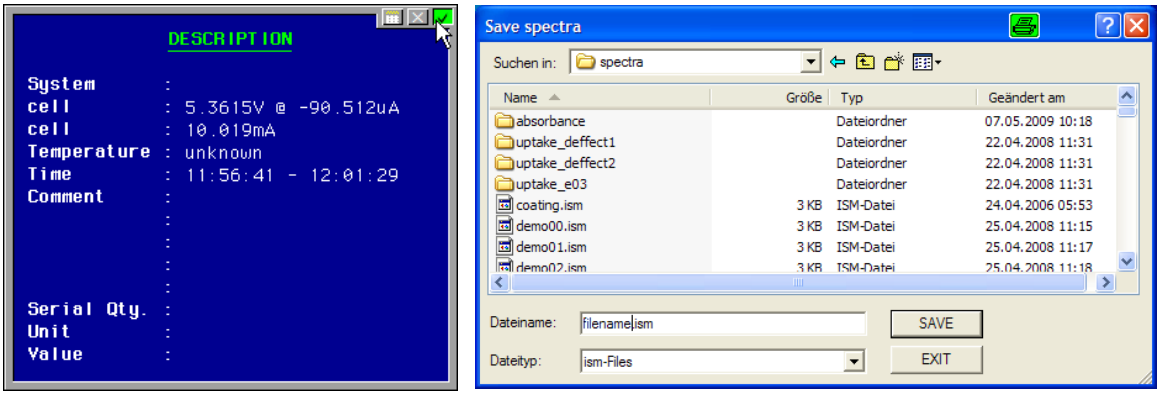


Fig. 16 Entering comments and choosing location and name while saving spectra

3.3.6. Text Export of Dynamic Transmittance Spectra

In order to export the measured data for use in third party software select “export ASCII list” in the display spectrum screen (Fig. 14 left hand side). Three options are available for ASCII text export (Fig. 17 left hand side). “Copy list to clipboard” passes the data to the Windows® clipboard from where it can be pasted to various Windows® applications. “Save list as textfile” opens a file dialog in order to save the ASCII list to disk.

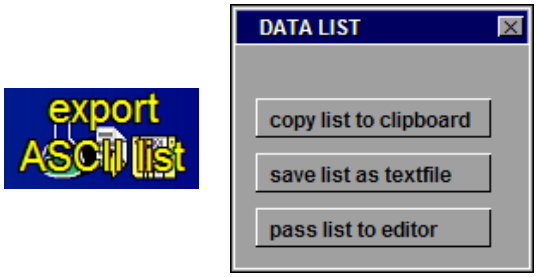


Fig. 17 Export of spectra as ASCII list

“Pass list to editor” transfers the ASCII data to the Thales editor where it can be further processed (Fig. 18).

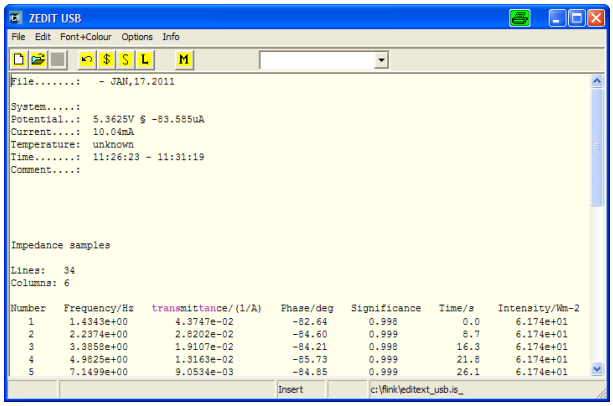


Fig. 18 Thales editor with exported ASCII data

3.3.7. Graphic Export of Dynamic Transmittance Spectra

The displayed spectrum (Fig. 14) can be exported as graphics. “Pass to clipboard” passes the graph to the Windows® clipboard from where it can be pasted to various Windows® applications. “Paste to CAD” transfers the graph to the Thales CAD application. For details concerning CAD refer to the CAD manual. “Save as EMF file” opens a file dialog in order to save a Windows® Enhanced Metafile. EMF is a vector graphics format which can be imported in various Windows® applications.

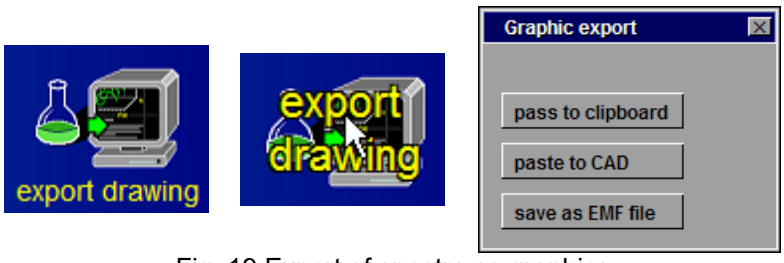


Fig. 19 Export of spectra as graphics

3.4. Static Transfer Functions

In addition to the frequency dependent transmittance/reflectance also measurements with changing DC bias can be recorded. Either control voltage sweeps or charge sweeps under current control can be selected.
Before recording static transfer functions the light source has to be activated and a transmittance full scale calibration has to be performed (refer to chapter 3.2).

3.4.1. Recording Voltage Scans

In order to record a voltage scan cell control has to be switched to potentiostatic mode. Therefore click the sample control icon (Fig. 20 left hand side and middle) to enter testsampling and potentiostat control (Fig. 20 right hand side). Here choose potentiostat and return to the CIMPS-dtr main screen by pressing the middle mouse button or by clicking the x button at the top right.

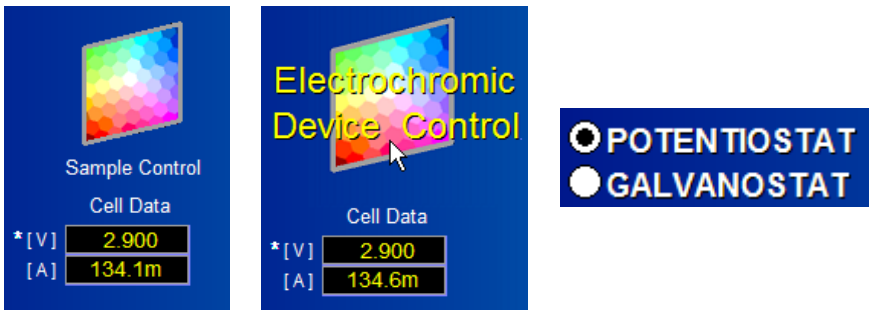


Fig. 20 Switching sample control to potentiostatic mode for voltage scans

Now the scan parameters are automatically switched to voltage scan (Fig. 21, left hand side). In order to set up the experiment click the parameters (Fig. 21, left hand side) to enter the parameter window (Fig. 21, right hand side).

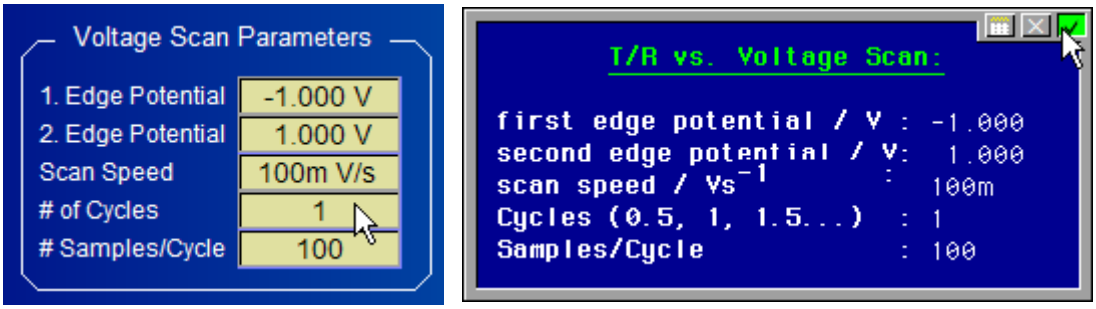


Fig. 21 Setting parameters of voltage scans

The limits of the parameters are:

- edge potentials: within the potential limits of the used potentiostat
- scan speed: 0.1 mV/s to 0.1 V/s
- cycles: 0.5 to 1000
- samples/cycle: 10 to 1000
- samples/s: max. 10. Samples are put in as samples/cycle. If the combination of the parameters violates the max. sample/s, this input will be rejected and corrected automatically.

One cycle is understood as sweep from the first edge potential to the second edge potential and back to the first edge potential. In order to stop the measurement at the second edge potential add a half cycle. After the parameters are set, start the measurement by clicking “Start voltage scan” as shown in Fig. 22 left hand side.

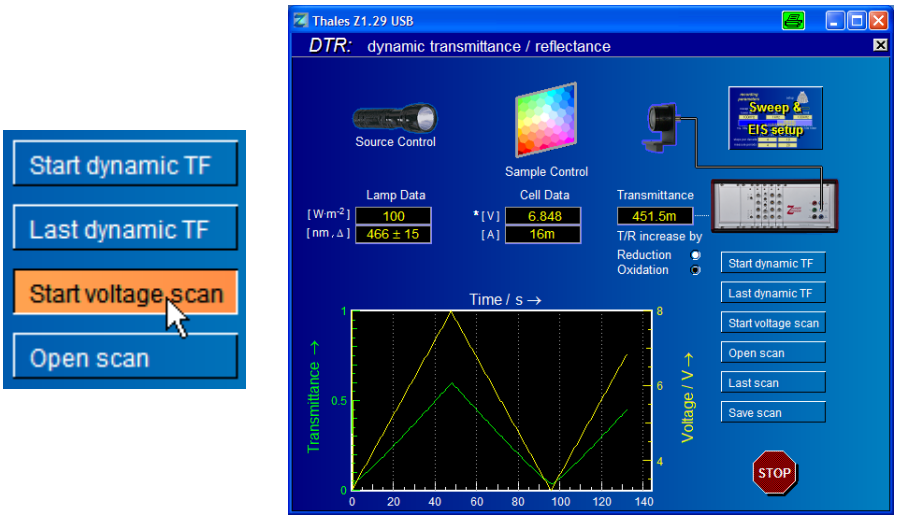


Fig. 22 Voltage scans: start button and online display

During the measurement recorded data are displayed online as shown in Fig. 22 right hand side, where a scan of 1.5 cycles is nearly finished.

3.4.2. Recording Charge Scans

Charge scans are recorded in galvanostatic mode at fixed current which is automatically integrated by Thales to yield the charge. In the first half of a cycle the sample is charged with the preset current (starting sign of current), in the second half of the cycle it is discharged again (inverse sign of current). In order to record a charge scan cell control has to be switched to galvanostatic mode. Therefore click the sample control icon (Fig. 23 left hand side and middle) to enter testsampling and potentiostat control (Fig. 23 right hand side). Here choose galvanostat and return to the CIMPS-dtr main screen by pressing the middle mouse button or by clicking the x button at the top right.

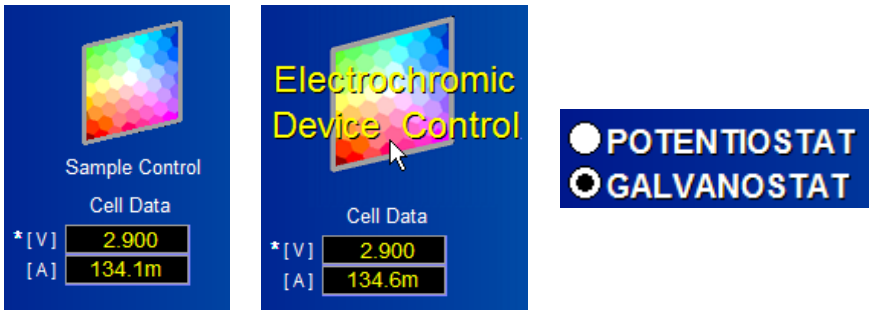


Fig. 23 Switching sample control to galvanostatic mode for charge scans

Now the scan parameters are automatically switched to charge scan (Fig. 24, left hand side). In order to set up the experiment click the parameters (Fig. 24, left hand side) to enter the parameter window (Fig. 24, right hand side).

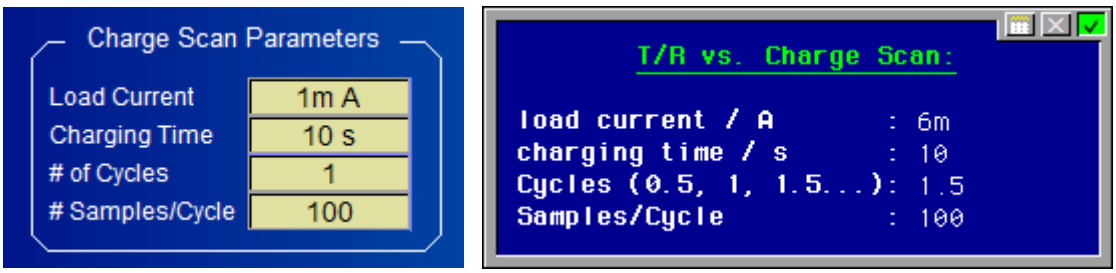


Fig. 24 Setting parameters of charge scans

The limits of the parameters are:

- load current: within the limits of the used potentiostat
- charging time: 1 to 3600 s
- cycles: 0.5 to 1000
- samples/cycle: 10 to 1000
- samples/s: max. 10. Samples are put in as samples/cycle. If the combination of the parameters violates the max. sample/s, this input will be rejected and corrected automatically.

One cycle is understood as a charging phase in the first half of the cycle and a discharging phase in the second half of the cycle. In order to stop the measurement after a charging phase add a half cycle. After the parameters are set, start the measurement by clicking “Start charge scan” as shown in Fig. 25 left hand side.

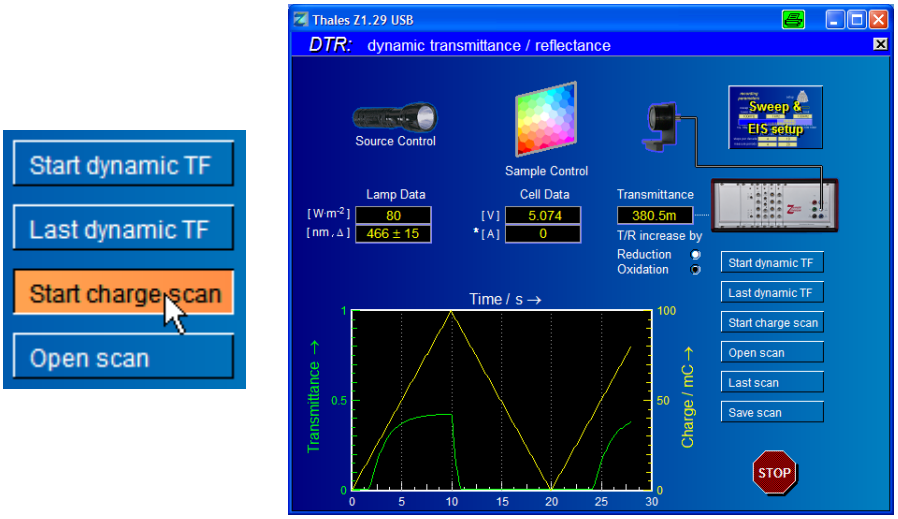


Fig. 25 Charge scans: start button and display during a scan.

During the measurement recorded data are displayed online as shown in Fig. 25 right hand side, where a scan of 1.5 cycles is nearly finished.

3.4.3. Display of Static Transfer Functions

After a voltage or charge scan has finished it is displayed for review (Fig. 26). By clicking “Select Graphic” different options for plotting the data are available (Fig. 27).

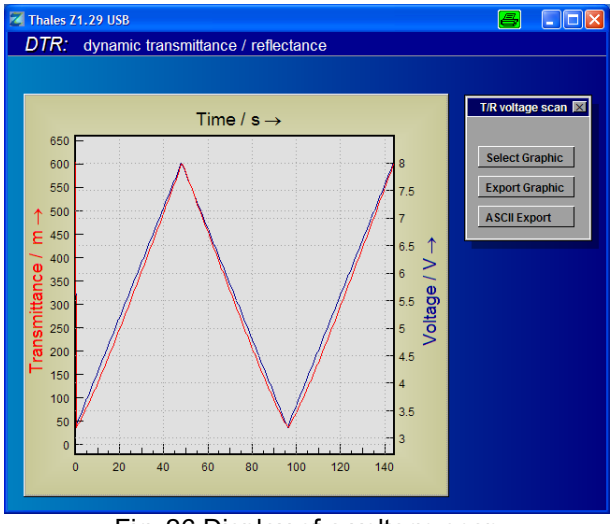


Fig. 26 Display of a voltage scan

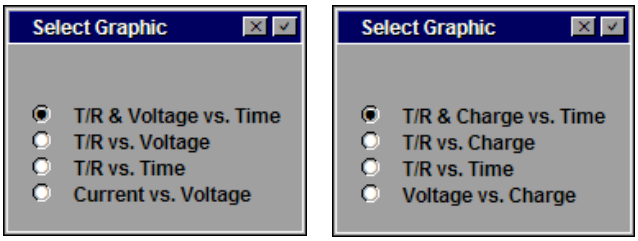


Fig. 27 Display options of voltage scans (left hand side) and charge scans (right hand side)

3.4.4. Graphic Export of Static Transfer Functions

The displayed scan can be exported as graphics (Fig. 28) using the “Export Graphic” button. “Pass to clipboard” passes the graph to the Windows® clipboard from where it can be pasted to various Windows® applications. “Paste to CAD” transfers the graph to the Thales CAD application. For details concerning CAD refer to the CAD manual. “Save as EMF file” opens a file dialog in order to save a Windows® Enhanced Metafile. EMF is a vector graphics format which can be imported in various Windows® applications.

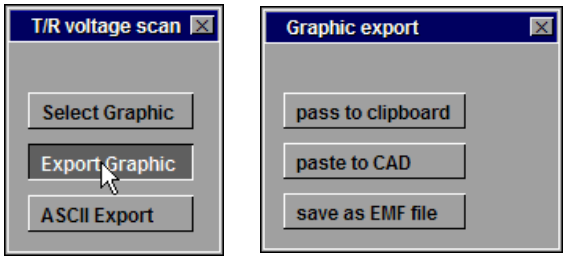


Fig. 28 Export of voltage scans as graphics

3.4.5. ASCII Export of Static Transfer Functions

Both voltage or charge scans can be exported as ASCII files. While the scan is displayed (Fig. 26) select ASCII Export (Fig. 29) in order to save an ASCII file to disk.

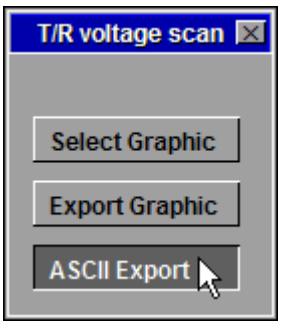


Fig. 29 ASCII Export of voltage and charge scans

3.4.6. File Operations for Static Transfer Functions

Voltage and charge scans can be loaded and saved using the buttons in the CIMPS-dtr main screen (Fig. 30). Please note the “Save scan” button is not displayed until measured data are available.

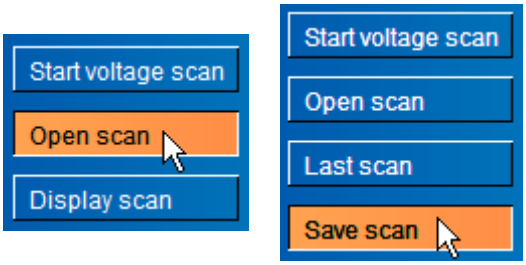


Fig. 30 Buttons for file operations of voltage and charge scans

After clicking the save button (Fig. 30 right hand side) a dialog for entering additional information about the experiment is opened (Fig. 31 left hand side). The data entered here will be saved in the header of the file and can be retrieved when opening or exporting the spectrum later. When finished click the green button on the upper right corner. In the file dialog (Fig. 31 right hand side) select a path and filename for saving the spectrum.

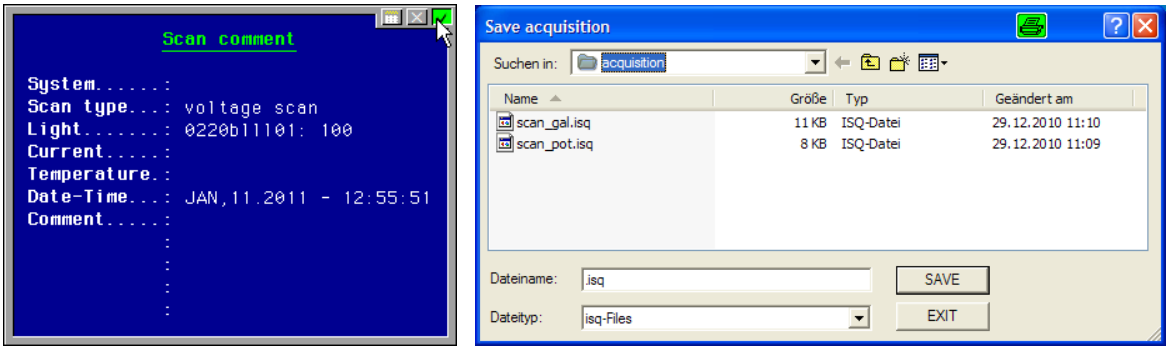


Fig. 31 Saving voltage and charge scans to disk