

Electrochemical Impedance Spectroscopy Using the BAS-Zahner IM6 and IM6e Impedance Analyzers

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This article discusses the IM6 and SIM modules of the Thales software system that is used for the operation of the BAS-Zahner IM6 and IM6e impedance analyzers. The IM6 module is used for data acquisition, whereas the SIM module is used for data analysis, equivalent circuit synthesis, and fitting of experimental data.

Electrochemical impedance spectroscopy is becoming increasingly popular as an analytical technique for a number of applications, including characterization of batteries, fuel cells, coatings, ceramics, semiconductors, sensors, and corrosion studies. The BAS-Zahner IM6 and IM6e Impedance Analyzers combine high precision hardware and powerful, user-friendly software to simplify the acquisition and analysis of high quality, reliable impedance data.

Although the hardware specifications of the IM6 and IM6e differ (**T1**), the operating system for both is the Thales software. This is a modular system, with separate programs for impedance data acquisition and data analysis, as well as programs for techniques such as cyclic voltammetry, linear polarization, and electrochemical noise data acquisition and analysis.¹ The pro-

grams for impedance data acquisition (IM6) and data analysis (SIM) are the subject of this article.

IM6 — Impedance Data Acquisition

Activating the IM6 icon in the Thales menu leads to the screen shown in **F1**. The first item to examine is the *check cell connections* screen (when this icon is activated, the potentiostat is automatically switched off, which allows the connections to be changed safely). This shows the cell lead BNC connections, and the order of connection for two, three, and four electrode operation (**F2**). Note that there are four cell leads, two for the working (test) electrodes, and one for each of the reference and counter (auxiliary) electrodes. The two connections for the test electrode are for the current-measuring circuit (*power* connec-

tion), and for the potential-control circuit (*sense* connection). A buffer amplifier is also available, if a higher input impedance is required for the reference electrode (this amplifier is plugged into the *Probe E* connection, and substitutes for the test electrode *sense* and *reference electrode* BNC connections).

Once the cell connections have been made, the experimental parameters can be entered. The DC potential and the AC amplitude are adjusted using the *test-sampling and potentiostat control* screen (**F3**).

When this screen is first entered, the potentiostat is switched off and the rest potential is displayed in the *DC POTENTIAL* display box. This allows the rest potential to be monitored as a check for system stability. Once the rest potential has stabilized, the potentiostat can be switched on² (the required value is entered in the *POTENTIAL* dialog

T1

Comparison of IM6 and IM6e.

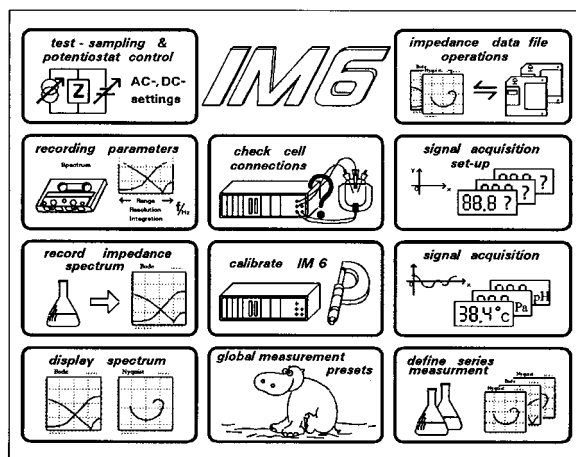
	IM6e	IM6
Upper frequency limit	1 MHz	8 MHz
Current range	± 1 A	± 3 A
Rise time	300 ns	100 ns
Expansion slots	1	4
Floppy disk drive	no	yes
IEEE-488 bus	no	yes

box). The background DC current is now displayed in the DC CURRENT display box. Once the DC parameters have been set, the AC parameters can be optimized by measuring the impedance at selected single frequencies. The required parameters are the FREQUENCY, the AMPLITUDE, and the number of COUNTS. While these single frequency meas-

urements are being made, the AC potential and current wave forms and spectra are displayed in the upper left corner. These provide an indication of the quality of the experimental data and the linearity of the system response, and the AC amplitude and number of counts can be adjusted if necessary. This provides an efficient method for optimizing the experimental parameters (the alternative method of running a full frequency spectrum for each set of parameters is considerably more time consuming).

F1

Menu for IM6 program.

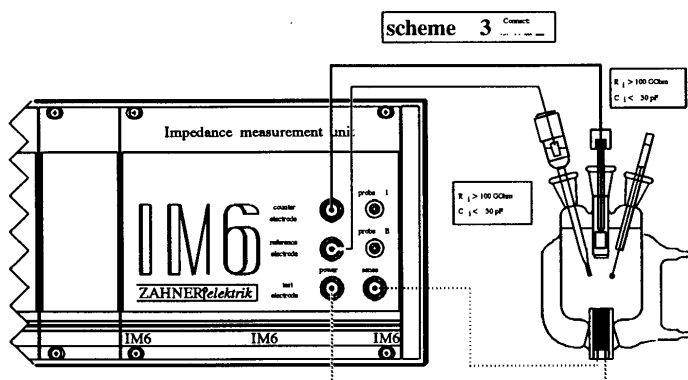


Once the AC amplitude and the number of counts have been optimized, the frequency range, the number of data points, and the number of cycles are entered using the recording parameters screen (F4).

Three parameters can be used to define the Frequency range: a Start at value, an Upper limit, and a Lower limit. The default measurement starts at an intermediate value, sweeps to the high frequency limit, and then sweeps to the low frequency limit. The measurement at the same high frequency points on the forward and reverse sweep provides an indication of system stability without adding significantly to the experimental time, as any change in the system over this time scale will alter the impedance and phase angle at a given frequency. A single sweep measurement from high to low frequency can be obtained by setting the Start at and Upper limit frequencies to the same value. Changing the Sweep Mode changes the initial direction of the frequency sweep.

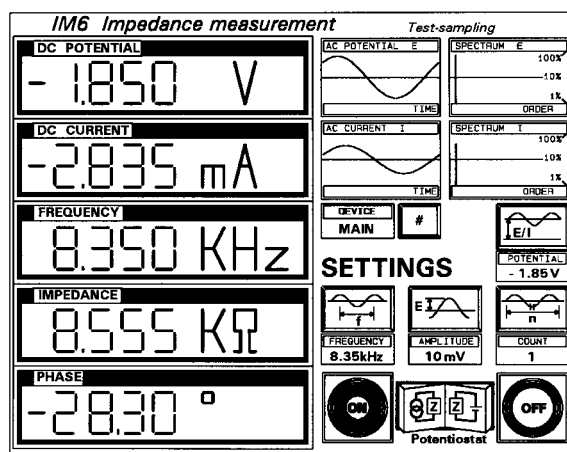
F2

Connection scheme for three electrode system without buffer amplifier.



F3

Test-sampling and potentiostat control screen.



One problem inherent in impedance experiments is the balance between the improvement in the data quality obtained by increasing the number of frequencies used and the number of cycles collected at each frequency and the increase in the time required for the experiment, which can lead to time-dependent artifacts. This problem is particularly pronounced when low frequencies are used. The IM6 program offers a partial solution by dividing the frequency range into two (greater than

and less than 66 Hz) when setting the number of frequencies (*Steps per decade*) and the number of cycles at each frequency (*Number of measure*

periods).³ This allows the number of frequencies and cycles to be increased at high frequencies without significantly increasing the time re-

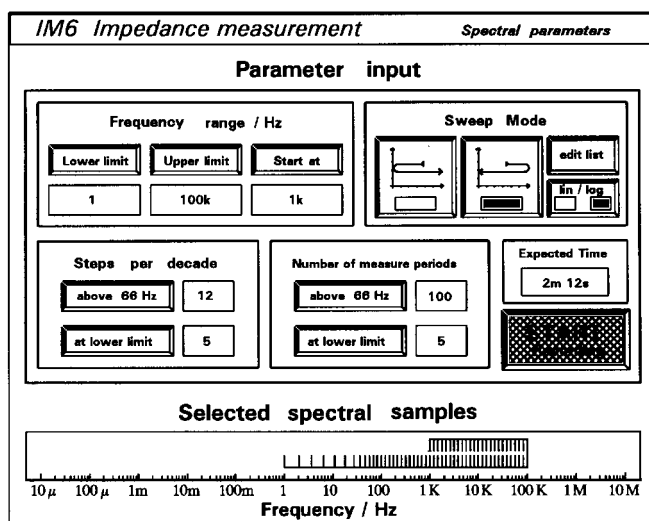
quired for the experiment (changes in the time are shown in the *Expected Time* display box).

Once the parameters have been set, the experiment can be started, by clicking either the *START Recording* icon in the recording parameters screen or the *record impedance spectrum* icon in the main IM6 menu. During the experiment, the data is displayed in real time in either a Nyquist or a Bode plot (other formats are available), as well as the AC wave forms and spectra, and the measured numerical values (**F5**).

When the experiment is complete, the data can be displayed using *display spectrum*. However, if more comprehensive data analysis is required, the data must be saved, and then loaded into the SIM program.

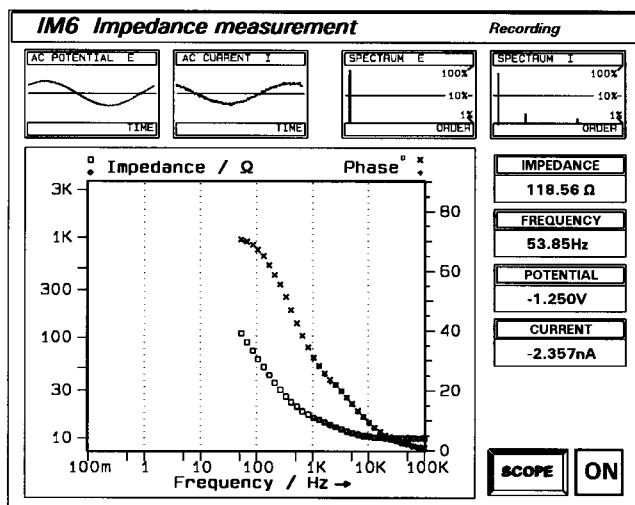
F4

Recording parameters screen.



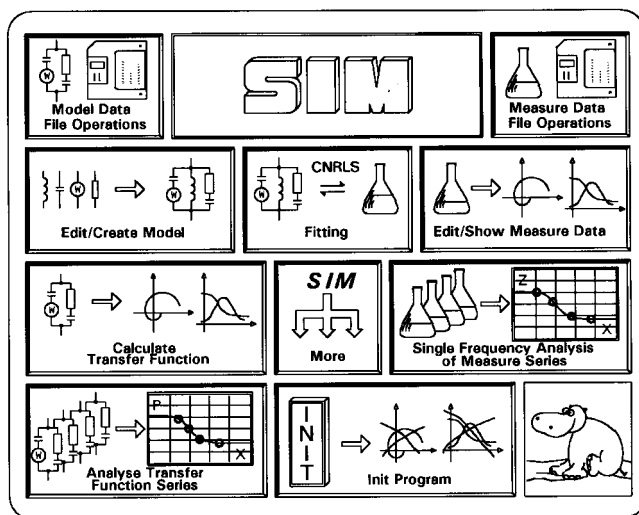
F5

Real time data display during experiment.



F6

Menu for SIM program.



SIM Impedance data analysis

The SIM program is used for data analysis, including equivalent circuit synthesis, and fitting of experimental and simulated data. Clicking the SIM icon in the main Thales menu produces the menu shown in **F6**.

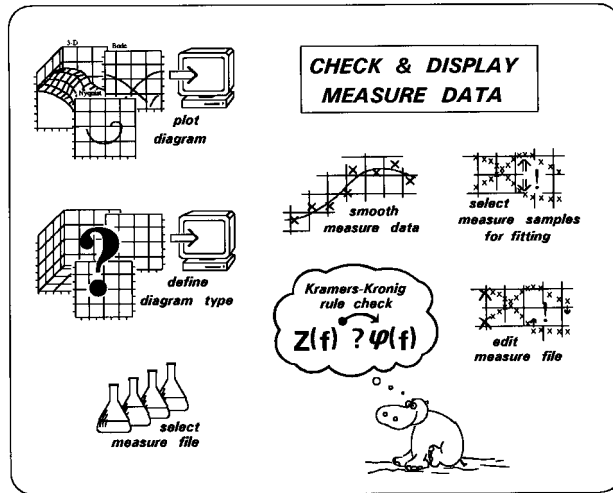
The first step is to load one or more experimental data files (multiple data files can be displayed simultaneously, either overlaid or in 3-D). These can then be viewed in the *Edit/Show Measure Data* menu (**F7**).

The impedance data can be displayed using either a Bode plot (**F8**) or a Nyquist plot (**F9**). Selection of the display mode, together with the axis scales, is made in the *define diagram type* screen. The data can be smoothed, edited (i.e., the phase angle and impedance values can be altered), printed, exported to the Thales CAD graphics program, or saved in an ASCII text format (for export to external data analysis and plotting programs).

The other menu items are *select measure samples for fitting* and *Kramers-Kronig rule check*. As noted above, the data density is typically higher at high frequencies than at low frequencies. Hence, if all the data points in the spectrum were

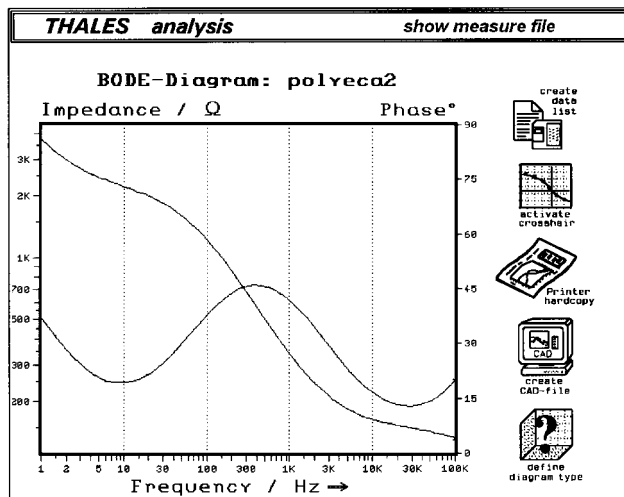
F7

Edit/Show Measure Data menu.



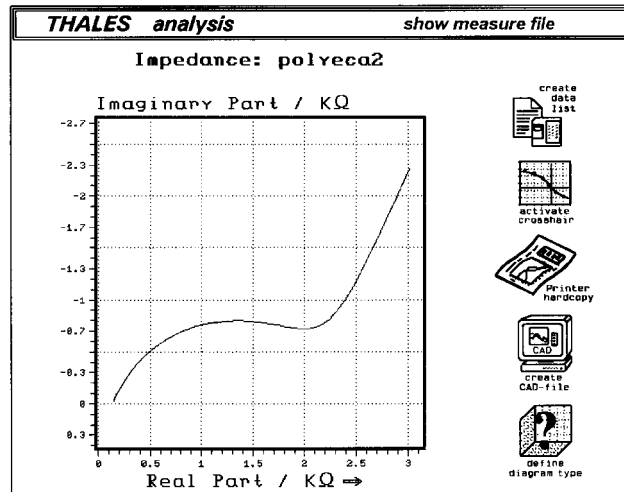
F8

Bode plot.



F9

Nyquist plot.



used when optimizing the fit of simulated data to experimental data, there would be a bias towards high frequencies. It is therefore advisable to select data points equally distrib-

uted on the logarithmic frequency scale when fitting simulated data to experimental data, and this is achieved using select measure samples for fitting.⁴

The basis of the Kramers-Kronig rule is that the phase angle and impedance are related; that is, the impedance values can be calculated from the phase angle values, and vice versa. However, the Kramers-Kronig rule only applies if the following four conditions are met by the system under investigation:

Causality The measured response of the system is due only to the applied perturbation, and there are no contributions from other sources.

Linearity The relationship between the perturbation and the response should be linear.

Stability The system must return to its original state when the perturbation is removed.

Finiteness The impedance must be finite at all frequencies.

In the *Kramer-Kronig rule check*, the impedance is calculated from the phase angle, and the calculated impedance is compared with the measured impedance. Any deviation between the calculated and experimental values shows that one of the above conditions has not been maintained during the experiment, and hence the measured data are not reliable. In practice, the most common cause of deviation is system instability, particularly during measurements at low frequencies, which may require several hours. This is illustrated in **F10**, which shows deviations at low frequencies.

Interpretation of impedance data is often based on the principle of equivalent circuits, which states that it is possible to build a circuit consisting of electronic components that gives an impedance spectrum identical to that obtained experimentally. This principle also requires that there is a correlation between the components of the equivalent circuit and the components of the experimental system.

The SIM program can be used to build an equivalent circuit, calculate

the theoretical impedance spectrum for this circuit, and optimize the values of the circuit components to provide the best fit with the experimental data. Equivalent circuits can be built using a graphical editor (**F11**), which is accessed by clicking the *Edit/Create Model* icon.

The available circuit elements are displayed on the right side of the model editor. These include a resistor, an inductance, a capacitor, a constant phase element, the Warburg impedance (semi-infinite diffusion), two finite diffusion elements (hyperbolic cotangent and hy-

perbolic tangent functions), and elements for spherical diffusion and homogeneous reactions. There are also specific models for surface relaxation, a passive layer (Young surface layer impedance), and a porous electrode. In addition, user-defined elements can be written, and used in equivalent circuits.

The method for building an equivalent circuit is as follows. The individual elements are selected from the table, the parameter value(s) are entered, and the connection of this element is then defined.

As each element is specified, it is displayed in the graphics box on the left of the screen. In the example shown in **F11** and **F12** (the Randles circuit), a resistor was first selected (**F12a**) (charge-transfer resistance). The next element was the Warburg impedance (semi-infinite diffusion), which was connected in series to the resistor (**F12b**). A capacitor was then selected (double-layer capacitance), and was connected in parallel with the first two elements (**F12c**). The final element was a resistor (solution resistance), which was connected in series (**F12d**).

This method can be used to build a wide range of circuits. Once constructed, the equivalent circuits can be edited, either to change a parameter value, or to change an element (e.g., a capacitor to a constant phase element). Elements can also be inserted or deleted, although this may not be advisable for more complicated circuits, since the linear order of the model may be affected.

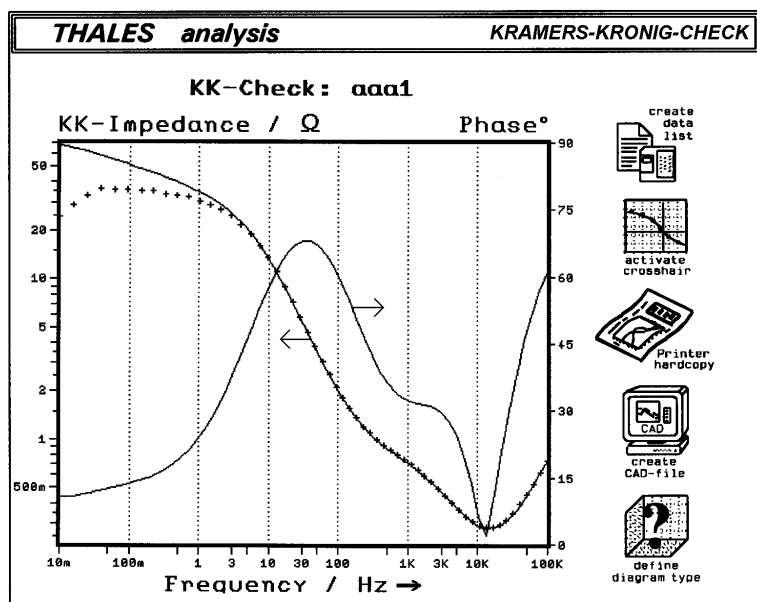
Once the equivalent circuit has been constructed, the theoretical impedance spectrum for this circuit can be viewed using *plot diagram* in the *Calculate Transfer Function* menu (the *plot diagram* and *define diagram type* functions in this menu are identical to the analogous functions in the *Edit/Show Measure Data* menu). The parameter values of the circuit can also be optimized to provide the best fit to a selected experimental impedance spectrum using the *CNRLS* (Complex Non-linear Regression Least-Squares) *Fitting* routine.

Before the fitting routine can be used, both an experimental data file and an equivalent circuit (model) must be specified. In addition, the number of data points used in the fitting routine must be specified (see above).

Before the fitting operation is started, the screen displays the equivalent circuit being used, and the initial parameter values. While the fitting operation is in progress, the parameters values used for each iteration are displayed, as well as the difference in the experimental and

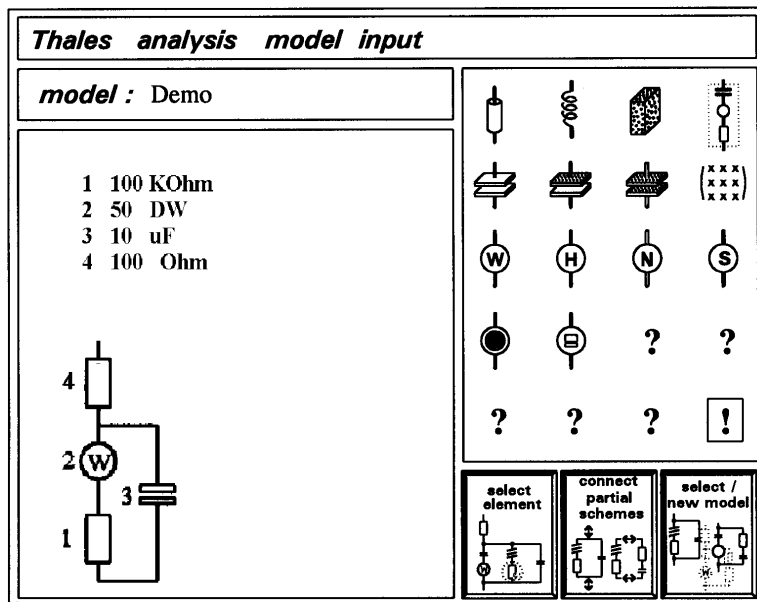
F10

Kramers-Kronig rule check.



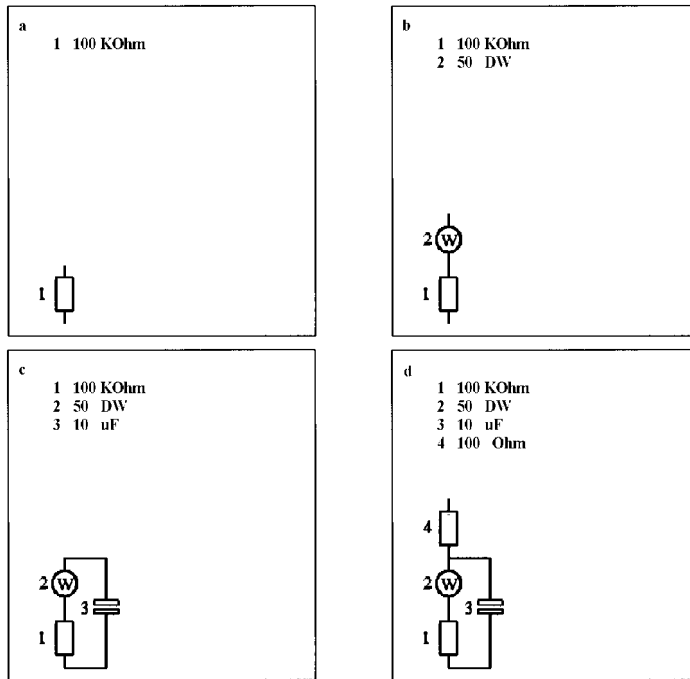
F11

Graphical editor for constructing equivalent circuits.



F12

Assembly of the Randles circuit using the SIM graphical editor.



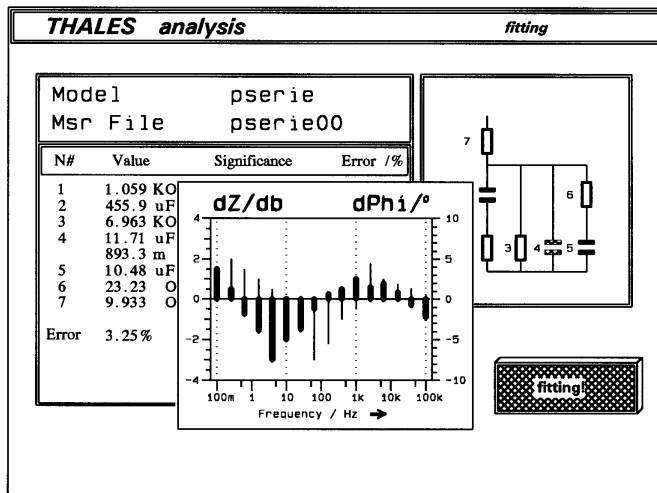
simulated impedance and phase angle values for each of the selected frequencies (**F13**). Iterations will continue until either the absolute error on consecutive iterations is less than 0.1%. The optimized parameter values will then be displayed, together with the maximum and mean errors in the impedance and phase angle (**F14**).

The significance and error are also listed for each parameter. The significance is the maximum value of dZ/dP ($P = \text{parameter value}$) (i.e., it is a measure of the effect of that parameter on the impedance; it is important to note that this is frequency dependent). The error is related to the difference between the experimental and calculated impedances at the frequency for which the significance is quoted.

The experimental data and the optimized calculated data can be compared using *plot diagram* in the *Calculate Transfer Function* menu (**F15**). The line represents the calculated data, and the crosses show the selected experimental data.

F13

Progress of the fitting operation.

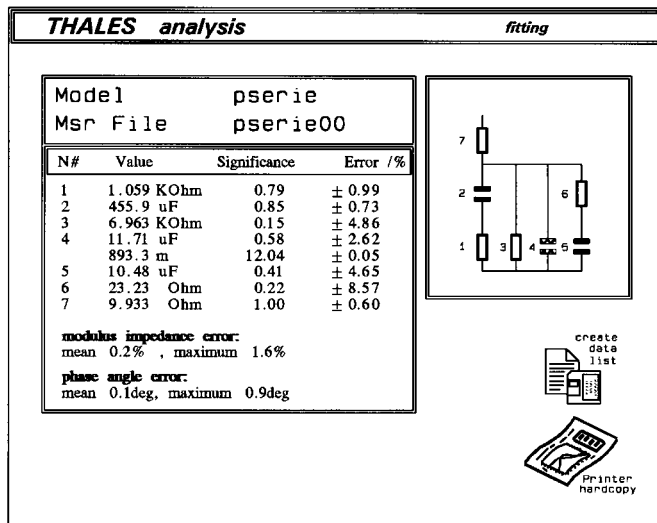


Automatic series measurement

A function that is standard on the IM6, but optional on the IM6e, is the ability to run series of measurements. This enables the user to record a series of impedance spectra either as a function of internal variables, such as time, potential, and current, or as a function of external variables, such as temperature. There are a number of features of SIM that can be used for such measurement series.

F14

Results of fitting operation.

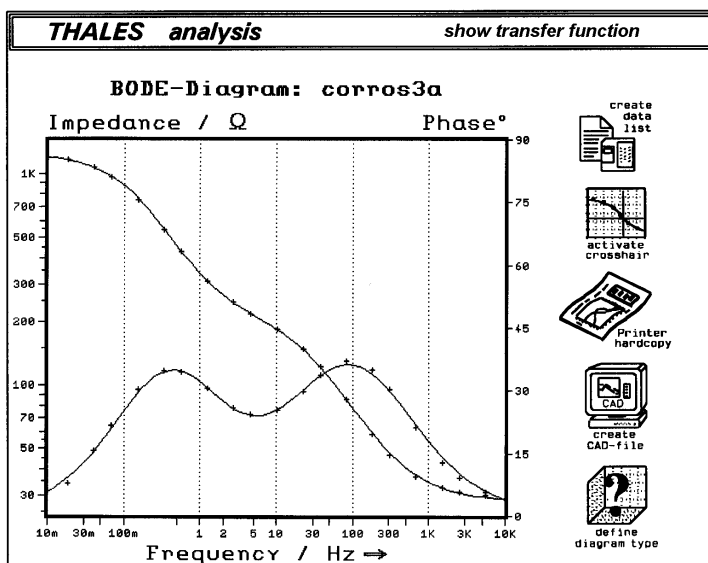


3-D plots

The data from series measurements can be plotted on the same set of axes, either as a 2-D plot, or as a 3-D plot, where the third axis is the parameters varied in the series measurement. The 3-D plot in **F16** shows how the impedance vs. frequency plot varies as a function of the applied DC potential.

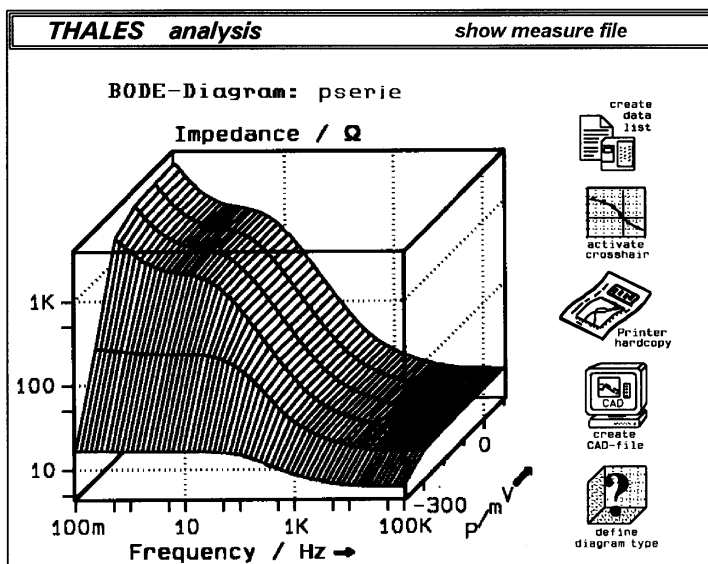
F15

Comparison of experimental and simulated data for a stainless steel electrode.



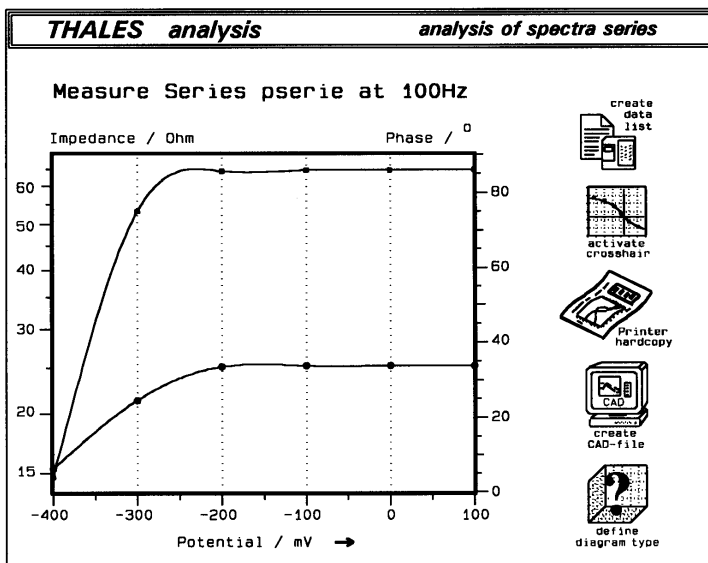
F16

3-D plot of impedance spectra as a function of applied DC potential.



F17

Variation of impedance and phase angle as a function of potential at 100 Hz.



Series fitting

The series fitting operation will fit all selected data sets of the series measurement to one selected equivalent circuit. The optimized parameter values for each data set are saved in separate files.

Single frequency analysis

The 3-D plot displays the variation of impedance and/or phase angle as a function of the varied parameter for the entire frequency spectrum. The variation of either impedance and/or phase angle as a function of the varied parameter at a single frequency can also be displayed (**F17**) (i.e., a cross-section of the 3-D plot). This display is available for both the experimental spectra and those calculated based on the equivalent circuits. The variation of the parameter values of the components of the equivalent circuits can also be plotted for the calculated spectra.

It has been shown in the above discussion how the Thales software used for the IM6 and IM6e impedance analyzers facilitates the acquisition and analysis of electrochemical impedance data. The capabilities of these instruments can be further extended by the addition of other modules of the Thales system, which use the same graphical approach for cyclic voltammetry, linear polarization, electrochemical noise analysis, and capacitance/potential measurements.

Endnotes

1. The additional modules are standard on the IM6 and optional on the IM6e.
2. In this discussion, the system will be under potentiostatic control. However, galvanostatic control is also available (the switch in the lower right corner is used to select the required mode).
3. Note that measurements are made at single frequencies over the whole frequency range.
4. The select measure samples for fitting also allows user-defined selection of data points to be used for fitting.