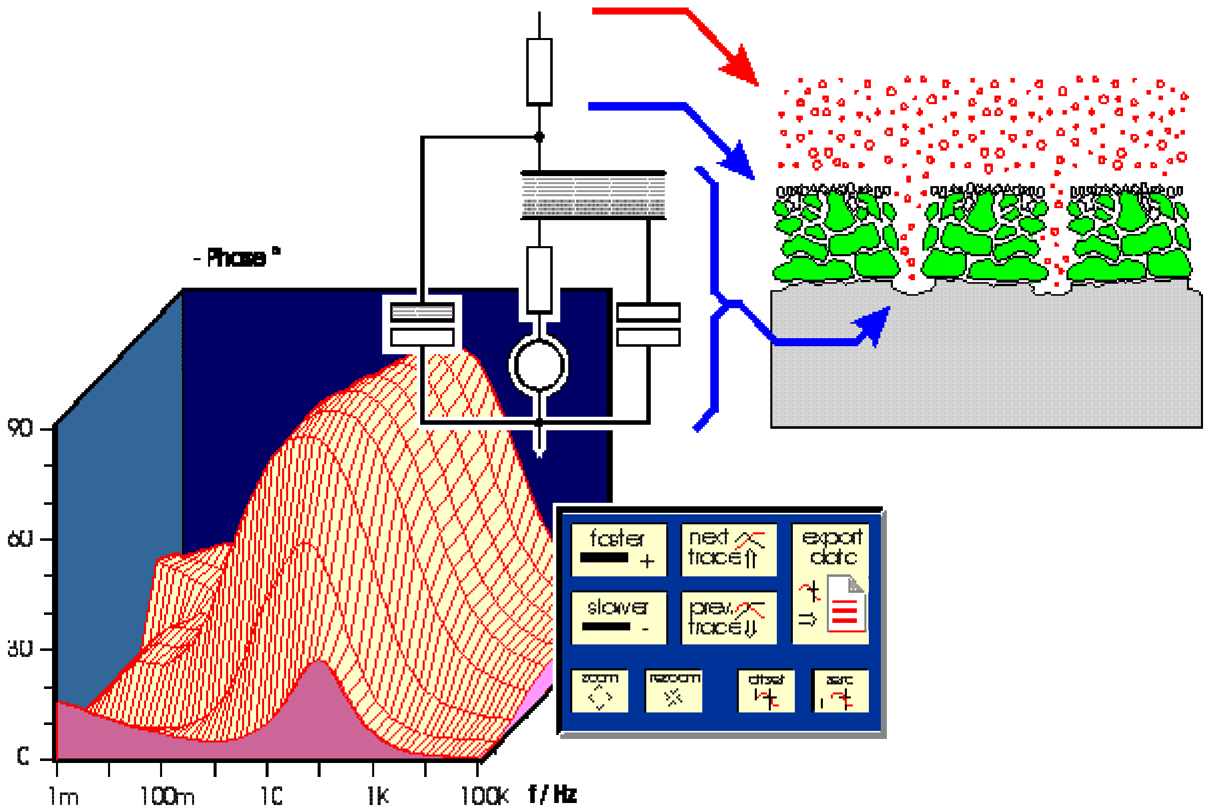
SIMULATION & FITTING

SIM

Part of the Thales software package

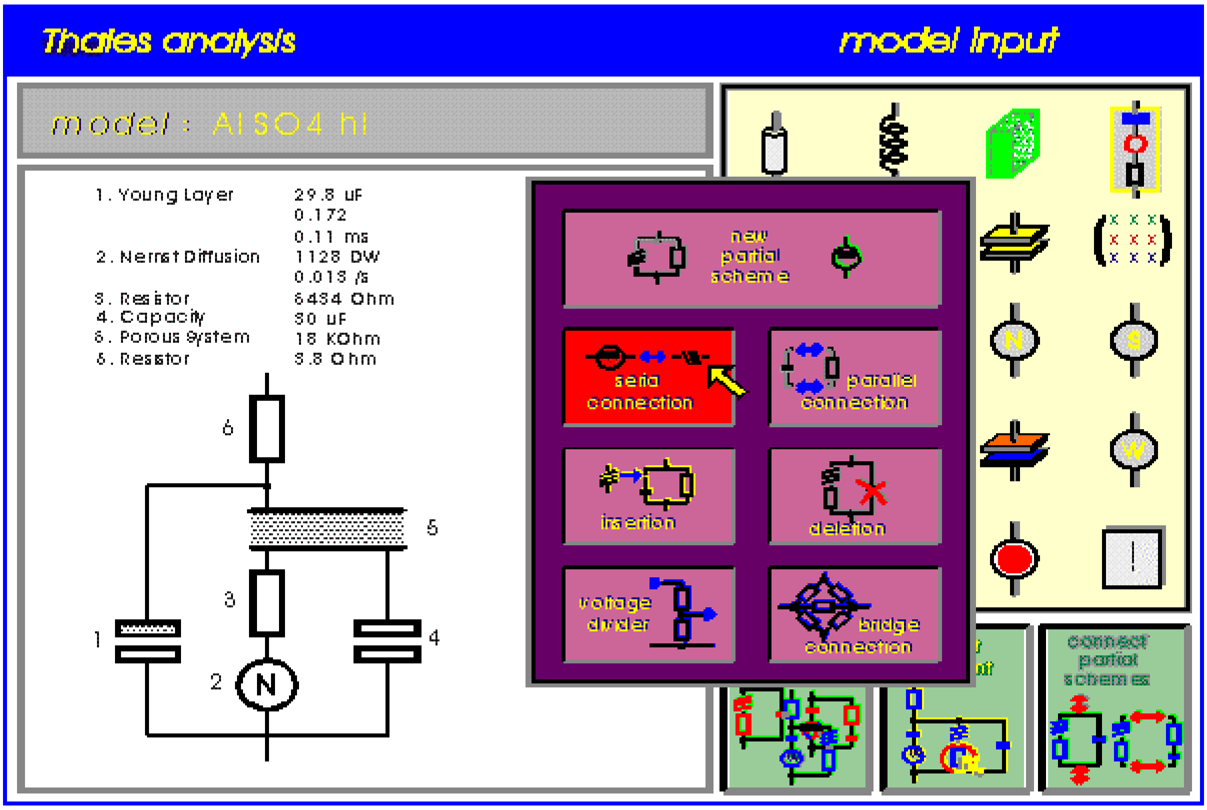


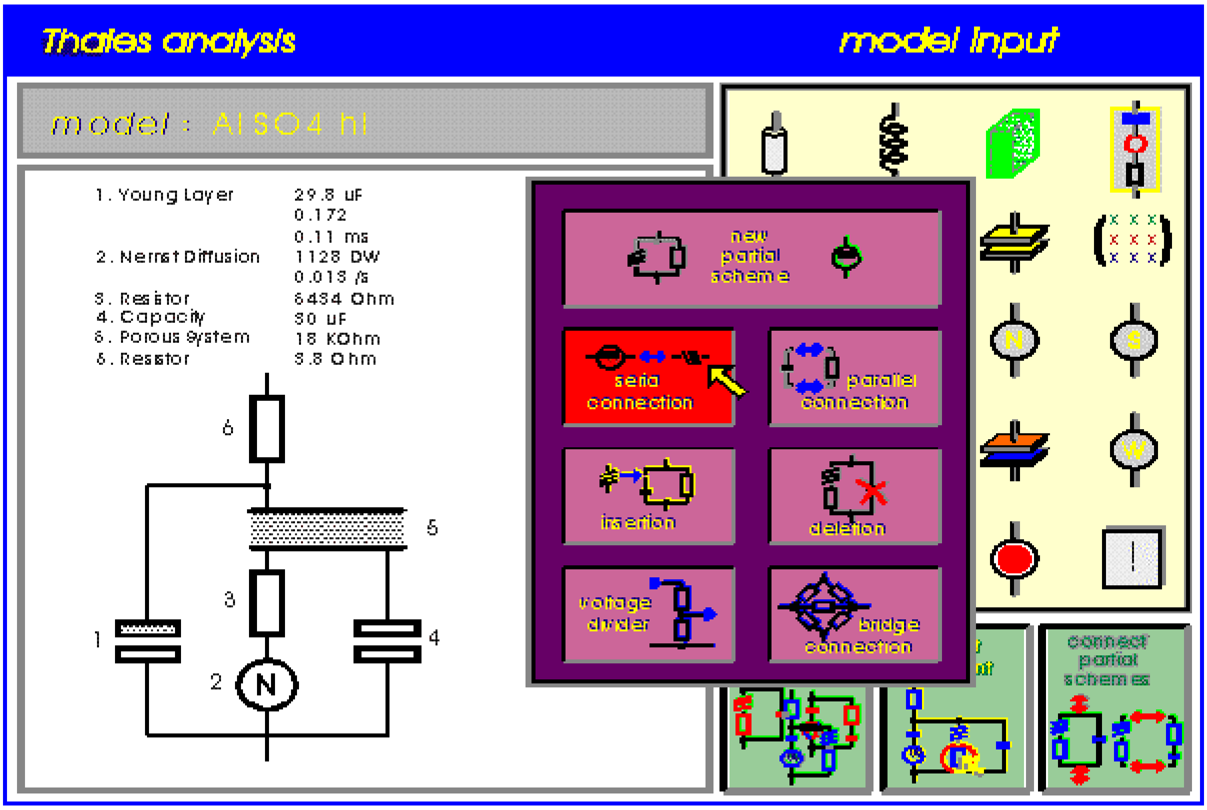
SIM is ...

the main analysis module of the ***THALES*** software package. With its powerful analysis functions, display modes, simulation capabilities and fitting algorithms, it provides unique possibilities worldwide - all this embedded in a user interface whose handling is extremely easy and comfortable. No commands have to be learned, no formulas to be derived - the models and parameters have simply to be clicked and defined.

The main idea of this software is to correlate measurement data with electrochemical models. When modeling the transfer function of an electrochemical system by means of an equivalent circuit (EC) a lot can be learned about its physics. As generally known, kinetic and thermodynamic properties determine the parameters and their values, whereas electrochemical mechanisms and topologies are mainly reflected in the connection scheme. The impedance elements in use provide information about, for example thickness of a layer, ion concentration, reaction rate, conductivity and many more characteristics of the examined object.

Equivalent Circuits

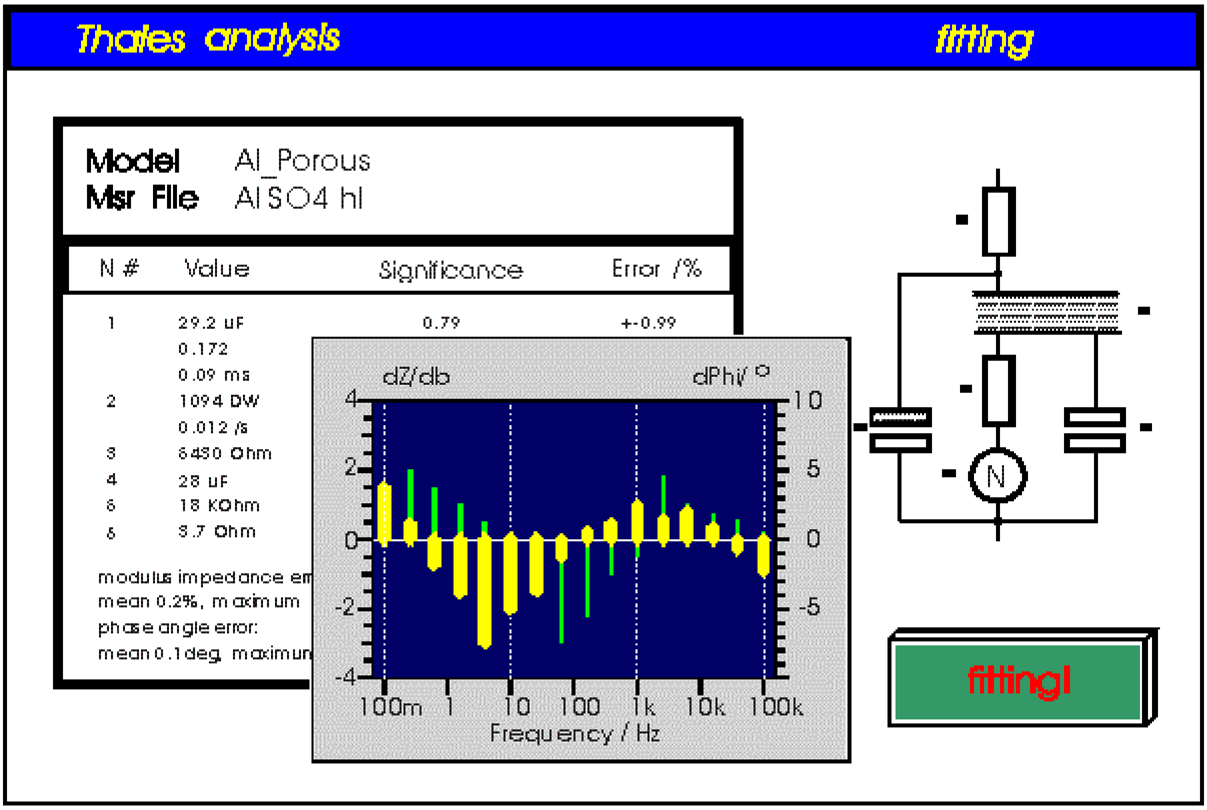




Initially an adequate electrical equivalent circuit (EC) has to be created. Unlike other programs, ***SIM*** allows any complex arrangement, and any connection of impedance elements. Even the results of artifacts caused by electrical interference, coupling and voltage divider effects can be involved and realistically modeled. Of course, all standard impedance elements are available in a library. Furthermore, the library provides a great number of transfer function elements (for example, six diffusion models for different geometries and coupling modes) which allow the modeling of almost all possible electrode impedance properties. All preset models have of course been scientifically proved.

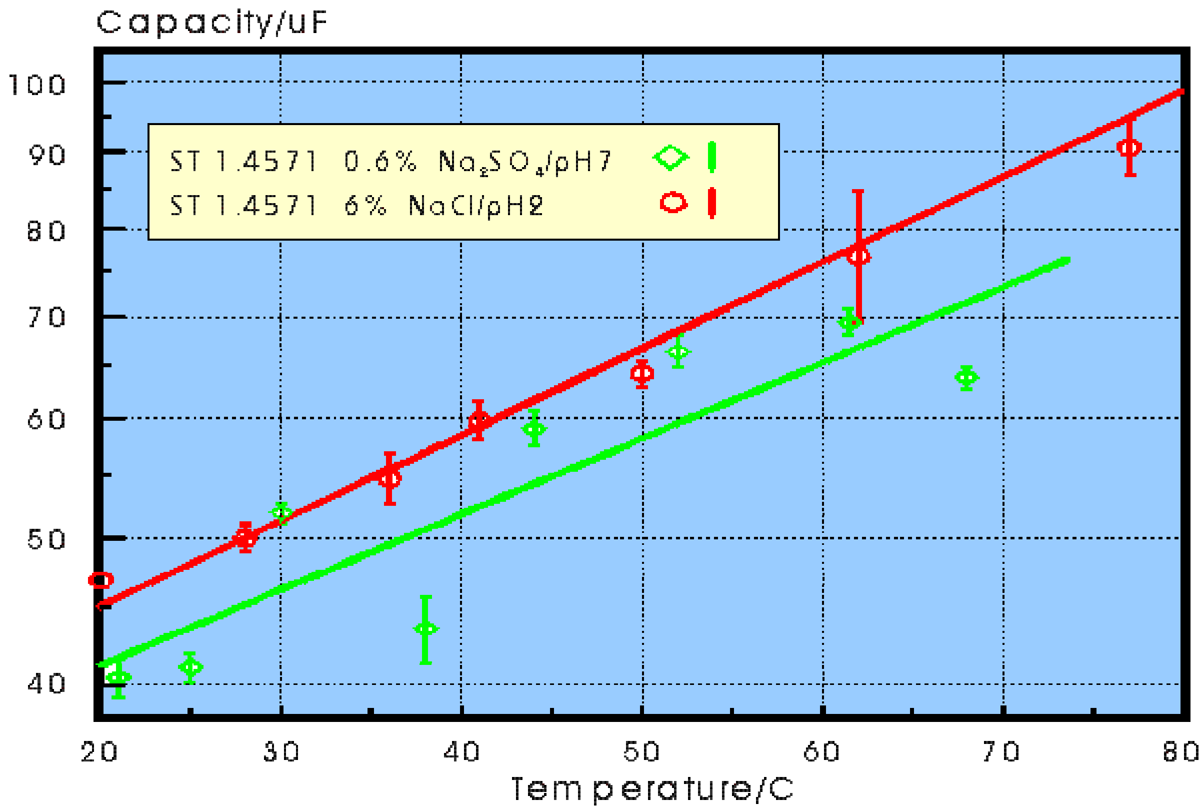
It is very easy to create a model scheme with the sophisticated ***SIM*** Editor: You select an element with the mouse, input its parameters and the connection needed - ready. A help function grants access to the physical meaning, the dimensions, the units and the used algorithms of each model. In case the preset models do not meet your requirements, additional user elements can be defined. These are entered in the library and can then be used in the same way as the preset elements. The ***SIM*** calculates a transfer function of the created scheme, displays it graphically and automatically passes it to the ***SIM*** fitter.

Automated Fitting



Kramers-Kronig Check

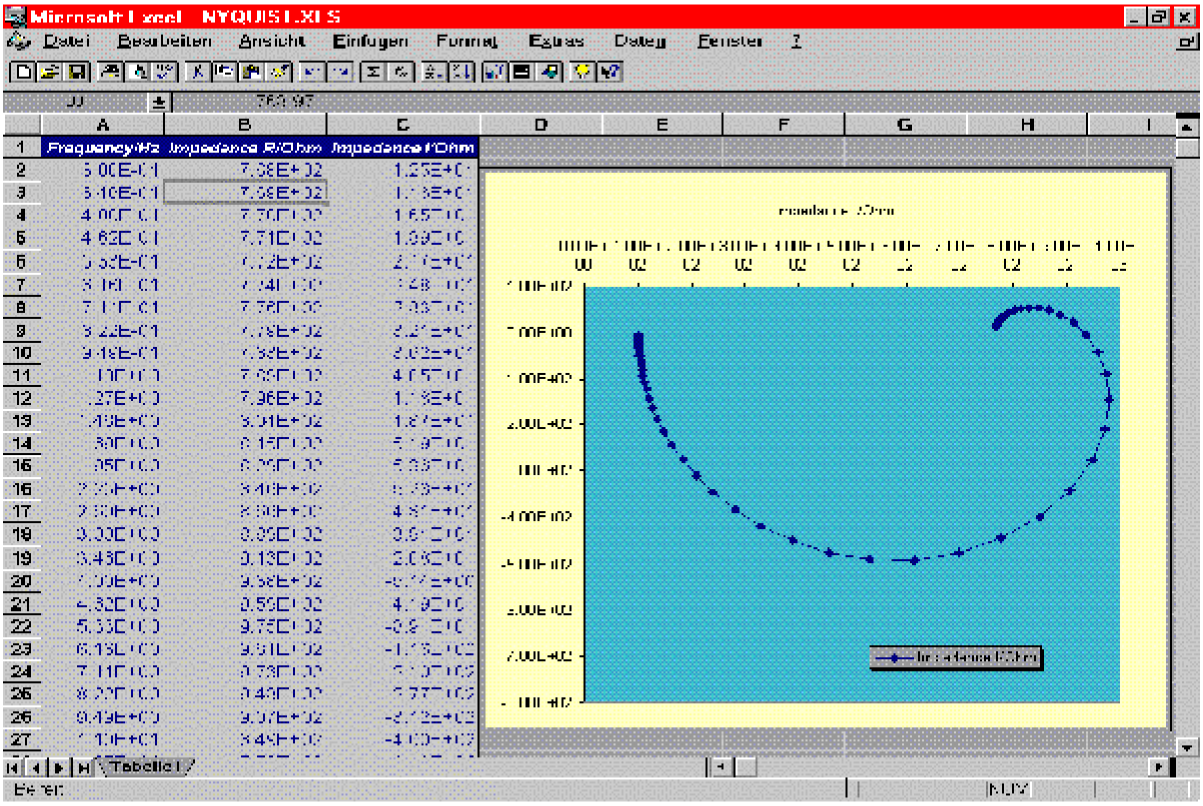
The incoming experimental data are carefully validated before entering the fitter. The spectra are passed through a special smoothing filter, while every sample is weighted with its individual measuring uncertainty. The goal is to suppress noise spikes and to evaluate the primitive function and several derivatives of the measured transfer function. This information is used to check the spectra against the logarithmic type of the Kramers-Kronig transform (LKKT). In contrast to the well-known linear one, this procedure detects not only instability of the examined system, but all deviations from proper two-pole impedance behavior. If non negligible time drift is found in a spectrum, the user can call a LKKT-correction routine. An almost perfect treatment of non steady-state behavior can be applied on spectra series vs. time: On demand, the SIM creates time-independent series by interpolation.



The ***SIM*** fitter allows adaptation of the model parameters to the measured data. The software, designed against the background of 20 years of know-how in the field of complex, non-linear mathematics, works with a sophisticated CNRLS fit (Complex Non-linear Regression Least Squares) algorithm. Im-plemented elements of evolution strategies and flood algorithms contribute to the extraordinary fitting results. By this the numerical values of the model parameters as well as all important statistical data are achieved. The significance as well as the error of data are registered and calculated from the data acquisi-tion till the end of the fitting process for each evaluated parameter.

In addition to single runs complete measurement series, e.g., those coming from the ***AS*** software module can be fitted in one pass. As a result one gets the courses of the impedance parameters vs. a third parameter. The resulting function (polarization resistance vs. temperature, concentration vs. time, capacity vs. potential etc.) is not only displayed as a diagram or a data list but can also be analyzed in a second step with other methods, for example, in the ***C/E*** software.

Data Export



This open analysis concept is completed by the ***ALEX*** software module and the Data Export function of the SIM. The ***ALEX*** allows the creation of all possible diagram types which one gets from the available data - without having to leave the ***THALES*** software environment.

The Data Export function implemented in the ***SIM*** enables the user to analyze data in any PC program which accepts the ASCII format data lists. With a mouse click data can be transferred to, for example, Microsoft Excel in order to do further analysis or to create a presentation sheet. Besides all this the diagrams created by the ***SIM*** can be printed out on a laser/color printer and can be exported as a HPGL file, which can be imported directly into other PC programs, such as Word, CorelDraw, PageMaker and all other programs with an HPGL import filter.

Table of Models and Impedance Elements

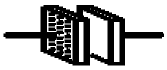
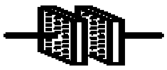
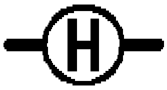
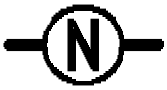
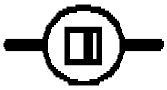
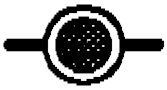
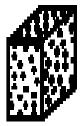
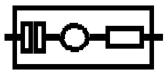
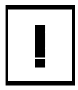
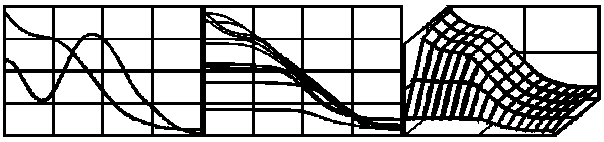
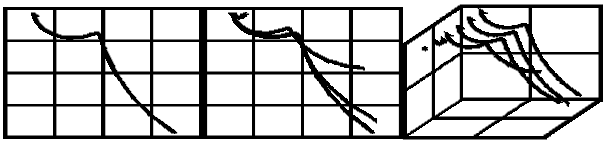
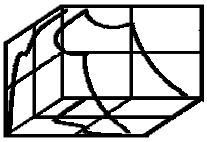
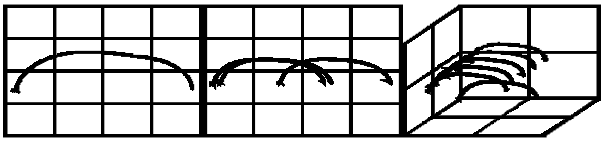
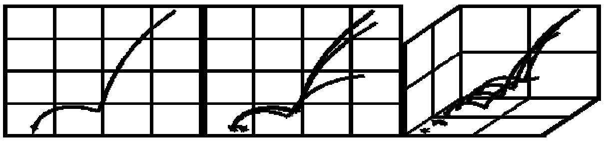
Element	Description	Example	Symbol
Resistive Element	impedance of a homogeneous conductor	electrolyte resistance, charge transfer resistance	
Capacitive Element	model of an proper capacitor	plate capacitor, double layer, pseudo capacity at adsorption	
Young Element	model of a dielectric layer with an exponential gradient of conductance	films, coatings, passive layers of oxides, nitrides ...	
Constant Phase Element	model of a loss capacitor	fractal porous electrodes, surface layers with conductance gradients	
Inductive Element	classical inductance	piece of wire, coil, pseudo inductivity	
Warburg Diffusion Element	model of infinite one-dimensional diffusion in a semi-infinite space	bulk solution diffusion in absence of boundary effects such as convection	
Homogeneous Reaction Element	finite length diffusion limited by a bulk chemical reaction	product/educt redox system in solution	
Nernst Impedance Element	finite length diffusion with a constant concentration boundary	diffusion layers with convection, rotating electrodes, membranes	
Finite Diffusion Element	finite length diffusion with phase change boundary	membranes, intercalation of kations in a battery electrode	
Spherical Diffusion Element	spherical diffusion from local spots	pitting corrosion	
Porous Electrode	model of homogeneous pores	fuel cell cathode, battery electrodes, porous layers	
Surface Relaxation	Faraday impedance at a non-equilibrium potential with a potential de-pendent reaction rate	surfaces with active-passive-transition, corroding electrodes	
USER Defined Impedance Models	user models of complex transfer functions which are defined by the user in mathematical terms	e.g. channel diffusion of oxygen in SOFCs	

Table of Diagram Types

Diagram	Description	Graphic
Bode 2D & 3D	impedance and/or phase vs. frequency. Bode plots vs. a third parameter as a 3D plot.	
Nyquist 2D & 3D	imaginary part vs. real part of the impedance. Nyquist plots vs. a third parameter as a 3D plot.	
Nyquist 3D/Freq	Nyquist plots vs. the frequency as a 3D plot	
1/Nyquist 2D & 3D	imaginary part vs. real part of the admittance. 1/Nyquist plots vs. a third parameter as a 3D plot.	
-Nyquist 2D & 3D	-imaginary part vs. -real part of the impedance. -Nyquist plots vs. a third parameter as a 3D plot.	
User Defined	resistance/capacitance vs. frequency, complex modulus of impedance vs. frequency, log. real/imaginary vs. frequency etc. via ALEX