# ZMAN ver2.5

User's Manual

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# Chapter 1 Overview

ZMAN is a scientific application for impedance analysis and modeling.

With ZMAN, you can integrate a series of impedance measurements and control parameters into a single file, and then present them in sophisticated 2D and 3D graphs including the familiar Nyquist plots and Bode diagrams.

With its powerful equivalent circuit model editor, you can easily add arbitrary circuit components, expressed by complex functions, to build and manage your own equivalent circuit models.

ZMAN's special equivalent circuit search engine lets you easily search for an appropriate equivalent circuit model which best fits the raw impedance spectrum from pre-defined and user-defined models.

In addition, ZMAN helps you fit model parameters with the equivalent circuit fitter employing the Levenberg-Marquardt (LEVM) algorithm and to compare the best-fit result against raw data in graphical form. In fitting impedance series, you can use previous best-fit parameters as initial values for fitting the next impedance spectrum.

#### A. What is new in ZMAN 2.5

- ZMAN can be used without Admin Right.
- You must run ZMAN with admin right to input license code.
- Ver2.5 Project file is not compatible with older version but it can read older version project file.
- Model searching default parameters were changed.
- Support Biologic's new data format files.

These exciting features will help you manage and analyze your impedance data in a more productive way than ever before.

# **B.** History of ZMAN 2.5

- Upgrade from ZMAN 2.3
- ZMAN 2.3
- ZMAN 2.2
- ZMAN 2.1
- ZMAN 2.0
- Upgrade from ZMAN 1.1

# C. Major New functions

# > in ZMAN version 2.5

- · Setup file including Labview runtime engine
- · Supporting Biologic new data format

#### > in ZMAN version 2.3

- · Labview runtime engine version RTE2013 32bit
- Frequency extension function of simulated data

#### > in ZMAN version 2.2

- · Ascii file reading extended option
- KK plot updated
- Interpolate Bad data
- Black-Nichols Plot
- 3D graph setting option
- · Improved Model editor
- · Application Model library for automatic searching
- · Parameter Simulation of model
- Genetic algorithm option for fitting
- Automatic initial guessing
- Trace movie function on fitting
- Data analysis for WonATech data format (SEO, SDE, Z# file) without a license code

#### > in ZMAN version 2.1

- Data analysis for WonATech data format (WDF, WIS file) without a license code. WDF file extension is from WEIS system, WIS file extension is from Z# and Z100 systems
- Data editing
- Circle fitting
- Add/remove element parameter
- Add/remove model parameter
- Impedance E,M,Y,Z in polar Admittance Modulus Dielectric constant Data display

## D. System requirements

In order to run ZMAN, you must ensure that your computer meets the following minimum software and hardware requirements:

Operating System: Microsoft Windows XP, 2000, Vista, or Windows 7/8 (32,64bit available)

Processor: Intel Pentium 4 or equivalent

RAM: 512MB

Display: 1280 x 1024 recommended

If you have lower resolution, you can use ZMAN by maximizing window.

Internet: An internet connection is required for registration

#### E. Installation and Setup

Installation and setup is performed by running "setup.exe" in volume folder from the ZMAN setup.

The ZMAN software will then be installed, along with the National Instruments libraries.

After installation, you can run ZMAN by going to the Start Menu, All Programs, WonATech,

#### ZMAN 2.3 and clicking ZMAN.

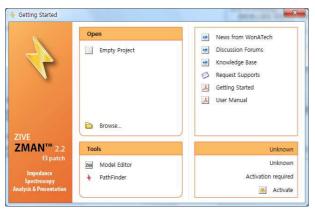


Figure 1. Intro Menu without license(Before license Request)

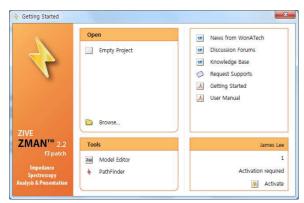


Figure 2. Intro Menu without license(After license Request)

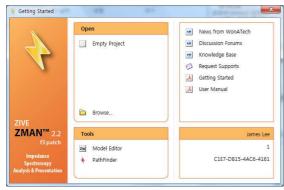


Figure 3. Intro menu with licensed

You can see intro menu of ZMAN2.5 as the above figure1.

You can select blank project at start or select recent project which you handled last time or you can browse specific file by clicking Browse button.

If you want to edit/create model only, you can directly enter Model editor

If you select blank project, the following window will appear.

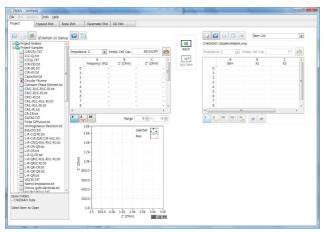


Figure 4. ZMAN starting

If you have purchased ZMAN and have not activated the ZMAN license, you will need to send some information to WonATech in order to be sent a valid license code.

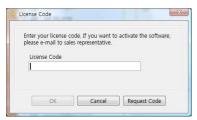


Figure 5. License Code Entry

Click the "Send e-mail" button, and fill in your registration details:

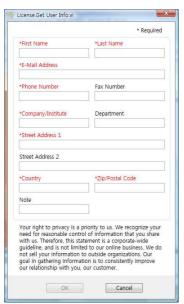


Figure 6. License code application form

If you have not purchased ZMAN and want to evaluate the software, click the "Cancel" button.

If you have purchased ZMAN, then fill in the required information and click the "OK" button.

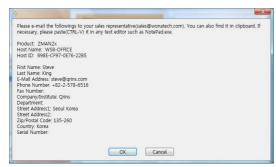


Figure 7. Send registration email

If you click "OK" button, the program will automatically e-mail this information to WonATech to obtain a license code. If your PC is not connected to the internet, please paste (Ctrl+V) the information into a text editor and email it to <a href="mailto:sales@WonATech.com">sales@WonATech.com</a>. You will then receive the license code for ZMAN by email. You must run ZMAN with admin right to input license code. Until the license code has been entered into ZMAN, you can only use it with WonATech generated data.

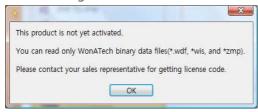


Figure 8. License notice

## F. Licensing Note

A ZMAN license code is required for each PC you use it on. You must install ZMAN into the PC you want to use ZMAN software for 3<sup>rd</sup> parties data analysis. Without License code, you can use ZMAN for WonATech generated data in any PC with full functions.

# G. Known Bug

ZMAN uses Microsoft Common Control to open a file; however, the file open dialog is not loaded in some machines. It is caused from a licensing issue of the ActiveX control. The easiest way to fix it is to install Microsoft Visual Studio or Visual Basic.

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Korea

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# **Limited Warranty**

WonATech Co., Ltd warrants to the original user of this product that it shall be free of defects resulting from faulty manufacture of the product.

WonATech Co., Ltd makes no warranties regarding either the satisfactory performance of ZMAN package including the software encoded in this product or the fitness of the system for any particular purpose.

WonATech Co., Ltd reserves the right to make revisions to the system at any time without

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# Chapter 2 About ZMAN

The basic concepts and features of  $ZMAN^{TM}$  are shown in the figure below.

In this section, you will learn about the main features and functions of ZMAN. To get an overview of some of the features of the software, follow these steps:

- Open a data file. Refer to EIS Data File for details. You can use your EIS data file or importing 3<sup>rd</sup> parties data file
- 2. Edit your data file. You may edit bad data or combine some series measurement for ZMAN analysis. Refer to **Preview data file** for details
- Project concept. You can use **Project function** to manage your series of data files measured with max 3 control variables. Refer to **Project** for details
- Check validity using the Kramers-Kronig relation. For details, see Kramers-Kronig
  Consistency. However, this is not a general procedure used to analyze impedance
  data.
- 5. Using the Levenberg-Marquardt algorithm, best fit the data to an Equivalent Circuit which is defined and selected in the Equivalent Circuit Model Editor. Refer to **Modeling**
- 6. Try circular fitting for your Nyquist plot's shape having semi-circle. Refer to **Circular fitting** for details
- 7. You can add or subtract some element or model from your data. Refer to **Manipulate** element or **Model** for details
- 8. You can create/manage your own model or models in libraries. Refer to **Equivalent Circuit Model Editor**.
- When you are uncertain what is an appropriate equivalent circuit or you are not familiar
  with equivalent circuit, you can use the ZMAN automatic Search Engine to find possible
  choices. Refer to Automatic Model Searching for details.
- 10. Plot the data file. Refer to **Impedance Data plot** for details. You may plot raw data with KK checked results or best fit results in various types of graphs. Best fit parameters are plotted against control variables.
- 11. There are many type of graph handling for impedance data presentation. Refer to **Graph** for details

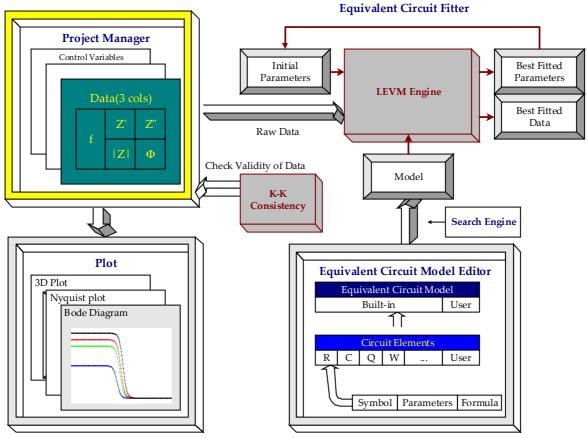


Figure 9. ZMAN Diagram

# Chapter 3 EIS DATA FILE

ZMAN use project concept. Each impedance data file(s) can be transferred to project file. Only if the data file was transferred to project section, it can be analyzed.

Project section can be handled as single file or multiple files. Main reason of project concept is series analysis from various data sets by experiment circumstance changing.

In the Project tab, there are 3 sections..

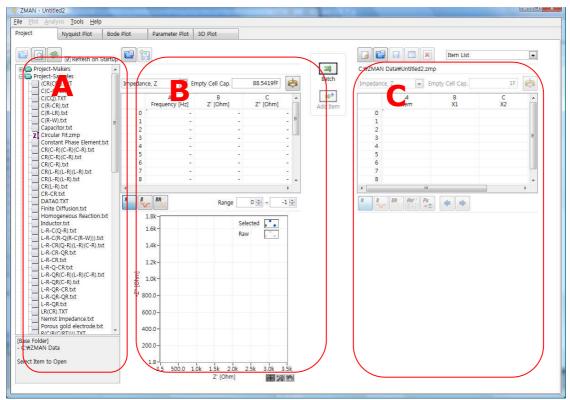


Figure 10. Main windows structure

You can select raw data as an individual file or you can group several data together and save them in a ZMAN project file in Project Tab. ZMAN Project files end with the extension .zmp.

You can see 3 sections as shown above.

"A" section: Data files Browser "B" section: Data file Preview

"C" section: Project files handling for ZMAN data analysis

#### A. Browse data files

#### 1. Base folder selection

ZMAN shows data file list which can be used in ZMAN. These file list is different by

licensing. Displayed data files are located on base folder which user can determine.

You may need to select folder which contains EIS data files. Data file browser ("A" section) will display data file list under base folder. To select base folder, click right mouse button at "A" section in Figure 10. Then pop up menu will appear.

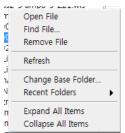


Figure 11. Data file handling pop up menu

You can change base folder by selecting "Change Base Folder.." on pop up menu, ZMAN will show file list including subsidiary folders.

Note: You can NOT select root folder as base folder. If you want to save data file in hard disk or usb memory etc., you must make some folder and save the data file into the folder.

If you check on Start Up , ZMAN will show the files which you set as base folder at last time when you open ZMAN program

```
[Base Folder]
- C:\(\pi\zMAN\) Data
[Current Item]
- C:\(\pi\zMAN\) Data\(\pi\repro)...\(\pi\repro)EMO.Z\)
```

Figure 12. Base folder display

You can see current base folder at bottom.

If you select the file, you can also see file information base folder information.



Figure 13. File information

#### 2. Recent folders

You can easily change highest path using recent folders. Recent folders displays folder which you did set as base folder.

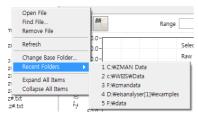


Figure 14. Recent folders

#### 3. Refresh list

If you select Refresh or click refresh button



, data file list is updated.

#### 4. Expand All Items

You can display All EIS data files in subsidiary folders when you select "Expand All item" Generally subsidiary folder's EIS data can be seen when you click this folder.

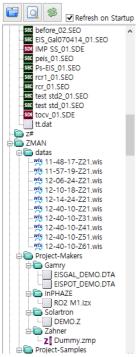


Figure 15. Open All items

# 5. Collapse All Item

If you select this, you can just see base folder data list. Sub folder's data list will be collapsed.

You can back to normal display by selecting "Collapse All items".

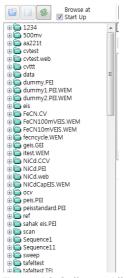


Figure 16. Collapse All items.

#### 6. Find File

You can find file using "Find file".

To use this function, you can click icon or select submenu on file list section "A"

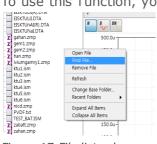


Figure 17. File list submenu

You can see following menu

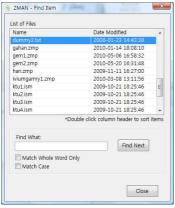


Figure 18. Find item menu

If you want to sort file name or date, double click on title then it will be sorted.

#### 7. Remove file

You can erase data file on hard disk.

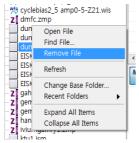


Figure 19. Remove file

Select data file which you want to erase and select "Remove file" You can see warning message box.

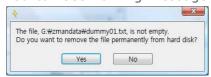
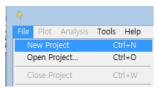


Figure 20. Warning message

# B. File Menu

ZMAN software is based on "project" concept. This project concept is that ZMAN software will make its own data set file format including multiple eis data with analysis result. Project file's extension is zmp. Project file's contents are listed on section "C" in above Figure 10.

# 1. New Project



When you select "New Project", Uploaded project contents will be cleared to make new project file.

# 2. Open Project

This is to open project file.

#### 3. Merge Project

This is to add other project file(s) into current project contents.

# 4. Batch: files to Project

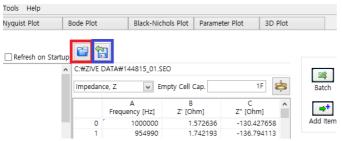
This is batch processing to add several EIS data files to current project

#### C. Data file Open

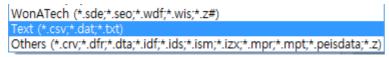
You can load data file(s) into ZMAN using two methods.

#### **Direct reading:**

Open EIS data file from target folder.



Click red boxed icon and select EIS data file format



If the EIS data file is on experiment, you can click blue boxed icon to update the data file.

#### From Data file browser

You can open EIS data file on data file browser by double clicking on data file name.

#### 1. Without License Code:

You can select data file in section "A" by double clicking on the file name, you can then see, EIS data preview of this selected file. If this is the file you want to load into Project for data analysis, click "add" button. You can then see selected files information in section "C". ZMAN can load the data files (zmp, wdf, sde, seo,wis,z# etc.) which come from WonATech products directly without a license code. If you want to load ASCII file produced by 3<sup>rd</sup> parties you will then need to obtain a ZMAN license code.

#### a) Single EIS data set

If a data file is a single EIS data set, Double Click on the data file in section "A" Then you can see data preview in section "B"

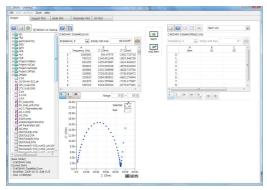


Figure 21. Data preview

#### b) Multiple EIS data set

WDF file (WEIS data file) or SEO/SDE file (ZIVE SM data file)

If your WDF/SEO/SDE data file includes multiple EIS data sets (e.g. Series measurement etc.). Double click on data file name on section "A"

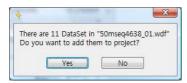


Figure 22. Multiple data loading

If you inserted Cycle marker to produce the above sequence file, the box above will appear. Click "Yes" then multiple EIS data will be split automatically and loaded in Project part (Section "C")



Figure 23. Parameter value editing

If you do not want to use all EIS data set, click "No" and the select box will appear.

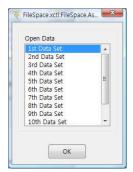


Figure 24. File select

You can then select one EIS data set for analysis.

• Other data file

If your data file have multiple eis data set, you can split the file as each EIS data using data range function.

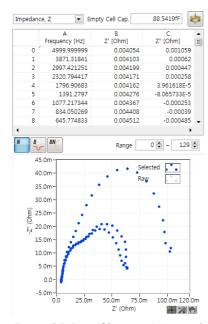


Figure 25. Data file containing multiple EIS data set

#### c) Project file

Double click on project data file (zmp) name in section "A" Then project data will be loaded in section "C"

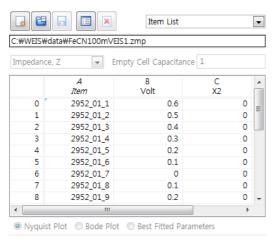


Figure 26. Parameter editing example

# 2. With License Code

Reading of ACSII and 3<sup>rd</sup> Party files requires a License Code to be obtained from WonATech.

# a) Direct reading 3<sup>rd</sup> parties data(Needs License Code)

ZMAN read Zahner Data file(\*.ism), Autolab Data file(\*.dfr), Gamry Data file (\*.dta), Solartron (\*.z), Inphaze (\*.izx), origalys (\*.crv), biologic (\*.mpt, \*.mpr), Ivium(\*.idf, \*.ids), palmsens(\*.peisdata) directly without text file importing menu.

# b) Ascii file and 3<sup>rd</sup> party's data (Needs License Code)

Select an ASCII file(needs license code) to analyze. You can read extensions among text formatted Data File (\*.dat, \*.txt , \*.csv) using text file importer

ZMAN supports ASCII data file containing several lines of header, which are automatically recognized and ignored in ZMAN, and three successive columns with numbers such as frequency, real and imaginary part of impedance. Available orders of columns are:

nth Column	(n+1) th Col		(n+2) th (	Column	
	Real(Z')		Imaginary(Z")	part	of
Frequency(f)	rear(Z)		Impedance		
or Angular Frequency(w)	Mod.( Z )	&	Phase of Impedance Imaginary(Y") part Admittance		
	Real(Y')	Ċ.			of
	Mod.( Y )		Phase of Admitta	ance	

If your data file does not have three successive columns as the above rule, you need to use extended option with which you can set each column for each parameter manually.

These columns should be delimited by delimiters such as space, comma and tab. Your ASCII data file format must have one of the following 3 successive column data rule.

- Frequency, Zreal, Zimg
- Frequency, |Z|, phase
- · Frequency, Yreal, Yimg
- Frequency, |Y|, phase

You can select frequency or w for fist column. If your data set do not have the above column rule, you need to use extended option with which you can set each column for each parameter manually.

If you attempt to open ASCII file or 3<sup>rd</sup> party's data file without license code, you can see the following message box.

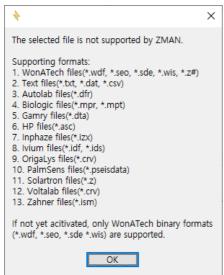


Figure 27. File format information

Once you select an ASCII format data file or after you checked the "Show dialog" check box ON, you may see the following window.

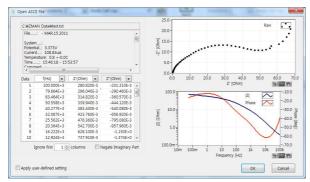


Figure 28. Read Text File

If the data file which you selected has no EIS data or invalid file format, the following message box will appear.

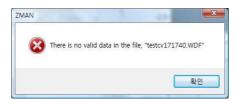


Figure 29. No data in file message

If additional columns are inserted before the three successive data columns, type the number of additional cols in the Ignore the first cols check box. With predetermined file formats, column skip function and negative colum3 selection will be inactive.

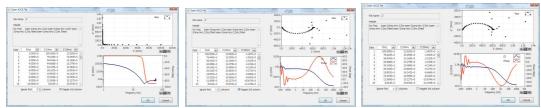
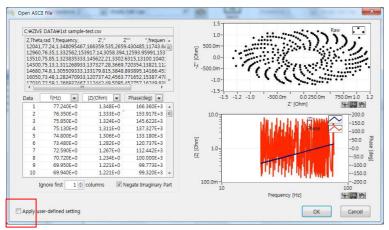


Figure 30. 1st column: serial number, Zimg polarity opposite

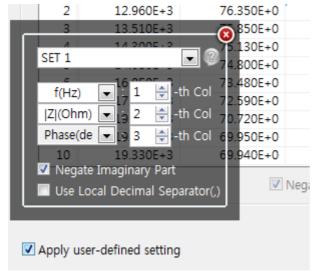
Sometimes, the sign convention of the third column may be inverted. In such a case, press **Negate 3<sup>rd</sup> Column** and plot it in Nyquist Plot and Bode Diagram. With predetermined file format, column skip function and negative colum3 selection will be inactive

Note: If your data file include time data having 00:00:00 format, ZMAN will read with 3 columns.

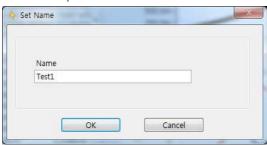
If your data set do not have the above column rule, click "apply user-defined setting" check box at left bottom side.

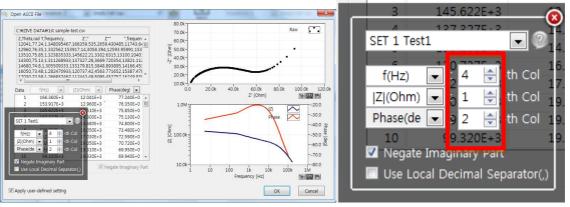


Then you can see pop up window for setting customized column rule.



you can save Max 10 set of profile. If you click "?" icon, you can make profile name for 10 set of profile.





You can set each parameter's column number column number input directly

# Chapter 4 Preview Data file

If you selected data file, The data file will move to preview section(B) or project section(C) when you selected project file.

#### A. Preview

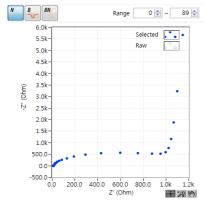


Figure 31. Preview EIS data in section "B"

When you open the data file, EIS data will be displayed at preview section. You can check the data by view various graphic or data list also you can edit the data file before EIS data analysis.

# **B.** Preview Data table

#### 1. Data format

You can select data format by selecting combo box on data list or by clicking right mouse on data list and selecting immittance .The following data formats are available for display

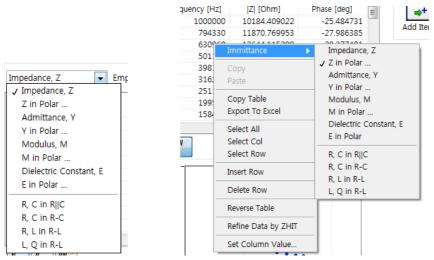


Figure 32. Data format select on combo box(left) & popup menu on data list (right)

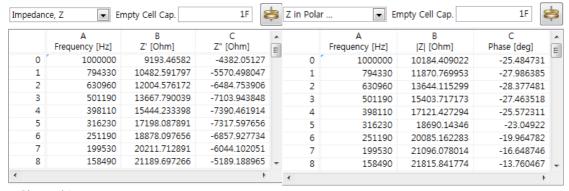
<sup>&</sup>quot;in Polar..." means in polar coordinate.



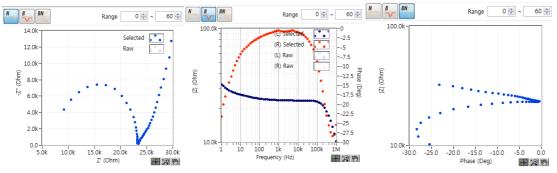
You can select Nyquist, Bode, Black-Nichols plot by selecting icon

## a) Impedance Z & Impedance Z in polar

#### a-1) Data display

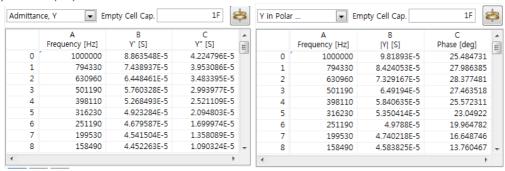


#### a-2) graphic

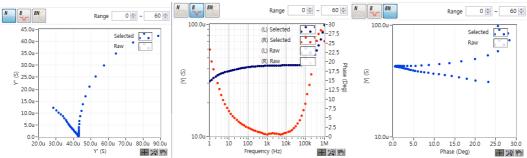


# b) Admittance Y & Admittance Y in polar

#### b-1) Data display

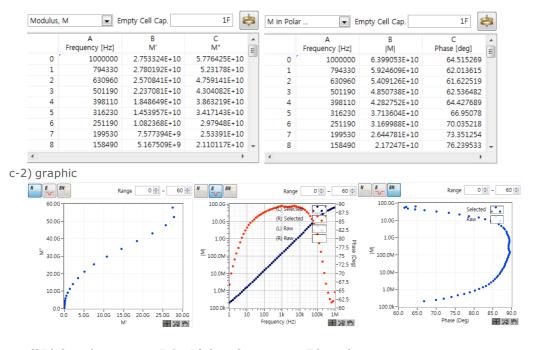


# b-2) graphic



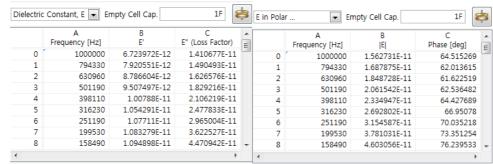
#### c) Modulus M & Modulus M in polar

c-1) Data display

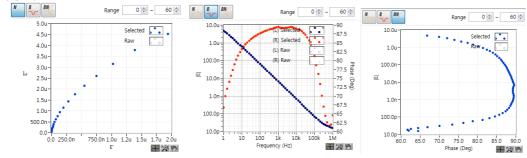


#### d)Dielectric constant E & Dielectric constant E in polar

#### d-1) Data display

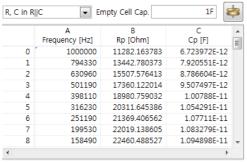




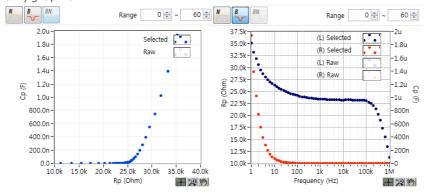


#### e) R,C in R||C (parallel connection)

e-1) Data display

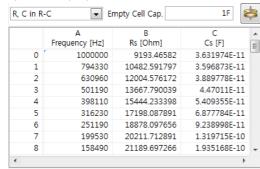


e-2) graphic

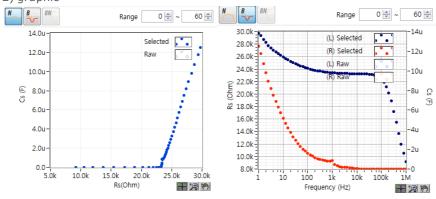


#### f) R,C in R-C(serial connection)

#### f-1) Data display

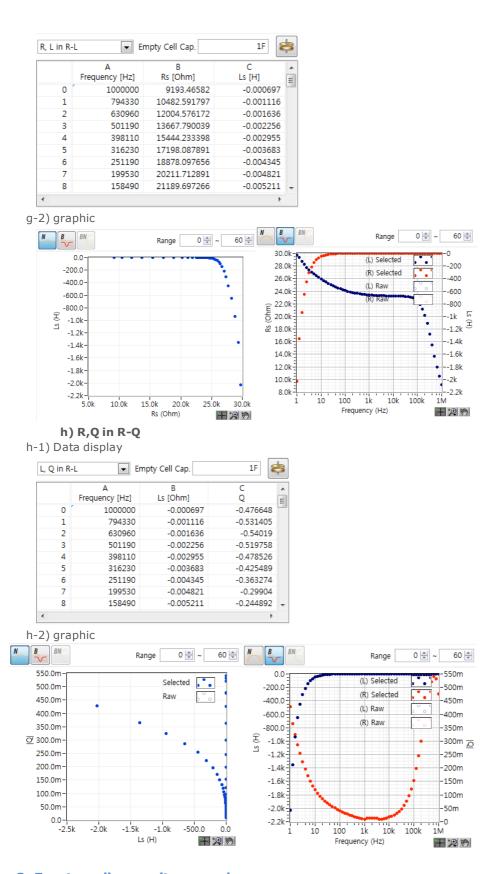


f-2) graphic



g) R,L in R-L

g-1) Data display



# 2. Empty cell capacitance value

To get dielectric constant and modulus, you must input empty cell capacitance value



Figure 33. Empty cell capacitance value input

If you do not know empty cell capacitance value, click area then you can see "set geometry"



button located on the input

Click this button then you can see the following menu

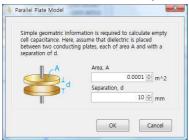


Figure 34. Parallel plate model parameter input

Area is electrode area(Unit is m<sup>2</sup>)

Separation is the distance between two electrode (Unit is mm)

If you input two parameter value and click "OK" then the calculated empty cell capacitance will be displayed on value input.

#### 3. Table Menu

To see table menu, click right button of the mouse then menu will appear.

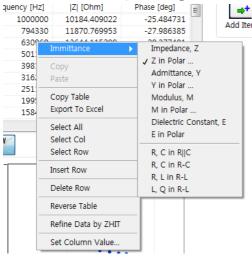


Figure 35. Table menu

#### a) Copy

If you want to copy row or column of table, click title or index number or "select Col" or "Select Row" and select "copy"

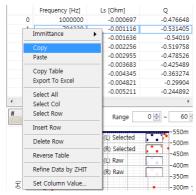


Figure 36. Row copy

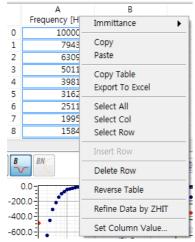


Figure 37. Column copy

#### b) Paste (Needs License Code)

This function is to paste the copied valued on the table. If you do not have license code, this will be inactive.

#### c) Copy Table

This command will copy entire table value.

#### d) Export to Excel

This function will transfer data to excel.

#### e) Insert Row

This will insert a new row above the current row. This can make generate new virtual data point if required

## f) Delete Row

This will delete data point.

## g) Reverse Table

This will reverse data order. If you want to make the data set from high frequency to low frequency when the data set has low frequency to high frequency order, you can do reverse data order by select this function.

#### h) Define Data by ZHIT

This will change the data by ZHIT function.

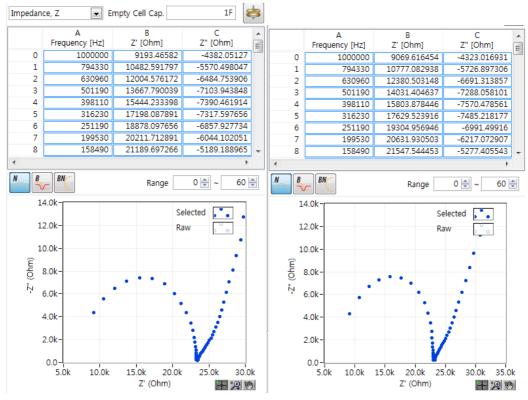


Figure 38. Before(left) & after ZHIT(right)

## i) Set Column Value

You can change the value of the user defined formula.

Click/select the column in which you want to change the data value and click right button of mouse to see the menu.

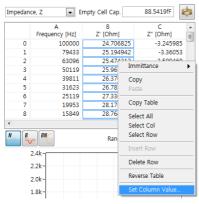


Figure 39. Set column value

The "set column value" menu will appear



#### Figure 40. Set column value

If you want to change the polarity of column C (Z"), type  $C[i]^*(-1)$ ;



Figure 41. Input formula directly

If you click OK button column C data's polarity will be changed.

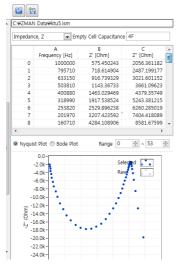


Figure 42. Polarity changed data

If you want use predefined function, Use the following rule.



Figure 43. Select column parameter

Select column parameter which you will change for the selected.



Figure 44. Dragging variable for usage of functions.

If you want to use the abs(x) function, double click or drag the parameter which you want to apply.

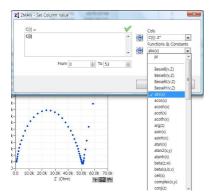


Figure 45. Select function

Select function or constant and click





Figure 46. Set colum value result

Click OK button and the data will be recalculated.

# C. Data Editing

If you want to modify the original data before analyzing, you can do it as follows.

# 1. Data region for analysis

You can use part of data for analysis

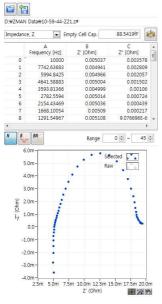


Figure 47. Preview

If you want to use positive data for Zimg, then zoom up the 0 point of Zimg by selecting regional zoom function and dragging the mouse in the area to zoom up.

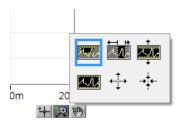


Figure 48. Zoom menu

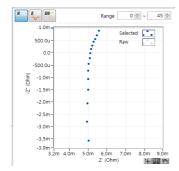


Figure 49. Zoom up

Place the mouse cursor on the graph and click right button of mouse then you can see the sub menu. Select the cursor as follows

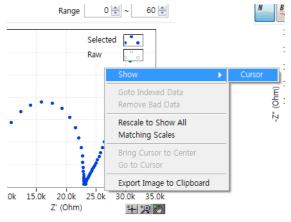


Figure 50. Cursor mode selection

You can select data point near the 0 value of Zimg by dragging the cross hair cursor and click right button of mouse.

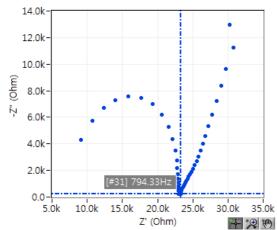


Figure 51. Select data point by cursor mode

or click right button of mouse. Then click "Goto indexed data"

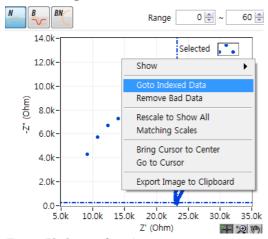


Figure 52. Cursor function

You can see the data point corresponding to the cursor location

Impedan	ce, Z ▼ E	■ Empty Cell Cap. 1F				
	A Frequency [Hz]	B Z' [Ohm]	C Z" [Ohm]	*		
31	794.330017	23250.30957	-236.620831			
32	630.960022	23266.873396	-312.90085			
33	501.190002	23296.095114	-382.616335			
34	398.109985	23340.050715	-443.652588			
35	316.230011	23394.106261	-515.264018			

Figure 53. Cursor pointed data

The cursor pointed is the 31th data point in data list.

You can input 31 in the Range box instead of 0 if you want analysis for right part of spectrum only.

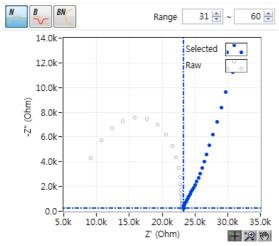


Figure 54. Selected data region

Selected data will be displayed as blue colored. These data points will be used for analysis.



Click the Add Item icon and the selected data set will be transferred to project section"C"

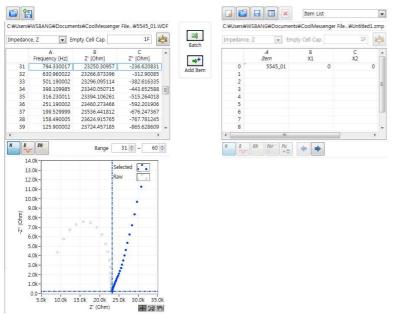


Figure 55. Transferring data set to project

You can see data preview by selecting file name at section "C" 's file name combo box or

click activated right arrow

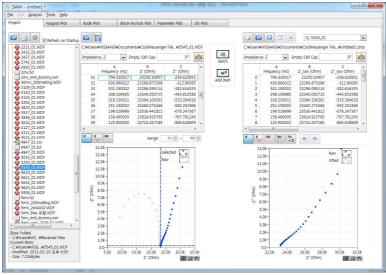


Figure 56. Data preview in project

#### 2. Delete Data points

If you want to delete bad data point(s) on original data before analysis, you can do it using the following process.

To find bad data, zoom up by selecting the regional zoom function and dragging the mouse on an area to zoom up.

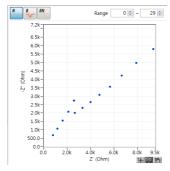


Figure 57.Zoom up

By cursor function, move the cross-hair cursor to the bad data

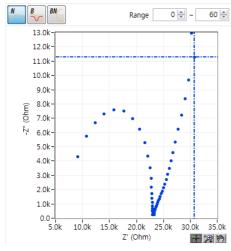


Figure 58. Cross hair cursor on bad data

Click right button on graph and select "Remove bad data"

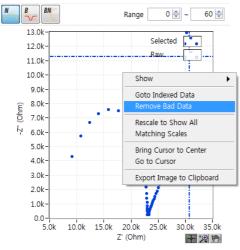


Figure 59. Remove bad data

Now the bad data point was deleted

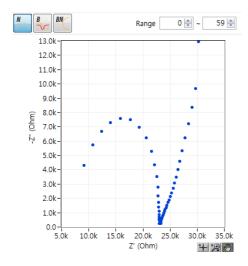


Figure 60. Bad data was deleted

## 3. Extrapolation Bad data

If you want to change bad data as expected data using extrapolation, you must change graph format as Bode plot at first.

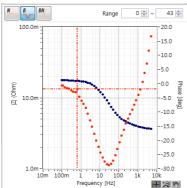


Figure 61. One point bad data on Bode plot

You can select bad data by cursor function and click right button of mouse. Then click interpolate bad data.

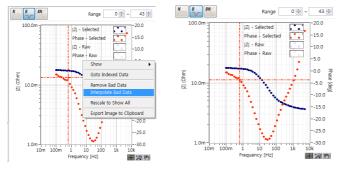


Figure 1. Interpolate bad data(before & after)

## 4. Editing Data points

If your data contains bad data points, you can change the point value

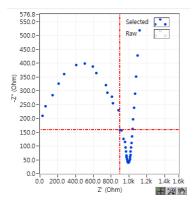


Figure 62. Select bad data by cursor function

You can select bad data by cursor function and click right button of mouse. Then click "Go to indexed data"

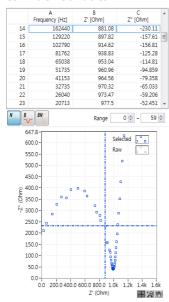


Figure 63. Bad data value list

You can change the value of Zimg to -180.

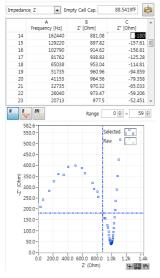


Figure 64. Data value changed

You can delete or modify the bad data points on project section

# D. Preview graph Menu

## 1. Nyquist Plot

If you want to see Nyquist plot, click button. To view pop up menu, click right button on plot region.

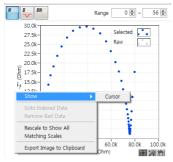


Figure 65. Nyquist pot

#### a) Cursor

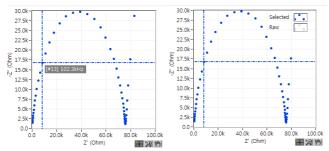


Figure 66. Nyquist plot cursor display

If you move mouse cursor to cross hair and click on it then you can see the point information as the left side graph (point number and frequency) If you release the mouse button, you can see the right side graph

At cursor mode, pop up menu is as the follows.

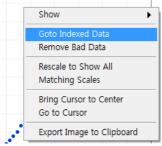


Figure 67. Pop up menu on Nyquist plot

Goto Indexed Data & Remove Bad Data is activated.

## b) Legend submenu

Only when pop up menu is displayed, you can move mouse cursor onto Legend. Then click right button of mouse.

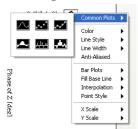


Figure 68. Legend submenu

You can change each line's properties using this pop up menu.

You can refer to this function in Graph section.

#### c) Goto Indexed Data

This will do pointing on data table for cursor selected data on graph

#### d) Remove Bad data

You can delete cursor pointed data.

#### e) Rescale to show all

If the graph was zoomed up, it will initiate scale to see whole graph

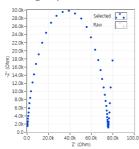


Figure 69. Rescale to show all in Nyquist

# f) Matching scale

This will display X axis scale equally to Y axis scale.

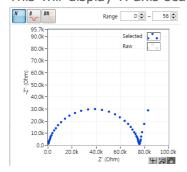


Figure 70. Matching scale in Nyquist

#### g) Bring cursor to center

Cursor will move on the center position of the current view graph region.

## h) Go to cursor

Graph will move to current cursor position as center.

## i) Export image to clipboard

Copy graphic into clipboard to use in other application software such as Word, Excel etc..

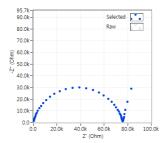


Figure 71. Clipboard image

#### 2. Bode Plot

If you want to see Bode plot, click button. To view pop up menu, click right button on plot region.

Same as Bode plot except matching scale.

## a) Cursor

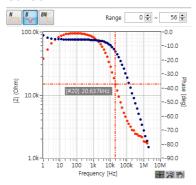


Figure 72. Bode Plot cursor display

Same function with Nyquist plot

Pop up menu on cursor mode is as the following.

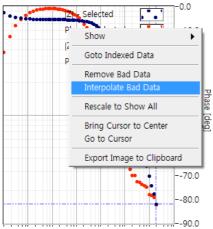


Figure 73. Pop up menu on Bode plot

Same function with Nyquist plot except Interpolate bad data function.

## b) Legend submenu

Only when pop up menu is displayed, you can move mouse cursor onto Legend. Then click right button of mouse.

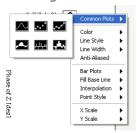


Figure 74. Legend submenu

You can change each line's properties using this pop up menu.

You can refer to this function in Graph section.

#### c) Remove Bad data

You can delete cursor pointed data.

## d) Interpolate Bad data

With this function, ZMAN changed cursor pointed data by interpolation with two data points.

#### e) Rescale to show all

If the graph was zoomed up, it will initiate scale to see whole graph

## f) Export image to clipboard

Copy graphic into clipboard to use in other application software such as Word, Excel etc..

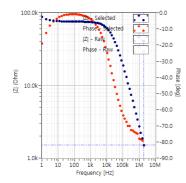


Figure 75. Clipboard image

# Chapter 5 Project

# A. How to Use the Project ("C" section)

ZMAN software was designed to handle impedance data file using a project concept. The Project can contain several EIS data files and this project can be used for analysis of serial measurement files or grouped data files. This can manage data files related among them by control variables. For example, for the evaluation of properties of a battery, one may measure impedance of the battery in its open circuit state. In such a case control variable is OCV.

These data files sets can be saved as a project file with analysis result.

If you have already opened a project file (\*.zmp), ZMAN automatically loads it in the Project section "C".

## B. Data file transfer to project

You can upload multiple files on project by the above process.

#### 1. Add item

You can transfer data file on preview section to project section by clicking "Add item" button.

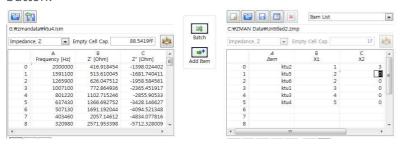


Figure 76. Upload EIS data file

#### 2. Batch transfer

You can transfer multiple data file to project section by clicking "batch" button or select batch on file menu (short key: ctrl + B). When you click "batch" button, you can select multiple data files. If these files need text file importing function, these function will do sequentially.

#### 3. Merge

You can merge other project file into current project without clearing the project. This function can be done by selecting Merge in File menu.

If you select other project file directly, current project will be cleared.

## 4. File part transfer to project

If your data file have cyclic impedance data then you can break down each impedance using data region transferring.

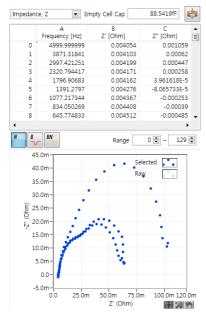


Figure 77. Data file containing multiple EIS data set

You can check how many data points included in one EIS data set on data list. And input each data set's range.

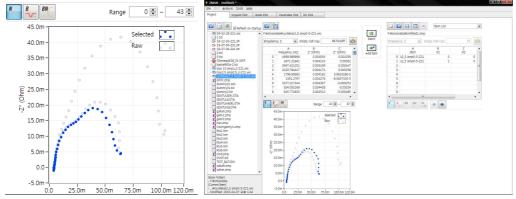


Figure 78. Data transfer by splitting.

You can transfer each data set to project.

# C. External parameter setting

## 1. Parameter value input

## a) Manual input

If you did upload multiple files, you can input values, at X1, X2, X3, such as temperature value, voltage value, distance value etc. for use in a parameter plot. To input a value, click

on the required cell and input the value as shown above. You can move the cell by using arrow keys.



Figure 79. Parameter editing

#### b) Using formula editing

If you data has rule for external parameter, you can use "set column value".

For example, your EIS data set was acquired by 50mV interval from 800mV, you can use the following formula instead of input each value by manually.

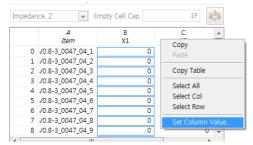


Figure 80. Formula editing for parameter input

Click right button of mouse on B column and select Set column value then the following window will appear.



Figure 81. Formula input on Set column value

Input 0.8+0.05\*i and click OK button then X1 column value will be changed automatically..

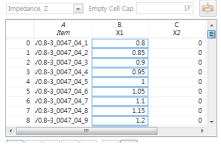


Figure 82. Parameter input result by set column value function

## 2. Parameter name



Also you can define (name) parameters (X1, X2, and X3) by clicking "Edit item" icon in "C" section such as Voltage(mV) or Time(sec) etc.

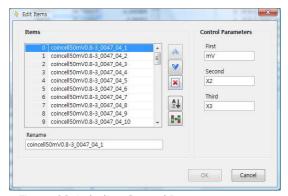


Figure 83. Labeling Control Parameters

If you change parameter name, these name will be used for parameter plot or 3D plot.

## D. Data file order change

## 1. Manual order change

For series fitting and data display for 3D plot, you need file order adjustment.

If you want to change the order of files of the list, Select one file name in the item list and click up or down icon to move to wanted location.



Figure 84. Edit item

#### 2. Sorting

You can sort by file name by clicking but

## 3. Reverse ordering



You can change item order reversely by clicking

When you want to analyse sequential data set then last measurement result was located as last one. The equivalent model for last data can be applied to other data set by using this function. These result will effect on 3D graph and sequential fitting.

# E. Open data file directly

## 1. Project file reading

You may open the project file(file extension: zmp) by clicking folder icon at "C section or double click project file at file browser (section "A")

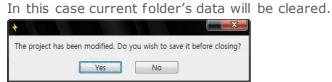
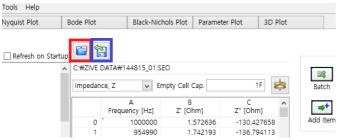


Figure 85. Warning message

#### 2. EIS data file reading

Open EIS data file from target folder.



Click red boxed icon and select EIS data file format

```
WonATech (*.sde;*.seo;*.wdf;*.wis;*.z#)
Text (*.csv;*.dat;*.txt)
Others (*.crv;*.dfr;*.ida;*.idf;*.ids;*.ism;*.izx;*.mpr;*.mpt;*.peisdata;*.z)
```

If the EIS data file is on experiment, you can click blue boxed icon to update the data file.

#### 3. Multiple EIS data file reading

If your EIS data file contains multiple multiple impedance data set by cycling such as WDF file(wonatech WEIS data file). SEO/SDE (wonatech SM data file), IDS(Ivium data file), It can be directly transfer set of data to project region(section"C")

When you did double click on those data file then following message box will appear

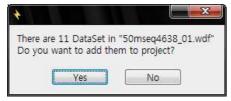
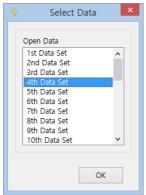


Figure 86. Multiple data set WonATech WDF/SEO/SDE file or Ivium IDS file opening

If you click Yes button, all set of data will transfer to project.

These files will be added to current project file configuration.

If you want one EIS data set in multiple EIS data set, click "NO", then you can select EIS data set which you want.



# F. Data preview on Project

If you want to preview data file from project, click index number for the data file name on item list or select file name on combo box.

Data preview function is same as in Preview section. You can refer to chapter4 Preview data file.

## 1. File selection to preview



Figure 87. Select file name on combo box

Or double click the index number on item list.

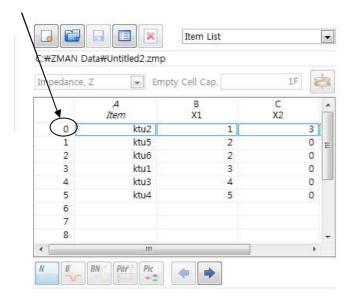


Figure 88. Select file name on item list

Then you can see preview for the data file as Nyquist, Bode, Black Nichols, Parameter value and model pictorial with data list

You can also change the preview file using arrow key



# 2. Preview type selection

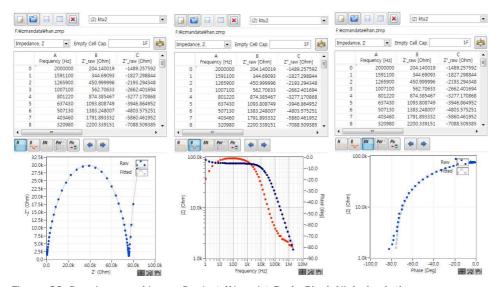


Figure 89. Preview graphics on Project (Nyquist, Bode, Black Nichols plot)

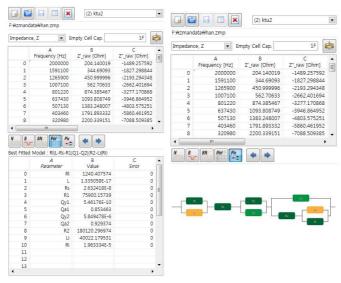


Figure 90. Preview parameter info & model pictorial

# G. Data Editing on Project

You can delete or modify the bad data on project section. Refer to Preview section regarding to data editing.

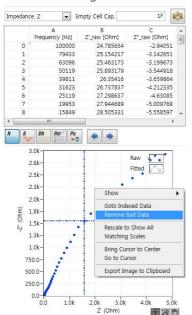


Figure 91. Data editing on project

# Chapter 6 Data analysis

# A. Kramers-Kronig Consistency

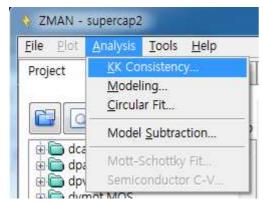


Figure 92.KK Consistency menu

# 1. Kramers-Kronig relation

The validity of Complex Impedance data may be checked by the Kramers-Kronig Relation. The Kramers-Kronig Relation is given by the following.

Z" to Z' Transform:

$$Z'(\omega) = Z'(\infty) + \frac{2}{\pi} \int_0^\infty \frac{x Z''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx$$

Z' to Z" Transform:

$$Z''(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx$$

In order to perform the calculation, ZMAN first interpolates impedance data with points equally spaced in the frequency domain. After that, the interpolated data is calculated by Maclaurin's series method.

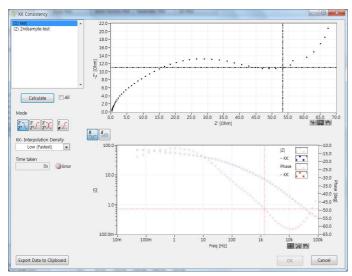


Figure 93.KK consistency menu

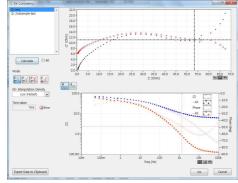
## 2. Data File Selection

Select a data file analyzed in the Filenames Box. If you want to analyze all data in the project, select one on the following option

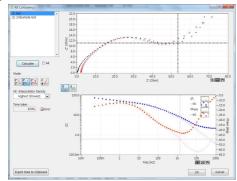
# 3. Mode Selection



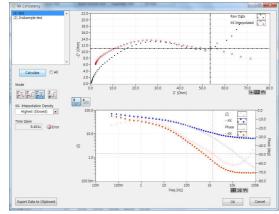
(a) Z' -> Z"



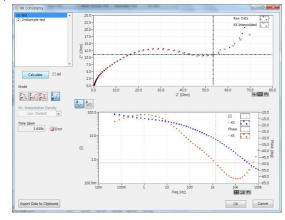




## (c) Z" <-> Z'



## (d) ZHIT



# 4. Interpolation Density option

Select an option in the "Interpolation Density" list box. There are three options: Low, Medium, High and Highest. If you select Highest, it may take around half minute to complete the calculation, depending on the performance of your computer.

### 5. Calculate

Click Calculate. After calculation if there is error, error color will change to red. Calculation time will be displayed.

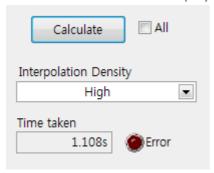


Figure 94. Calculated result

#### 6. Graph

There are Nyquist plot and Bode plot to show KK consistency result.

To view pop up menu for graph, click right mouse on graph region.

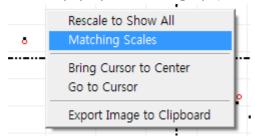


Figure 95. Nyquist plot pop up menu

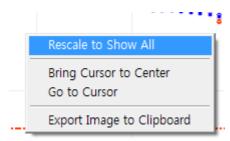


Figure 96. Bode plot pop up menu

## 7. Check Validity

After completion of the calculation, you may check the validity of your impedance data by comparing data and result in the Nyquist Plot and Bode Diagram. The difference between both is shown in the Error Graph, where  $\Delta Z$  and  $\Delta P$  hase is calculated by the following equations:

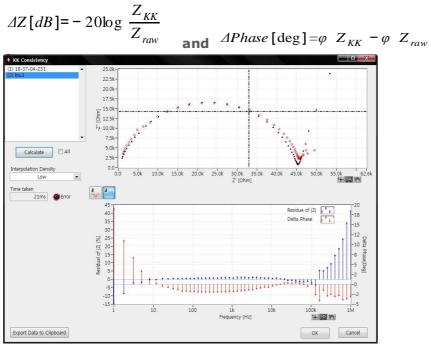


Figure 97.KK consistency error diagram

## 8. Export data to clipboard

When you click "Export data to clipboard" button, KK consistency calculation result will be copied to clipboard.

When you click OK button, KK consistency result will be applied on project. If you click "Cancel" button, result will be discarded

# **B.** Modeling

In order to fit your EIS data to equivalent circuit, Enter to Modeling Menu..

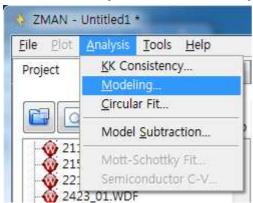


Figure 98. Modeling menu selection

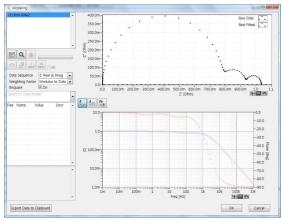


Figure 99. Modeling

# 1. Select data

If your project has multiple EIS data set, From the left-upper list box, select the data that you want to fit.

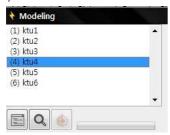


Figure 100. Data selection

When you click the data set name, Nyquist plot and Bode plot will be displayed at right side.

#### 2. Search Model

When you are uncertain as to which model best fits the data, click search model button. You can quickly and easily search available models that best fit the data. See "Automatic Model Search" for details. This step may be skipped.

#### 3. Select Model

You can select model directly from model editor or by input equivalent circuit symbol.

#### a) From Model editor

Click Select Model button in order to select an equivalent circuit to be applied to the data. See **Equivalent Circuit Model editor** for details.

You can select model in model library. Each library has same model with different initial parameter values. If you selected one model in equivalent circuit model editor

by clicking button, its initial value in the model will transferred to Modeling window

## b) Direct Input Model symbol

You can input Symbol in model input combo box as same rule in model editor.



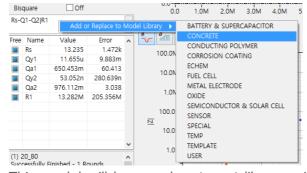
Figure 101. Symbol input box

If you did not complete it, following error message will appear.



Figure 102. Error message box

You can add this model into model library by clicking right mouse button on model



This model will be saved on target library with fitting value as initial value.

#### See "Equivalent Circuit Model editor" for details

#### c) Select Model in combo box.

You can select model list on combo box. The listed models are from libraries.

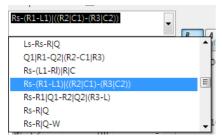


Figure 103. Model selecting combo box

#### 4. Data sequence and Weighting

Select a data sequence and a weighting method.

## a) Data sequence

You can select data set which will be used to fit.

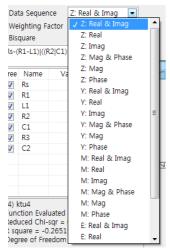


Figure 104. Data sequence selecting

Default data set is Zreal and Zimg for Nyquist plot

You can change other data set following data characteristics to get more accurate fitting result

## b) Weighting Factor

You can select weight factor on fitting process.

Default is modulus to data.

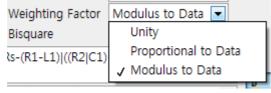


Figure 105. Weighting factor

The aim of Least Square Fitting is to find a set of parameters  $\vec{\mathbf{F}}$  which minimize the quantity

$$\chi^2 = \sum \omega_i \big[ X_i - X(f_i; \vec{P}) \big]^2$$

called the "chi-square".

1. Selection of Data Sequence

```
A. For "Z: Real & Imag" Data Sequence: X_i = \{ Zr[0], Zr[1], Zr[2], ... Zr[Ns-1], Zi[0], Zi[1], ... Zi[Ns-1] \}
```

- B. For "Z: Real" Data Sequence:  $X_i = \{ Zr[0], Zr[1], Zr[2], ... Zr[Ns-1] \}$
- C. For "Z: Mag & Phase" Data Sequence:  $X_i = \{ \ |Z[0]|, \ |Z[1]|, \ |Z[2]|, \ ... \ |Z[Ns-1]|, \ \phi[0], \ \phi[1], \ ... \ \phi[Ns-1] \ \}$
- D. For "Y: Real & Imag" Data Sequence:  $X_i = \{ Yr[0], Yr[1], Yr[2], ... Yr[Ns-1], Yi[0], Yi[1], ... Yi[Ns-1] \}$
- E. and so on
- 2. Selection of Weighting Factor  $\omega_i=\frac{1}{\sigma_i^2}$  is calculated from the uncertainty  $(\sigma_i)$  of the i-th data point..
  - A. "Unity" : no weighting.  $\sigma_i = 1$
  - B. "Proportional": the uncertainty of the real component of the data is proporti onal to its magnitude, and the uncertainty of the imaginary component is proportional to its magnitude

```
\sigma_i = { Zr[0], Zr[1], ... Zr[Ns-1], Zi[0], Zi[1], ... , Zi[Ns-1] } for "Z: Real & Imag"
```

$$\sigma_i = \{ Zr[0], Zr[1], ... Zr[Ns-1] \}$$
for "Z: Real"

$$\sigma_i = \{ \text{ Zr[0], Zr[1], ... Zr[Ns-1], Zi[0], Zi[1], ... , Zi[Ns-1] } \} \text{ for ``Z: Mag \& Phase''}$$

$$\sigma_i = \{ Yr[0], Yr[1], ... Yr[Ns-1], Yi[0], Yi[1], ... , Yi[Ns-1] \} for "Y: Real & Imag" *1$$

and so on...

C. "Modulus to Data": the uncertainty of the each data is proportional to its modulus.

$$\sigma_i = \{ \ |Z[0]|, \ |Z[1]|, \ ... \ |Z[Ns-1]|, \ |Z[0]|, \ |Z[1]|, \ ... \ , \ |Z[Ns-1]| \ \} \ for \ ``Z: \ Real \ \& Imag''$$

$$\sigma_i = \{ |Z[0]|, |Z[1]|, ... |Z[Ns-1]| \}$$
 for "Z: Real"

$$\sigma_i = \{ \ |Z[0]|, \ |Z[1]|, \ ... \ |Z[Ns-1]|, \ |Z[0]|, \ |Z[1]|, \ ... \ , \ |Z[Ns-1]| \ \} \ for \ ``Z: \ Mag \ \& Phase''$$

$$\sigma_i = \{ \ |Y[0]|, \ |Y[1]|, \ ... \ |Y[Ns-1]|, \ |Y[0]|, \ |Y[1]|, \ ... \ , \ |Y[Ns-1]| \ \} \ for \ ``Y: \ Real \ \& \ Imag'' \ ^{1}$$

and so on...

\*1 I have designed the ZMAN according to a rule that <u>bigger Z, bigger uncertainty.</u>

However, please note that this is not valid for Y, E data sequence in current ZMAN version.

#### 5. Model Parameters

Free	Name	Value	Error	•
1	Rs	100	-	
<b>V</b>	R1	100	-	
V	L1	10n	-	
1	R2	100	-	
1	C1	1m	-	
1	R3	100	-	
1	C2	1m	-	
				•

Figure 106. Model parameter window

You can modify model parameters value to use as initial values of fitting process. When you input value, Nyquist plot and bode plot display(fitting curve) will be changed following this value.

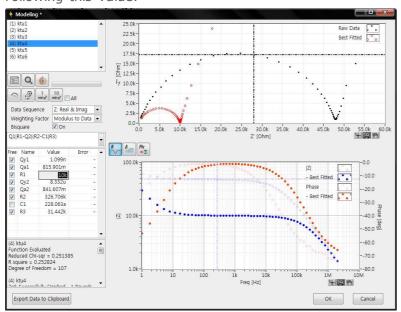


Figure 107. Parameter input result

## 6. Initial guessing



There are 3 initial guessing method.

- a) Direct parameter value input
- b) Simple circular initial guessing
- c) Genetic algorithm initial guessing

For details See "Automatic Model Search"

#### 7. Fit Data

Click Fit Data one round minimize or 10 round minimize to fit mode parameters to the model. You can do fitting with 3 options

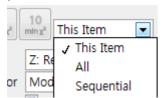


Figure 108. Fitting option

- a) This item: With this option ZMAN will do fitting for only selected file.
- b) All: With this option, ZMAN will do fitting based on parameters current values. Also this can be used for initial guessing for all data.
- c) Sequential: With this option, The fitting process will done sequentially data by data.

After fitting routine is finished, you may compare the best-fitted data against raw data in Nyquist Plot and Bode Diagram. Check All TRUE to fit parameters of impedance series. ZMAN automatically use best-fitted parameters as initial values to fit the next impedance data set. So you need to locate data set in order as changing control test conditions such as time, voltage etc.

You can change file location order in project tab's edit items.



Figure 109. File location order change

Note: If you use series fitting using check on All, Fitting process will use 1st data's model with its parameter setting in fixed or free for all other data sets even if you selected other model for other data set.

In Error Graph,  $\Delta Z$  and  $\Delta Phase$  is calculated by the following equations:

$$\Delta Z[dB] = -20\log \frac{Z_{\textit{BestFitted}}}{Z_{\textit{raw}}} \quad \text{and} \quad \Delta Phase [\deg] = \varphi \quad Z_{\textit{BestFitted}} - \varphi \quad Z_{\textit{raw}} \quad .$$

Figure 110. Error graph

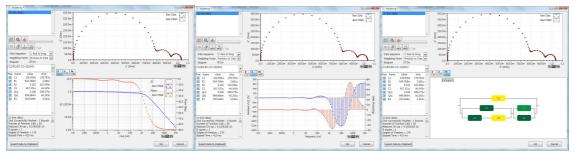


Figure 111. Model fitting result

You can view the equivalent circuit model by clicking "PIC" button. Left bottom side information is fitting result. If you see "Singular matrix...", fix the parameter in model by check out "Free" section and do fitting again.

## 8. Bisquare option

Check on Bisquare option, you will get more accurate result but it takes more time.

## 9. Parameter free/fix

Only free parameters will be used for fitting. If some parameter(s) are set as fixed, those parameter will not be used for fitting process.

There are two free condition by fitting value range

## a) Positive value acceptable only

ZMAN will fit the parameter value within positive value. If you set this one, free mark will be  $\blacksquare$ 

### b) All value including negative acceptable

ZMAN will fit the parameter value with all value. If you set this one, free mark will be

If parameter was fixed free mark will be  $\ \square$ 

You can set all parameter as positive value only or all parameter by clicking right mouse button on "Free" characters then following pop up menu will appear.

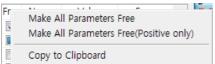


Figure 112. Free option pop up menu

You can change free status per parameter by click this mark then mark will be changed by every clicking.

If you select copy to clipboard, each parameter's setting information will copied to clipboard as;

```
Free,Rs,100,-
Free(+),R1,100,-
Fixed,C1,0.001,-
Free,R2,100,-
Free,C2,0.001,-
Free,R3,100,-
Free,C3,0.001,-
```

## 10. Fitting history information

Every fitting process will be logged and displayed at left bottom side

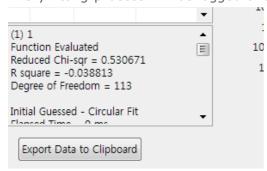


Figure 113. Fitting history information

## a) Initial guessing log.

If you do initial guessing, following information will be logged.

#### Simple circular

```
(1) 1
Function Evaluated
Reduced Chi-sqr = 0.530671
R square = -0.038813
Degree of Freedom = 113
Initial Guessed - Circular Fit
Elapsed Time = 0 ms
```

## Genetic algorithm

```
(1) 1
Function Evaluated
Reduced Chi-sqr = 0.075619
R square = 0.963088
Degree of Freedom = 113

Initial Guessed by Genetic algorithm
Fitness(Chi-sqr) = 0.075619
Number of Populations = 100
Number of Generations = 175
Elapsed Time = 13135 ms
```

## b) Fitting log

## Successful fitting result

(1) 1

3rd: Successfully Finished - 1 Rounds Number of Function Calls = 56 Reduced Chi-sqr = 0.000364 R square = 0.999826 Degree of Freedom = 113 Elapsed Time = 167 ms

2nd: Successfully Finished - 1 Rounds Number of Function Calls = 45 Reduced Chi-sqr = 0.000316 R square = 0.999799

.

# Singular Matrix result

(1) 1
Singular Matrix - Fix Qa2 - 1 Rounds
Number of Function Calls = 184
Reduced Chi-sqr = 0.000412
R square = 0.999952
Degree of Freedom = 112
Elapsed Time = 694 ms

If you meet singular Matrix result, there will be no Error value on the result.

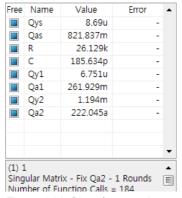


Figure 114. Singular matrix result

In this case, you must FIX by clicking parameter which log informed and do fitting again.

Free	Name	Value	Error	
	Qys	8.924u	64.171m	
	Qas	814.867m	1.391k	
	R	26.129k	1.828P	
	C	177.627p	1.055u	
	Qy1	1.131u	185.281m	
	Qa1	375.987m	10.71k	
	Qy2	1.241m	2.677M	
	Qa2	222.045a	-	
	Successf	ully Finished - unction Calls :		

Figure 115. Fitting result after fixing parameter

# 11. Export Data to clipboard

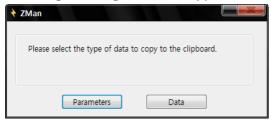


Figure 116. Fitting result clip board copy

Click Okay to close this window. If you click OK button, fitting result will be accepted and can be saved in project file. If you click Cancel button, fitting result will be discarded.

# C. Circular fitting

If your EIS data's Nyquist plot has circle(s), you can get circle information using this fitting function.

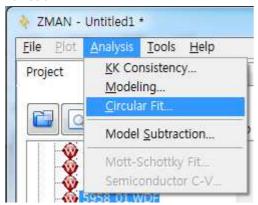


Figure 117. Circular fit menu

When you selected Circular fit function, circular fit menu will show with 1<sup>st</sup> data. ZMAN will do circular initial fitting automatically. If there are no previous analysis including circular fit, modeling, ZMAN will set data range for circular fitting as full range which data contains. If there was previous analysis, data range will be changed following previous result.

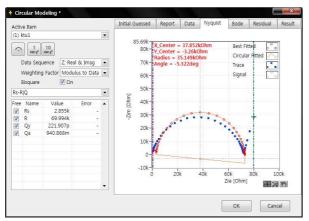


Figure 118. Circular fit menu

#### 1. Data file selection

Select data file for circular fitting on Active item

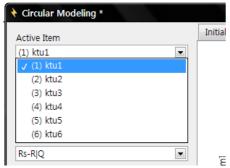


Figure 119. Data file selection

When you select new data file, ZMAN will do circular initial fitting again automatically.

# 2. Data range setting for circular fitting

If you did not analyse selected data before, data range will be show all range.

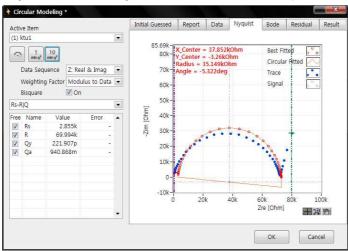


Figure 120. Before range setting

Move left(violet) & right(olive) cursor bar into circle region by clicking and dragging the cursor bar.

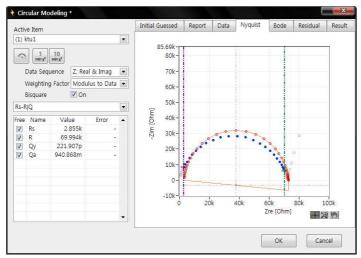


Figure 121. After range setting

Data points color outside of range bar will be change to grey. Blue colored data points will be used in calculation for circular fitting.

# 3. Graph pop up menu

You can get pop up menu by clicking right mouse button on graphic region.



Figure 122. Graph pop up menu

#### a) Initialize cursors

This will relocate two cursor bar to initial position.

# b) Violet cursor/Olive Cursor

- 1) Go to center: Cursor bar will locate at center
- 2) Go to cursor: Graphic window will locate at cursor

## c) Rescale to show all

#### d) Matching scales

Adjusting Nyquist plot X, Y axis with same scale

# 4. Circular Initial guessing

After setting data range by moving cursor bars.

If you click the circular Initial guessing icon—, then circular fitting will be done with new setting data range.

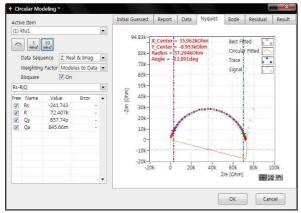


Figure 123. Circular fitting data range setting

If there are multiple circles and you want to fit other circle, move cursor bar to the circle region and click guessing icon.

10

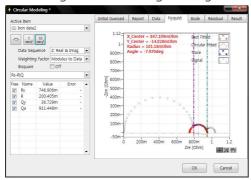


Figure 124. Other circle fitting

# 5. Circular fitting

Click fitting icon for 1time or 10 time fitting

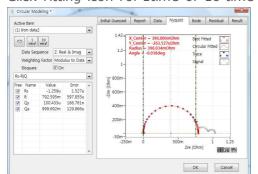


Figure 125. Fitting process

Fitting process is same as described in above modeling. See " Modeling" for details

# 6. Including Warburg impedance

If the circular data has Warburg diffusion element as simple circuit, you can select the model as the follows.

a. Select Model Rs-(R-W)|Q or Rs-(R-W)|C

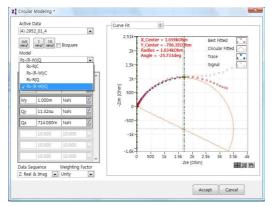


Figure 126. Model change

- b. Move right(olive) cursor bar to linear region
- c. Click fitting icon for 1time or 10 time fitting



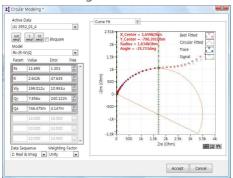


Figure 127. Fitting again

#### 7. Circular fit result

You can see the data list, Report, Initial Guess information, Result, Residual, Bode as follows...

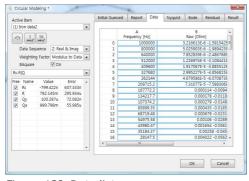


Figure 128. Data list

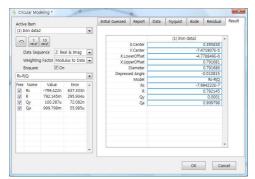


Figure 129. Circular fitting result display

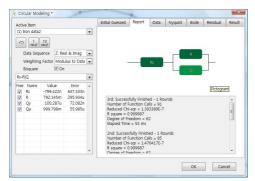


Figure 130. Circular fit report display

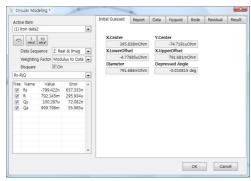


Figure 131. Initial guessing data

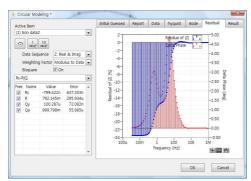


Figure 132. Residual

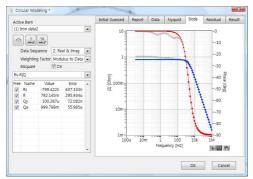


Figure 133. Bode plot overlay with result

Click accept button if you want use this parameters This fitting result parameter values will transfer to model parameter for Modeling and can be used as further fitting initial value.

You can see fitted data in plots if you select raw data + fitted data.

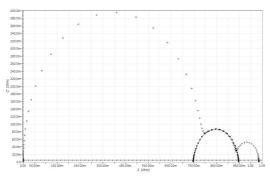


Figure 134. Raw data + circular fitted data in Nyquist plot after circular fitting

# 8. Circular fit result for Modeling

#### Example 1)

You can use these circular fitting result parameter values as fixed parameter and other parameters are free then further fitting can be done for other free parameters.

If there are 3 circles on Nyquist plot, you can do circular fit for 1<sup>st</sup> circle and can use this result for other 2 circle's fitting data in Modeling.

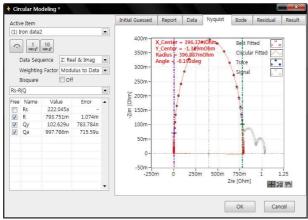


Figure 135. 1st circles circular fit

After circular fit finished, click OK button and enter Modeling menu. You can find same fitting result value was transferred to Modeling.

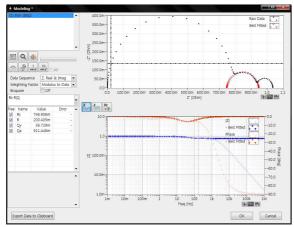


Figure 136. Circular fitting result transferred to Modeling

You can input adding Symbols to current circuit formula.

Rs-R Q <mark>-R1 Q1-R2 Q2</mark>				•
Free	Name	Value	Error	•
	Rs	222.045a	-	
1	R	793.751m	1.074m	
1	Qy	102.629u	783.784n	
1	Qa	997.786m	715.59u	

Figure 137. Input Adding Symbols for new model to fit

After input adding symbols and press enter key, then adding symbol(parameter) list will displayed.

Free	Name	Value	Error		
		222.045a	LITOI		Т
<b>V</b>	Rs			-	
1	R	793.751m		-	
1	Qy	102.629u		-	
1	Qa	997.786m		-	
1	R1	100		-	
1	Qy1	1u		-	
1	Qa1	800m		-	
<b>V</b>	R2	100		-	
1	Qy2	1u		-	
1	Qa2	800m		-	

Figure 138. Added parameter list

You can fixed Rs, R, Q values by clicking Free parts.

Free	Name	Value	Error	•
	Rs	222.045a	-	
	R	793.751m	-	
	Qy	102.629u	-	
	Qa	997.786m	-	
1	R1	100	-	
1	Qy1	1u	-	
1	Qa1	800m	-	
1	R2	100	-	
1	Qy2	1u	-	
1	Qa2	800m	-	

Figure 139. Fixed parameters from circular fit

Click simple circular initial guessing or genetic algorithm initial guessing to set added parameters initial value.

Now you can do further fitting for other circles by clicking fitting buttons

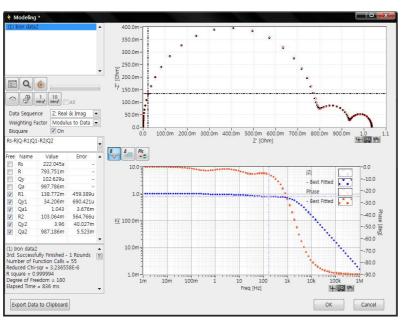


Figure 140. 1st Fitting result

Check free for parameters from circular fitting and click fitting button again.

10 min x²

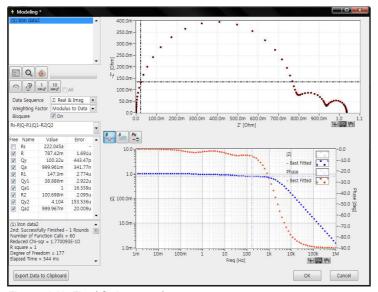
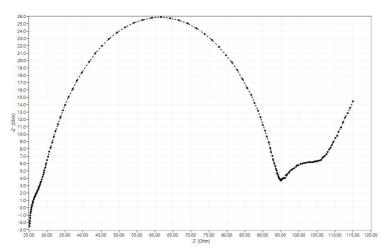


Figure 141. Final fitting result.

# Example2)

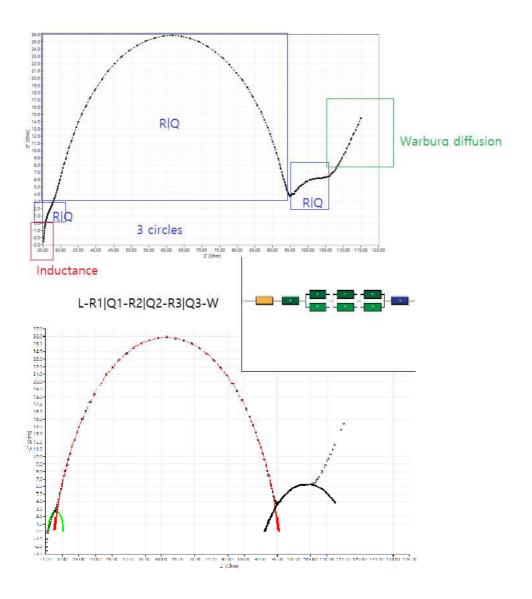
Modeling & fitting using circular fitting for impedance spectrum having 3 circles. Data file loading

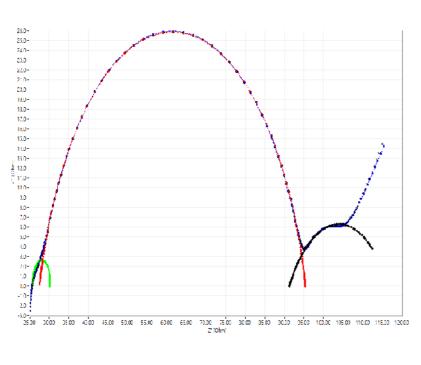


The Nyquist plot shape has 3 circle and diffusion.

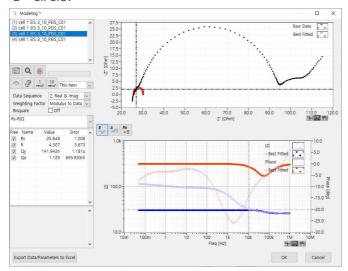
Equivalent circuit example is

Rs-R1|Q1-R2|Q2-R3|Q3-W

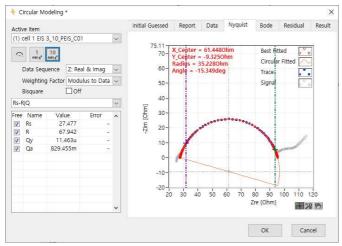




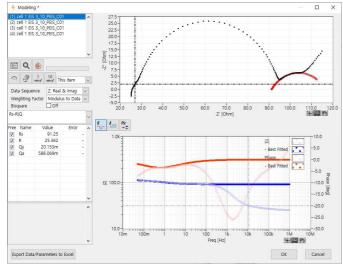
The 3 circles might be fitted using circular fitting as the follows.  $1^{st}$  circle.



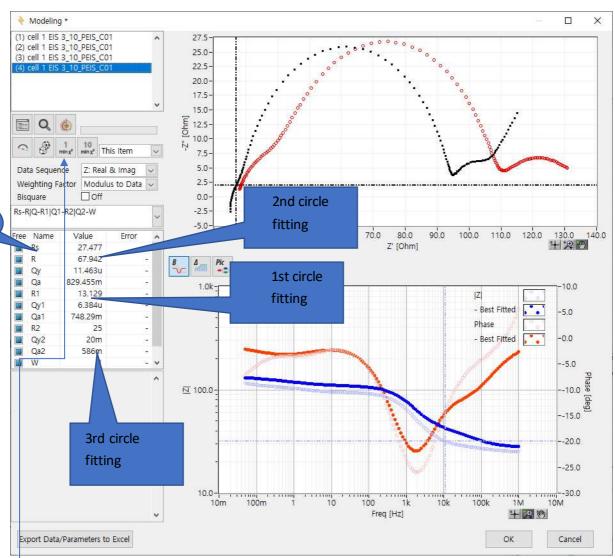
#### 2<sup>nd</sup> circle



#### 3<sup>rd</sup> circle

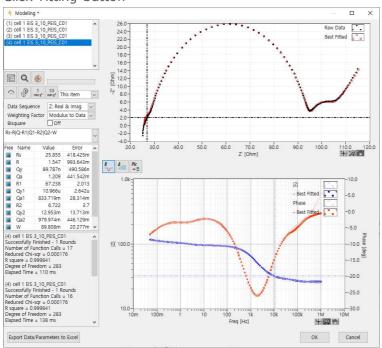


We can use each parameters using above 3 circles.

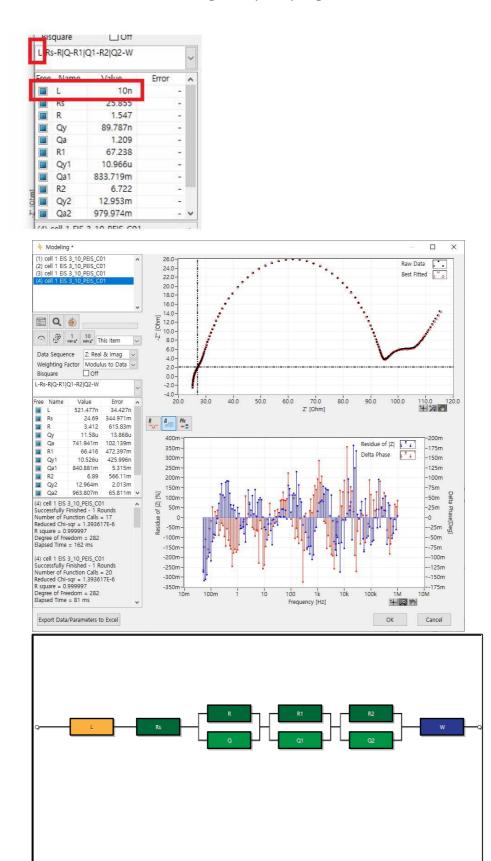


#### Click fitting button

Input



Add Inductance element for high frequency region data.



# D. Manipulate element or Model

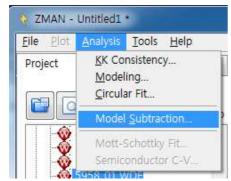


Figure 142. Model Subtraction menu

If you want to add or subtract element/circuit model from data, select Manipulation data model. You can select Add or subtract

If you select element or model in combo box or from model editor by clicking input the value for manipulation, you can select subtraction or Addition of this value. You can input Model symbol directly but if there is such model in library, input is not available. You must make same model in model editor before doing this.

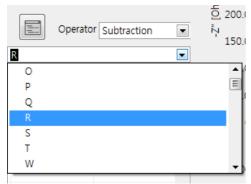


Figure 143. Select element or model for manipulation

#### 1. Element subtraction/Addition

If you want 6kOhm resistor from data, select R for element and input 6kOhm then origianl data and subtracted data will be displayed as overlayed.

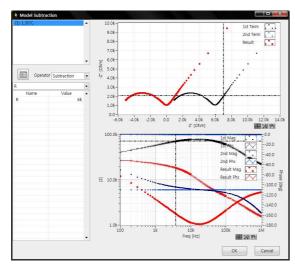


Figure 144. Manipulation result display

If you click Add & close, you can see the original data and the manipulated data at same time on the graph menu as the follows.

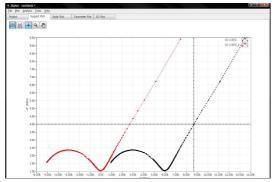
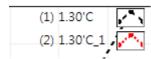
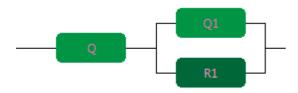


Figure 145. Overlay (original data and manipulated data)

Manipulated data will be new data named adding "\_1" at end of original file name. So this manipulated data can be used for fitting etc independently.



The above data is assumed Q-Q1|R1



Q is straight line at right side Q1|R1 is semi circle at left side.

If you subtract Q from original data, semi circle will remain.

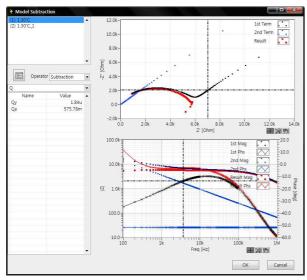


Figure 146. Q subtraction

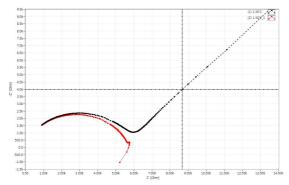


Figure 147. Q subtracted result (red line)

# 2. Model Subtraction/Addition

You can subtract or add model. For example If you subtract Q1 $\mid$ R1 model, straight line will remain.

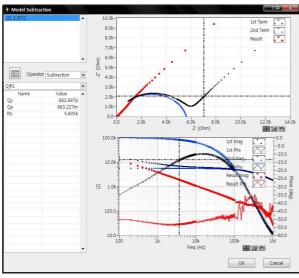


Figure 148. Q1|R1 subtraction

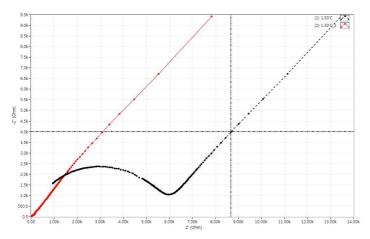


Figure 149. Q1|R1 subtracted result (red line)

# E. Mott-Schottky Fit & Semiconductor C-V

This menu is only activated series data having same frequencys and voltage value were loaded. These data file can come from fixed frequency Mottschottky technique or dynamic mottschottky technique using ZiveLab EIS instruments.

When you try to load these data file, You can see the following dialog box.

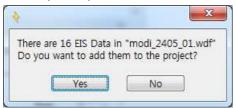


Figure 150. Confirm dialog box

Click "Yes" button then data series will be loaded on section "C" (project section)

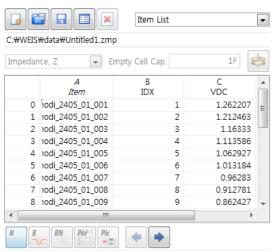


Figure 151. Series data loaded on section "C"

#### 1. Mott-schotky fit

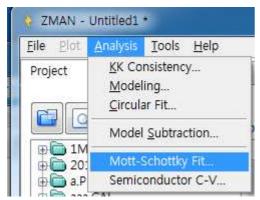


Figure 152. Mott-Schottky fit menu

If you select this menu, Mott-schottky analysis sub windows will be appear.

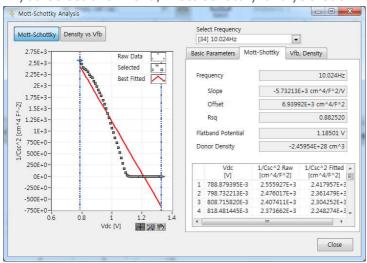


Figure 153. Mott-Schottky Analysis window

# a) Basic Parameter Input

For analysis, you must input parameters on "Basic parameter tab"

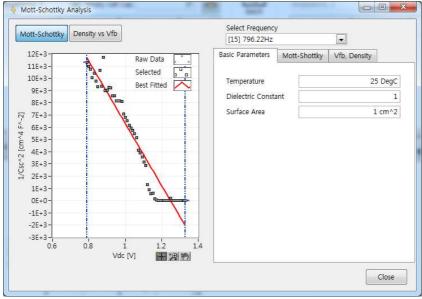


Figure 154. Basic parameters input

# b) Mott-Schottky analysis

## i) Select Frequency

If you loaded dynamic mot-schottky data set, you can select frequency which you want analysis.

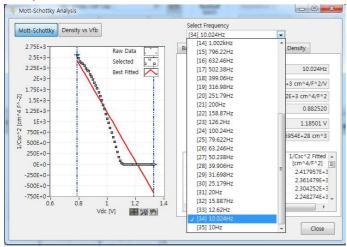


Figure 155. Frequency selection

# ii) Selecting data region for analysis

Moving blue lines for data which you want analysis.

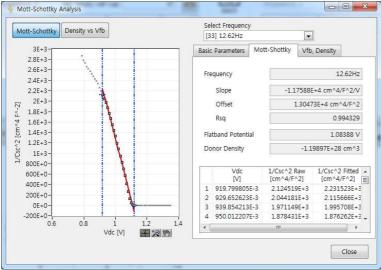


Figure 156. Selecting data region for analysis

You can see Mott-schottky analysis result at right side on Mott-Schottky Tab

# c) Donor Density vs. Vfb graph and analysis

If you click "Density vs Vfb" button you can see the graph and analysis result. This can be done only with Dynamic Mott-Schottky data set.

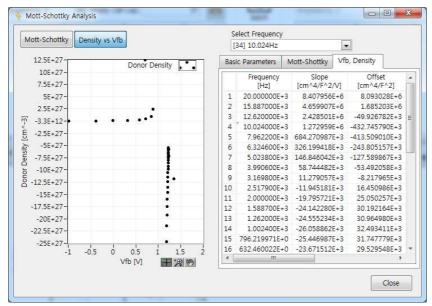


Figure 157. Donor density vs. Vfb graph and analysis

You can export analysis result to Excel using "export to Excel" or make Ascii file using copy and paste on pop up menu. (By clicking right button of mouse on result list)

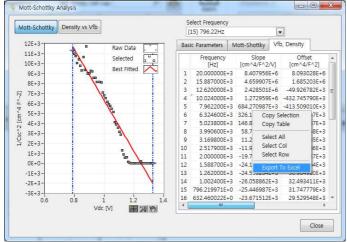


Figure 158. Analysis result pop up menu

#### 2. Semiconductor C-V

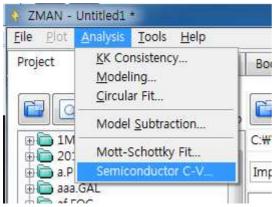


Figure 159. Capacitance vs voltage menu

If you want to see Capacitance vs. voltage curve, select this function. Then you can see following "Semiconductor C-V" window.

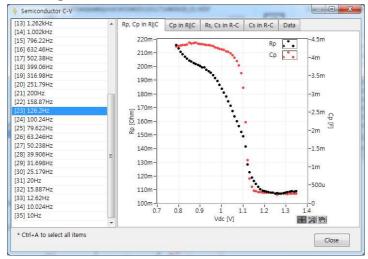


Figure 160. Semiconductor C-V menu

If you loaded dynamic mott-schottky data, you can see multiple frequency at left side of window. You can select one frequency or multiple frequency using CNTRL+click or shift+click. (If you want to select all frequency, press CNTRL+A)

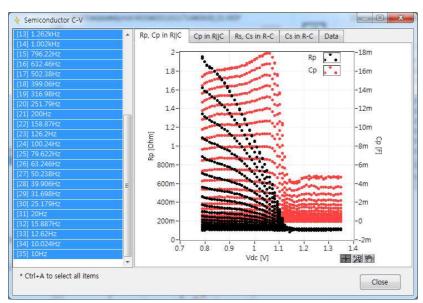


Figure 161. All frequency selected

If you want to see line instead of dot, click right button of mouse on graph and move cursor to legend which you want to change and click left or right button of mouse. You can see graph property setting menu.

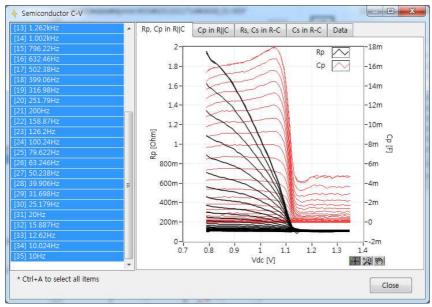


Figure 162. Graph property change

You can see 4 kinds of graph by selecting Tab.

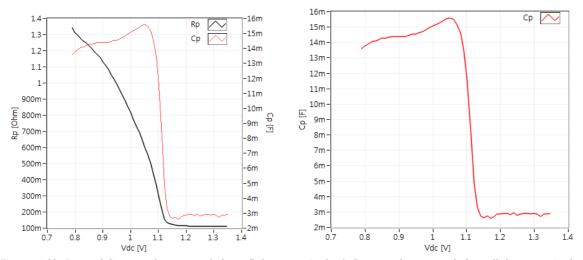


Figure 163. Rp and Cp vs voltage graph (parallel connection) & Cp vs voltage graph (parallel connection)

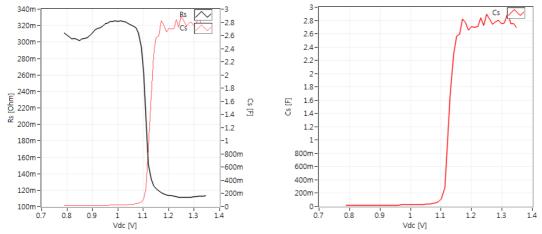
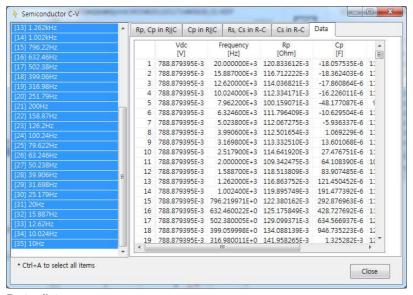


Figure 164. Rs and Cs vs voltage graph (serial connection) & Cs vs voltage graph (serial connection)



Data list

You can export data to excel on popup menu by clicking right button of mouse.

# Chapter 7 Equivalent Circuit Model Editor

You can use this menu on intro menu or tool-Model editor.



Figure 165. Model editor menu

When you select this function, you can see independent window as the follow.

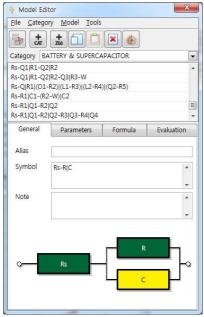


Figure 166. Equivalent Circuit Model Editor

#### A. Model file

You can backup/import/initialize model file if you want.

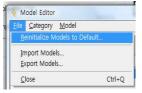


Figure 167. Model file menu

## 1. Reinitialize Models to Default

If you want to clear current models/categories and come back to default, then click this menu. You can see the warning message box.

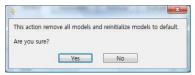


Figure 168. Confirmation of initialize model file

# 2. Import Models

If you want import model/category from backup file, ZMAN old version model file or other person's model file which he/she made using ZMAN, you can import it into current model file.

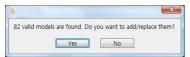


Figure 169. Model Importing

# 3. Export Models

Using this function, you can backup current model file including model/category information. Default file name format is "Backup(today's year-mnth-day-hour-minute-second).models"

# **B.** Category Menu

There are several predefined category for each application's library. You can make your own category(library). These category will be used when you search the model. You can search the model for all of categories or some category only.

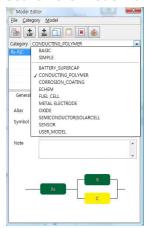


Figure 170. Predefined categories

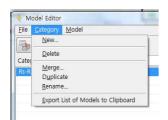


Figure 171. Category Menu

#### 1. New category

If you want make your own category(library), Select New in Category menu.

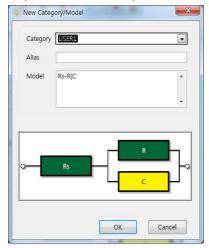


Figure 172. New category/model

You can input your category name(eg. Test1 etc) by typing then the category will be created. (Note: Each category must have minimum one model)

#### 2. Delete category

If you want to delete category which has models, Select Delete in Category menu.

Please note;

deleted category with models can NOT be recovered(permanently erased).

Before delete category, you must select category which you want to delete as the following window.



Figure 173. Delete category

And select delete in category menu the following window will appear.

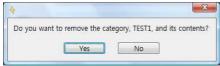


Figure 174. Delete confirmation box.

If the category has just one model, you can delete model then its category will be deleted.

#### 3. Merge categories

If you want merge several categories into one new category, you can use this function.

Note: If you did merge function, source category will be disappeared.

Example) If you want TEST1, TEST2, TEST3 categories into one TEST\_total category, select 3 category in left window and click right side arrow and change the New Category name as TEST\_total and click OK button then 3 source categories will be disappeared and all models in 3 categories will move to new category named TEST\_total.

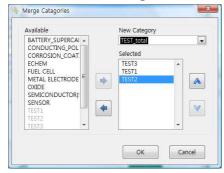


Figure 175. Merge Menu

When you click the OK button, you can see warning message as the follows

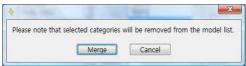


Figure 176. Merge confirmation

If you confirm it, click the Merge button.

TEST1, TEST2, TEST3 category and its models will be erased and merged TEST\_total including all models ,which 3 model had, category will be created

#### 4. Duplicate

This function will make clone of source category.

#### 5. Rename

You can change category name using this function

# 6. Export list of models to clipboard

You can copy the model list which included in category into clipboard

# C. Model Menu

Each category can contains several models(equivalent circuit model). Each model can be included in multiple categories with different default parameter value to meet each application.

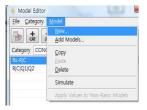


Figure 2. Model Menu

#### 1. New

You can make new model by clicking Model-New on the menu or clicking Model New button. New model editor will be displayed as the follow.

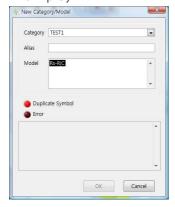


Figure 177. New Model/Category Menu

Firstly you must select Category which you want the new model into.

If you need new category, just type on Category input then new category will be created.

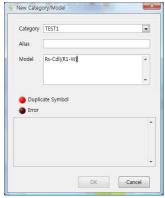
#### Example)



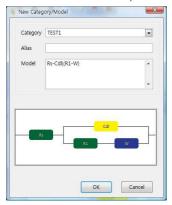
If you selected Category, input the model following Model editor rule described in the following "model design rule"



If you want to make above equivalent circuit model, type "Rs-Cdll(R1-W)" on Model input. And enter key or click other part.



If there is no error, the following window will be displayed.



If you click OK button, this model will be saved in TEST1 category.

If there is an error in Model description, the following error will be displayed.

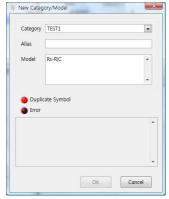


Figure 178. Duplicated Model

If there is same model in target category, the above error will be happened.

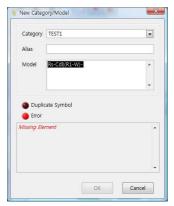


Figure 179. Missing element

If element is missing on the above model, the above error will be happened.

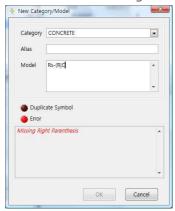


Figure 180. Missing Right Parenthesis

Need Right Parenthesis to complete the formula.

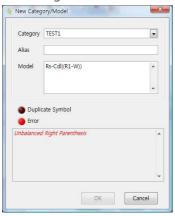


Figure 181. Unbalanced Right Parenthesis

There is missing left Parenthesis on the formula.

#### 2. Add Models

You can add model(s) into category by typing symbols or paste model list if you did "Export list of Models to clipboard" on category menu. Before this action, you must select category at first.

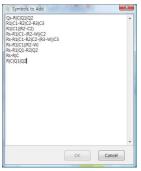


Figure 182. Symbols to add

After typing or paste symbol list as the above, click OK button then following box will appear. If valid model exist, valid model color will be change to blue and OK button activated. When you click OK button, valid models will be added to target category.

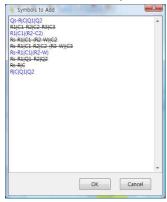


Figure 183. Model check for symbol to add

# 3. Model Copy

If you want copy a model to paste into other category, click model copy icon or select copy on Model menu.

#### 4. Model Paste

If you did copy some model, you can paste it into other categories.

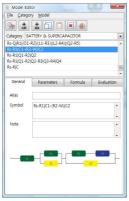
#### 5. Model Delete

You can delete the model in specified category. Same model in other categories will NOT be erased.

# 6. Model Edit/Create

You can edit current model in parameter default value, alias, note field. If you modify symbol(model circuit), software will accept it as new model.

#### a) Model Edit



You can input some information in Alias by typing.(It may be used as comment for application). Also you can input the information in Note field. If you double click on Note field, New memo window will be displayed.



Figure 184. Memo input window.

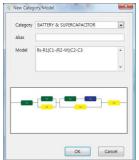
# b) Model create

If you want to create new model using current model modification, ZMAN will recognize it as new model.

Eg) If you want add C3 as serial connection, then type "-C3" end of formula.



And press enter key. If there is no error on symbol connection then the following New category/Model window will appear.



But if there is any error, the following error message will appear.



# D. Model Design Rule

An equivalent circuit is made of combination of circuit functions. ZMAN already has 12 basic circuit functions. See **Basic Elements** to know details. If you want to have your own circuit function, refer to **Single Elements**.

In ZMAN, a circuit model is described as symbols of functions and 4 special operators standing for relation of functions or their combinations. You can identify each symbols with an ASCII characters (0 to 9, a to z, and A to Z) next to symbols such as R1, R2, and Rs.

# Those 4 operators are

- : Serial Operator. For example, "R-C" means a resistor is serially connected with a capacitor. "+" operator can be used instead of "-" operator.
- | : Parallel Operator. For example, "R|C" means a resistor is connected in parallel with a capacitor. "/" operator can be used instead of "|" operator.

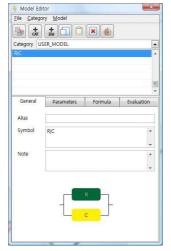


Figure 185. Equivalent Circuit Model Editor

(and): Left and Right parentheses are used to clearly define a group of elements. For example, "Rs-(Rct|Cdl)" means a resistor (Rs) is serially connected with a bundle of a resistor (Rct) and a capacitor, in which each is parallel, connected the other.

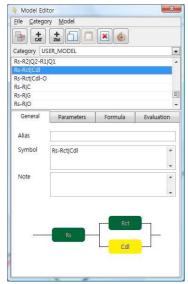


Figure 186. Rs-(Rct|Cdl)



Figure 187. (Rs-Rct)|Cdl

In ZMAN, the Parallel Operator has a higher priority than the Serial Operator similar to the  $\ast$  and + operators in normal Math calculations. It is quite natural that Parentheses operators are the highest among them. This means, if a circuit is expressed as "L-(R|C)", then "L-R|C" is equivalent in ZMAN.

# Example) Complicated model designing

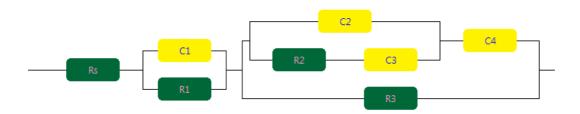


Figure 188. Sample Model

The above circuit can be grouped as the follows. Each group should be identified by Parenthesis.

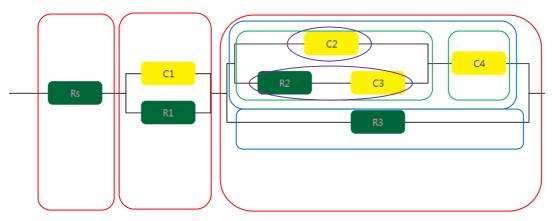


Figure 189. Sample model group analysis

1<sup>st</sup> step: Red group is; Rs-(C1|R1)-(blue group)

2<sup>nd</sup> step: Blue group is

Rs-(C1|R1)-((Green group)|R3)

3<sup>rd</sup> step: Green group is

Rs-(C1|R1)-(((violet group)-C4)|R3)

4th step: Violet group is

Rs-(C1|R1)-(((C2|(R2-C3))-C4)|R3)

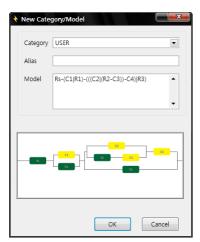


Figure 190. Check the symbol for sample model designing

#### E. Basic Elements

There are 12 basic elements in BASIC category which already defined in ZMAN software. These elements cannot be deleted nor modified in formula.

When you click right button of mouse at symbol area, pop up menu will appear as the follows.

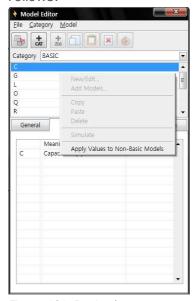


Figure 191. Basic element

You can change parameter default value and it can be applied to other category as their default value by selecting "Apply Values to Non-Basic Models"

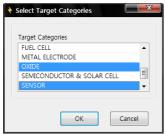


Figure 192. Default parameter value change in target category

## Each element in Basic category

Note: s represents jw, where j is imaginary unit,  $\sqrt{-1}$ , and w is angular frequency.

#### 1. Resistive Element

Symbol: R

Parameter(s): R

Formula:  $Z_R = R$ 

## 2. Capacitive Element

Symbol: C

Parameter(s): C

$$Z_C = \frac{1}{sC}$$

Formula:

#### 3. Inductive Element

Symbol: L

Parameter(s): L

Formula:  $Z_L = sL$ 

## 4. Constant Phase Element (CPE)

Symbol: Q

Parameter(s): Qy, Qa

$$Z_{Q} = \frac{1}{Q_{y} s^{Qa}}$$

Formula:

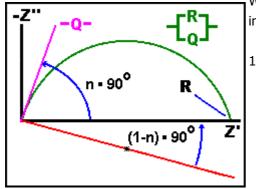
The Constant Phase Element (CPE) is a non-intuitive circuit element that was discovered (or invented) while looking at the response of real-world systems. In some systems the Nyquist plot (also called the Cole-Cole plot or Complex Impedance Plane plot) was expected to be a semicircle with the center on the x-axis. However, the observed plot was indeed the arc of a circle, but with the center some distance below the x-axis.

These depressed semicircles have been explained by a number of phenomena, depending on the nature of the system being investigated. However, the common thread among these explanations is that some property of the system is not homogeneous or that there is some distribution (dispersion) of the value of some physical property of the system.

Mathematically, a CPE's impedance is given by

$$1 / Z = Y = Q^{\circ} (j \bullet)^{n}$$

where Q° has the numerical value of the admittance (1/ |Z|) at m=1 rad/s. The units of Q° are S·s<sup>n</sup> .



When n=1, this is the same equation as that for the impedance of a capacitor, where  $Q^{\circ} = C$ .

$$1/Z = Y = j Q^{\circ} = j C$$

When n is close to 1.0, the CPE resembles a capacitor, but the phase angle is not  $90^{\circ}$ . It is constant and somewhat less than  $90^{\circ}$  at all frequencies. In some cases, the 'true' capacitance can be *calculated* from  $Q^{\circ}$  and n

The Nyquist (Complex Impedance Plane) Plot of a CPE is a simple one. For a solitary CPE (symbolized here by  $\mathbf{Q}$ ), it is just a straight line which makes an angle of (n\*90°) with the x-axis as shown in **pink** in the Figure. The plot for a resistor (symbolized by  $\mathbf{R}$ ) in parallel with a CPE is shown in **green**. In this case the center of the semicircle is depressed by an angle of (1-n)\*90°

http://www.consultrsr.com/resources/eis/cpe1.htm

#### **5. Warburg Diffusion**

Symbol: W

Parameter(s): Wy

 $Z_W = \frac{1}{W_v \sqrt{s}}$ 

Formula:

The most common diffusion circuit is the so-called "Warburg" diffusion element, but it is not the only one! A Warburg impedance element can be used to model semi-infinite linear diffusion, that is, unrestricted diffusion to a large planar electrode. This is the simplest diffusion situation because it is only the linear distance from the electrode that matters.

The Warburg impedance is an example of a constant phase element for which the phase angle is a constant 45° and independent of frequency. The magnitude of the Warburg impedance is inversely proportional to the square root of the frequency (  $1/\omega^{1/2}$  ) as you would expect for a CPE with an **n**-value of 0.5. The Warburg is unique among CPE's because the real and imaginary components are equal at all frequencies and both depend upon  $1/\omega^{1/2}$ 

http://www.consultrsr.com/resources/eis/diffusion.htm

#### **6. Diffusion Circuit Element**

Symbol: 0

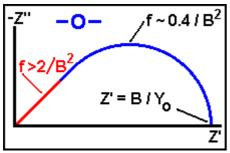
Parameter(s): Oy, Ob

 $Z_O = \frac{1}{O_v \sqrt{s}} \tanh[O_b \sqrt{s}]$ 

Formula:

The most commonly used diffusion circuit element is the Warburg, but it is not always the most appropriate one! It is often wise (and fairly common) to use a **rotating disk electrode** (RDE) in impedance studies. It is particularly wise when studying reactions involving diffusing species when the "DC" current is different than zero -- studies at potentials away from the open circuit or equilibrium potential ( away from the rest

potential or the corrosion potential: ). If a stationery electrode and unstirred solution were used instead, the current would slowly decay. The changing and non-steady state "DC" current would corrupt the interpretation of the lower frequency measurements. In systems such as the RDE, there is a region close to the electrode in which mass transport happens only by diffusion. Outside of this "Nernst Diffusion Layer" the solution is homogeneous due to the stirring produced by the rotating electrode assembly. The concentration of the diffusing species in the bulk solution remains unchanged by the experiment (i.e., the reaction vessel is big!) The material simply diffuses through the Nernst Diffusion Layer (NDL) to reach the electrode. The impedance in this case is described by the so-called **O** circuit element. The RDE is not the only case where the **O** element might be seen. Often the rate of corrosion is limited by the slow diffusion of oxygen through a coating or a passive film. This situation is quite similar to the RDE example, above. The oxygen concentration is homogeneous in the solution phase due to mixing and the concentration just outside the coating or film is fixed and constant. The impedance in this example also fits the **O** element model



The figure to the left shows the Nyquist plot for the  $\mathbf{O}$  diffusion element. The  $\mathbf{O}$  element is characterized by two parameters, an "admittance" parameter,  $\mathbf{Y_0}$ , and a "time constant" parameter,  $\mathbf{B}$  (units:  $\sec^{1/2}$ ). At high frequency ( f > 2 /  $B^2$ ) the  $\mathbf{O}$  circuit element is indistinguishable from a Warburg impedance! This frequency range is shown in  $\mathbf{red}$  in the figure. Since the time for a molecule to diffuse across the thin layer is much longer than the period of the AC stimulus applied, the electrode does not 'see' that the film or coating is of finite thickness.

Equations for the O element.

The equations for the complex admittance ( $Y(\mathbf{m})$ ) and complex impedance ( $Z(\mathbf{m})$ ) are given by the equations below. The O circuit element gets its name from the hyperbolic cotangent (coth[]) admittance response.

$$\vec{\mathbf{Z}}(\omega) \!=\! \left\{ \! \frac{1}{\mathbf{Y}_0 \sqrt{j\omega}} \right\} \! \tanh\! \left[ \mathbf{B} \sqrt{j\omega} \right] \qquad \vec{\mathbf{Y}}(\omega) \!=\! \left\{ \mathbf{Y}_0 \sqrt{j\omega} \right\} \! \coth\! \left[ \mathbf{B} \sqrt{j\omega} \right]$$

**Yo** has the same <u>definition</u> as for the Warburg impedance. **Yo** can be used to calculate a diffusion coefficient for the mobile species **within** the film, coating, or in the NDL using the same <u>equations</u>. For large values of the argument (the **red** region of the Nyquist plot, above), the tanh and coth functions both approach unity and the impedance has the same **w**dependence as the Warburg. This region can be used to estimate **Yo**.

If the thickness of the NDL (for RDE) or the thickness of the film is  $\delta$ , then the constant **B** is related to that thickness and the diffusion coefficient, D. **B** characterizes the time it takes for a reactant to diffuse through the NDL or thin film.

$$B = \delta/\sqrt{D}$$

(http://www.consultrsr.com/resources/eis/diff-o.htm)

#### 7. Finite Diffusion

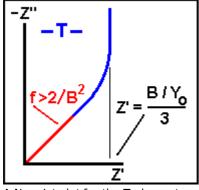
Symbol: T

Parameter(s): Ty, Tb

$$Z_T = \frac{1}{T_v \sqrt{s}} \coth[T_b \sqrt{s}]$$

Formula:

The **T** circuit element is characteristic of another type of film -- a film which contains a fixed amount of electroactive substance. The classical "thin layer electrochemistry" cell is an example of such a system. Batteries or supercapacitors also may share this behavior. The common feature is the fixed amount of electroactive material present. Once it has been consumed, it can not be replenished.



A Nyquist plot for the  $\boldsymbol{T}$  element

The figure to the left shows the Nyquist plot for the  $\mathbf{T}$  diffusion element. Like the  $\underline{o}$  element, the  $\mathbf{T}$  element is characterized by two parameters, an "admittance" parameter,  $\mathbf{Y_o}$ , and a "time constant" parameter,  $\mathbf{B}$  (units:  $\sec^{1/2}$ ). At high frequency ( $f > 2 / \mathbf{B}^2$ ) the  $\mathbf{T}$  circuit element is indistinguishable from a Warburg impedance! This frequency range is shown in redi in the figure. Since the time for a molecule to diffuse across the thin layer is much longer than the period of the AC stimulus applied the electrode does not 'see' that the film or coating is of finite thickness.

At low frequency, the **T** element looks like an R and a C in series, with  $R=(\mathbf{B} / \mathbf{Yo}) / 3$ 

The equations for the complex admittance ( $Y(\mathbf{m})$ ) and complex impedance ( $Z(\mathbf{m})$ ) are given by the equations below. The T circuit element gets its name from the hyperbolic tangent (tanh[]) admittance response.

$$\vec{z}(\omega) = \left\{ \frac{1}{Y_0 \sqrt{j\omega}} \right\} coth \left[ B \sqrt{j\omega} \right] \qquad \vec{y}(\omega) = \left\{ Y_0 \sqrt{j\omega} \right\} tanh \left[ B \sqrt{j\omega} \right]$$

**Yo** has the same <u>definition</u> as for the Warburg impedance. **Yo** can be used to calculate a diffusion coefficient for the mobile species **within** the film, coating, or thin layer cell using the same <u>equations</u>. For large values of the argument (the red region of the Nyquist plot, above), the tanh and coth functions both approach unity and the impedance has the same **u**dependence as the Warburg. This region can be used to estimate **Yo**.

If the thickness of the thin layer is  $\delta$ , then the constant B is related to this thickness and the diffusion coefficient, D. The parameter B characterizes the time it take for a reactant to diffuse from one side of the layer to the other.

$$B = \delta/\sqrt{D}$$

http://www.consultrsr.com/resources/eis/diff-t.htm

## 8. Homogeneous Reaction(Gerischer)

Symbol: G

Parameter(s): Gy, Gk

$$Z_G = \frac{1}{G_v \sqrt{G_k + s}}$$

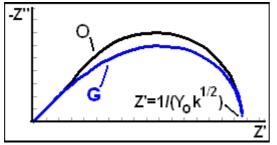
Formula:

The Gerischer (  ${\bf G}$  ) circuit element was first derived for a preceding chemical reaction happening in the bulk solution. This is the so called  ${\bf CE}$  mechanism.

$$A \xrightarrow{k} Ox \xrightarrow{ne} Red$$

A Gerischer has also been used to model a porous electrode ( $\underline{ref 2}$ ).

On a Nyquist plot, it looks quite a lot like the <u>O diffusion element</u> (diffusion through a thin layer).



A Nyquist plot for the **G** element. It is not as high as an **O** element with the same intercept. The value of

The figure to the left shows the Nyquist plot for the  ${\bf G}$  diffusion element. The  ${\bf G}$  element is characterized by two parameters. an "admittance" parameter,  ${\bf Y_0}$  (units S-s<sup>1/2</sup>), and a "rate constant" parameter,  ${\bf k}$  (units: s<sup>-1</sup>). At high frequency the  ${\bf G}$  circuit element is indistinguishable from a <u>Warburq</u> impedance! At high frequency, it presents

the low frequency intercept for the Gerischer is shown.

a 45° line on the Nyquist plot and a straight line with slope of -1/2 on the Bode magnitude plot

The equations for the complex impedance ( $Z(\mathbf{m})$ ) and complex admittance ( $Y(\mathbf{m})$ ) are given by the equations below. (Ref 1)

$$\vec{\mathbf{Z}}(\boldsymbol{\omega}) = 1/\{Y_0\sqrt{k+j\boldsymbol{\omega}}\}$$
  $\vec{\mathbf{Y}}(\boldsymbol{\omega}) = Y_0\sqrt{k+j\boldsymbol{\omega}}$ 

Yo has the same definition as for the Warburg impedance. Yo can be used to calculate the diffusion coefficient for the mobile species using the same *equations* as for the Warburg. The high frequency region can be used to estimate Yo

http://www.consultrsr.com/resources/eis/gerischer.htm

#### 9. Spherical Diffusion

Symbol: S

Parameter(s): Sy, Sk

 $Z_S = \frac{1}{S_v} \frac{1}{\sqrt{S_k} + \sqrt{S}}$ 

#### 10. Finite-Length diffusion at planar particles

Symbol: X

Parameter(s): Xr, Xc

Formula: Zx=sqrt(3\*Xr/Xc/s)\*CotH(sqrt(3\*Xr\*Xc\*s))

#### 11. Finite-Length diffusion at spherical particles

Symbol: Y

Parameter(s): Yr, Yc

Formular:Zy=Tanh(sqrt(3\*Yr\*Yc\*s))/(sqrt(3\*Yc\*s/Yr)-Tanh(sqrt(3\*Yr\*Yc\*s))/Yr)

#### 12. Finite-Length diffusion at cylindrical particles

Symbol: Z

Parameter(s): Zr, Zc

Formula: Zz=Zr\*BesselI(0,sqrt(2\*Zr\*Zc\*s))/sqrt(2\*Zr\*Zc\*s)/BesselI(1,sqrt(2\*Zr\*Zc\*s))

## F. Simple elements (User defined elements)

Simple element is User defined element. User can define specific symbol as functional element in SIMPLE category.

Note: It is for only advanced users. If you want to use this function of ZMAN, please make contact with us.



Figure 193. Simple category editing.

#### 1. New/Edit element

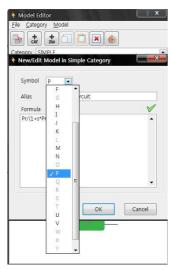


Figure 194. New/Edit Model in simple category

Select one Symbol. Available Symbols are one among A, B, D, E, F, H, I, J, K, M, N, P, U and V. Valid symbol is dark and used symbol is grey

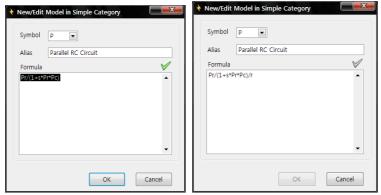


Figure 195. Formula input for user defined model.(Left: formula correct)

Type "Pr/(1+s\*Pr\*Pc)" in the Formula tab. If the formula is correct, then green check mark will appear but if it is incorrect then check mark's color will be changed to grey. and click OK button

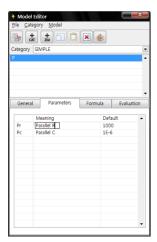


Figure 196. Default parameter input

Input each default value in the table of Parameter tab and type each parameter's meaning.

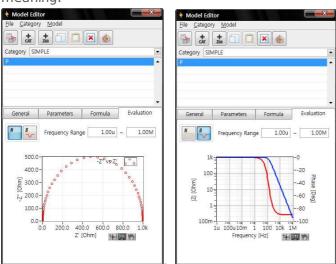


Figure 197. Evaluation tab

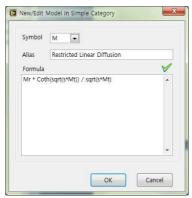
Click Save to save it.

#### Example: How to Add M Symbol

1. Open Model Editor



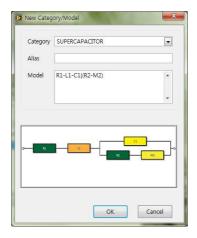
- 2. Select **SIMPLE** in **Category** List box
- 3. Select Model >> New/Edit...
- Select "M" in **Symbol** List box
   Type "Restricted Linear Diffusion" in **Alias** blank
- 6. Type "Mr \* Coth(sqrt(s\*Mt)) / sqrt(s\*Mt)" in **Formula** blank



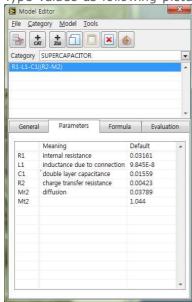
7. Click **OK** button

#### **Add Category**

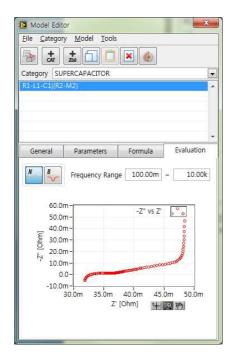
- 1. In Model Editor, select **Category >> New...** in menu bar
- 2. Type "Supercapacitor" in **Category** combo box
- 3. Type "R1-L1-C1|(R2-M2)" in **Model** blank



- 4. Click **OK** button
- 5. Click **Parameters** tab in lower tab control
- 6. Type values as following picture



7. See whether the model is properly created.



#### 2. Delete element

Click Delete to erase element in Simple category

#### 3. Apply values to Non-Basic Models

You can change parameter default value and it can be applied to other category as their default value by selecting "Apply Values to Non-Basic Models"

## 4. Set color codes

You can set color for each element for modeling. You can select " set color codes" on tools menu.

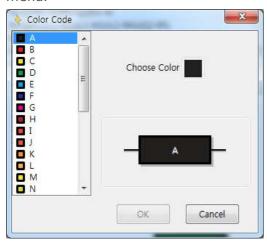


Figure 198. Color code setting

#### **G.** Parameter Simulation

ZMAN provides unique simulation function. This function can display multiple impedance spectra following parameter value change as matrix.

There are two way to simulate.

#### 1. From Model editor

This function can be used for default parameter change for the selected model or for study the impedance spectra for the selected mode.

You can select model in model editor for simulation.

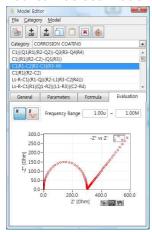


Figure 199. Model selection for simulate

Click simulation button the simulation window will appear.

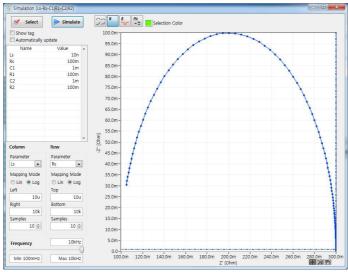


Figure 200. Parameter simulation window

#### a) Select parameter

You can select two parameters to view simulation result following these two parameter value changes.

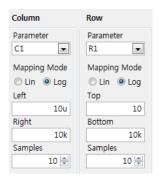


Figure 201. Parameter selection

- 1) You can select log scale or linear scale for matrix.
- 2) Parameter value range setting: Max. Min value for simulation
- 3) You can change matrix value for X, Y samples (default value is each 10).

#### b) Simulation

- Show tag
  Automatically update
- 1) Show tag: If you checked on show tag, matrix simulation spectra will be displayed with X,Y value.
- 2) If you check on Automatic update, then simulation will be done automatically whenever you change the parameter.

If you did not check on above two check box then when you click button you can see simulated matrix view.

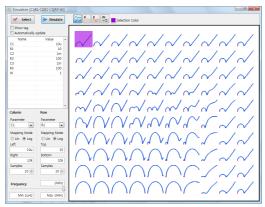


Figure 202. Parameter matrix display

#### c) Frequency range for simulation

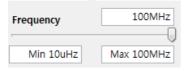


Figure 3. Frequency range

You can extend frequency range by input minimum frequency and Maximum frequency at left bottom side.

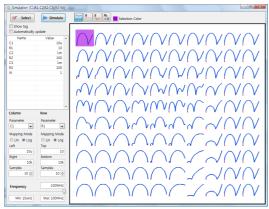


Figure 203. Change frequency range 10uHz to 100MHz for simulation

#### d) Selected Spectra

You can select one of simulated spectra by clicking on it. Selected color can be changed.

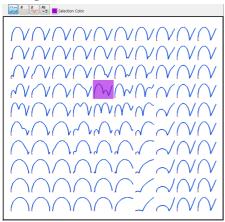
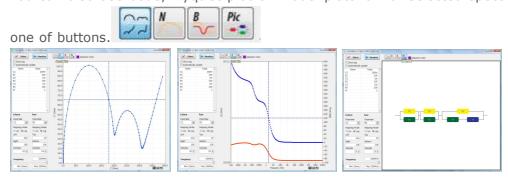


Figure 204. Simulated spectra selection

If one spectra was selected, those parameter value will be displayed at left side parameter information.

You can also see bode, Nyquist plot or model pictorial for selected spectra by clicking



## e) Model default parameter value

If you selected spectra on simulation and click button, then selected spectra's parameter value will be saved as the model's default value.

If you do not want to change model's parameter default value inside the category, do NOT click Select button

## 2. From data fitting

This function can be used for determining initial parameter value for further fitting or for study the impedance spectra for the selected mode.

You can enter simulation from fitting result

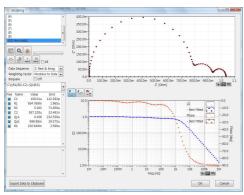
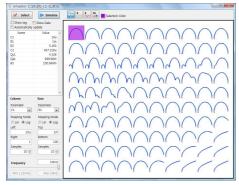


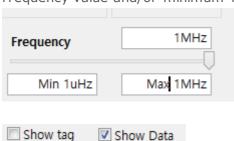
Figure 205. Fitting result

Click simulation button the simulation window will appear



If you check on show data, you can see simulated spectra(blue color) with raw data(grey color).

You can extend max frequency or min frequency for fitted result by inputting maximum frequency value and/or minimum frequency value.



Automatically update

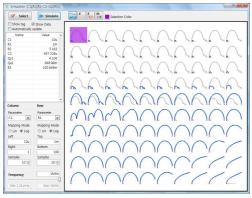


Figure 206. Matrix simulated spectra with raw data

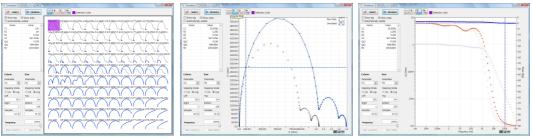


Figure 207. Simulated graphic display

Regarding to other function, refer to the above "1. From the model".

If you selected one of simulated spectra and click select button, the parameter will transfer to fitting menu. You can fit from these initial parameter values

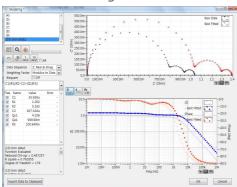


Figure 208. Fitting display

## Chapter 8 Automatic Model Search

ZMAN has unique function namely Automatic Model Search. User who is not familiar with EIS model, they can find suggested models which are better fitted with their data.

To do automatic model search, you need to upload your data to project side.

And select Analysis-Modeling in menu.

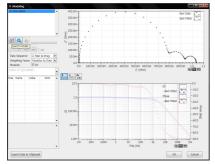


Figure 209. Automatic Model search selection

## A. Searching Parameter Setting

Click search model button then the following box will appear.



Figure 210. Automatic Searching Condition

## 1. Target Category selection

You can select single category or multiple categories which will be used for searching. Default selection is all categories selected. It will take longer time to search models than with selection of single category.

Option: Remove duplicates On/Off

If this option is ON, duplicated model in various categories will be skipped in searching.

If user make their own categories which contains proper models for their test, searching

time will do not take long time to get best result.

If you want to use multiple categories for searching, select categories by mouse click under pressing ctrl key

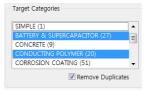


Figure 211. Multiple categories selection

#### 2. Parameter value range

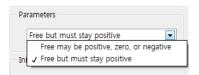


Figure 212. Parameter range selection

You can select searching condition in parameter value range.

If you select "Free may be positive, zero, or negative", Fitting parameter value can be under zero value (artificial value).

If you want positive value only for parameter value, you must select "Free but must stay positive"

## 3. Initial guessing method

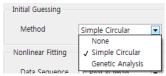


Figure 213. Initial guessing method selection

There are 3 methods.

- None: If you select None, Searching process will start from default parameter value in each model. If you have proper model library for your data, this is recommended for initial guessing.
- b) Default method is Simple circular method. This is assumed that Nyquist plot contains circular shape and finding initial value to start fitting.
- c) Genetic algorithm. This method put random value matrix as initial value and try to find proper initial value. It takes much longer time than simple circular method. If you fail to find proper model, you may use this method.

With Simple circular method or Genetic algorithm method, parameter default value in model will not be used.

#### 4. Nonlinear fitting



Figure 214. Nonlinear fitting

#### a) Data sequence

You can select data set which will be used for nonlinear fitting. Default data set is Zreal & Zimg.(Nyquist)
For some data, you can use Zmag & Zph (Bode)

#### b) Weighting factor

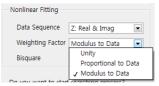


Figure 215. Weight factor selection

You can select weighting factor as unit, proportional to data or Modulus to data. Default setting is Modulus to data

#### c) Bisquare

Bisquare obtains the slope and intercept using an iterative process and calculates the residue using the same formula as in the Least Square method. This option takes longer time but more accurate.

Default setting is off.

When you select searching condition, click OK button then searching process will start.

## **B.** Model finding Criteria Setting

You can set model finding criteria for model searching by selecting options in Tools.

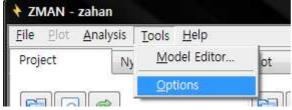


Figure 216. Option Menu

#### 1. For Simple circular initial guessing and no initial guessing

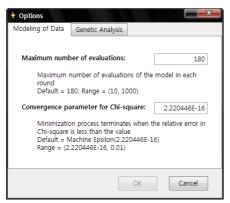


Figure 217. Modeling of Data for searching criteria

If you select no initial guessing or simple circular initial guessing for automatic model searching, you can set limit criteria for ZMAN to determine the model.

#### a) Maximum number of evaluations; Default value (180)

This setting value is maximum number of evaluations of the model initial guessing and fitting in each round.

Input number range: Minimum 10 to Maximum 1000

If you input larger number, the searching result is more accurate but it takes much longer time.

If the fitting result in Chi-square meet following "Convergence parameter for Chi-square" before setting "Maximum number of evaluations" number, Model searching to move to next model.

#### b) Convergence parameter for Chi-square; Default value (2.220446E-16)

Minimization process terminates when the relative error in Chi-square is less than the setting value

Input number range: Minimum 2.220446E-16 to Maximum 0.01

If you input small number, the searching result is more accurate but it takes longer time.

#### 2. For Genetic algorithm

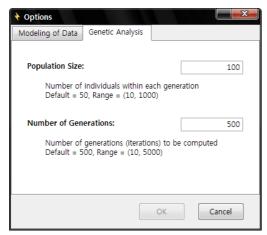


Figure 218. Genetic algorithm for searching criteria

If you select genetic algorithm initial guessing for automatic model searching, you can set limit criteria for ZMAN to determine the model.

#### a) Population size: Default (100)

Number of individuals within each generation Input number range: Minimum 10 to Maximum 1000

## b) Number of Generations: Default(500)

Number of generations(iterations) to be computed Input number range: Minimum 10 to Maximum 5000

#### C. Searching process

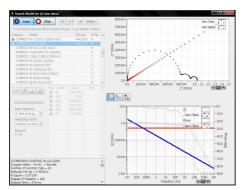


Figure 219. Searching process

#### 1. Start searching

During searching process, searching engine is trying to find proper model and displaying spectra matching process graphically in real time. You can see the tracing process in Nyquist plot, Bode plot and error diagram.



Figure 220. Process bar

If the process bar is working, The software is running (complicated model may take long time).

#### 2. Stop searching

If you need to stop during searching, click button.

If fitting process is complicated with multiple parameter model, it could not be stopped promptly. In this case stop button will be changed button. After calculation, searching process will be stopped.

#### 3. Change searching condition

If you stopped or finished searching process, you can change searching process by clicking button then searching condition menu will appear. You can restart searching with new condition.

## D. Searching Result

When searching process finished, you can see the model list on left upper side. List will be arranged by chi square value.

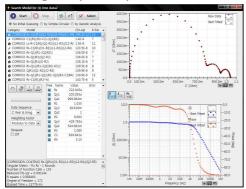


Figure 221. Searching result

#### 1. Extensive fitting

If you did not set Bi-square option when you search, you can use it at this moment to find best model.

To do this, check on Bi-square option and click "minimize 1 round" button.

If fitting process look to need further process by tracing trend, you can click "minimize 10 round" button. This button will do 10 times repetition of "Minimize 1 round".

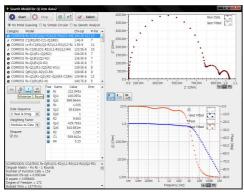


Figure 222. Bi-square fitting

If the result(chi-square value) order is different from previous, you can rearrange the order by clicking button.

#### 2. Fitting by parameter range

You can check the fitting result and if you want to change parameter range, you can change all parameter range by clicking right button of mouse at "Free" character's area then popup menu will appear.

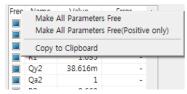


Figure 223. All parameter range selection

You can change parameter range by clicking parameter range marker. Parameter range setting markers are

: Fix

: Positive value only free

: Negative/Positive value free

## 3. Initial guessing/fitting

From the result, you can try to fitting for each model on result list. Generally do not use initial guessing on result.

: Simple circular method

: Genetic algorithm method

### 4. Re-searching model

Based on searching result, you can search the result model again in chi square order.

In this case, select "no initial guessing" and click start button

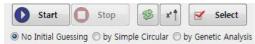


Figure 224. Re-searching model

#### 5. Singular matrix result

At category display region, If the result is singular matrix error, 2 tag will be displayed. If the result is successful, 4 tag will be displayed.

If the singular matrix happens, you can see the reason at left bottom side.



Figure 225. Fitting process report

As following to fitting process report, fix some parameter by clicking parameter range setting marker to status and try to fit again.

#### 6. Ending Search process

If you find proper model by automatic model searching function, you must click button.

# Chapter 9 Impedance Data Plot

## A. How to plot data in a graph.

#### 1. Select a data set

Select a data set from a data series or individual data files from Project (Section "C"). This will be shown in a graph.

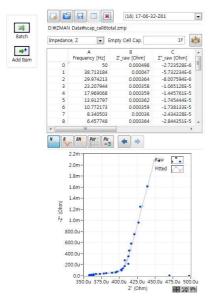


Figure 226. Project file data preview

#### 2. Select Plot Option

Select one among the following three options from Plot menu. If you want a parameter plot, skip this step.

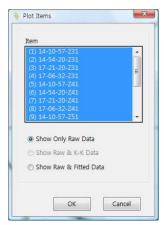


Figure 227. Plot display selection for 2D plots (except parameter plot)

- Show only Raw Data
- Show Raw and K-K
- Show Raw and Fitted-Data

#### 3. Plot formats

Available graph types are listed in the following table.

	Туре	х	У	z
2D	Nyquist	Real part(Z')	-Z"	
		Y'	Υ"	_
	Bode	f	y1 y2	
			$ Z $ $\Phi_Z$	_
			$Z'$ , $-Z''$ , $ Z $ , $\Phi_Z$	_
			$Y'$ , $Y''$ , $ Y $ , $\Phi_Y$	
	Parameter	CtrlVar13	P <sub>1</sub> P <sub>n</sub>	
3D	Nyquist	Z'	No, f,	-Z"
		Y'	CtrlVar13	Υ"
	Bode	f	#, CtrlVar13	Z', -Z",
				$ Z ,\Phi_Z$
				Y', Y",  Y ,
				Фү
	Parameters	Not available		

Where f is frequency,  $Z=Z'+jZ''=\mid Z\mid e^{j\Phi_Z}$  , and  $Y=\frac{1}{Z}=Y'+jY''=\mid Y\mid e^{j\Phi_Y}$  .

## a) 2D Nyquist Plot

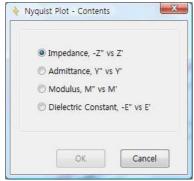
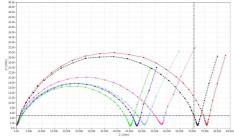
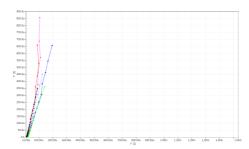


Figure 228. 2D Nyquist plot's display selection







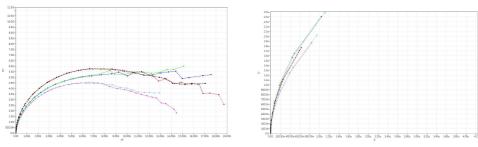


Figure 230. Modulus & Dielectric constant plots

## b) 2D Bode Plot



Figure 231. 2D Bode plot's display selection

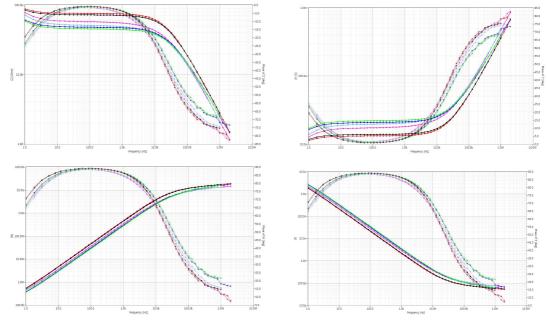
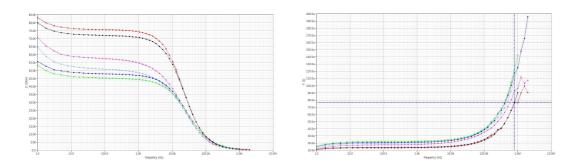
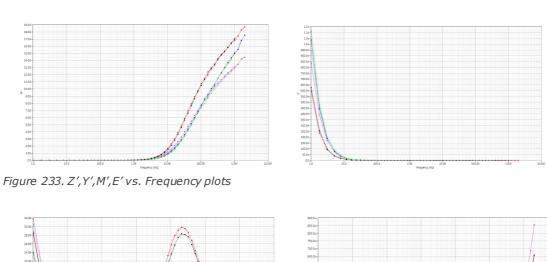


Figure 232. |Z| & phase, |Y| & phase, |M| & phase, |E| & phase plots





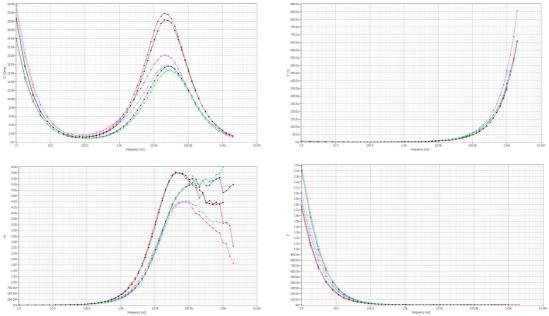


Figure 234. Z", Y", M", E" vs. Frequency plots

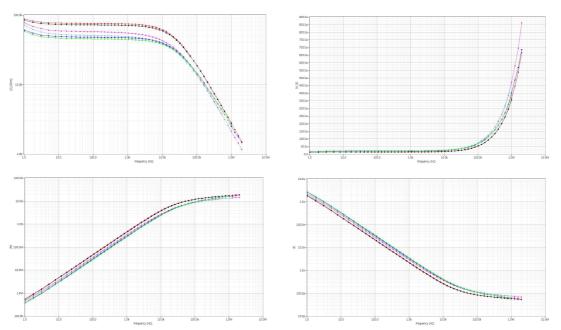


Figure 235. |Z|, |Y|, |M|, |E| vs. Frequency plots

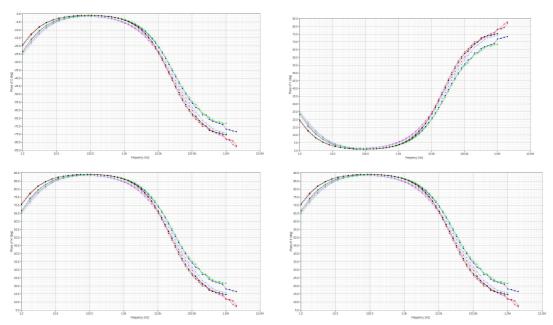


Figure 236. Phase of Z',Y',M',E' vs. Frequency plots

## c) Black Nichols Plot



Figure 237. Black Nichols Plot's display selection

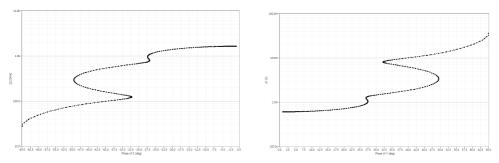


Figure 238. Impedance & Admittance plot

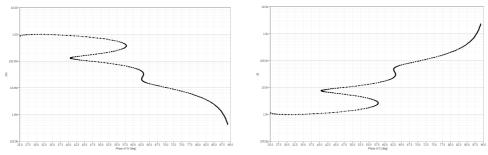


Figure 239. Modulus & Dielectric constant plot

#### d) Parameter Plot

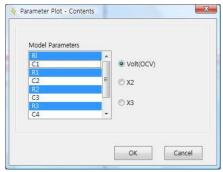


Figure 240. 2D Parameter plot's parameter selection

#### e) 3D Nyquist plot

For more details regarding to 3D plot, refer to chapter 10. Graph

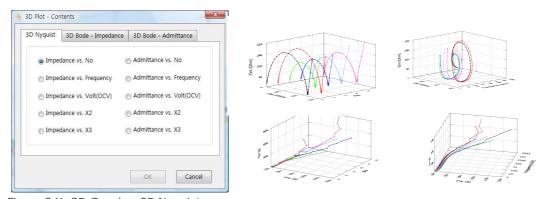


Figure 241. 3D Graph > 3D Nyquist

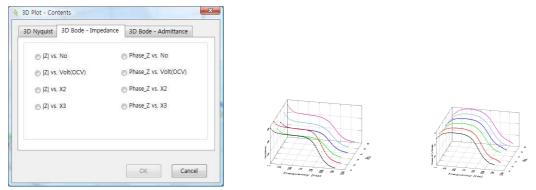


Figure 242. 3D Graph > 3D Bode -Impedance

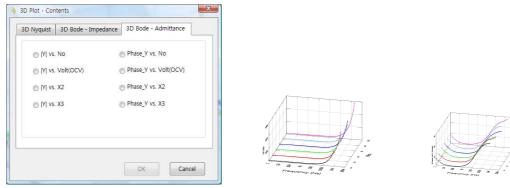


Figure 243. 3D Bode-Admittance

#### **B.** How to Format Axis Scales

#### 1. Select 2D or 3D Plot settings

Select **2D Plot Settings** or **3D Plot Settings** from the Plot menu. **Y2 axis** is available only in 2D-Bode Plot.

## 2. Configure Axis/Scale properties

Configure the axis scale properties. Modifications are immediately reflected in the graph.

- Use the **Format** and **Precision** to format Tick Label on an axis.
- Click **Major Grid** and **Minor Grid** Box to change color of major and minor grid color, respectively. "T" means transparency.
- Make Auto scale ON to automatically adjust the scale.
- Make Loose Fit ON to round the end markers to a multiple of the increment used for the scale.
- Make Flip Axis ON to reverse min and max positions on the scale.
- Change **Logarithmic** ON/OFF for logarithmic/Linear scale mapping mode.
- Make **Show Cursor** ON/OFF to show/hide cursor on the graph.
- Make **Show Graph Palette** ON/OFF to show/hide graph palette on the graph.

Click **Apply** to apply the modification to the graph.

## 3. Setting

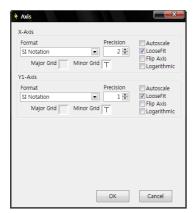


Figure 244. 2D Setting



Figure 245. 3D Setting

# Chapter 10 Graph

## A. 2D Graph common functions



#### 1. Legend

You can display Legend on graphic region by clicking



### File name change on graph(Just displaying)

If you click Legend button you can see legend right upper side and you can change the name by clicking on the name.

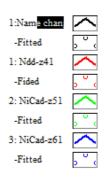


Figure 246. Legend

Click on file name and change it.

#### 2. Side function of Graph

You can use this function only when Legend is ON.

Move the cursor to Legend and click on box right side of file name then pop up menu will appear.

## a) Common plot

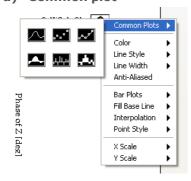


Figure 247. Legend menu

#### b) Line color

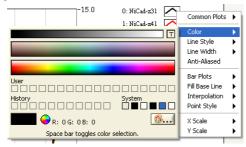


Figure 248. Line color setting

#### c) Line style

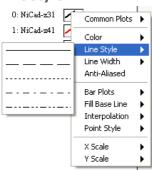


Figure 249. Line style setting

#### d) Line width

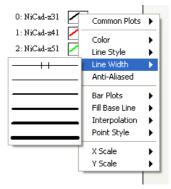


Figure 250. Line width setting

## e) Bar plot

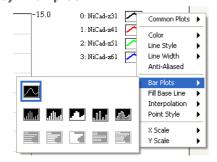


Figure 251. Bar plot setting

#### f) Interpolation

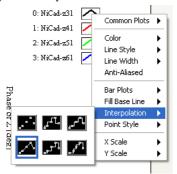


Figure 252. Interpolation setting

#### g) Point Style

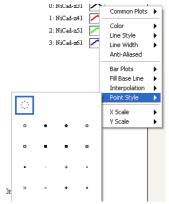


Figure 253. Point style selection

#### 3. Rescale to show all

This function will redraw the graph to initial scale by clicking button on graphic tool bar.

#### 4. Cursor Mode

Cursor On/Off: You can make cursor mode on by clicking button on graphic tool bar. If it is enable, you can see cross hair type cursor.

If you click on cross hair cursor location, you can see the cursor value display at nearby cursor point.

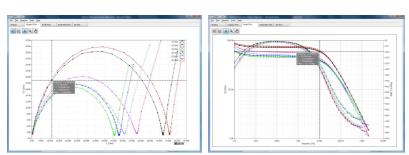


Figure 254. Cursor data display

Cursor will be displayed as cross hair. You can move the cursor position with your mouse or keyboard left/right direction key. Cross hair cursor's color will be changed by file's color. By keyboard up/down direction key, you can select data file which were overlaid.

When cursor mode is activated (on), 3 menus will be activated.

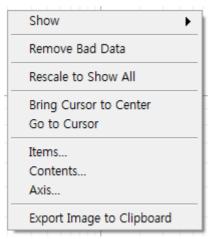


Figure 255. Pop up menu on 2D graph

# a) Remove Bad data; You can delete bad data on cursor located.

You must check on cursor for this function. Select bad data using cursor function and click "Remove bad data"

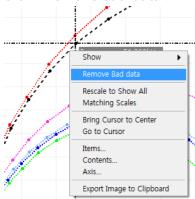


Figure 256. Remove bad data

#### b) Bring Cursor to Center:

If you check on this function, cursor will be located on center point of zoomed area.

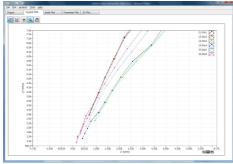


Figure 257. Zoom up display

If you click cursor button but cursor was not displayed on the screen then select "Bring cursor to center".

The cursor will be located nearby center position.

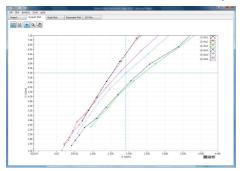


Figure 258. "Bring cursor to center" function

Please note that the data should be located in center position. You can use move

button to move the display position.

#### 5. Zoom

For zooming Click button and drag the area

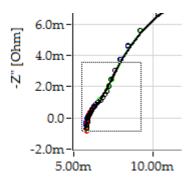
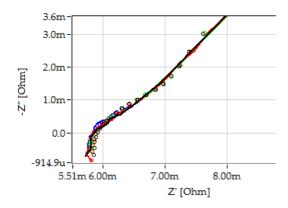


Figure 259. Before Zoom up

Mouse selecting an area to zoom up



#### 6. Axis scale

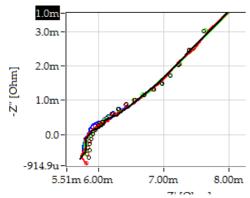


Figure 261. Before Max value change

Change maximum axis value by clicking on a value

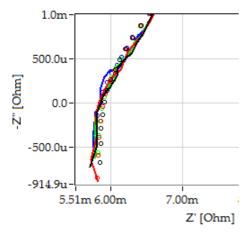


Figure 262. After max value change

# B. Graph internal function for Bode, Nyquist & Black Nichols plot

Move the cursor inside the graph and click right button, the following sub menu will then appear.

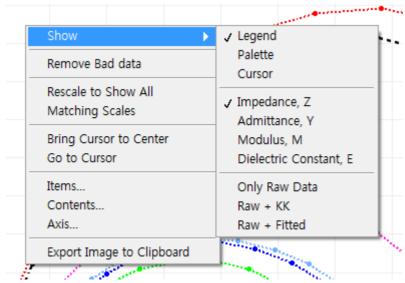
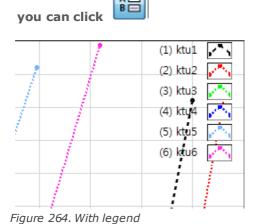


Figure 263. Graph function menu

#### 1. Show

# a) Legend On/Off: If you check on Legend you can see Legend on the graph



b) Palette on/off

You can enable/disable the palette function. Graph Pallet



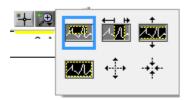


Figure 265. Graph pallet

#### c) Cursor On/Off

Refer to the above Cursor mode

If You can select Impedance, Admittance, Modulus or Dielectric constant

# d) Impedance

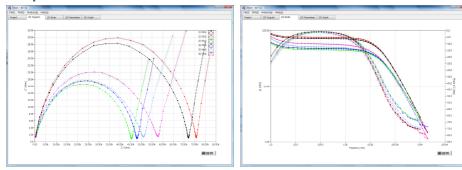


Figure 266. Impedance

# e) Admittance

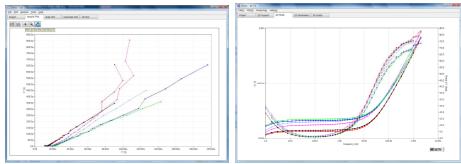


Figure 267. Admittance

# f) Modulus

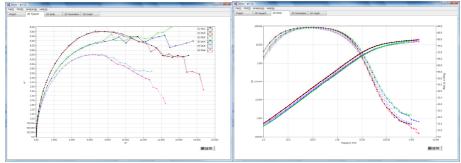


Figure 268. Modulus

# g) Dielectric Constant

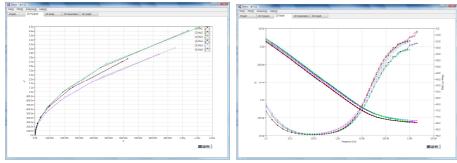


Figure 269. Dielectric Constant

# h) Only Raw data

Plot with raw data only

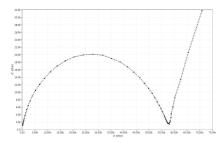
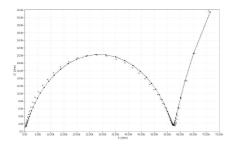


Figure 270. Raw data only

#### i) Raw+Fitted

Plot with raw data and fitted data together.



#### 2. Remove Bad data: You can delete bad data.

Refer to the above cursor mode

# 3. Rescale to show all

Initiate graph scale.

# 4. Matching Scale (Only for Nyquist Plot)

The Nyquist plot will be displayed with the same scale for X axis and Y axis.

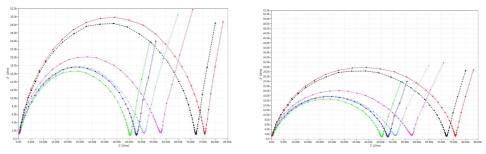


Figure 271. Show all scale(Left) & Matching scale(Right)

# 5. Bring cursor to center

Move cursor location to center of graph at Y axis value

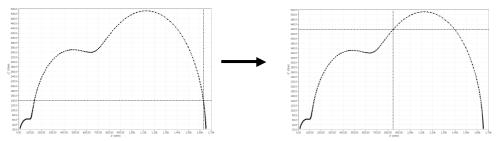


Figure 272. Bring cursor to center

#### 6. Go to center

Move graph location to current cursor location as center.

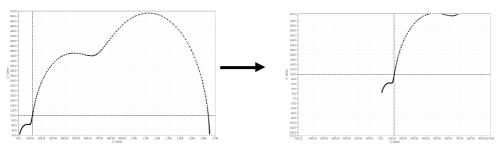


Figure 273. Go to cursor

#### 7. Item

You can select file to plot and select raw data or raw + fitted data or Raw+K-K Data.

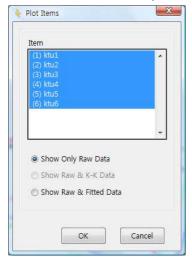


Figure 274. Plot item selection

# 8. Contents

You can select plot type

#### a) Nyquist plot

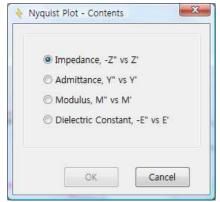


Figure 275. Nyquist plot contents

#### b) Bode Plot

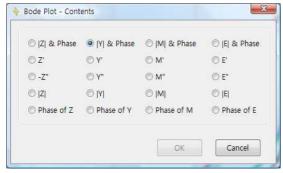


Figure 276. Bode plot contents

# c) Black Nichols plot



Figure 277. Black Nichols plot contents

# 9. Axis

You can set graph properties.



Figure 278. 2D graph setting

# 10. Export Image to Clipboard

You can use image in other program Using Windows Paste(Ctrl+V) function

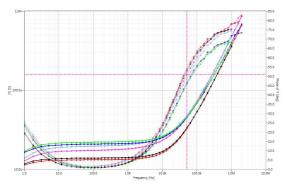


Figure 279. Paste result

# C. Graph internal function for Parameter plot

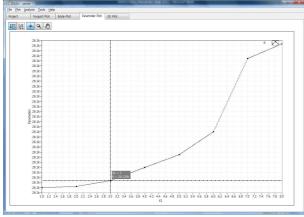


Figure 280. Parameter plot

Move the cursor to inside the graph and click right button, the following sub menu will appear.

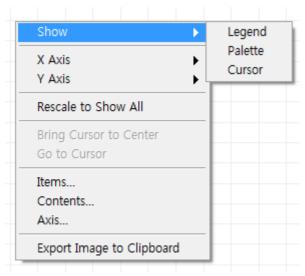


Figure 281. Parameter plot menu

#### 1. Show

#### a) Legend On/Off:

If you check on Legend you can see Legend on the graph

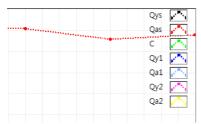


Figure 282. With legend

- b) Palette On/Off
- c) Cursor On/Off

#### 2. X axis setting

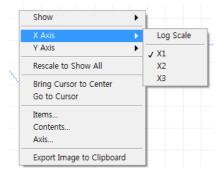


Figure 283. X axis setting

X1, X2, X3 will be replaced if you input name for these parameters.

# 3. Y axis setting

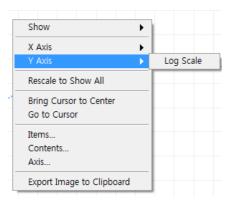


Figure 284. Y axis setting

# 4. Contents

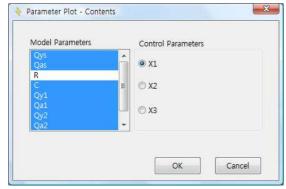


Figure 285. Parameter plot contents

• Other functions are referred to above 2D plot

## D. 3D Plot

3D plot can be used for multiple EIS data display or Multiple axis plots.

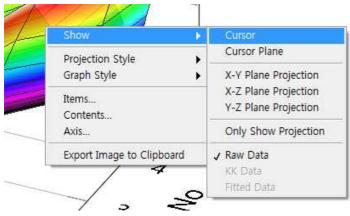


Figure 286. 3D graph Internal function

#### 1. Cursor

#### a) Cursor On/Off

You can select Cursor On/Off on Show option or click button at left upper side.

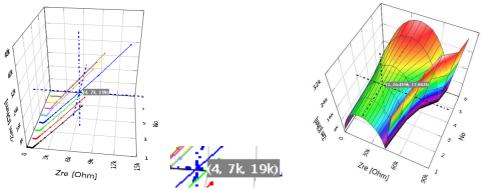


Figure 287. Cursor On at 3D graph Nyquist plot per parameter

With Cursor On, there is X, Y, Z coordinate value with data color. Cross hair cursor can be moved to other point or other data file by mouse dragging. Up and downward key on keyboard can be used for moving data on same data file.

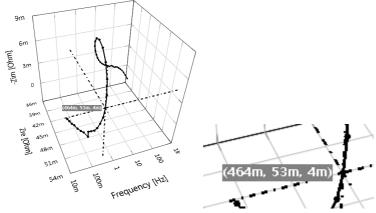


Figure 288. Cursor on at 3D graph Nyquist plot per frequency

#### b) Cursor plane

Cursor plane can be visible by selecting cursor plane on Show option.

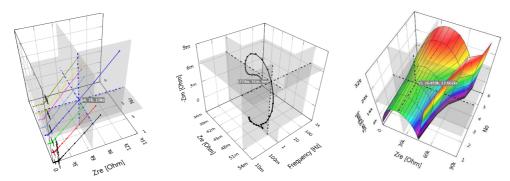


Figure 289. 3D plot with cursor plane

# 2. Plane Projection

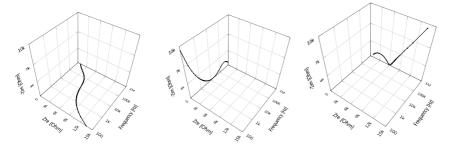


Figure 290. XY, XZ, YZ plane projection

You can select plane projection in Show option.

#### 3. Projection Style

There is two type depending on projection style (orthographic or perspective)

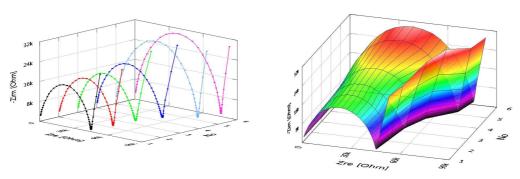


Figure 291. 3D Nyquist plot (orthographic style)

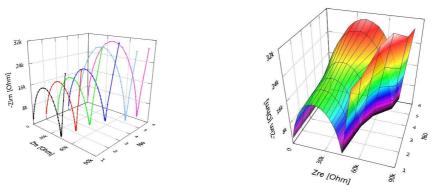


Figure 292. 3D Nyquist plot(perspective style)

Version 2.2 does not provide surface plot which have provided in previous versions.

You can change the view angle by dragging on the graph

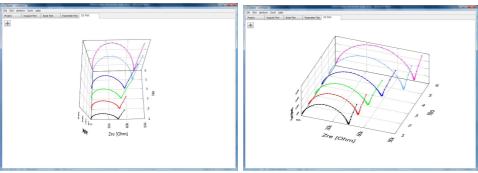


Figure 293. View angle change(Left: orthographic, Right perspective)

# 4. Graph Style

#### a) Curve plot

This graph style displays plot as individual plot. Line and dot for each data set is available. You can show raw data with simulated data or KK plot only in this style.

#### b) Surface plot

You can show 3D plot with surface.

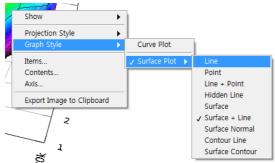


Figure 294. Surface plot option

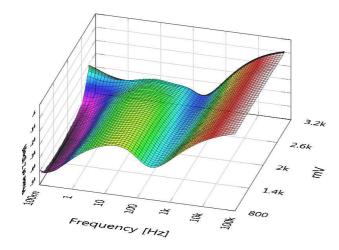


Figure 295. Surface plot with "surface+line"

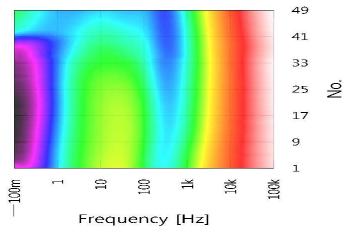


Figure 296. Surface plot for phase data with "surface"

#### 5. Plot Item

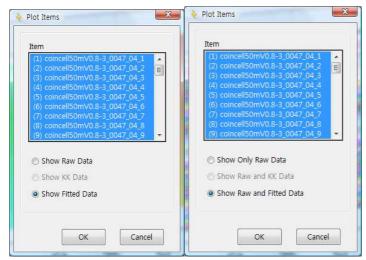


Figure 297. 3D graph plot item (left for surface plot, Right for curve plot)

#### a) For curve plot

- You can select file(s) to plot and select "Show Only Raw Data" or Show Raw & K-K Data" or "Show Raw & Fitted Data"
- K-K data and Fitted Data selection is only enable status after analysis of fitting or K-K
- If you select "Show Only Raw Data", then Raw data will be plot as solid line with dot.
   But if you select "Show Raw & Fitted Data", then Fitted data is solid line and raw data is dot

#### b) For surface plot

- You can select file(s) to plot and select "Show Raw Data" or Show K-K Data" or "Show Fitted Data"
- K-K data and Fitted Data selection is only enable status after analysis of fitting or K-K

#### 6. Contents

You can select one of 3D plot in followings.

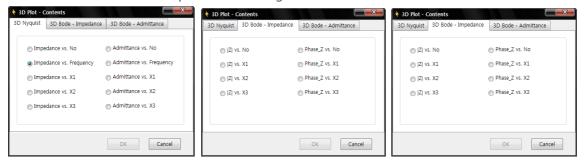


Figure 298. 3D Plot contents

#### **E.** Parameter Plot

After fitting result, you can get parameter plot with fitting result

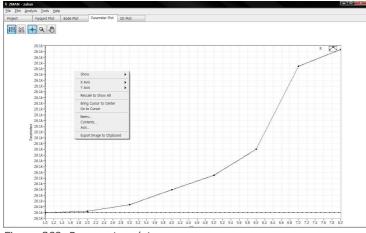


Figure 299. Parameter plot

#### 1. Parameter to display

You can select parameter(s) to display on plot by selecting contents in the pop up menu.

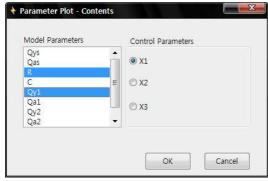


Figure 300. Parameter to display

Multiple parameters can be selected by clicking ctrl+click or shift+click

#### 2. File select

You can select file(s) to display parameter(s) by selecting items in the pop up menu.

#### 3. Axis

Parameter plot can select X1, X2, X3 control value as X axis. X & Y axis can be displayed as linear scale or log scale.

# F. Print

You can print each graph format using File menu- Print

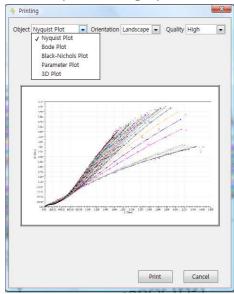


Figure 301. Print Menu

#### 1. Graph object

You can select Nyquist, Bode, Black Nichols, Parameter, 3D plot.

#### 2. Orientation

You can select Landscape or Portrait

#### 3. Quality

You can select High, Middle, Low

# Appendix 1. User defined Element Guide1

#### How to add a new user-defined element?

Introduced by ZMAN 2.3, the "SIMPLE" category provides you with a functionality to easily make and edit your own circuit elements.

"BASIC" and "SIMPLE" categories are the sets of circuit elements. Each element is written in a form of analytical formula. Table 1 shows the elements of BASIC category. Its formula cannot be edited by a user. On the other hand, you can add and edit your own circuit elements under the category of SIMPLE. The other categories are for equivalent circuit models.

In this note, you can learn how to add a new user-defined element in SIMPLE category.

#### **Preparations**

Let's think about the following model:

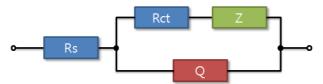


Figure 1. The model to be considered in this note is as shown here.

In the model shown in Figure 1, diffusion impedance element Z is defined as the following equation:

$$Z = \frac{R_W \coth [(T_W j\omega)^{Wp}]}{(T_W j\omega)^{Wp}}$$
(1)

Whilst you will easily find Rs, Rct, and Q(Constant Phase Element) in the BASIC category, there is no such element describing the analytical function Z. Therefore, you need to make a new circuit element of your own as realizing eq. (1).

First, you may symbolize Z as an arbitrary but unused symbol; i.e. V.

Second, you must substitute suitable parameters for Rw, Tw, and Wp elements from eq (1):

Vr = Rw

Vt = Tw

Vp = Wp

It is due to the specific rule of naming parameters which is as the following in the box:

#### **Parameters for circuit Element**

ZMAN accepts only the following parameters:

```
A, AA, AB, AC, ..., Aa, Ab, Ac, ...
B, BA, BB, BC, ..., Ba, Bb, Bc, ...
...
Z, ZA, ZB, ZC, ..., Za, Zb, Zc, ...
```

- A parameter must consist of symbol and (or) an alphabetical character.
- A parameter name is case sensitive; i.e. AA and Aa are considered to be distinct parameters.

Then, the next step is to rephrase eq (1) into a formula acceptable in ZMAN, i.e. V equals to:

```
Vr * Coth(pow(Vt*s, Vp)) / pow(Vt*s, Vp)
```

where s is  $\underline{i}\omega$ , Coth(x) is the hyperbolic cotangent of x, and pow(x, y) is the x raised to the power of y. Table 2 shows the list of functions you can use in formula.

Now, the model depicted in the Figure 1 can be described as the following expression.

The rule for naming elements is as the following in the box.

#### **Elements in Model**

Variables are distinguished by names. There are the following rules of naming variables:

The first character should be a Symbol character(A to Z) and followed by alphabe tical characters (capital and small letters), decimal digits, and underscore ( \_ ) A name is case sensitive; i.e. lowercase and uppercase letters are considered to b

e distinct characters

There is no limit of name length; herewith all characters are significant

Now, let's start to register V element to Model Editor.

#### Make a new element in SIMPLE category

Complete the following steps to register a user-defined element in the model editor.

- 1. Launch ZMAN.
- 2. In the 'Getting Started' window, click the 'Model Editor'.

**Note** Use one of the following methods to access the Model Editor dialog box:

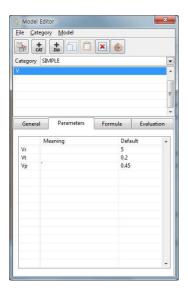
- · Click the Model Editor link from the Getting Started Window after you launch ZMAN; or
- Select **Tools** >> **Model Editor...** from the menu bar of the ZMAN main window.
- 3. From the **Category** list, select SIMPLE. This displays its elements in the below list box.
- 4. Select **Model** >> **New/Edit...** to display "New/Edit Model in Simple Category" dialog.
- 5. From the **Symbol** list, select **V**. Disabled items means that they are used in BASIC category.
- 6. Type "Closed Warburg" in the Alias field. This is not necessary but for your convenience.
- 7. Type "Vr \* Coth(pow(Vt\*s, Vp)) / pow(Vt\*s, Vp)" in the formula box. If the formula is acceptable, you can see green Validation checkmark and the OK button that is enabled.



8. Click the **OK** button to complete the steps. You can see V element is added in the **Element** list.



9. Click **Parameters** tab and type the suitable values in the "Default" column of the **Parameter Table**.



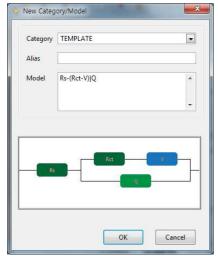
10. See the Nyquist and Bode Plot by clicking **Evaluation** tab.

Now we are ready to handle the model depicted in Figure 1.

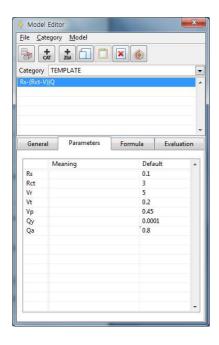
#### Add a new model in user category

Complete the following steps to make a user-defined model in the Model Editor.

- 1. From the **Category** list, select TEMPLATE. You can see its models in the below list. Select **Model** >> **New...** and the New Category / Model dialog is showed. If the TEMPLATE category is not existing, you can add it to the list by selecting **Category** >> **New...**. In this case, you can see the same dialog box.
- 2. Select "TEMPLATE" or type it in the **Category** box and "Rs-(Rct-V)|Q" in the **Model** box. The OK button should be enabled.



3. Click the **OK** button to come back to Model Editor. You may see the model is added in the Model Editor. To observe the behavior of the model, select **Parameters** tab and type suitable values in the table.



4. Check its Nyquist plot by clicking **Evaluation** tab. In order to have a close look, change frequency range from 0.1 Hz to 1 MHz and select **Matching Scales** in the right-click menu of the plot.

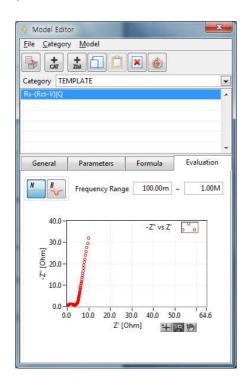


Table 1. Circuit elements defined in BASIC category are summarized.

Sy m bo I	Description	Param eters	Formula	N o t e
R	Resistive Element	R	R	
С	Capacitive Element	С	1 sC	* 1
L	Inductive Element	L	sL	
w	Warburg Diffusion	W	$\frac{1}{W\sqrt{s}}$	
Q	Constant Phase Element	Qy Qa	$\frac{1}{Q_y} \frac{1}{s^{Q_a}}$	
0	Nernst Impedance	Oy Ob	$\frac{1}{O_y\sqrt{s}} \tanh(O_b\sqrt{s})$	
т	Finite Diffusion	Ty Tb	$\frac{1}{T_y\sqrt{s}} \coth(T_b\sqrt{s})$	
G	Homogeneous Reaction (Gerischer)	Gy Gk	$\frac{1}{G_y\sqrt{G_k+s}}$	
S	Spherical Diffusion	Sy Sk	$\frac{1}{S_y} \frac{1}{\sqrt{S_k} + \sqrt{s}}$	
х	Finite-Length diffusion at planar particles	Xr Xc	$\sqrt{\frac{3X_{ m r}}{X_{ m c}s}} { m tanh}(\sqrt{3X_{ m r}X_{ m c}s})$	*
Y	Finite-Length diffusion at spherical particles	Yr Yc	$\frac{\tanh(\sqrt{3Y_{\rm r}Y_{\rm c}s})}{\sqrt{\frac{3Y_{\rm c}s}{Y_{\rm r}}} - \frac{1}{Y_{\rm r}}\tanh(\sqrt{3Y_{\rm r}Y_{\rm c}}}$	*
Z	Finite-Length diffusion at cylindrical particles	Zr Zc	$\frac{I_{0}(\sqrt{2Z_{\mathrm{r}}Z_{\mathrm{c}}s})}{\sqrt{2Z_{\mathrm{r}}Z_{\mathrm{c}}s}\cdot I_{1}(\sqrt{2Z_{\mathrm{r}}Z_{\mathrm{c}}s})}Z$	* 2 , * 3

<sup>\*1.</sup> Complex argument,  $s=j\omega$ , where imaginary unit, j equals  $\sqrt{-1}$  and  $\omega$  is angular frequency.

<sup>\*2.</sup> Impedance Spectroscopy: Theory, Experiment, and Applications, 2<sup>nd</sup> edition, Ed. E. Barsoukov, and J. R. MacDonald, John Wiley & Sons, Inc., Hoboken, New Jersey, 2005

<sup>\*3.</sup>  $I_0(x)$  and  $I_1(x)$  are modified Bessel-functions of the first kind, with 0 and 1 order correspondingly.

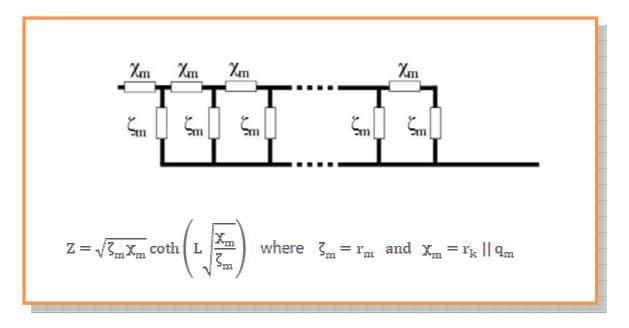
Table 2. List of functions.

Constants		
Constants	Returns pi	
•	Returns pi	
Functions	commutes the sheet the value of v	
abs(x)	computes the absolute value of x	
acos(x)	inverse cosine of x	
acosh(x)	inverse hyperbolic cosine of x	
acot(x)	inverse cotangent of x	
acoth(x)	inverse hyperbolic cotangent of x	
asin(x)	inverse sine of x	
asinh(x)	inverse hyperbolic sine of x	
atan(x)	inverse tangent of x	
atan2(x,y)	inverse tangent of x/y	
atanh(x)	inverse hyperbolic tangent of x	
ceil(x)	computes the smallest integer greater than or equal to x	
cos(x)	cosine of x	
cosh(x)	hyperbolic cosine of x	
cot(x)	cotangent of x	
coth(x)	hyperbolic cotangent of x	
Coth(x)	Coth(x) is modified to avoid failure at limit condition of $x$	
csc(x)	cosecant of x	
csch(x)	hyperbolic cosecant of x	
deg(x)	converts radians to degrees (x*180/p)	
e(x)	returns e or the argument multiplied by e	
erf(x)	Error function	
erfc(x)	complementary Error function	
exp(x)	e raised to the x power (exponential function)	
factr(x)	Factorial of x	
floor(x)	computes the largest integer less than or equal to x	
fract(x)	computes the fractional part of x	
gamma(x)	Gamma function	
gammai(a,x)	Incomplete Gamma function	
getexp(x)	computes the exponent of a floating-point value	
getman(x)	computes the mantissa of a floating-point value	
int(x)	computes the integer part of x	
ldexp(m,e)	computes a floating-point number from mantissa and exponent	
ln(x)	natural logarithm of x (logarithm to the base e)	
log(x,y)	logarithm of y to the base x	
log10(x)	logarithm of x to the base 10	
log2(x)	logarithm of x to the base 2	
pi(x)	returns pi or the argument multiplied by pi	
pow(x,y)	x raised to the y power	

pow10(x)	10 raised to the x power
pow2(x)	2 raised to the x power
rad(x)	converts degrees to radians (x*p/180)
random(x,y)	generates random numbers within the specified range
sec(x)	secant of x
sech(x)	hyperbolic secant of x
sign(x)	returns the sign of x
sin(x)	sine of x
sinc(x)	sin(x)/x
sinh(x)	hyperbolic sine of x
spike(x)	Spike function
sqrt(x)	computes the square root of x
square(x)	square function
step(x)	step function
tan(x)	tangent of x
tanh(x)	hyperbolic tangent of x
Tanh(x)	Tanh(x) is modified to avoid failure at limit condition of $x$
Special Functions	
BesselJ(n,x)	Bessel function of the first kind, denoted as $J_n(x)$
BesselY(n,x)	Bessel function of the second kind, denoted as $Y_n(x)$
BesselI(n,x)	modified Bessel function of the first kind, denoted as $\mathrm{I}_{n}(x)$
BesselK(n,x)	modified Bessel function of the second kind, denoted as $K_n(x)$
·	

# Appendix2. How to make bisquert

#### **Bisquert Open Model**



Constant Phase Element qm can be represented as ;

$$q_{\rm m} = \frac{1}{Q_{\rm y} s Q_{B}} \ \ \mbox{where} \ s = j \omega \ \mbox{and} \ j = \sqrt{-1}$$

$$\chi_m = \frac{r_k}{1+\,r_k Q_y s^{\,Q_B}}$$

$$Z = \sqrt{\frac{r_{m}r_{k}}{1 + r_{k}Q_{y}s^{Q_{\underline{a}}}}} \coth\left(L\sqrt{\frac{r_{m}}{r_{k}}(1 + r_{k}Q_{y}s^{Q_{\underline{a}}})}\right)$$

Let's guess that this model is Element A and add this user defined model into ZMAN library as the following steps.

1. Add "A" ele	ment in SIMPLE category	
Categ	SIMPLE	
ory		
Model	A	
Formu	coth(AL * sqrt(Am / Ak * (1 + Ak * Ay * pow(s, Aa)))) *	
la	sqrt(Am * Ak / (1 + Ak * Ay * pow(s, Aa)))	
Note	Refer to Appendix 1 and 2	
	$\cdot$ AL = L	
	• Am = $r_m$	
	• Ak = $r_k$	
	• Ay = $Q_y$	
	• Aa = $Q_a$	
	<ul> <li>s = jω</li> </ul>	
Steps	Refer to Fig. 1 ~ 3	
	<ul> <li>(1) Open Model Editor dialog</li> <li>(2) Select SIMPLE item in the Category list</li> <li>(3) Select Model &gt; New/Edit in menu</li> <li>(4) Select A as Symbol</li> <li>(5) Type "Bisquert Open" in the Alias blank</li> <li>(6) Type above formula in the Formula blank</li> </ul>	
	(7) Click the <b>OK</b> button	
2 Make Ps-A-I	(8) Select <b>Parameter</b> tab and type default values  L1 Model in USER category	
Categ	USER	
ory		
Model	Rs-A-L1	
Steps	Refer to Fig 4 ~ 5	
	<ul> <li>(1) Select USER item in the Category list</li> <li>(2) Select Model &gt; New in menu</li> <li>(3) Type "Rs-A-L1" in the Model blank</li> <li>(4) Click the OK button</li> <li>(5) Select Parameter tab and type default values</li> </ul>	

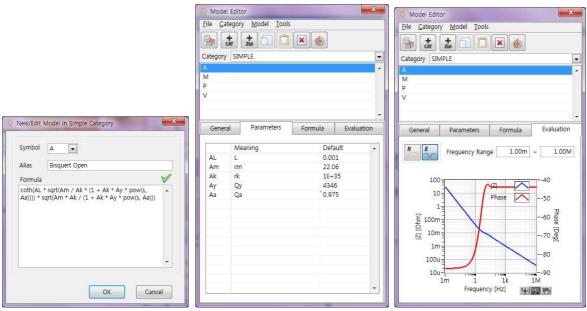


Figure 302.

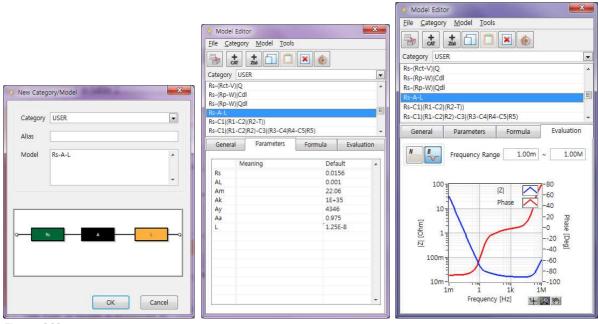


Figure 303.

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# Modeling & Fitting Flow Chart using ZMAN software



Manufactured by WonATech Co, Ltd

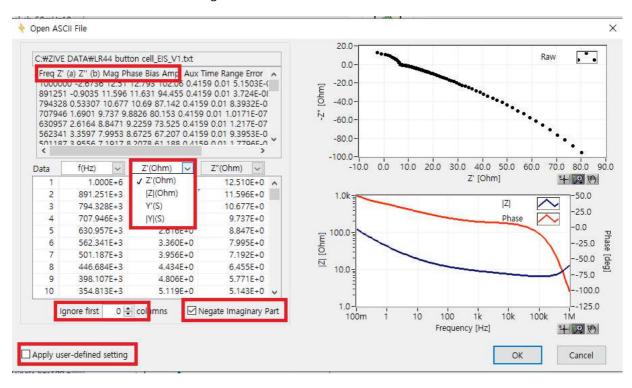
WonA Bldg, 7, Neunganmal 1-gil, Seocho-gu, Seoul, 137-180, Korea

Phone: +82-2-578-6516
Fax: +82-2-576-2635
http://www.wonatech.com
e-mail: service@ wonatech.com

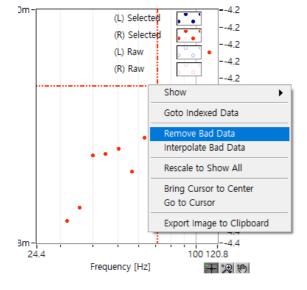
1. Round1:

```
ZiveLab Files (*.sde;*.seo;*.wdf;*.wis;*.z#)
ASCII Files (*.csv;*.dat;*.txt)
Others (*.asc;*.crv;*.dfr;*.dta;*.idf;*.ids;*.ism;*.izx;*.mpr;*.mpt;*.pseisdata;*.z)
```

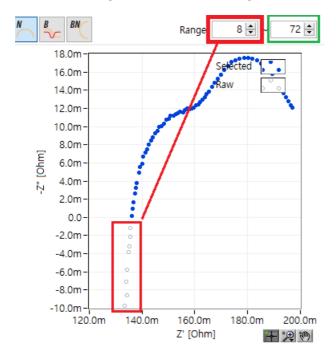
- A. WonATech(Zivelab) data files: No requirement of License
- B. 3<sup>rd</sup> parties EIS data format (others)
- C. ASCII files
  - i. Define user-defined setting value



- 2. Round2. (Data pre-treatment): Refer to operation manual
  - A. Abnormal data=> delete(Remove Bad Data) or modify (Interpolate Bad data or input modified value directly in goto indexed data)

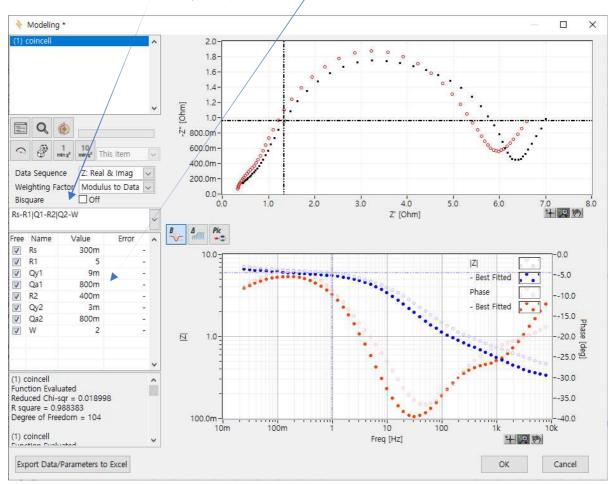


# B. Select data range to be used for fitting.

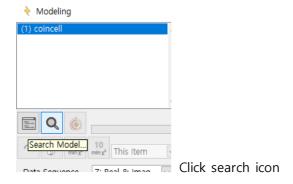


#### 3. Round3

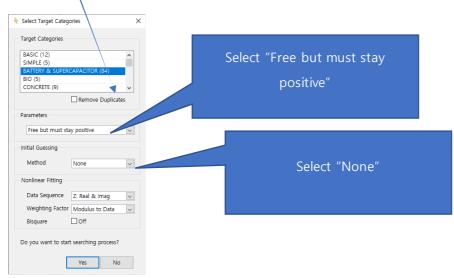
Input model (serial: - parallel: | ) \* input parameter value



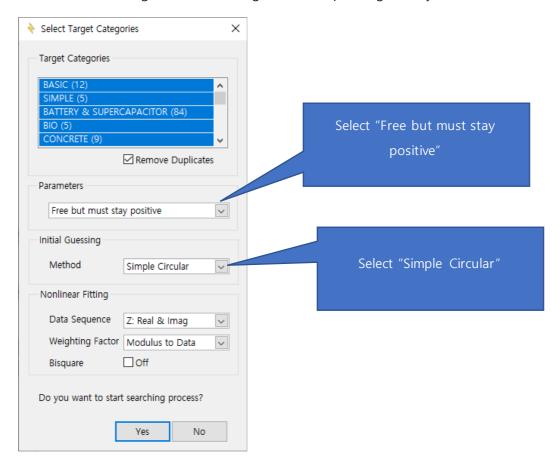
# 4. Round 4-1 Automatic fitting



A. Select category if you know.

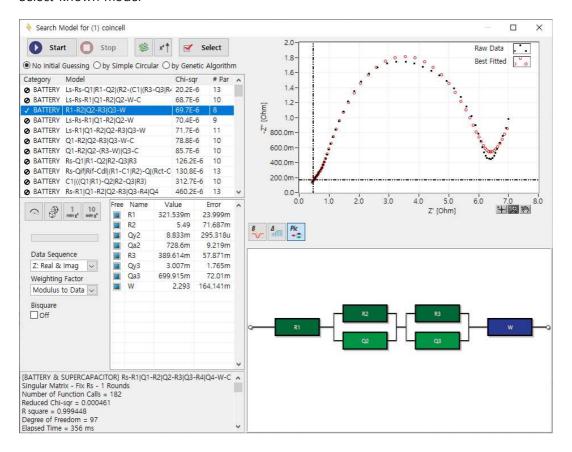


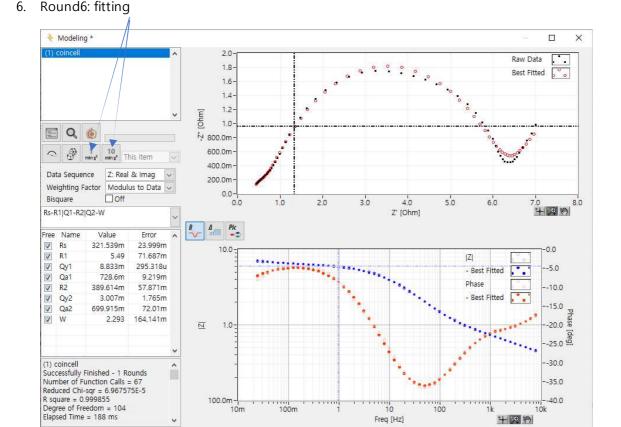
B. If not, select all categories (Select categories under pressing ctrl key).



#### 5. Round 5

#### Select known model





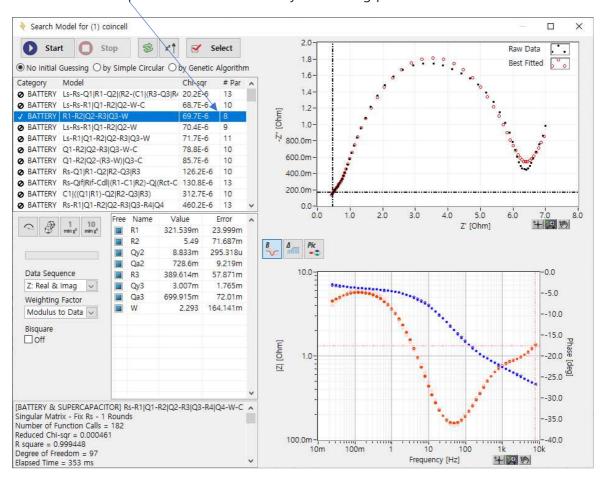
Freq [Hz]

Cancel

Click OK to select the primary fitting result

Export Data/Parameters to Excel

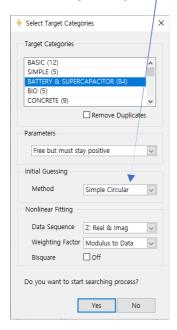
7. Round 7 Select simpler model in visual overlay without big problem



- 8. Round 4-2: You need several trials with following cases
  - A. Change Parameters to "Free but must stay positive" and goto next step

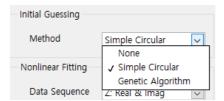


B. Use Initial guessing to Simple circular and goto next step



B. Change Nonlinear fitting data sequence and or weighting factor and goto next step

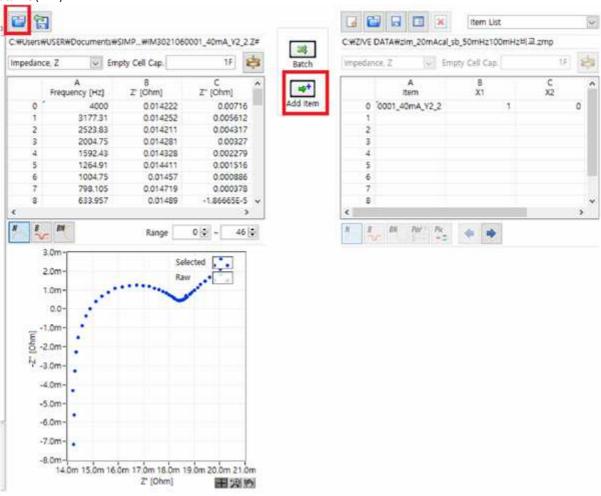
D. Use Initial guessing to genetic algorithm and goto next step



# Model Searching Example

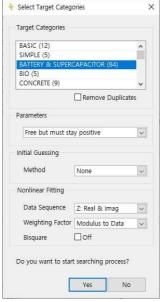
# 1. EIS data file loading

Load the BZA data file (\*.z#)

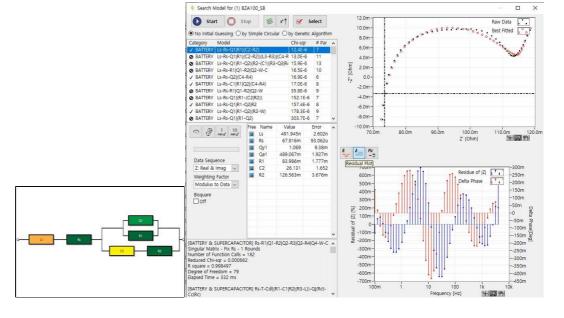


### 2. Model searching

# (1) Model searching based on default value



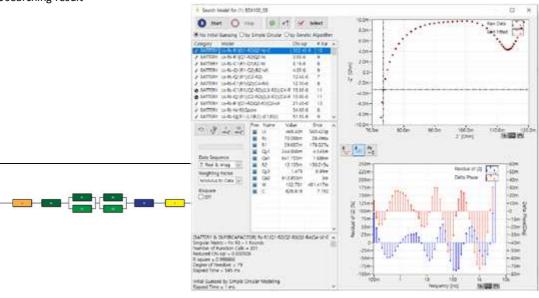
Automatic searching result



# (2) Initial guessing using simple circular



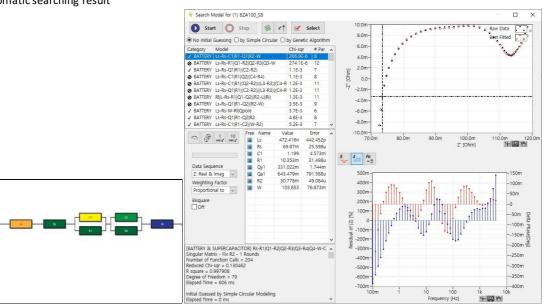
Automatic searching result



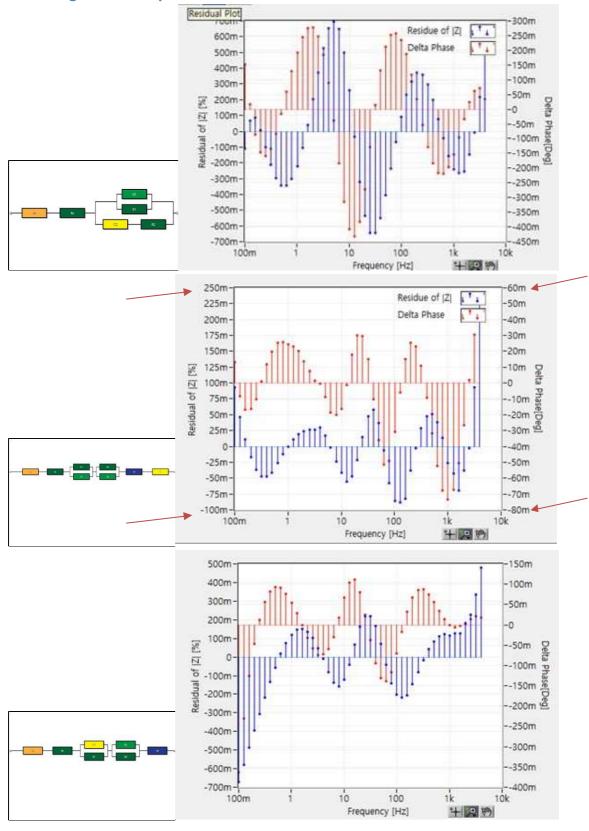
# (3) Initial guessing using simple circular with proportional weighting



Automatic searching result



# 3. Searching result comparison



Initial guessing using simple circular is good choice for this model searching