Series EIS Test by Cyclic Voltage step using sequence file with tag function

Purpose

2 mM potassium ferricyanide(K3Fe(CN)6) with 1 M potassium nitrate(KCN) in water is used for typical cyclic voltammetry test. The voltage scanning range is 0V to 600mV. EIS test will be done by each 100mV step after constant voltage is applied and reverse scan. With this example, you can test your electrochemical cell by same manner to get EIS graph per specific voltage automatically. This application note guides to make this experiment using sequence file to demonstrate how to use sequence file. This complex procedure can be tested with just 6 steps sequence file using "tag" function on constant control parameter. But this procedure is only available with constant step voltage value. If you want to test this kind of test with variable voltage step, please refer to ZIVE application note7.

More simple method for this test is batch file using frequency scanning potentiodynamic PEIS in technique menu. See ZIVE application Note8

This demonstration's test condition is;

- ◆ Start potential: 600mV
- ◆ Middle potential: 0V
- ◆ Final potential: 600mV
- ◆ Voltage step: 100mV
- ◆ EIS measurement at each potential step
    - ● Initial frequency: 100kHz
    - ● Final frequency: 0.1Hz
    - ● Amplitude: 10mV
    - ● Points per decade: 10

Preparation

- ● ZIVE SP/MP electrochemical workstation
- ● Pt working electrode
- ● Ag/AgCl reference electrode
- ● Graphite rod counter electrode
- ● Universal Electrode Holder
- ● Cell vial
- ● Electrolyte:2 mM potassium ferricyanide(K3Fe(CN)6) with 1 M potassium nitrate(KCN) in water.

- ✓ **Preparation of the Test Solution**

    1. Weigh 16.5 mg potassium ferricyanide and place in a 25 mL volumetric flask.
    2. Weigh 2.53 g potassium nitrate and add to the same volumetric flask.
    3. Add about 20 mL deionized water to dissolve the potassium ferricyanide and potassium nitrate.
    4. Dilute to 25 mL with deionized water.

Cell Connection

Platinum Working Electrode (Green lead & Blue lead)
Graphite Counter Electrode (Red lead)
Ag/AgCl Reference Electrode (White lead)

Add 10-15 mL of the ferricyanide solution to the cell vial and place in the cell holder.
Insert Pt working electrode on one of hole in cell top and screw right the electrode holding screw.
Insert Graphite counter electrode as same way of Pt electrode
Insert Ag/AgCl reference electrode as same way of Pt electrode (Reference electrode body is fragile. Be careful on holding screw.
Too much forced screwing might break the electrode)
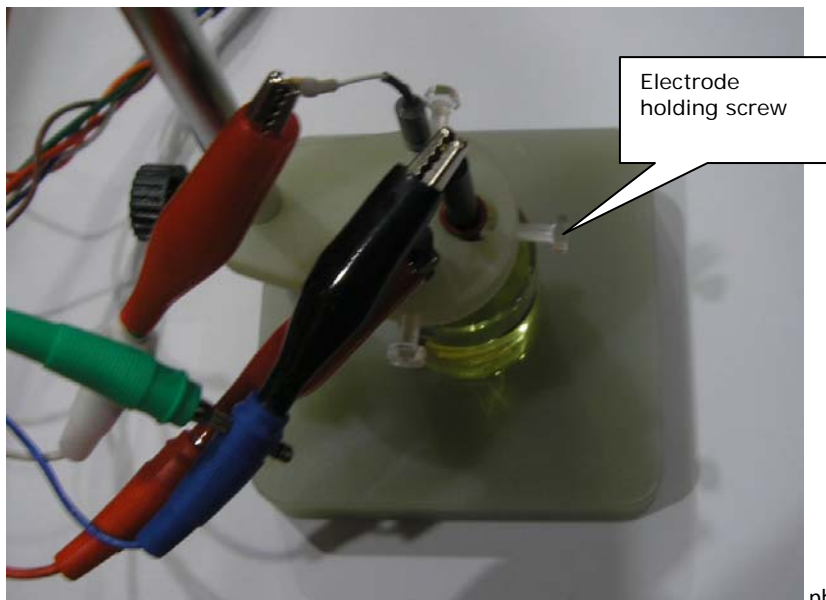
photo: Universal holder (model: UEH)

Procedure

1. Turn the Power switch on the ZIVE SP/MP electrochemical workstation
2. Open the SM software by clicking the SM icon. The following progress box will appear, and will show the progress of checking instrument configuration and communication between ZIVE SP/MP electrochemical workstation and PC.

If the link is successfully connected, Click "OK" button on the box then the progress box will automatically disappear and SM software will appear. If the link failed, The following progress box will display then click the "Retry" button.
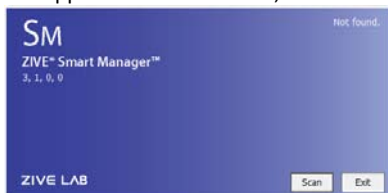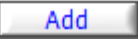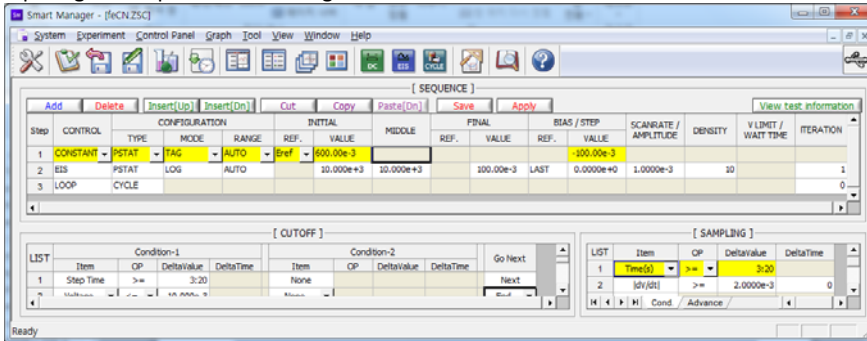

If the link failed again after clicking "Retry" button, you need to check USB cable connection.
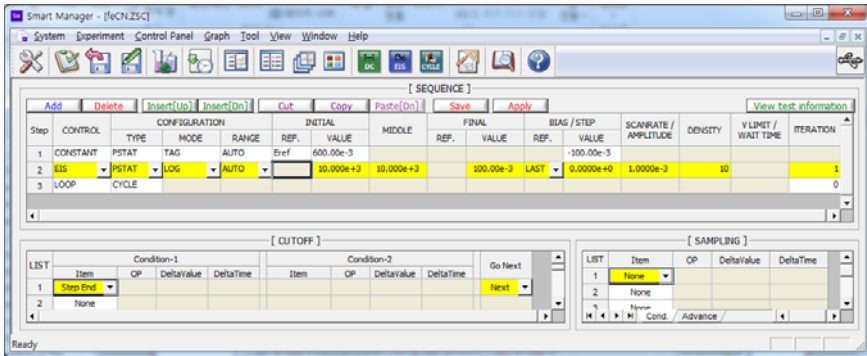
3. Click New Sequence function icon (or select Sequence function-New on Experiment menu)
   Then you can see the following menu
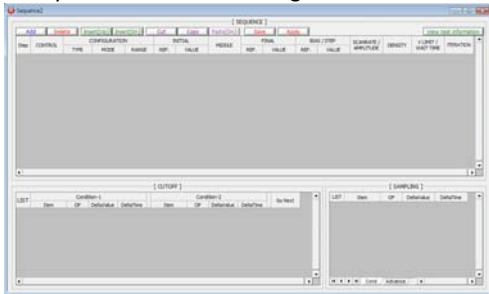
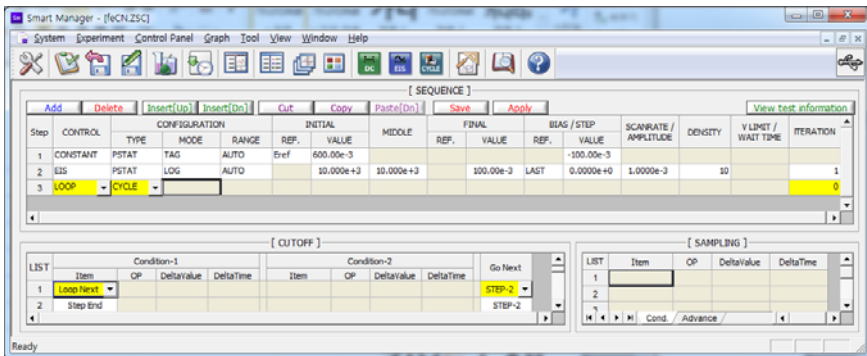4. Click Add button .
   Input figure for parameter setting as the follows.

   1st step(constant voltage)


   2nd step(EIS)

   3rd step(Loop)

The above 2 steps are for constant voltage applying and EIS measurement. 3rd step is to mark cycle. This cycle mark will be used to separate each EIS data when you analyze EIS data using Zman software. If you do not insert Loop(cycle) step after EIS measurement, You must separate each EIS data by manually.

To copy the above 3 steps, drag mouse from step numbers them selected region will be changed with yellow color
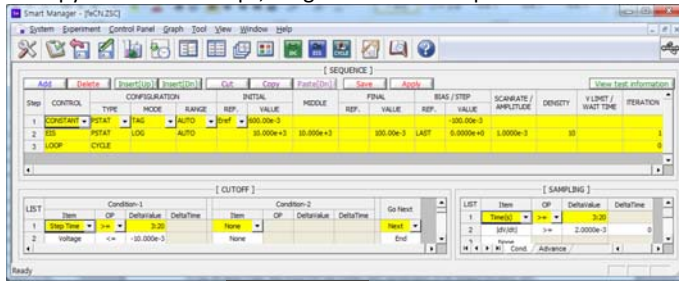
Then click copy button [Copy]

Click on step 3
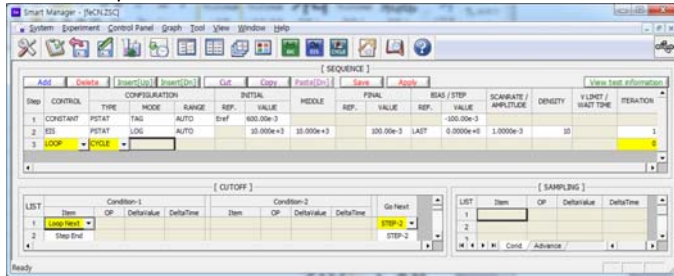
Click Paste(Dn) button [Paste[Dn]]
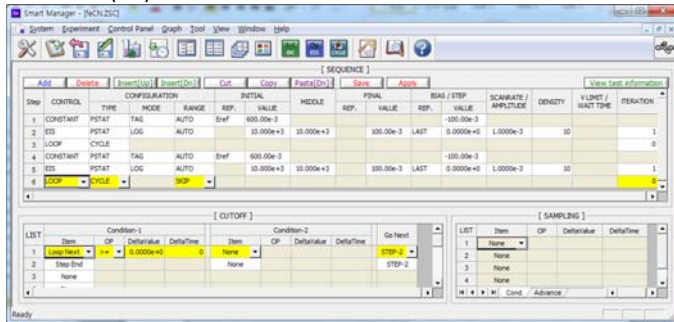
Change the voltage value from 600mV to 0V and -100mV to 100mV for step value at step4 and change cutoff condition from voltage<0 to voltage>0.6.
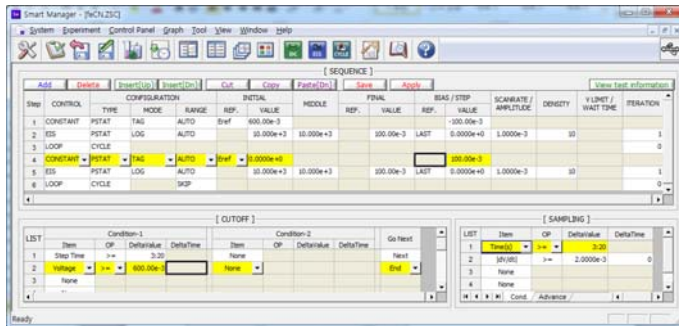

Click 1st step and change cutoff condition from V<0 's target from end to step4.
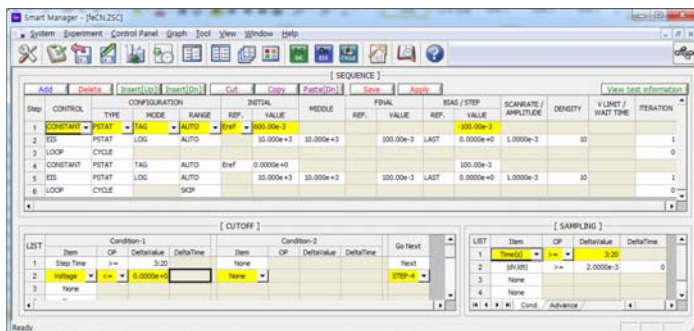
5. Click "Save" button to save the technique file which contains the above parameter and setting file name.
6. You can assign this technique file to channel(s) which you want by click "APPLY" button or select schedule file using file selection on "Single channel control/monitor" or "multi channel control/monitor"
   If you click "apply" button on technique menu, You can see the following channel selection menu.
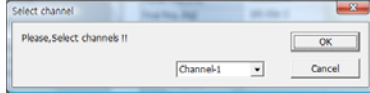
Select channel and click OK then this technique file will be assigned on the channel.
Click "Close" button or minimize technique window.
7. If you want control ZIVE SP/MP electrochemical workstation using "Single channel control/monitor", you can see following windows.

To start experiment, click Start button

If you want control ZIVE SP/MP multichannel, you can see the following window

To start experiment for specific channel, click Start button on the channel. If you want to start experiment for multiple channel,

click on Group column which you want to start and click Start button **at bottom side.**

8. After click start button, you can see the following box.
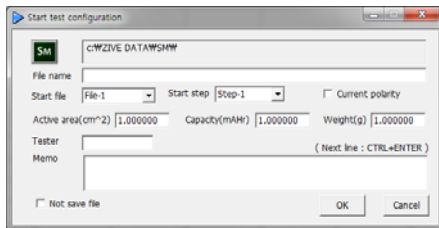
The data file name is automatically determined as default value but if you want to change data file folder then click icon

You can make new folder which you want to save.
   ◆ If you want use your file name, input your file name on "File name"

◆ If you did not make file name manually, new data folder which named as sequence file name or technique file name under data folder and it's subfolder will be created with name as date. The data file will be saved in this folder. The data file name will be determined automatically as string with sequence file name or technique file name and hour and minute and second, finally channel number will be added.

example) If you used sequence file for test and its file name is testabc.zsc and channel number is 1 and test date is 2000 year January 1st time is 15:30: 1 then the data file will be saved as

C:\Zive data\sm\data**testabc.zsc\2000010115\3001_01**.sdo (If data file have DC data only)

Or

C:\Zive data\sm\data**testabc.zsc\2000010115\3001_01**.sde (If data file have DC data and EIS data)

Or

C:\Zive data\sm\data**testabc.zsc\2000010115\3001_01**.seo (If data file have EIS data only)

e.g.) schedule file name with extension\yearmonthdayhour\minutesecond_channel number

If you input file name as "tommy" then

C:\Zive data\sm\data**testabc.zsc\2000010115\tommy3001_01**.sdo (sde,seo)

① Start Step: If your sequence file has several steps, you can select starting step.

② Start file: If batch file is loaded, select file number

③ Current polarity: If you want reverse polarity for measured current, check on this box.

④ Active area: For calculation of current density

⑤ Capacity: For C-rate value calculation

⑥ Weight: For specific capacity calculation

⑦ Tester: Operator name

⑧ Memo: Text information for test (For line change, use CTRL+ENTER)

➢ No Save file: If you click this check box, the data will NOT be saved.

If you are ready to test, click OK button then experiment will be started.

You can see real time plot as the following.
When experiment done, the display will be changed as following.

Constant voltage step display

EIS measurement step display

Real time EIS graph shows sub window at right upper side. This window display sine wave or E vs. I graph to check data quality. Default display is sine wave.

58m	266.277m	1.493	1.493

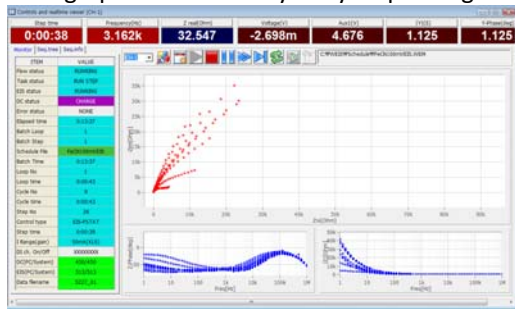C:\ZIVE DATA\SM\Schedule\cap.MOS
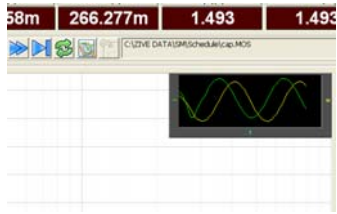
This shows two sine wave graphs. One is for current (green line) and the other is for voltage (Yellow line).

If you switch this graph to I vs E, double click on the graph then graph format will be changed.

Yim(S)	|Y|(S)	Y-Phase(de
8.819m	1.512	1.51:

C:\ZIVE DATA\SM\Schedule\cap.MOS
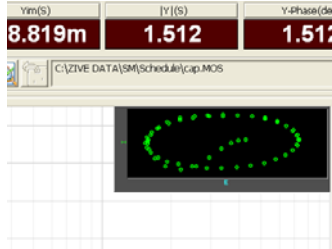
Each graph will be overlayed by step voltage change.

9. You can display graphic by clicking button on tool bar

Click "Open data file" icon and select data file which you run the experiment.
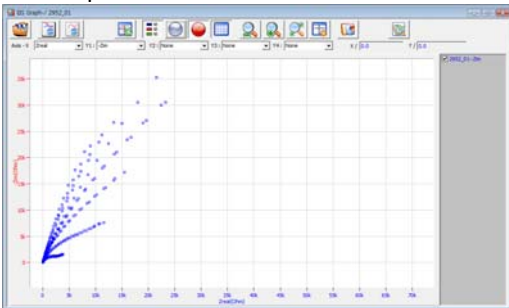
You can select Bode plot by clicking icon or Nyquist plot by clicking icon.
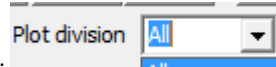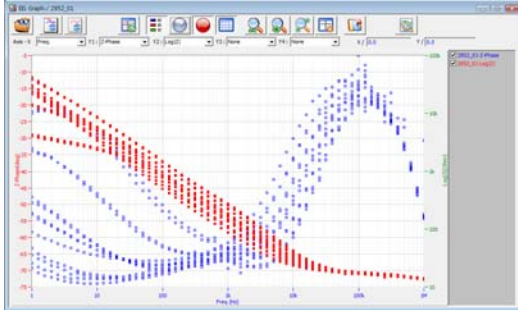
SM can split each EIS graph by selecting "step" in "division".

You can split data by file, cycle or step. Splitted data set's color was changed and graph line will be broken

ZMAN will split each EIS data automatically if you insert "cycle" mark.

For user defined graphic, you can select X axis and Max 4 Y axis parameter as you wanted.
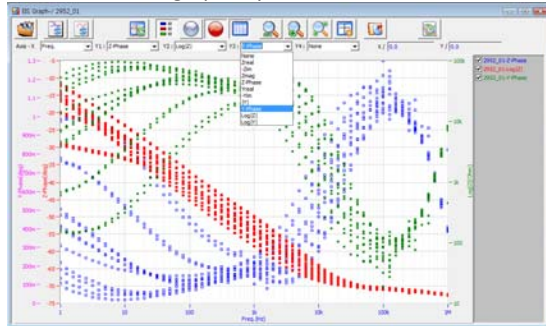
Data Analysis

1. Open "ZMAN" by clicking ZMAN icon. ZMAN program is located c:\program files\zivelab\zman2.2 folder.
2. You can see the following window.
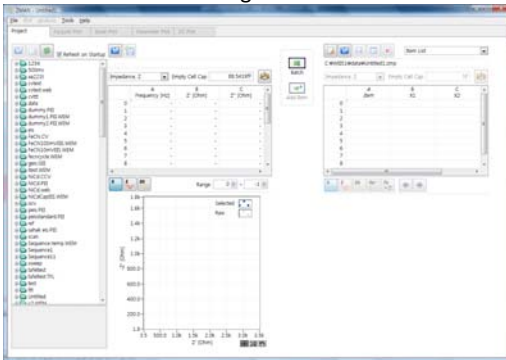
3. Click Right button of mouse
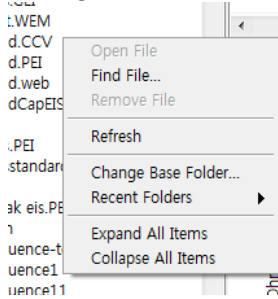
Select Change Base folder and select the folder which contain SM data.

4. Select data file by double clicking
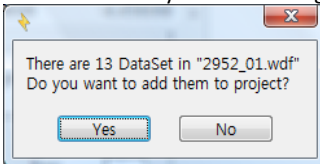
If you inserted Cycle market as we used the above sequence file, above box will appear. Click "Yes" then multiple EIS data will be split automatically.
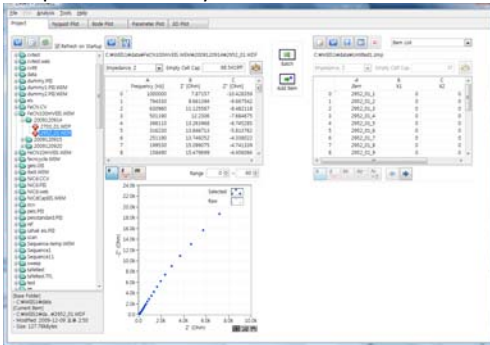
If you do not want to use all EIS data set, Click "No" then you can see select box.
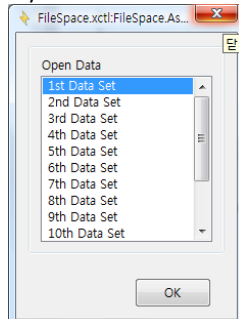
You can select one EIS data for analysis.

5. Parameter for voltage name can be changed from X1 to Voltage for example by clicking "edit item" button
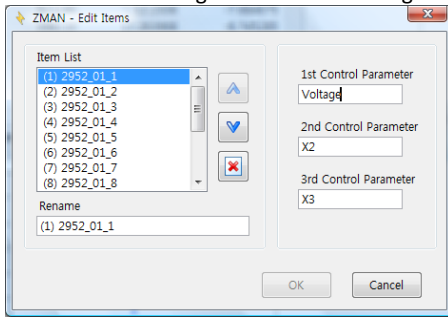
6. You can input each voltage value for each EIS data using X1 colum.

	A Item	B Volt	C X2
0	2952_01_1	0.6	0
1	2952_01_2	0.5	0
2	2952_01_3	0.4	0
3	2952_01_4	0.3	0
4	2952_01_5	0.2	0
5	2952_01_6	0.1	0
6	2952_01_7	0	0
7	2952_01_8	0.1	0
8	2952_01_9	0.2	0

○ Nyquist Plot ○ Bode Plot ○ Best Fitted Parameters
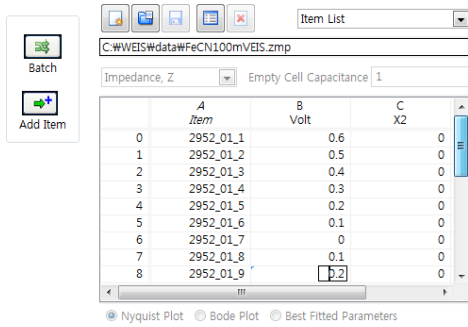
7. You can see Impedance,Admittance,Modulus,Dielectric Constant by selecting as the following
a) Select data set
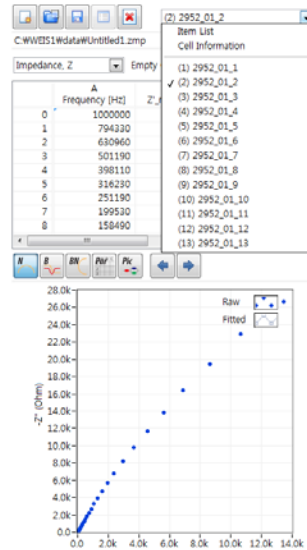
b) Seelect Impedance,Z in polar,Admittance,Y in Polar, Modulus, M in polar, Dielectric Constant, E in polar. (in polar = in Polar Coordinate)
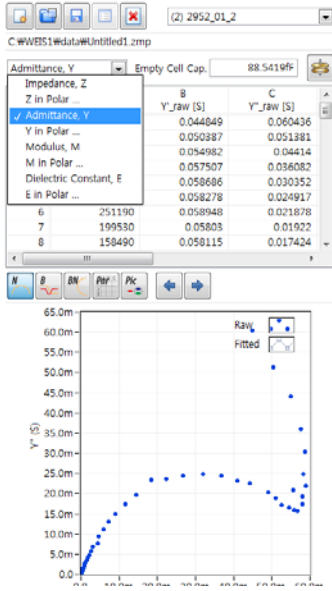
8. Click 2D nyquist plot
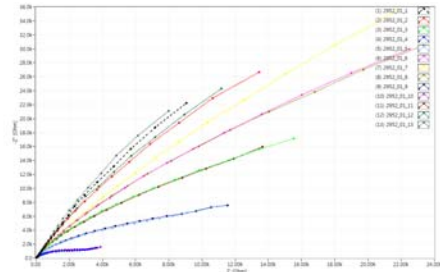
You can see "Matching scale" by clicking right button of mouse and select "Matching scale"
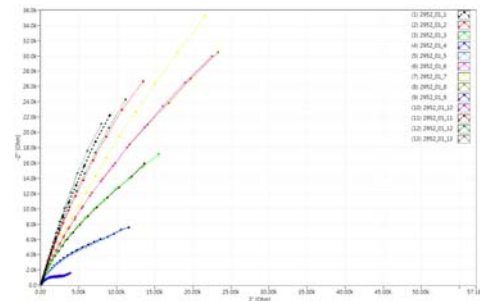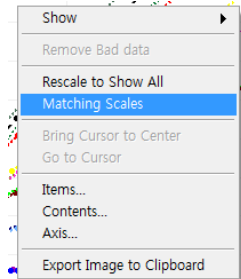
Matching scale is X axis scale and Y axis scale on graph is same.
You can check each data value by selecting "cursor" with clicking right button of mouse .

You can move the point by dragging the mouse or by keyboard arrow key .

9. Click 2D Bode
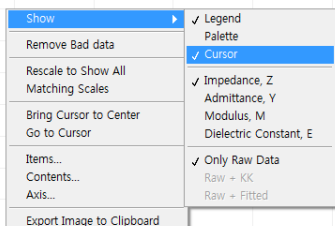
EIS Anaysis

- Select Modeling on Analysis

1. Select data
   Choose one data set having more complicated shape
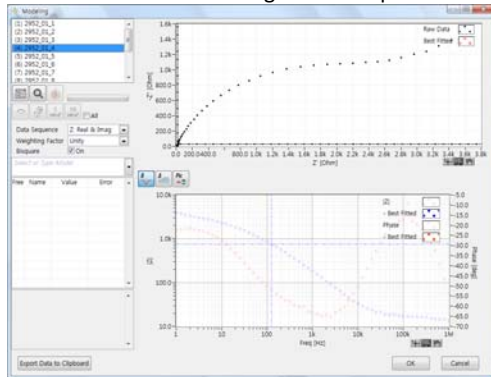
2. Search Model by clicking "search" button
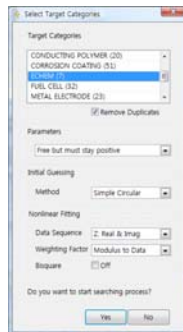
3. Select Battery & Supercapacitor in Target category
4. Select Parameters range as Free but must stay positive
5. Select initial guessing method as simple circular
6. Select data sequence as Zreal & Zimg
7. Select weight factor as modulus
8. Click Yes button then automatic model searching will be done
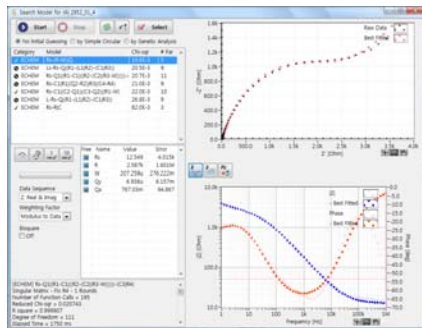
   Result was rearranged by chi square value order.
9. Check on Bisquare for more accurate searching.
10. Click Start button and press stop button about 10th model searching finished or until end of similar fitting overlay plot on Nyquist & Bode..
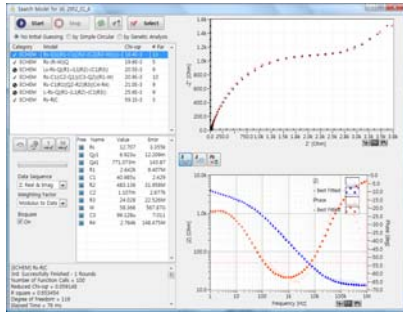
searching result will be rearranged by chi square value and it may be different from previous result.

11. If the error level per parameters are too high, you can search again with other weighting factor.

12. By clicking you can change searching parameters. Select weighting factor as unit and search again.
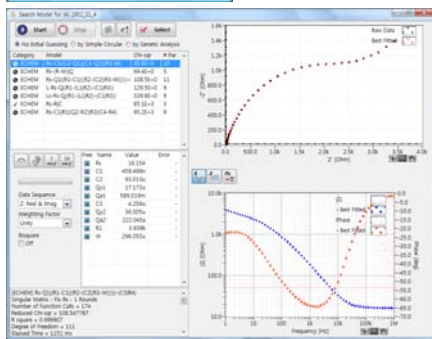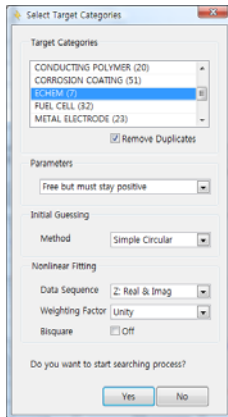
13. Repeat previous 9-10 steps.

14. If top listed model have parameters which needs lock, then lock parameter and fit again.
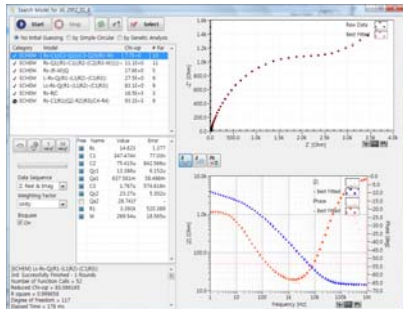
Suggested 1st model by automatic model searching is Rs-C1|(C2-Q1)|(C3-Q2)|(R1-W)
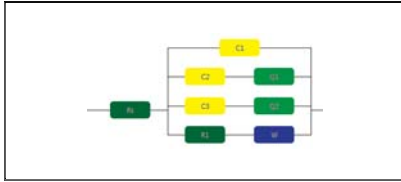
15. Check on "ALL" and click fitting button for series fitting
16. If there are data sets having singular matrix after series fitting, click initial guessing(simple circular fitting) and click fitting button until showing normal result (no singular matrix) for each data set. If singular matrix remains, try to use genetic analysis as initial guessing and click fitting
    To compare each element(parameter) for series measurement data sets, do not lock parameter anymore.
17. If all data set fitting result are normal, Click select button to take this model
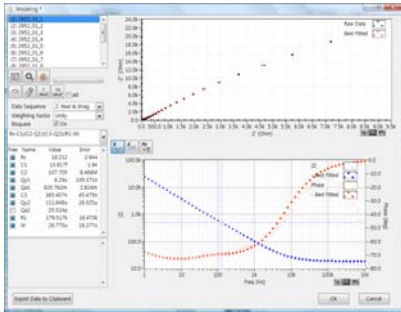
18. You can get this result or do fitting again by clicking fitting button.
19. If you want to accept this result, click OK button
20. If you want to choose other model, click right mouse on searching button
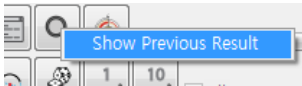
21. Click Show previous result pop up menu
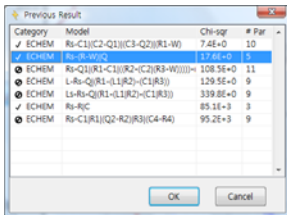
22. Select Minimum parameters on the top list. It is Rs-(R-W)|Q
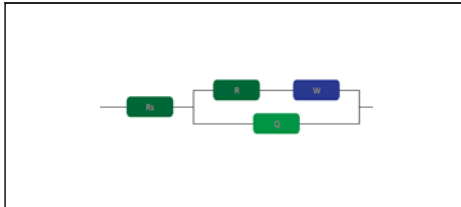
23. Check on Bisquare option and click fitting button
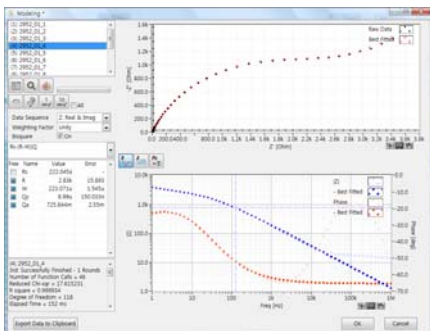
24. Do step 15-18 again.
25. If you accept this result, click OK button

26. If you want overlay raw data and fitted data, Plot detail in Plot menu
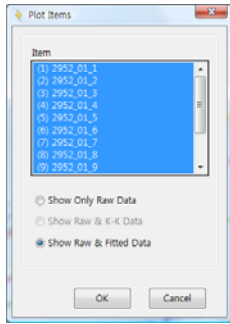
- You can see Nyquist or Bode data with fitted data
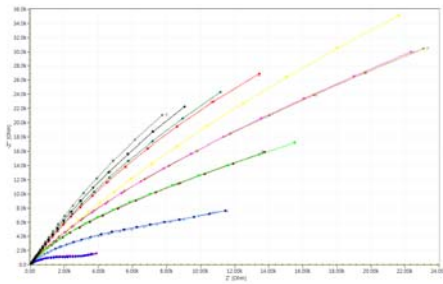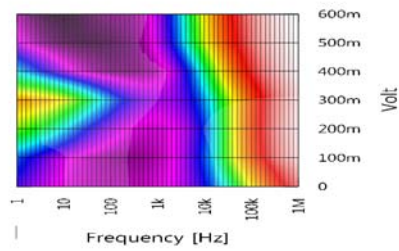

- 3D graph
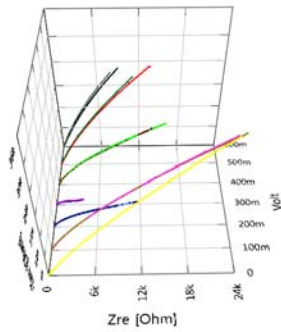
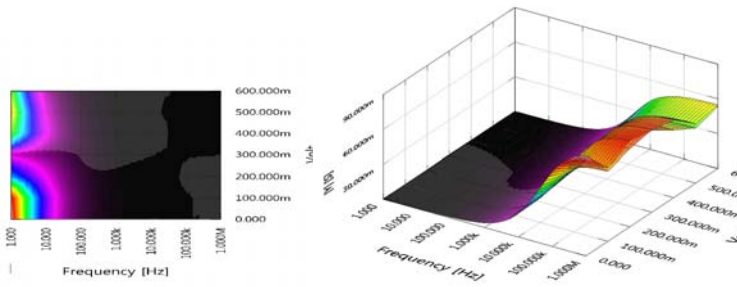Curve plot (Nyquist)
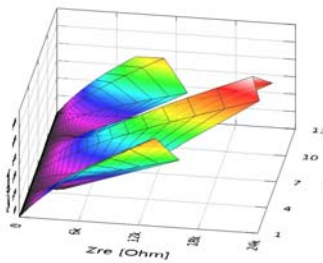
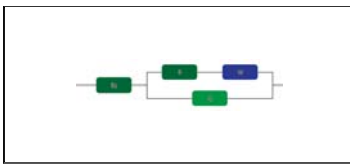Surface plot (Nyquist)   Surface plot(Bode, Phase)
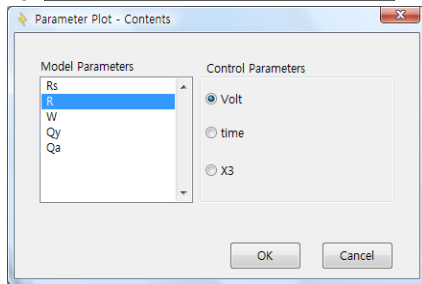
Surface plot(Bode, impedance)   Surface plot(Admittance)
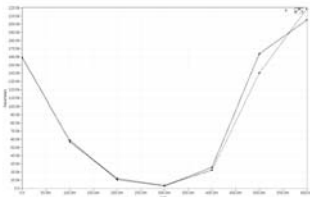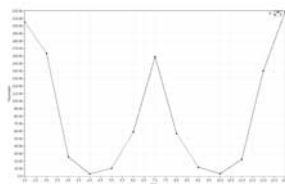
- To view parameter plot, Select Plot-2D parameter

For

Select parameter(s) and click apply button
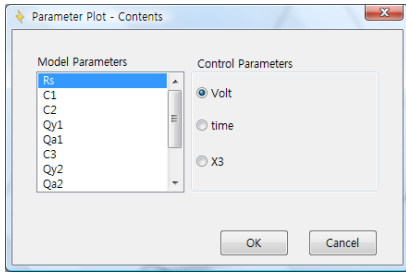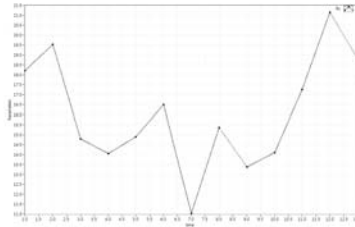

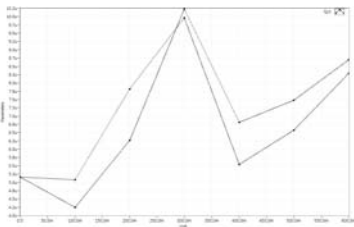R vs. voltage   R vs. time
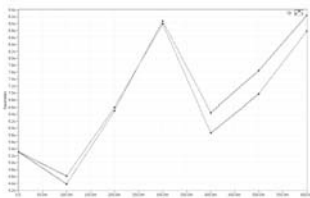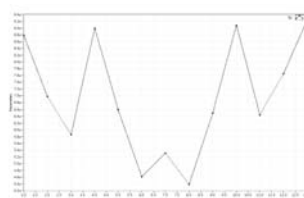
Qy vs time   Qy vs. time
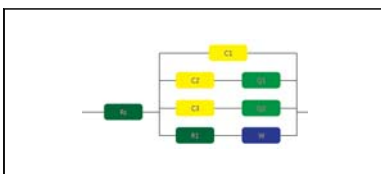
For
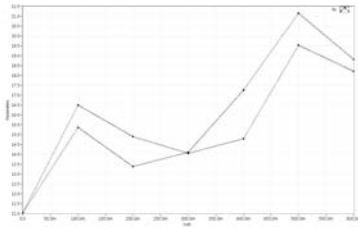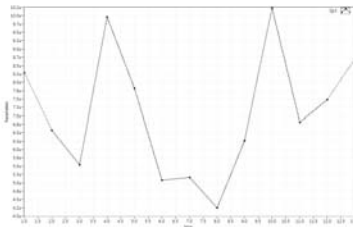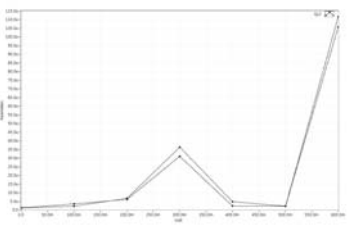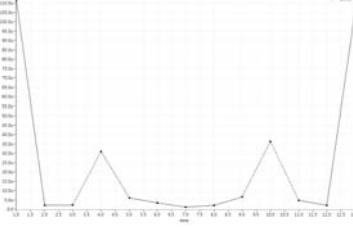
Rs vs. voltage

Rs vs. time

Qy1 vs voltage

Qy1 vs time

R1 vs. voltage

R2 vs. voltage

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