

# **\_\_AMRY** Echem Analyst™ Software

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# **Introduction to This Guide**

The Echem Analyst<sup>™</sup> is Gamry's dedicated data-analysis program, the companion to Gamry's data-acquisition program called Framework<sup>™</sup>. Data files generated by experiments in Gamry Framework then can be analyzed in the Echem Analyst. The Echem Analyst is a single program that runs data-analysis for all types of experiments, such as those used in DC Corrosion, EIS and Physical Electrochemistry.

The Echem Analyst is designed with the specific functions to make data analysis as straightforward as possible. This manual will explain the most common analysis routines. The tools discussed here in the examples are common to many data files created by other experiments. This document is a guide, and is not intended to have the same scope as the on-line help or a complete operating manual. In order to create a concise document, we assume the user has a working knowledge of Windows®-based applications. Details on common functions, such as opening, saving, and closing files, are intentionally ignored, so as not to obscure the goal of this guide.

This textbox indicates a helpful hint to know about Echem Analyst.

# **General Information and Overview**

#### **Installation**

Echem Analyst installs separately from other Gamry software. If Echem Analyst is not installed yet, you can find it on the CD-ROM, or—if you already own one of our potentiostats—on our website at <a href="https://www.gamry.com">www.gamry.com</a>.

You may install copies of the Echem Analyst on multiple computers. Often users prefer the convenience of performing data-analysis at an office workstation, rather than the laboratory setting.

#### **File Formats**

Gamry data files acquired using Framework software have the extension \*.DTA. DTA files are ASCII text, and therefore may be opened directly into various programs, such as Excel® or Origin®. When DTA files are opened in Echem Analyst, then saved, their extension becomes \*.GData. Gdata files include information on curve-fits and graphing options, thus Gdata files are only viewable in Echem Analyst.

Do not delete your DTA files! They are the raw data and may need to be reloaded for certain analyses, such as area normalization.

#### To Open a Gamry Data File

There are several different methods to open data files in the Echem Analyst:

- 1. Launch the Echem Analyst icon on your desktop. Then use the *File\Open* function.
- 2. Use the link on your desktop to open the *My Gamry Data* folder. Double-click on the data file. You may have to instruct your computer to associate the \*.DTA extension with the Echem Analyst program.

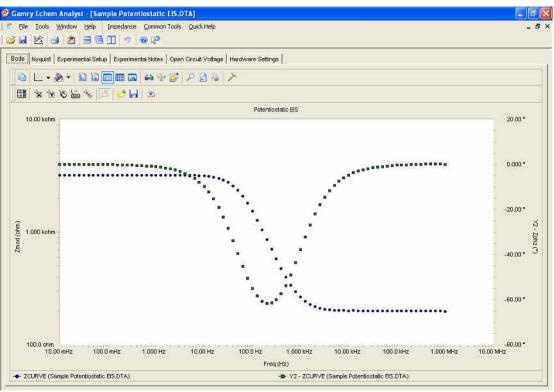


- There are two quick ways to open a recent Gamry Data File.
  - a. A recently generated file can be opened using the hotlink in the *Analysis* menu in the Gamry Framework. (The last eight generated data files are listed there for quick access.) The Echem Analyst automatically launches and opens your selected data file.
  - b. A recently opened file in the Echem Analyst is shown at the bottom of the *File* menu. This is similar to how other Windows®-based programs display links to *Most Recently Used* documents.

By default, files acquired in the Framework are saved into the *My Gamry Data* folder. A shortcut for *My Gamry Data* installs on the Windows® desktop. You can change this default under *Tools\Options*, which opens the **Gamry Analysis Framework Options** window. Choose the *General* tab, and change the *Path* for each type of data file as desired.

Don't change the directory for *Analysis Script* Files. These are the VBA programs that do the actual analysis.

The data set appears in the main window. The menu items, tabs, and toolbar are adjusted for the particular type of data set you chose. In the example below, a Potentiostatic EIS data set is shown:



Note the tab-based display. The *Experimental Setup* tab displays all the information from the parameters used to run the experiment, such as Voltage, Time, etc. The *Experimental Notes* tab stores any notes written into the setup screen in Framework. The *Open Circuit Voltage* tab shows the voltage measured during the Initial Delay of the experiment. The *Hardware Settings* tab records information on the filters, ranges, gains. Additional information on date of last calibration, software version, etc. is also stored here.

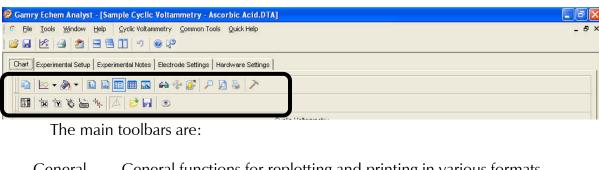
# **Working with Plots in Echem Analyst**

#### Introduction

Echem Analyst boasts a number of graphical tools to help you get the most information out of your data. Once you open a data set, these tools appear in the toolbars immediately above the plot:

In the data file, Framework writes a line that indicates the type of experiment used to generate that file. Echem Analyst displays both general and specific menus containing the analysis routines pertinent to your experiment.

#### **Toolbars:**



General functions for replotting and printing in various formats

Toolbar

Selection Toolbar

Toolbar

The following charts are references for buttons on the default toolbars. Descriptions of the most commonly used functions are highlighted in blue.

# **General Toolbar Functions**

Button	Name	Action
	Copy to clipboard	Copy the selection to the Windows® clipboard. Can paste directly in Microsoft programs for reports or presentations.
<u></u>	Gallery	Choose, via the dropdown menu, from scatter (no line), line, curve, and steps between data points
<b>→</b>	Color	Choose the color of the selection from the dropdown menu. To change the color menu, use the <i>Palette</i> button on the <i>PaletteBar</i> .
	Vertical Grid	Toggle between showing and hiding vertical grid lines on the plot
	Horizontal Grid	Toggle between showing and hiding horizontal grid lines on the plot
	Legend Bar	Toggle between showing and hiding a legend bar underneath the plot
	Data Viewer	Toggle between showing and hiding numerical data to the left of the plot
	Properties	Open the <b>GamryChart Properties</b> window, so that you can adjust effects, colors, markers, 3-D effects, lines, etc.
44	3D/2D	Toggle between two-dimensional and three-dimensional graphing
4	Rotate	Rotate the three-dimensional graph. Only active if the graph is 3D.
	Z-clustered	Offset two data sets so that they can be distinguished within one plot. Only operates in 3D mode.
P	Zoom	Zoom in on a selected region. Also open a zoom slider at the bottom of the graph for continuous adjustment of zoom.
	Print preview	Open the <b>Page setup</b> window to adjust orientation of plot and printer margins
\$	Print	Print the plot
>	Tools	Open a dropdown menu, for choices of various toolbars and viewers to appear on the screen

# **Selection Toolbar Functions**

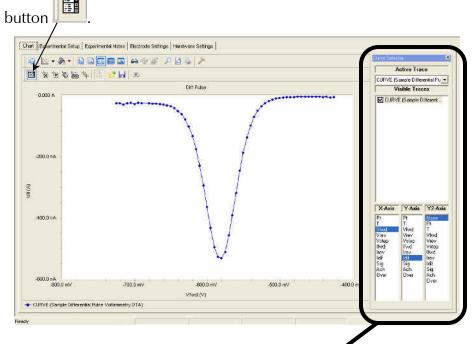
Button	Name	Action
	Show curve selector	Open the Curve Selector area to the right of the plot, so that you can choose which data are used as the <i>x</i> -, <i>y</i> -, or <i>y</i> 2-coordinate, and which curve is the active trace.
<b> </b>   <b>x</b>	Select x region	Select a desired region of the plot across the x-axis. Commonly used to specify a region for <i>Quick-Integrate</i> .
-l <b>y</b> i	Select y region	Select a desired region of the plot across the y-axis Commonly used to specify a region for <i>Quick-Integrate</i> .
Ø	Select Portion of Curve using the Mouse	Left-click on the active trace using the mouse to select a section of the curve
[ · ~ ·	Select Portion of Curve using the Keyboard	Open an area to the right of the plot, in which you can choose a segment of the trace numerically. See below for more details.
-k <sub>Sj-</sub>	Draw Freehand Line	Draw a line on the plot
A	Mark Found Peaks	Place a tag on peaks that the software finds. A portion of the curve must be selected first.
<b> </b>	Apply Template	Open the <b>Apply User-Defined Chart Template</b> window, and choose a previously created template to apply to the plot
	Save Template	Open the <b>Save User-Defined Chart Template</b> window, and save the template
0	Show Disabled Points	Show data points not being used in the plot

#### Changing the Axes on a Plot (the Curve Selector):

To choose a different variable plotted on an axis, use the *Curve Selector* button as follows:

(The example shown below is a Differential Pulse Voltammetry plot.)

1. With the plot open and displayed on the screen, click the Curve Selector



The *Curve Selector* area appears on the right side of the window.

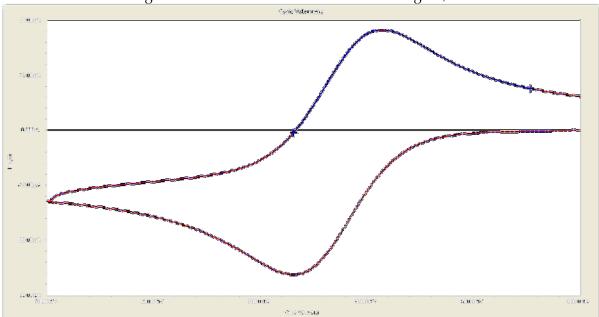
- 2. Choose which trace is active by clicking on the drop-down menu in the *Active Trace* area.
  - The Active Trace is the data series on which the analysis will be performed. Use this, for example, if multiple files or cycles are displayed on the graph.
- 3. Choose which trace is visible on the plot by activating the checkbox next to the desired trace(s) in the *Visible Traces* area.
  - Visible Traces also contain any data fits that are performed.
- 4. Choose which variable is plotted on the *x*-axis by highlighting the variable in the *X*-Axis column.
- 5. Choose which variable is plotted on the *y*-axis by highlighting the variable in the *Y-Axis* column.
- 6. Choose which variable is plotted on the second *y*-axis by highlighting the variable in the *Y2-Axis* column.

If there is a data column graphed on the Y2-Axis, those data appear in a different color and a different scale.

# **Selecting Portions of a Curve for Analysis**

For certain types of analysis, you must select a region of the curve, for example, within the *Peak Find* function in Cyclic Voltammetry or *Tafel Fit* function in Potentiodynamic. You can select regions by mouse or keyboard.

- 1. Left-click the mouse on the *Mouse* button in the *Selection toolbar*.
- 2. Use the left mouse-button to select each endpoint of the curve. Each endpoint is marked with a blue cross. The selected portion of the curve is shown as a thick blue line. (In the figure below, the color of the data has been changed to red for contrast to the selected region).



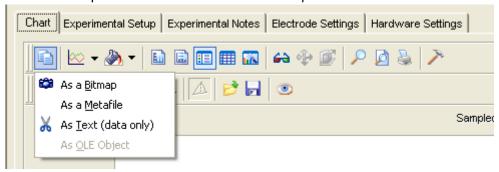
3. Another click on the *Mouse* button clears the selected region, and readies the graph for a different region to be selected.

#### **Cutting and Pasting Images and Data**

Many users want to present, publish, or otherwise share their data and charts from the Echem Analyst. To create a bitmap image of the graph,

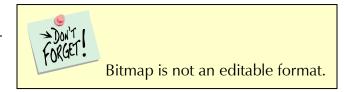
#### As a Bitmap:

- 1. Choose the Copy to Clipboard button from the General Toolbar.
- 2. In the drop-down menu select As a Bitmap.



3. A bitmap image of the graph enters the clipboard. This bitmap may be pasted into a presentation program such as Word® or Powerpoint®.

This is a quick and easy way to import a picture of the graph for a presentation or report.



#### As Text:

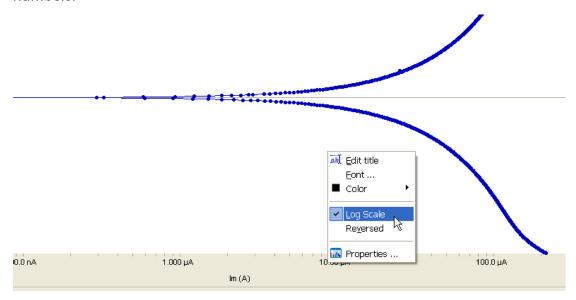
Because Gamry Data Files are ASCII text, they can be opened easily in other graphing programs, such as Excel® or Origin®. Right-click on the DTA file and select *Open With...* and select for favored program. These programs, however, do not contain fitting routines specific to the analysis of electrochemical data. This *As Text* feature lets you fit the data in Echem Analyst and then copy and paste the data and fit into another graphing program.

This is a quick and easy way to import both the data and the fit into another graphing program.

If you are using the *As Text* feature, be sure to note the currently graphed parameters. The coordinates of this currently displayed graph are copied and can be pasted to graphing programs.

#### **Plotting Conventions**

By right-clicking the mouse on a non-zero value on an axis, you can choose to show that axis in logarithmic or linear scale, or to reverse the direction of the numbers.



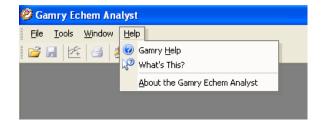
Alternatively, you can use the *Transform Axes* selection (if available) under the *Common Tools* menu.

Default plotting of graphs is auto-scale. Therefore, please note the y-axis's scale when a plot first appears. If bad data points obscure your data because of auto-scaling, you can choose to disable and hide those offending points.

## To Get On-Line Help:

In the toolbar, choose Help.

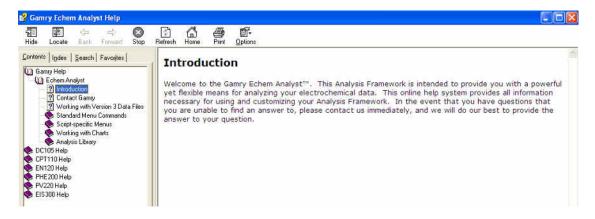
 a. Click Gamry Help to obtain information about various commands and functions within Echem Analyst.



A separate Gamry Echem Analyst Help

window appears. You can find much information about the details of Echem Analyst here, such as plotting and analysis.

On-line help is a great resource for more involved questions. Help is divided up according to software package.



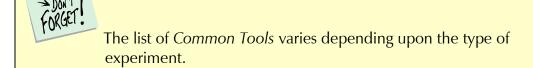
b. Click About the Gamry Echem Analyst to view the software version number.

# **Common Tools** and Tabs

While each type of experimental data has its own method and parameters, there are certain commands that are common to many analyses. This section shows you these *Common Tools*.

#### **Accessing Common Tools**

- Open a dataset.
   In the toolbar, the function Common Tools appears.
- 2. Choose 🥝 Gamry Echem Analyst - [Sample Chronoamperometry.DTA] Common File Tools Window <u>H</u>elp Chronoamperometry Common Tools Quick Help Tools. Add I Constant 1944 | 🗐 | 🏂 | A drop-Linear Fit down Chart | Second Chart | Experimental Setup | Experimental Smooth Data На menu appears.
- Select the desired command.
   In this example, chronoamperometry's Common Tools includes three commands, Add I Constant, Linear Fit, and Smooth Data.

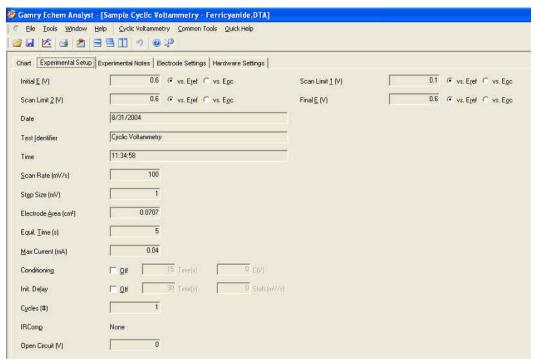


#### **List of Common Tools**

Command	Type of experiment	Result
Add E	Cyclic Voltammetry, DC Voltammetry,	Adds a constant
Constant	Differential Pulse Voltammetry, Galvanic Corrosion, Normal Pulse Voltammetry, Pitting Scan, Polarization Resistance, Potentiodynamic Scan, Square-Wave Voltammetry	potential to all voltages in the plot. Used to easily convert between different Reference Electrode's scales.
Add I Constant	Chronoamperometry, Chronopotentiometry, Cyclic Voltammetry, Galvanic Corrosion, Pitting Scan, Polarization Resistance, Potentiodynamic Scan	Adds a constant value to all currents in the plot.
C from CPE, omega(max)	Potentiostatic EIS, AC Voltammetry, Mott- Schottky	Calculates capacitance from previously fit CPE values and data

		from the Nyquist plot.
C from CPE, R(parallel)	Potentiostatic EIS, AC Voltammetry, Mott-Schottky	Calculates capacitance from previously fit CPE and fit R data.
Linear Fit	Chronoamperometry, Potentiostatic EIS, AC Voltammetry, Chronocoulometry, Chronopotentiometry, Cyclic Voltammetry, DC Voltammetry, Differential Pulse Voltammetry, EMF Trend, Galvanic Corrosion, Mott-Schottky, Normal Pulse Voltammetry, Polarization Resistance, Potentiodynamic Scan, Square-Wave Voltammetry	When a region of the plot is selected, fits the data to y = mx + b.
Post-Run iR Correction	Cyclic Voltammetry, Polarization Resistance, Potentiodynamic Scan	Corrects a previously run scan for voltagedrop caused by <i>iR</i> .
Smooth Data	Chronoamperometry, Chronopotentiometry, Cyclic Voltammetry, DC Voltammetry, Differential Pulse Voltammetry, EMF Trend, Galvanic Corrosion, Normal Pulse Voltammetry, Pitting Scan, Polarization Resistance, Potentiodynamic Scan, Square-Wave Voltammetry	Smoothes the data. Useful for locating peaks in regions of high data-density.
Transform Axes	Galvanic Corrosion, Pitting Scan, Polarization Resistance, Potentiodynamic Scan	Changes x- and y-axes from linear to logarithmic, etc.

#### **Experimental Setup**



This particular *Experimental Setup* tab is from a Cyclic Voltammetry experiment. This example has many of the same parameters as other experiments. It shows:

Initial E, Scan Limit 1, The potentials defining the waveform, and whether measured vs. a reference electrode ( $E_{ref}$ ) or the open circuit potential ( $E_{oc}$ ). Test Identifier Read from the Framework Setup. This field also becomes the

default title of the plot.

Time Time the experiment was started

Scan Rate How fast (in mV/s) the scan was taken

Step Size The interval between potentials

Electrode Area The size of the electrode

Equil. Time How much time was spent letting the electronics settle before

the scan was started

I/E Range Mode Automatically adjusted or fixed I/E (Current) Range mode.

Max Current The current value that sets the I/E Range in Fixed Mode and

determines the range in which to start in Auto Mode

Conditioning Whether off or on, for how long, and under what potential.

This Potential is vs. Reference.

Init. Delay Whether off or on. This is when the  $E_{\rm oc}$  is measured. Cycles Number of how many voltammetry cycles were run

IR Compensation was used and the mode.

Open Circuit The value of the Open circuit voltage (Corrosion Potential). It is

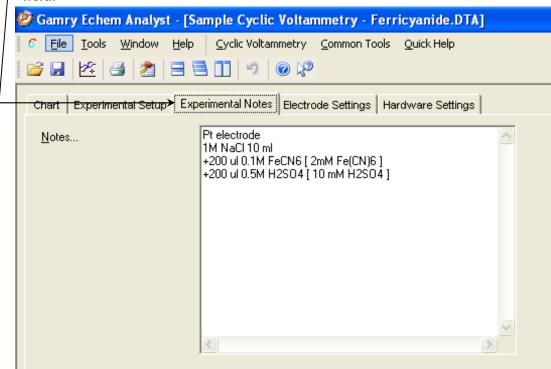
the value of the last point in the Initial Delay.

Sampling Mode Data-acquisition mode (for Reference Family Potentiostats)

#### **Experimental Notes**

Click the Experimental Notes tab:

Any notes entered in the Framework are automatically displayed here. You may enter any additional comments about the experiment in the *Notes*... field.



This is a version of a modern laboratory notebook. Enter as many details about your experiment as you can. Information here can help you avoid having long strings of descriptive file names.

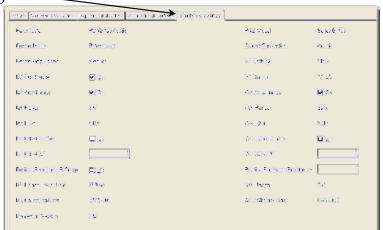
#### **Hardware Settings**

This section documents the hardware settings that were used when the experiment was run, e.g., everything from the offsets, filters, and gains to the last time the potentiostat was calibrated.

This information is used primarily by Gamry Technical Support staff to help troubleshoot. Gamry determines defaults for these settings based on experience. Advanced users can adjust these settings manually before the experiment is run.

For DC Corrosion experiments, the *Hardware Settings* are set in the experiment code. For Physical Electrochemistry experiments, users have access to these features through the *Advanced Panel*, but Gamry recommends that only advanced users make changes to these settings. Consult *Help* or Gamry Technical Support for advice.

Click the Hardware Settings tab: -



The hardware settings displayed here are:

Potentiostat Shows the potentiostat's label

Control Mode How the experiment was controlled
Control Amp Speed Shows the speed of the control amplifier

I/E AutoRange Shows if the I/E autorange function was enabled Shows if the  $I_{ch}$  autorange function was enabled Ich Range Shows the  $I_{ch}$  range (gain). 3 Volts = x1 Gain.

 $\begin{array}{lll} \hbox{Ich Filter} & \hbox{Shows the $I_{ch}$ cut-off filter frequency} \\ \hbox{Ich Offset Enable} & \hbox{Shows if $I_{ch}$ Offset was enabled} \\ \hbox{Ich Offset} & \hbox{Shows the $I_{ch}$ offset voltage} \\ \end{array}$ 

Positive Feedback IR Shows if the IR positive feedback was enabled

Comp

I/E Range Lower Limit Shows the lowest available I/E Range available to use in this

experiment

Ach select Shows the input connector for  $A_{ch}$ 

DC Calibration Date Shows the date of last DC calibration

Framework Version

Pstat Model Gives the model number of the potentiostat

Current Convention Shows which currents are positive I/E Stability Shows the I/E stability speed

I/E RangeShows the I/E (or current) range usedVch AutoRangeShows if  $V_{ch}$  autoranging is enabledVch RangeShows the maximum value for  $V_{ch}$ Vch FilterShows the  $V_{ch}$  cut-off filter frequencyVch Offset EnableShows if  $V_{ch}$  Offset was enabledVch OffsetShows the  $I_{ch}$  offset voltage

Positive Feedback Shows the positive feedback resistance applied to the system

Resistance

Ach Range Shows the voltage range of the auxiliary channel

Cable ID (for Reference Family Potentiostats only.) Gives the type of

cable connected to the system

AC Calibration Date Shows the date of last AC calibration

Instrument Version Shows the Firmware Version of a Reference Family Pstat

Detailed explanations of these parameters are beyond the scope of this guide.

# **Open Circuit Voltage (Corrosion Potential) Data**

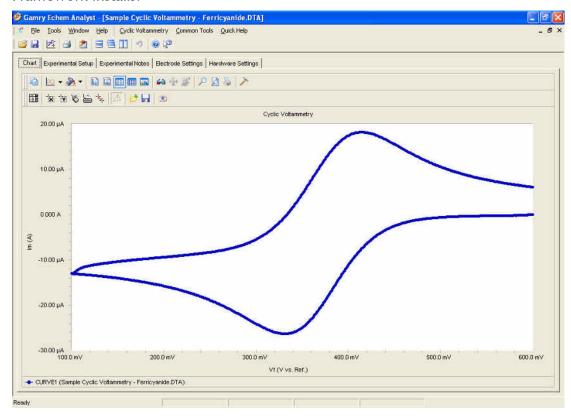
Click the Open Circuit Voltage tab: Gamry Echem Analyst [Sample Polarization Resistance.DTA] File Tools Window Help Polarization Resistance Chart | Experimental Setup | Experimental Notes | Open Circuit Voltage | Hardware Settings | 1 1x 1y 🗞 🔚 🦘 🔼 🥩 🔒 💿 Open Circuit Voltage 50,00 µV 0.000 V Vf(V vs. Ref.) -50.00 µ∨ -100.0 µV -150.0 µV 0.000 s 5.000 s 10.00 s 15.00 s T(s)

OCVCURVE (Sample Polarization Resistance DTA)

Because default plotting of graphs is auto-scale, please note the *y*-axis's scale when the *Open Circuit Voltage* first appears.

# **Analysis of Cyclic Voltammetry Data**

This is a sample cyclic voltammetry file that installs in \My Gamry Data\ when Framework installs.



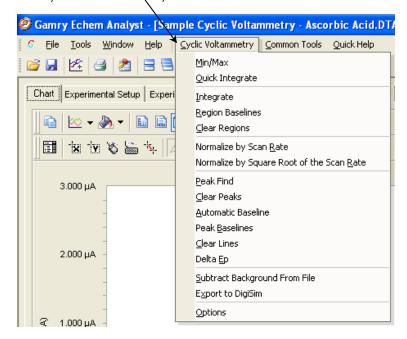
# **Cyclic Voltammetry Special Tools**

This menu analyzes the cyclic voltammetry data.

1. In the main menu, choose Cyclic Voltammetry.

A drop-down menu appears.

2. Choose the desired tool:



Tool	Function	Notes
Min/Max	Finds the minimum and maximum currents and voltages within the dataset. Results appear in a window below the plot.	
Quick Integrate	Integrates to find the total charge. Results appear in a window below the plot.	For multi-cycle CV experiments
Integrate	Integrates over a specified portion of the plot to find the total charge.	Portion of the curve must be selected
Region Baselines	Defines a line as the baseline for a specified region.	Region must be selected
Clear Regions	Clears all baselines from the dataset.	Region must be selected
Normalize by Scan Rate	Normalizes the dataset based on the scan rate.	
Normalize by Square Root of the Scan Rate	Normalizes the dataset based on the square-root of the scan rate.	
Peak Find	Finds peaks within a specified region of the dataset.	Portion of the curve must be selected
Clear Peaks	Clears all peaks found within the dataset.	Peaks must be identified
Automatic Baseline	Finds the baseline automatically.	Peaks must be identified
Peak Baselines	Defines a line as a baseline for a specified peak.	Peaks must be identified
Clear Lines	Clears all lines from the dataset.	Lines must be associated with graph
Delta Ep	Finds the potential difference between two peaks.	Peaks must be identified
Subtract	Subtracts a background amount from the	
Background from File	dataset.	
Export to DigiSim	Exports the file to a DigiSim <sup>®</sup> -compatible format.	
Options	Changes units and grids for plotting the data.	

# **Integrating the Voltammogram**

All integration methods integrate current versus time to get the total charge. There are two different ways to integrate under a curve with Echem Analyst.

#### **Quick Integrate**

Quick Integrate breaks the data into "curves". Each curve is integrated to a zero current. Quick Integrate integrates the entire area of each curve, unless an area is specified using the x-region icon.

#### Integrate

Integrate requires you first to select a portion of the curve. (See how to select a portion of the curve in the "Starting Echem Analyst" chapter.) After an integration is performed, you can change the baseline from the default 0 A to another line, either a line that you draw, or an *Automatic Baseline*.

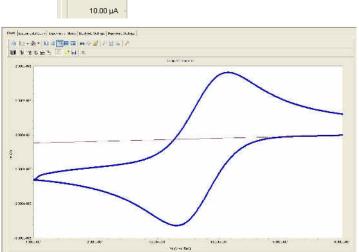
1. Open the data file.

2. Select the *Draw a Freehand Line* button: —

 Left-click and hold on the graph to place an anchor point.
 Holding down the mouse button, extend the line with the mouse.
 Move or extend the line as you wish.

Directions to accept the line are printed at the bottom of the window.

- Right-click the mouse on the line and either Accept or Delete.
   After you accept the line, it turns from dashed to solid.
- Select the portion of the curve to integrate.
   This function is described in detail earlier.



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File Tools Window Help Cyclic Voltammetry Common Tools Qu

Chart Experimental Setup | Experimental Notes | Electrode Settings | Hardware Settings |

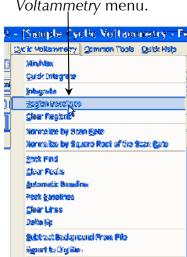
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Draw Freehand Line

6. Select *Integrate* from the *Cyclic Voltammetry* — menu.

This integrates the section between the curve and the zero amp line.

7. To change the baseline to the desired user-drawn line, select *Region Baselines* from the *Cyclic Voltammetry* menu.

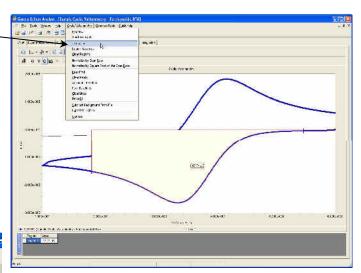


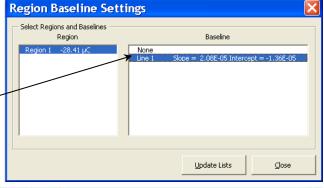
The **Region Baseline Settings** window appears.

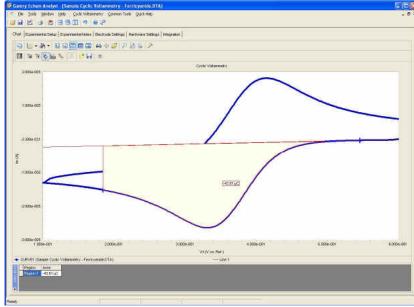
8. Select the Region Baseline from the available lines. You may draw multiple lines from which to choose.

Note that the integrated region moves from the default 0 Amps baseline to the userdrawn line.

<u> Ajablana</u>





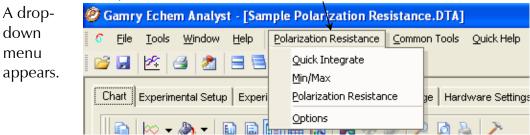


# **Modeling Polarization Resistance Data**

#### **Polarization Resistance Special Tools**

This menu analyzes the polarization resistance data.

1. In the main menu, choose Polarization Resistance.



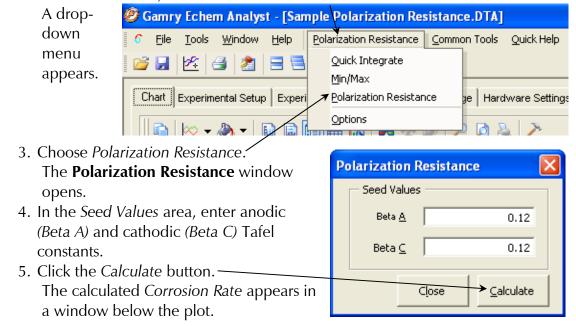
2. Choose the desired tool:

Tool	function
Quick Integrate	Integrates to find the total charge. Results appear in a window below the plot.
Min/Max	Finds the minimum and maximum currents and voltages within the dataset. Results appear in a window below the plot.
Polarization Resistance	Within a selected portion of the curve, finds the polarization resistance.
Options	Changes units and grids for plotting the data.

#### **Finding the Polarization Resistance**

#### Method 1: Manual Eentry of the Tafel Constants

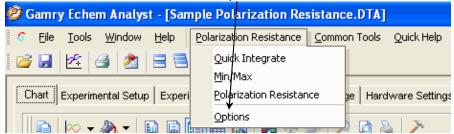
- 1. Select the desired portion of the curve. (See section....)
- 2. In the main menu, choose *Polarization Resistance*.



#### Method 2: Automatic Selection of Voltage Region

Gamry offers another way to select automatically the voltage region over which this analysis is done.

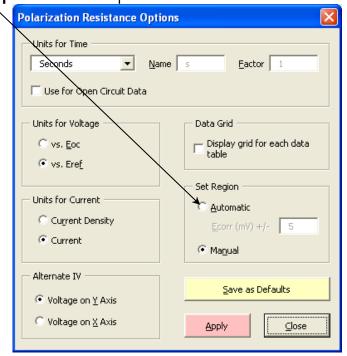
1. In the *Polarization Resistance* menu, choose *Options*.



The **Polarization Resistance Options** window opens.

2. Select this *Automatic* radio button, specify the region around Ecorr to use, and *Save as Defaults*. You are prompted directly for Tafel constants when a polarization resistance file is opened.

This is how Gamry's RpEc Trend experiments calculate corrosion rate.



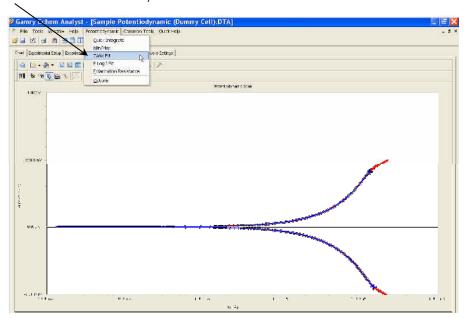
# **Modeling Potentiodynamic (Tafel) Data**

A Tafel experiment is also a very popular electrochemical corrosion technique. The following analysis is performed on the sample Potentiodynamic data file.

#### **Tafel Fit**

- 1. Select the region over which to perform the Tafel fit.

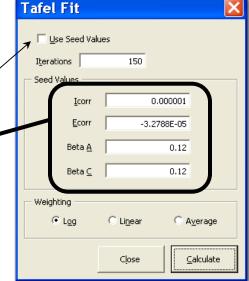
  This region must encompass the Ecorr (Open Circuit Potential).
- 2. Select Tafel Fit from the Potentiodyanmic menu:



3. A **Tafel Fit** window appears where you may input seed values optionally for the fit. The better the information we provide the fitting routine, the more likely it will be able to generate an acceptable fit.

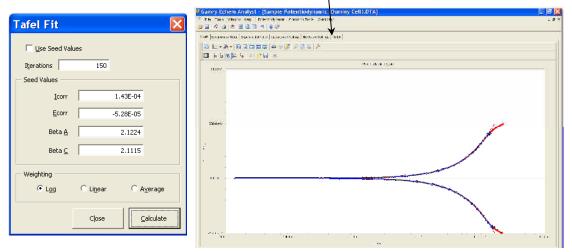
If you have reasonable starting parameters for the fit, input them in the Seed Values area, and check the Use Seed Values checkbox. If you do not have any confidence at all in your range of parameters, do not check the Use Seed Values checkbox.

We recommend using the seed values supplied by the Echem Analyst.



- 4. Click the *Calculate* button. When the *Calculate* button is pressed, the changes can be subtle. The
  - following events occur:
    The parameters in the **Tafel Fit** window become the fit parameters.

- A fit line is displayed on the graph.
- A new *Tafel* tab is created (to the right of the *Hardware Settings* tab) that holds the information about the fit.



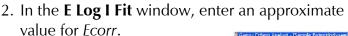
#### E Log I Fit

The *E Log I* fit is a useful fit if you want to fit the data one branch (anodic or cathodic) at a time. This can be important if one branch doesn't show linear behavior, but the other does.

The fit is called *E Log I* because of the semi-logarithmic nature of a Tafel plot. The x-axis is the logarithm of current, while the y-axis is potential on a linear scale.

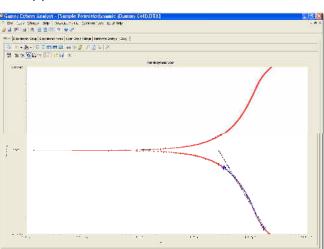
#### Method

Select a portion of the curve.
 Here you need only the linear section of one of the branches. This selection does not include Ecorr (Eoc (open circuit potential)).



3. Click the *Calculate* button. A single branch of the Tafel data is fit. The fit is shown on the graph, and the results of the fit are contained in a new *E Log I* tab.

You can run a Polarization Resistance fit on this Potentiodynamic data, if the axes of current are changed to the linear scale. Generally



E Log | Fit

Close

Ecorr |

-9.28802E-06 Volts

Calculate

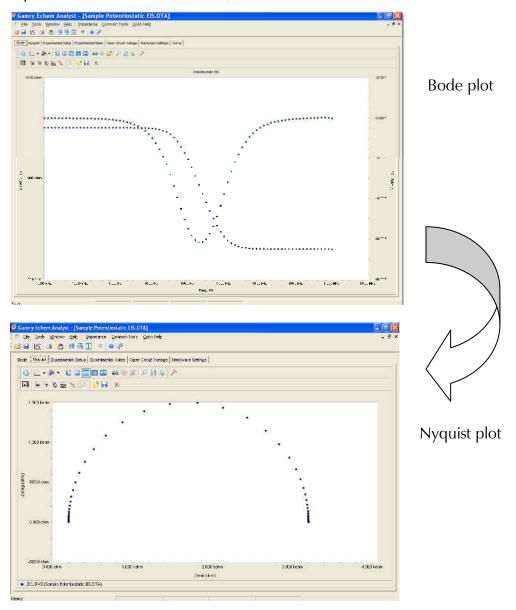
we suggest running a separate experiment on a new sample of the same material because of the more-polarizing, more-destructive nature of the Potentiodynamic experiment.

# **Modeling EIS Data**

The data-analysis features shown here are common to many of the AC-based techniques. By far the most popular type of AC experiment is Potentiostatic EIS.

# **Bode and Nyquist Plot View**

Click the *Bode* tab or the *Nyquist* tab of the plot you prefer to work with. All fits are displayed on both the Bode and Nyquist plots. Because they are different representations of the same data, the fit results are identical.



#### **EIS Special Tools**

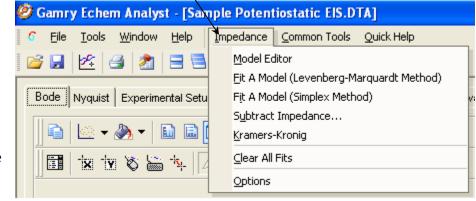
EIS data-analysis uses an equivalent-circuit approach. This menu creates and runs fits for EIS data. Commands in this menu allow you to build an equivalent-circuit model in the *Model Editor*, then fit that model to your data. This menu also lets you run advanced procedures, such as *Subtract Impedance*, and run Kramers-Kronig transforms.

1. In the main menu, choose *Impedance*. A drop-down menu appears.

2. To create or edit an equivalent circuit, choose Model Editor. The Impedance

Model

**Editor** 



window appears. See the next page for how to use it.

3. To fit the data using the Levenberg-Marquardt method, choose *Fit A Model* (Levenberg-Marquardt Method).

The **Select Model File** window opens.

Choose the appropriate model file, and click the OK button.

4. To fit the data using the Simplex method, choose Fit A Model (Simplex Method).

Simplex method weighs the user's seed values less. We recommend using the Simplex method.

5. To subtract an impedance from the data, choose Subtract Impedance....

The **Impedance Subtraction** window appears.

Choose:

Element Choose a circuit element from the drop-down menu.

Model Browse for a previously defined model.

Spectrum Browse for a data-set.

Click the Close button.

6. To use the Kramers-Kronig method,

Choose Kramers-Kronig.

Kramers-Kronig is a model-independent transform that checks the EIS data for consistency.

The **Kramers-Kronig** window appears.

7. To clear all fits from the plot,

Choose Clear All Fits.

8. To change time or impedance units,

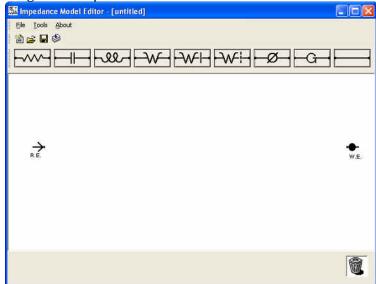
Choose Options.

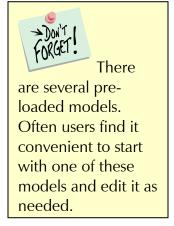
This option let you normalize the data and fits to the normalized area.

#### The Model Editor

The Impedance Model Editor allows you to create an equivalent circuit, via a

drag-and-drop method.





#### **Circuit Elements**

Symbol	Element	Comments
	Resistor	Abbreviated as R. $Z = R$
$-\parallel$	Capacitor	Abbreviated as C. $Z = -i/\omega C$
-بالك-	Inductor	Abbreviated as L. $Z = iL\omega$
$-\alpha$	Constant	Models an inhomogeneous property of the system, or a
_~	Phase	property with a distribution of values. Often abbreviated as
	Element	CPE.
	Wire	Connects one element to the next.
$-$ C $\rightarrow$	Gerischer	Models a reaction in the surrounding solution that happened
<u> </u>	element	already; also used for modeling a porous electrode. Often abbreviated as G.
$\rightarrow \wedge \leftarrow$	Infinite	Models a linear diffusion to an infinite planar electrode.
• • • • • • • • • • • • • • • • • • • •	Warburg	Often abbreviated as W.
$\rightarrow \lambda \neq \vdash$	Bounded	Models diffusion within a thin layer of electrolyte, such as
V V 1	Warburg	electrolyte trapped between a flat electrode and a glass microscope slide. Often abbreviated as T.
$-\lambda \wedge F$	Porous	Models diffusion through a thin layer of electrolyte, such as
V V 1	Bounded	electrolyte trapped between an electrode and a permeable
	Warburg	membrane covering it. Often abbreviated as O.

#### Building an Equivalent Circuit

#### 1. Adding an element

a. Click on an element symbol.

The element appears in the central window.

b. Place the mouse cursor over the element. Left-click and drag to move the element to its desired position.

#### 2. Connecting elements

- a. Click on the Wire symbol
- b. Left-click one end of the wire and drag the end to the element.

The element's border turns green when the wire's end reaches the element.

#### 3. Deleting an element

a. Right-click on the element.

The Delete command Pelete appears.

b. Left-click on the *Delete* command.

The element vanishes.

Here is an example of a simple equivalent circuit (a Randles model) constructed

in the **Impedance** 

#### **Model Editor:**

4. Relabeling and fixing parameters for an element

This lets you rename the element, and specify a Lower and Upper Limit for its value. Renaming the element helps you distinguish between elements of the same type during fitting. Giving the

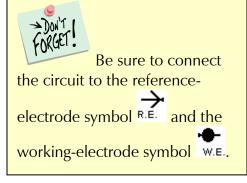
program limits on the parameters may help the mathematical algorithm. For example, we know values are generally positive, so a Lower Limit = 0 is reasonable to set.

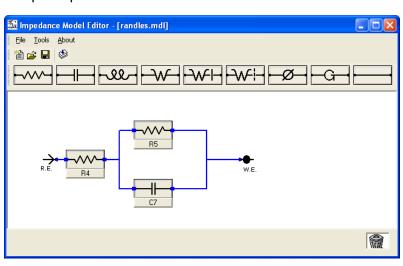
a. Left-click on the name of the element (here, R4).

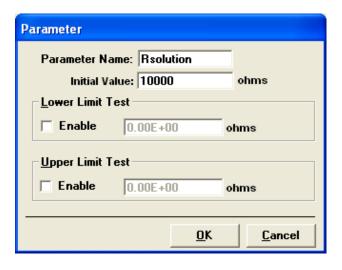
The **Parameter** window appears.

- b. Enter a new Parameter Name.
- c. Enter an *Initial Value*, i.e., the first trial value for fitting.
- d. In the Lower Limit Test and Upper Limit Test fields, enter lower and upper limits, and check the Enable checkbox, as desired.
- e. Click the OK button.

The **Parameter** window closes, and the element is set to these parameters.







#### Compiling the Equivalent Circuit

When the equivalent circuit is complete, the circuit can be compiled before use to check for connectivity of the wires. Compiling is only used to check connections

1. In the toolbar, choose Tools. 🌃 Impedance Model Edit A drop-down menu appears. Eile Tools About F5 2. Choose Compile or click the Test Compile button in the toolbar. Compile Error The software compiles the equivalent Wiring Error One or more components has missing wires, If there is a problem, such as a missing OK connection, an error message appears,

3. Click the OK button to continue.

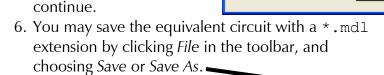
and a red box outlines the problem

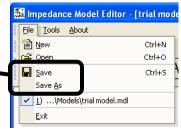
4. Inspect the schematic and make necessary corrections.

If the equivalent circuit compiles properly, the **Model Editor** window appears:

element:





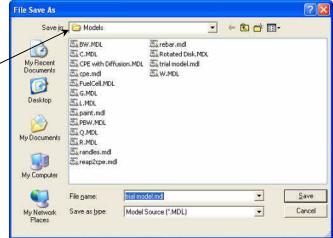


7. The **File Save As** window appears.

The default folder for saving model equivalent circuits is the Models folder.

8. Name and save the file here, or choose a different folder. The model shown above was saved as trial model.mdl.

The **File Save As** window closes.



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#### Fitting the Data to the Equivalent-Circuit Model

 With the data open and plotted, click Impedance, and choose Fit A Model (Simplex — Method).

The **Select Model File** window appears.

2. Choose the desired model.

The default folder for models is the *Models* folder. This *Models* folder is in the

<u>File Tools Window Help</u>

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Bode Nyquist Experimental Setu

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Gamry Echem Analyst - [Sample Potentiostatic EIS.DTA]

Impedance Common Tools Quick Help

Fit A Model (Simplex Method)

Subtract Impedance...

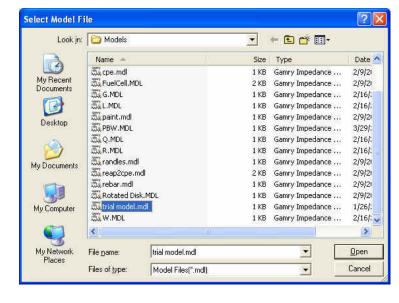
Kramers-Kronig Clear All Fits

Options

Fit A Model (Levenberg-Marquardt Method)

Model Editor

C:\Documents and Settings\All Users\Application Data\Gamry Instruments\Echem Analyst\Models by default. As our example, we choose the model trial model.mdl created previously.



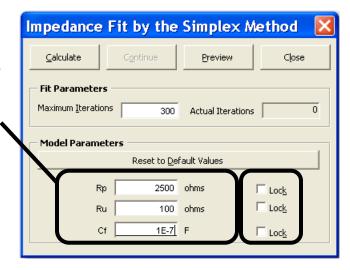
3. Click the *Open* button.

The **Select Model File** window closes, and the **Impedance Fit by the Simplex Method** window appears.

4. Set parameters.

Choose the maximum number of *Iterations* to loop before stopping the fit. Enter estimates for all the circuit elements in the *Model Parameters* area. Fix particular elements by enabling their *Lock* checkboxes.

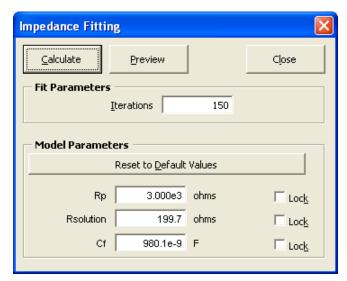
In our example, we try 100  $\Omega$  for Ru, 2500  $\Omega$  for Rp, and 100 nF for Cf and leave all of them free (unlocked).



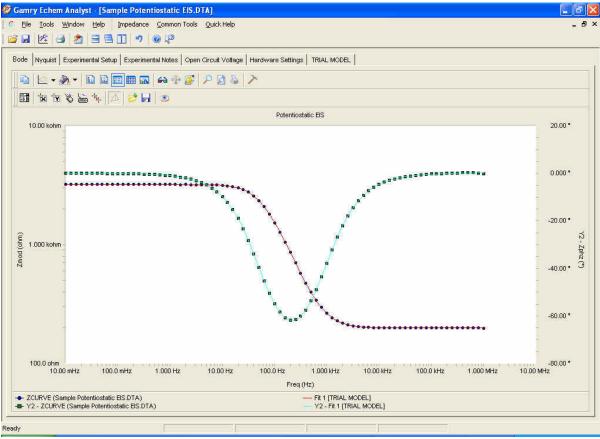
5. Click the *Calculate* button to start the fit.

The software attempts to fit the model to the data. When finished, the fitted parameters appear next to each circuit element.

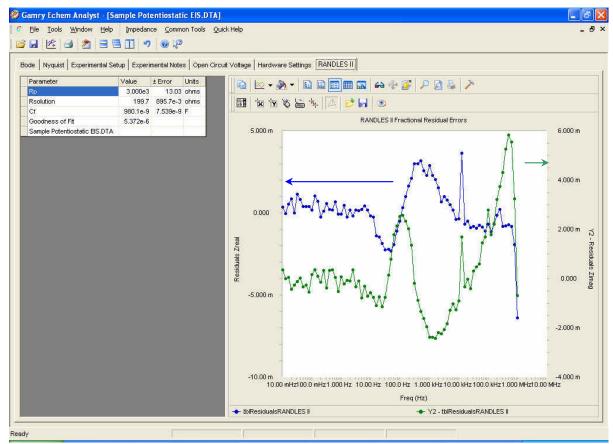
Our model results give  $Rp = 3 k\Omega$ Rsolution = 199.7  $\Omega$ Cf = 980 nF



Like other Echem Analyst fits, the fit also appears superimposed upon the data and a new tab is created that contains those results.



If you try another fit using the same model, this fit will be overwritten. If you fit to another model, the fit results of both models will be displayed.



This new tab shows the residual errors and goodness of fit, along with the various plotting tools. Residuals are a point-by-point *Goodness of Fit*, which quantifies how closely the data match the fit. A smaller number indicates a better fit.

The blue data (Zreal) correspond to the y1-axis (on the left); the green data (Zimag) correspond to the y2-axis (on the right).

# **Headings in Data-File Columns**

#### DC Data Files

**Abbreviation Meaning**Pt Point number

T Time

Vm, Vf Measured voltage Im Measured current

Vu Uncompensated voltage

Sig Signal from the signal generator

Ach Auxiliary channel

IE Range I/E (Current Measurement) range on which measurement was

nade

Over Any overloads. Numeric record of different overload types

0 No overloads

#### EIS Data Files

AbbreviationMeaningFreqFrequency

Zreal, Zimag, Zmod, Zphz Calculated values of impedance

Idc, Vdc DC component of current and voltage,

Yreal, Yimag Admittance (calculated from Z)

# Current Conventions According to Framework™ and Echem Analyst

The current convention in the Framework for all experimental packages is that an anodic/oxidation current is positive.

To change the current convention (whether anodic/oxidation currents or cathodic/reduction currents are positive), in the menu <code>Tools\Options\Units</code> tab, specify the current you want represented as positive. The current convention can be changed by editing the experimental script (contact Gamry or your Gamry representative if you need to do this). Regardless of the current convention used in the Framework, it can be changed in the Echem Analyst to the one you desire by the user (see below for exceptions).



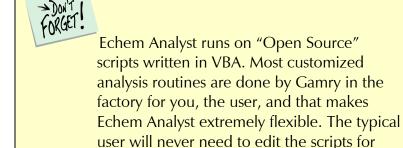
The current convention affects all experiments run under the PHE200 Physical Electrochemistry and PV220 Pulse Voltammetry heading. No other data files are affected.

To change the current convention in the Echem Analyst, in the menu *Tools/Options/Units* tab specify the current you want represented as positive.

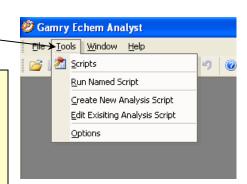
To change the current convention in other experimental packages (DC105, EIS300 etc) please contact Gamry or your Gamry representative.

## **To Edit Visual Basic Scripts:**

1. In the toolbar, choose *Tools*. A dropdown menu appears.



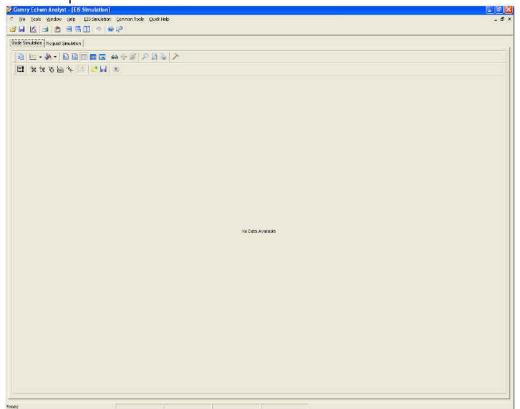
electrochemical analysis.



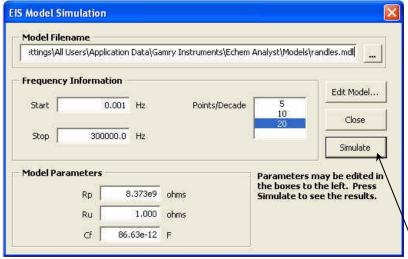
### Simulating an EIS Curve

It is often useful to simulate the response of an equivalent circuit.

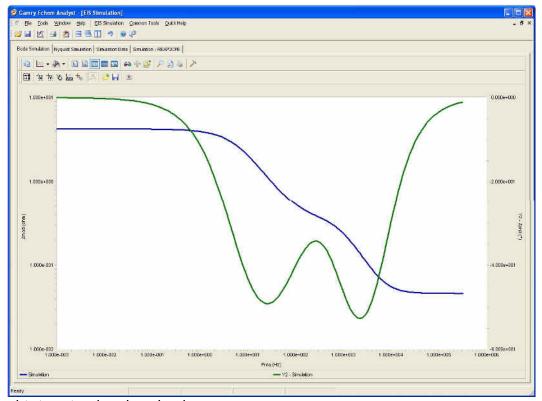
- 1. Launch the Echem Analyst.
- 2. Select *Tools/Run Named Script/s*elect *EIS Model Simulation Script*. Gscript. This opens a blank chart.



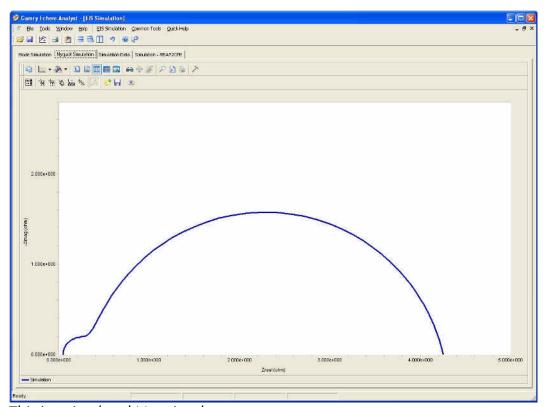
3. Select *EIS Simulation/Simulate* (use the *Model Editor* to build or edit the model). The **EIS Model Simulation** window appears.



- 4. Select the saved model, and input parameters for the experiment (frequencies and data-point density) and values of all circuit elements.
- 5. Click the *Simulate* button. The simulation appears under new tabs.



This is a simulated Bode plot.



This is a simulated Nyquist plot.

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