

## ***Electrochemical Impedance Spectroscopy Software***

Electrochemical impedance spectroscopy (EIS) is a powerful electrochemical technique that has enjoyed wide acceptance in the modern electrochemical laboratory. EIS is routinely employed in battery development, sensor evaluation, fuel cell characterization, corrosion science, and paint testing.

The Electrochemical Impedance Spectroscopy Software from Gamry is an exceptional value in EIS with unsurpassed performance and versatility. Use the EIS ~~Software~~ to measure the impedance between 10  $\mu$ Hz and 1 MHz. With four research Potentiostats and three modes of EIS measurement, a Gamry EIS system can reliably measure impedances as low as 1 m $\Omega$  or as high as 10<sup>13</sup>  $\Omega$ !

The EIS experiment places some critical demands upon potentiostat performance. Gamry understands sometimes-subtle potentiostat behavior and how it is affected by the sample. More than anyone, Gamry designs potentiostats for EIS – *every* Gamry Potentiostat leaves the factory ready to perform EIS!

In 1995, Gamry pioneered a novel single-sine EIS technique called Sub-Harmonic Sampling. Every Gamry Potentiostat includes the electronics for Sub-Harmonic Sampling, so there's no need to purchase any additional instrumentation. When the EIS software is installed, the Potentiostat is ready to record impedance spectra.

A Gamry EIS System with Sub-Harmonic Sampling has several benefits:

- Accuracy and precision are equal to or better than other EIS techniques.
- The instrumental footprint is small, saving bench space.
- The instrumental configuration is simplified -- no tangled web of BNC cables connecting several instruments.
- Your ability to tailor the Gamry EIS System to your specific sample is not compromised.
- Lower cost than alternative techniques.

If a special application arises, Gamry's **Open Source Scripting** allows you to make software changes to perform your custom experiment -- either in the data acquisition or the data analysis! If you like, Gamry can modify the software under your direction.



*The Electrochemical Impedance Spectroscopy System packs a powerful punch in a pristine package! The clean, space-saving design liberates bench space in your lab.*

You can also use the **Sequence Wizard** with the EIS Software to combine an EIS measurement with other electrochemical techniques to form a single experiment.

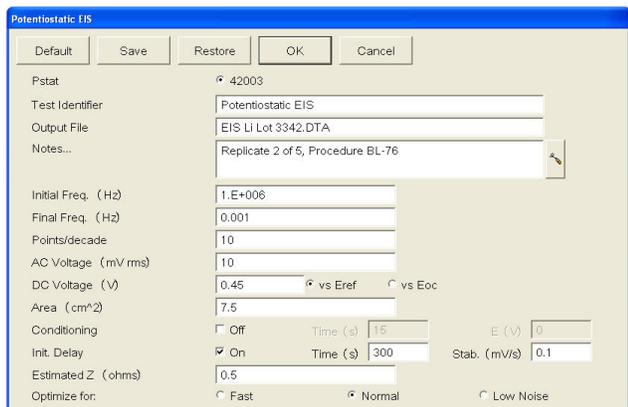
A Gamry EIS System can be configured in a desktop or in a notebook computer for experiments in the field or for convenient transport to other locations. All Gamry Potentiostats are electrically floating, so you can perform experiments on grounded samples.

This Software performs the following electrochemical impedance spectroscopy techniques:

- Potentiostatic EIS
- Multiplexed Potentiostatic EIS
- Galvanostatic EIS
- Hybrid EIS
- Single Frequency EIS
- Mott Schottky

### ***Potentiostatic EIS***

Potentiostatic EIS measures the impedance by applying a sinusoidal voltage to the sample and measuring the current. A DC voltage of  $\pm 8$  volts and an AC voltage of 3600 mV rms may be applied to the sample. Measure up to 1000 points/decade and collect up to 262,143 data points! Potentiostatic EIS is the most popular EIS technique and is favored by corrosion scientists and sensor developers.



**Setup Window for Potentiostatic EIS.** Every parameter required to make the EIS measurement is available on the single Setup Window.

### **Multiplexed Potentiostatic EIS**

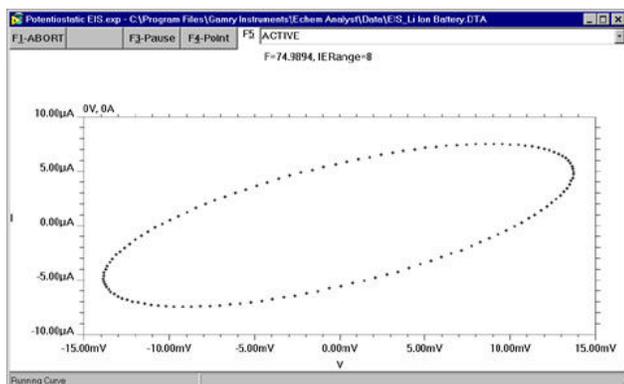
Multiplexed Potentiostat EIS is used with the ECM8 Multiplexer to automate the measurement on as many as eight samples. The ECM8 is an excellent tool to move more samples through your laboratory and is commonly used in paint testing and corrosion inhibitor testing programs.

### **Galvanostatic EIS**

Galvanostatic EIS involves the application of an AC current and measurement of the potential. Galvanostatic EIS is commonly used in battery and fuel cell studies. It is also often recommended for corrosion samples with an unstable open-circuit potential.

### **Hybrid EIS**

Galvanostatic EIS is a perfectly valid technique for EIS, but it must be used carefully to obtain valid results. It is possible for the sample to encounter voltage levels during Galvanostatic EIS that threaten the integrity of the experiment. For example, a sample impedance of  $1 \Omega$  at 100 kHz will result in a voltage of 10 mV with a 10 mA excitation. If the impedance increases to  $100 \Omega$  at 100 Hz, however, the 10 mA excitation will produce a voltage of 1000 mV, almost certainly outside the linear range and possibly even damaging to the sample.



**A Lissajous Figure Displayed During Data Acquisition** provides a snapshot of the data quality and potentiostat performance.

Hybrid EIS<sup>1</sup> is a modified form of Galvanostatic EIS in which the applied AC current is continually adjusted to optimize the value of the measured potential. In the Setup for Hybrid EIS, the user specifies the desired AC Voltage and the estimated impedance of the sample. Based on these values, the EIS Software calculates and applies an AC current at the Initial Frequency. The actual AC voltage is measured and the AC current is adjusted to bring the measured voltage into agreement with the desired AC Voltage.

The impedance at all other frequencies is performed by adjusting the applied AC current throughout the frequency range to obtain the desired AC Voltage as the impedance of the sample changes. In this manner, the amplitude of the AC current is continually regulated so that the AC voltage does not extend beyond the linear, non-destructive range.

<sup>1</sup> Orazem *et al*, *Electrochimica Acta*, 41, 977 (1996).

A galvanostatic EIS measurement provides higher accuracy and precision than potentiostatic EIS on low impedance samples such as batteries and fuel cells. This is because the potential can be measured (galvanostatic) with higher accuracy than it can be controlled (potentiostatic).

### **Single Frequency EIS**

Single Frequency EIS measures the impedance at a fixed frequency versus time. The user controls the experiment with a Repeat Time and a Total Time. Single Frequency EIS can be used for sensor evaluation, process monitoring, or to evaluate slow time-dependent changes in a sample.

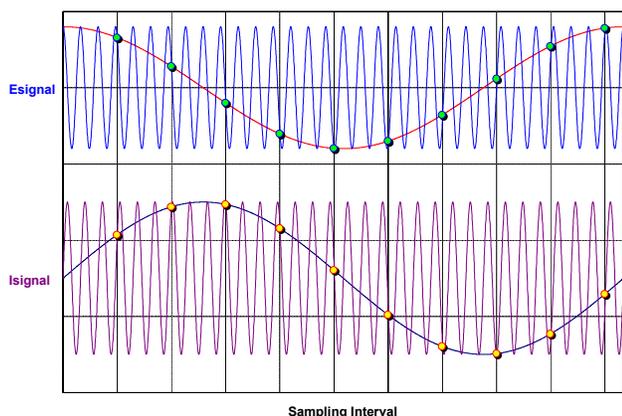
### **Mott Schottky EIS**

In Mott Schottky EIS, the impedance is measured at a fixed frequency as a function of applied DC potential. It is used most often in the studies of semiconductor interfaces or space charge regions.

### **Sub-Harmonic Sampling**

The AC waveform for EIS is generated using Direct Digital Synthesis (DDS). The DDS electronic circuitry is built into every Gamry Potentiostat. DDS employs digital signal processing techniques to generate a low-distortion, true sine wave excitation at the desired frequency (1 MHz – 1 Hz). Gamry's unique circuit design insures that the excitation waveform from the DDS is precisely synchronized with the Potentiostat's data acquisition.

Sub-Harmonic Sampling transforms high frequency AC waveforms to lower frequency waveforms. The Potentiostat's Analog/Digital Converter samples the excitation and response (voltage and current) waveforms at many points on different cycles of the waveform. The exact sampling position on the waveform is precisely controlled because the data acquisition frequency is an exact sub-harmonic (fractional harmonic) of the excitation waveform.



**Sub-Harmonic Sampling** transforms the high-frequency voltage and current signals to a lower frequency while maintaining the amplitude and the phase relationship.

The result is a sine wave of lower frequency but with the same amplitude as the original current or voltage waveform. The relative phase shift between voltage and current is also preserved in these lower frequency curves because current and voltage are synchronously sampled. After the current and voltage curves have been sampled, they are each transformed into the frequency domain using a discrete Fourier Transform. The impedance is calculated from the voltage and current signals.

The AC waveform for frequencies less than 1 Hz are generated using the D/A converter in the Gamry Potentiostat. The voltage and current are measured directly by the A/D Converters.

### Other Technical Details

The precision of a dynamic electrochemical measurement such as EIS is an important issue. Unlike other instruments where the user can only control the number of cycles, the Gamry EIS **CEKUFY** performs a statistical analysis of the data at each frequency during acquisition. The data is accepted only after the precision criteria are met. The precision criteria can be adjusted by the user.

An electrochemical system is a dynamic sample and it can be important to make the measurement quickly. The EIS **CEKUFY** user has a choice of optimizing speed or accuracy during acquisition. When Fast is selected, the precision criteria are relaxed, a minimum number of cycles are applied, and a minimum amount of information is displayed during the experiment. For Low Noise, the precision is enhanced and more cycles are allowed. If your system is stationary, operating in Low Noise can significantly improve the quality of your data. The measurement time for a Potentiostatic EIS measurement on the Gamry Universal Dummy Cell from 100 kHz to 0.1 Hz with 6 points per decade is only 54 seconds in Fast mode. The EIS scan is completed in 116 sec in Normal mode and 217 seconds in Low Noise mode.

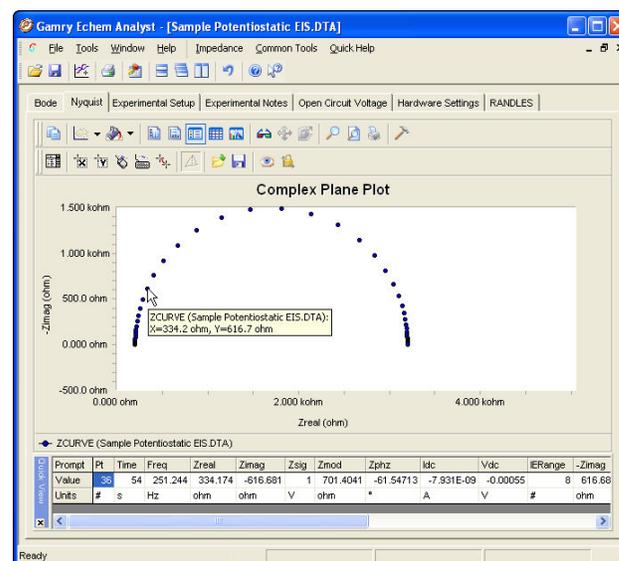
The accuracy of the EIS measurement is very, very dependent upon the Potentiostat, but also on the

impedance of the sample and frequency. The Accuracy Contour Plot details the accuracy of a potentiostat as a function of impedance and frequency and is available for all Gamry Potentiostats (see [www.gamry.com](http://www.gamry.com)). Every potentiostat is less accurate at high frequencies than at low frequencies, particularly at the extremes of impedance.

For corrosion, EIS is usually measured at open-circuit where the DC current is zero. For batteries and fuel cells, the EIS response is typically made under conditions of high background current. In this case, the EIS Software System offsets these DC levels to zero so that the AC values can be measured at a high gain for maximum accuracy.

### Data Presentation and Analysis

Presentation and analysis of your EIS data is done in the Echem Analyst. Bode and Nyquist Plots are standard and a wide range of other plotting formats are available through the Curve Selector. Multiple EIS curves can be easily overlaid. Place the cursor over a data point and detailed information (frequency, Zreal, Zimag, etc.) is displayed, particularly useful for Nyquist Plots.



**A Nyquist Plot in the Echem Analyst.** Notice the detailed information on the selected data point.

Convenient tabs are available to quickly display the Experimental Setup and Experimental Notes. Notes can be entered during setup for a detailed description of your sample. The data for Open Circuit Voltage vs. Time, measured prior to the EIS curve, is always saved and is available from a tab. The Hardware Settings tab contains detailed information on the Potentiostat during the EIS experiment.

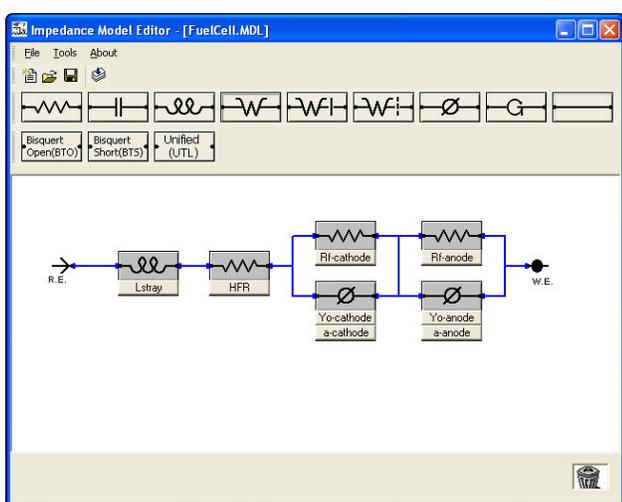
The quality of EIS data can be evaluated with the Kramers-Kronig Transform in the Echem Analyst. If the system's EIS response is not K-K compliant, then the system is not linear, causal, or stable and the EIS data will not model well.

## Modeling the EIS Results

The EIS300 includes a complete modeling package for interpretation of the results. Use the various pre-configured models or build and save your own model using the graphical Model Editor. The following elements are included in the EIS **CeZkUfY**:

- Resistor
- Constant Phase Element
- Infinite Warburg
- Porous Bounded Warburg
- Transmission Line (Open)
- Transmission Line (Short)
- Capacitor
- Inductor
- Bounded Warburg
- Gerischer
- Unified Transmission Line

The EIS **CeZkUfY** also allows you to implement your own circuit element. All you need are the equations defining the frequency response of your circuit element. See the App Note section of our website for details.



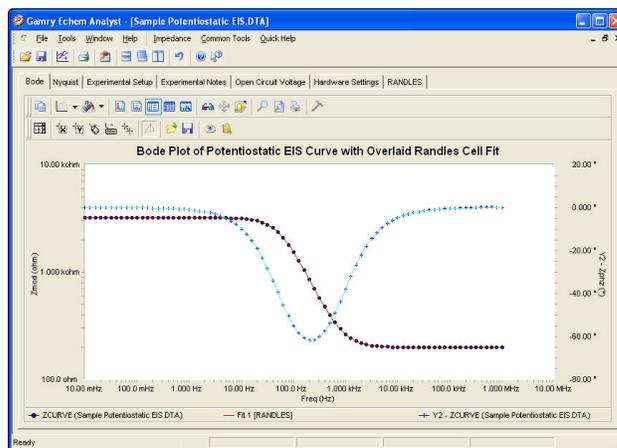
*The EIS300 Model Editor employs an easy-to-use click-and-drag mechanism to build an equivalent circuit. Build it once and save it.*

The equivalent circuit is fit to the data using a Marquardt-Levenberg or Simplex algorithm. The EIS **CeZkUfY** overlays the fit onto the data and generates a goodness-of-fit coefficient that approximates the relative error. If you wish, you can model a portion of the EIS curve and undesirable data points can be excluded from the fit. The data with the fit can be saved in the Echem Analyst.

If you prefer, you can use other commercial EIS modeling programs. The EIS data can be easily imported into other EIS data analysis software such as Equivalent Circuit, Zview 2, or ZsimpWin.

## Applications Assistance

If you're new to EIS, we can help. Pay a visit to [www.gamry.com](http://www.gamry.com), go to the App Note section, and take a look at the "Basics of EIS". There's an excellent list of references at the end of the Application Note. For specific questions, call us at our factory or your local Gamry sales office.



*A Bode Plot of a Randles Cell with the fit overlaid on the data. Click the "Randles" tab to view the values of the elements in the equivalent circuit and the Goodness of Fit coefficient.*

## System Information

The Electrochemical Impedance Spectroscopy Software requires a Gamry Potentiostat to conduct experiments. Gamry Potentiostats are described in a separate brochure.

Microsoft Windows 7™, Vista, or XP is required for operation of the EIS **CeZkUfY**.

Like most Gamry software, the EIS **CeZkUfY** and a Gamry Potentiostat use the Gamry Framework™ for data acquisition and the Echem Analyst™ for data analysis. The general features of the Gamry Framework and the Gamry Echem Analyst are described in a separate brochure entitled "An Overview of Gamry Software".

Gamry has an instrument for virtually every technique in the electrochemical laboratory. Other Gamry software includes DC Corrosion Techniques, Cyclic Voltammetry, Pulse Voltammetry, Electrochemical Noise, and Critical Pitting Temperature. Measure the impedance of a fuel cell with the FC350 Fuel Cell Monitor. You can be confident that your Gamry system can adapt as your electrochemical needs expand.

Gamry Instruments can supply complete systems installed in a desktop or notebook computer. Custom computer configurations, software, training, and installation are available by special order. Contact the factory or your local Gamry Distributor for further details on these systems

## Specifications

See Potentiostat specifications for additional information.

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