GAMRY INSTRUMENTS

Redefining Electrochemical Measurement

Physical Electrochemistry Software

The Physical Electrochemistry Software is used with a Gamry Potentiostat to perform in-depth studies of the structure of the electrode interface and the mechanisms of electrochemical reactions. The software brings Cyclic Voltammetry and other recognized electrochemical research techniques to the Gamry user. The Physical Electrochemistry Software is a useful tool for fundamental studies, sensor development, small-scale energy storage devices, electrophysiology, etc.

This software incorporates the following electrochemical techniques:

- Cyclic Voltammetry
- Linear Sweep Voltammetry
- Chronoamperometry
- Repeating Chronoamperometry
- Multiple-Step Chronoamperometry
- Chronopotentiometry
- Repeating Chronopotentiometry
- Chronocoulometry
- Controlled Potential Coulometry

Like most Gamry software, the D\ngJW 9YWfcWWa]gfm CcZlkUfY and a Gamry Potentiostat use the Framework™ for data acquisition and the Echem Analyst™ for data analysis. Gamry electrochemical techniques, therefore, have a common look-and-feel. Moving from one technique to another is easy. The general features of the Gamry Framework and the Gamry Echem Analyst are described in a separate brochure.

If your test methods are more complex than single experiments, you will appreciate the flexibility of the Gamry **Sequence Wizard**. The Sequence Wizard gives an intuitive drag-and-drop interface for combining these experiments with those in other Gamry software packages to tailor your testing protocol. Details on the Sequence Wizard are in the Overview of Gamry Software and on the Gamry website.

Cyclic Voltammetry

Cyclic Voltammetry is among the world's most commonly used techniques for studying electrochemical systems. The potential limits are defined with the Initial E, Scan Limit 1, Scan Limit 2, and Final E. For both a single cycle or a multiple cycle CV, the scan proceeds from one potential to the limit. You can define the potentials as absolute voltages or by their relationship to the Open-Circuit Potential.

The scan rate (mV/s) is determined by the interval between data points (sample period) and the Step Size (mV):

$$Scan\ Rate\,(mV/s) = \frac{Step\ Size\ (mV)}{Sample\ Period\ (s)}$$

The minimum sample period may be as low as 3.3 μs. The maximum Scan Rate is a function of Step Size. For example, the maximum Scan Rate with a 2 mV step is 600 V/s. Higher steps provide faster scan rates, but at the expense of resolution. Step Sizes greater than 10 mV are likely to result in unsatisfactory data.

The D\ngJW 9YWfcWWa]gfm CcZlkUfY can save, *and display*, up to 262,143 data points! The number of CV cycles that can be displayed is dependent upon the scan parameters.

$$No.\,of\ Cycles = 262,143 \times \frac{Step\ Size\ (mV)}{Voltage\ Span\ of\ the\ CV\,(mV)}$$
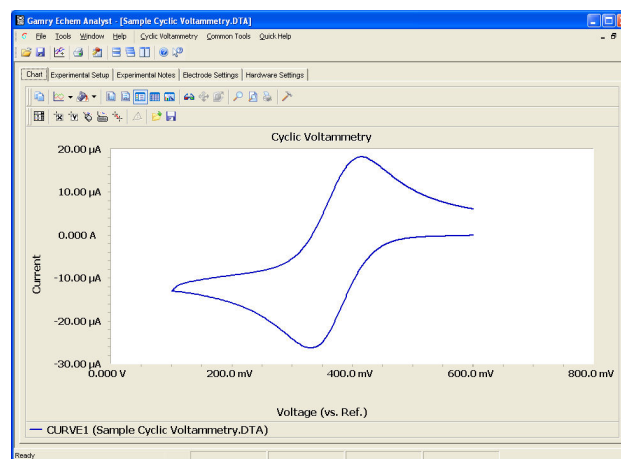

Typical Cyclic Voltammogram in the D\ngJW 9YWfcWWa]gfm CcZlkUfY" *You can easily change virtually anything in the display – color, line width, the title, tic marks, add markers, or add annotation.*

Scan rates higher than about 2000 V/s may be performed with a low-cost Function Generator and an oscilloscope. The signal from the Function Generator is applied to the External Signal Input of the Gamry Potentiostat. The current signal from the I Channel Output connector is

measured by the oscilloscope. A special script called "Pstat Panel" is available to simplify this procedure.

The mode of the current measurement during a CV experiment may be specified by the user as auto-ranging or fixed. Auto-ranging is most convenient – the Gamry Potentiostat can select the most appropriate current range. Auto-ranging, however, should only be used for relatively low scan rates (less than 100 mV/s). Higher scan rates require Fixed mode in which the user enters the maximum current and the *gΖkUϒ* sets the appropriate current range.
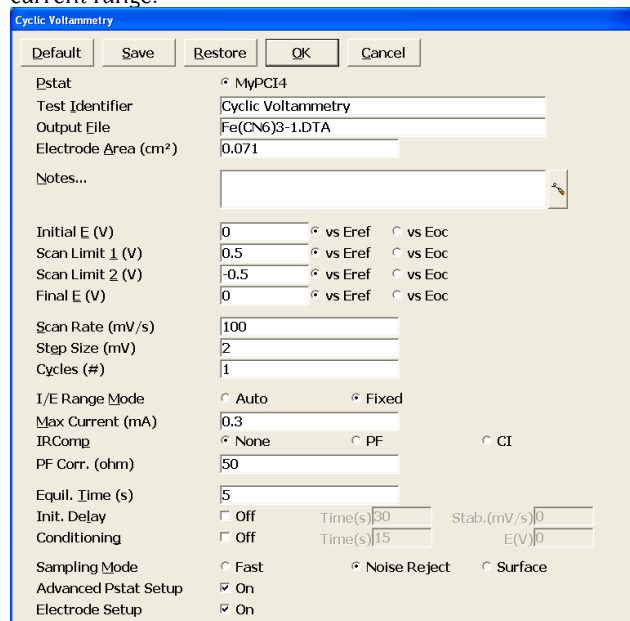
Setup Window for Cyclic Voltammetry. *The CV waveform starts at Initial E and continues to Scan Limit 1, Scan Limit 2, then Final E. iR Compensation can be performed with Positive Feedback or Current Interrupt. The value of the parameters that you entered for your last experiment is shown in each data field. Parameters for routine experiments can be Saved for easy Restore.*

iR Compensation has received an extraordinary level of attention in th*gΖkUϒ*. (For an enlightening discussion on solution resistance, see the Application Notes section of www.gamry.com.) There are two modes of compensation: current interrupt and positive feedback.

Current interrupt works great as long as the scan rate is less than 50 mV/s. Simply turn Current Interrupt on with the radio button and the *gΖkUϒ* takes it from there.

For higher scan rates, positive feedback is required if you want to compensate for iR drop. The age-old nemesis of positive feedback, of course, is selecting the proper amount of feedback. As usual, Gamry takes a totally new approach. We use Electrochemical Impedance Spectroscopy to measure the uncompensated resistance of the cell! We make the EIS measurement at a high frequency to make sure the resistance is valid (the limiting impedance at high frequency is the solution resistance). That impedance is employed as the solution resistance in

positive feedback iR compensation. We use that resistance and the current range to apply the correct amount of positive feedback to make sure your applied potential is accurate, but not so much that the potentiostat is pushed into oscillation. Neither the EIS measurement of R_u nor current interrupt increases the cost of your instrument – both are standard on every Gamry Potentiostat!

Three data acquisition modes are available when the *gΖkUϒ* is combined with a Reference 600 Potentiostat. These will significantly improve the signal-to-noise ratio leading to more accurate results. "Fast" mode takes one data point per sample period just before the voltage is updated for the next data point. "Noise Reject" mode is a noise rejection method where data are collected for the last 20% of the sample period at a rate of 60 kHz. They are then averaged into a single point. Finally, "Surface" mode samples data for the entire sample period and averages to a single point, essentially "integrating" the current. This is particularly useful for the researcher interested in batteries, fuel cells, supercapacitors, surface-confined electroactive species, and double-layer effects.

The Advanced Pstat Setup checkbox will open the Hardware Settings window if selected. This feature allows convenient, flexible access to the Potentiostat electronics to manually control the speed and stability of the instrument. Stability controls on the control amplifier and the current-to-voltage converter are available at this point. In addition, the analog filters in the Potentiostat may be selected. These settings may be adjusted in concert with the scan rate to maintain an optimum balance between the time scale of the experiment and the noise level in the potential and current measurement. The Advanced Pstat Setup is available in all techniques in the *gΖkUϒ*.
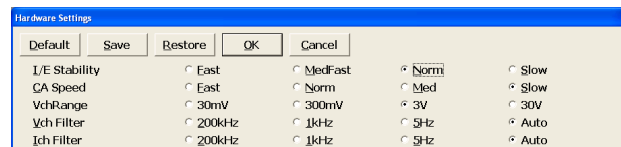
The Advanced Potentiostat Setup dialog box gives control of the potentiostat to you! *Adjust the speed of the Control Amplifier and the I/E Converter to optimize your instrument speed or discriminate against noise.*

The Electrode Setup checkbox will open the Electrode Setup window to specify your electode. For instance, if you select the rotating electrode, you will be prompted to input a rotation rate for the experiment. The Gamry software supports popular Mercury Electrodes as well as Gamry Instruments' RDE710 Rotating Electrode.
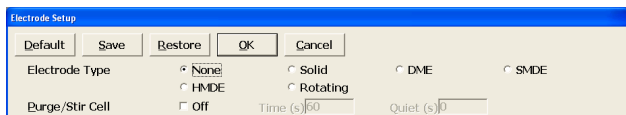
The Electrode Setup dialog box is used to select your electrode. With Gamry's RDE710 Rotating Electrode, the rotation rate is software-controlled in this window and written in your data file.

On the analysis side, the Gamry Echem Analyst brings an unprecedented combination of flexibility and simplicity to Cyclic Voltammetry. For example, the following data analysis routines are available for Cyclic Voltammetry:

Peak Find: Select a portion of the curve, then select Peak Find to identify the peaks and measure the peak height. The peak heights are normally measured above zero current. If your experiment exhibits a sloping baseline, you can either draw a freehand baseline using the mouse, or you can use the Automatic Baseline feature. When Peak Find is selected, the peak is located, then the peak height is measured directly above the selected baseline.

Delta Ep: The difference between two peaks is an important piece of information in CV. Delta Ep automatically reports the potential difference between two peaks. In cyclic voltammograms with multiple peaks, you can easily select the two peaks used in the Delta Ep calculation.

Subtract Background From File: Subtract a background curve from your sample curve. It is not necessary that all the experimental parameters be identical in both curves.

Integrate: Select a portion of the CV and integrate to calculate the charge.

Normalize by Scan Rate: Divide the CV peak current by the scan rate or the square root of the scan rate. Multiple files at different scan rates can be normalized and overlaid. The square root of the scan rate is used to assess diffusion-controlled processes while the scan rate dependence is best suited for the interpretation of surface reactions.

Min/Max: Automatically identify maxima and minima current in the curve.

Baselines: Create baselines for peak current or integration from a freehand line or using our Automatic Baseline function.

Post-Run iR Compensation: Correct for iR Compensation after the experiment is complete. This simple feature takes a user-input value for the Uncompensated Resistance and corrects for it in an approach similar to Positive Feedback, however, with no affect on data acquisition.
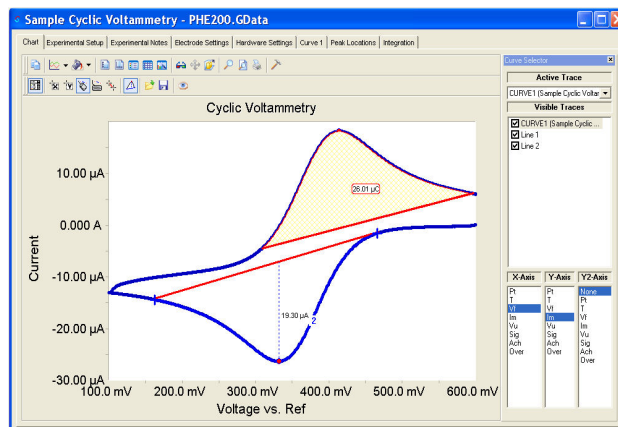
CV Data Analysis in the Gamry Echem Analyst
Peak Find located the peak in the negative portion of the curve and measured the peak height below the Freehand Line. Integration calculated the charge under the positive section of the curve above another baseline. The results are reported both displayed on the graph and reported in the new tabs. The Curve Selector has been activated and is shown on the right side of the graph.

A voltage signal from an external device may be connected to the Auxiliary A/D Input of the Gamry Potentiostat and automatically saved in the data file. This feature is particularly useful for Quartz Crystal Microbalances, thermocouples, and spectroelectrochemistry. The data format of the Explain is simple tab-delimited ASCII text. The data can be easily imported into other data analysis or presentation software.

Given the breadth of electrochemistry, it is impossible for any manufacturer to provide standard acquisition and analysis procedures for every conceivable application.

That's why we developed Open Source Scripting™. We perform our experiments in scripts that can be rapidly customized. All acquisition procedures in the Framework are written in Explain™, the Gamry electrochemical control language. The analysis routines in the Gamry Echem Analyst are written in Microsoft® Visual Basic® for Applications. For special electrochemical experiments, the scripts can be customized by either the user or by Gamry. With Gamry's Open Source Scripting, you're never locked out of the experiment you need!

Linear Sweep Voltammetry

Linear sweep voltammetry is best described as the first portion of a cyclic voltammogram. The Linear Sweep Voltammogram is displayed as the initial portion of a CV from Initial E to Scan Limit I. Most of the CV parameters of the Explain apply in the same fashion to Linear Sweep Voltammetry. Linear Sweep is used primarily for semi-quantitative measurement of electroactive species.

Analysis routines included in the Gamry Echem Analyst for Linear Sweep Voltammetry are the same as Cyclic Voltammetry, excluding the Delta Ep command.
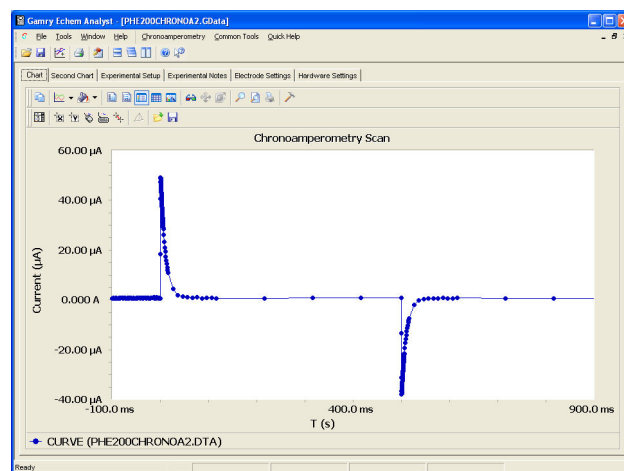
Chronoamperometry

Chronoamperometry is used to study diffusion-controlled electrochemical reactions and complex electrochemical mechanisms. It is performed by applying an initial potential at which no faradaic reaction is occurring, then stepping the potential to a value at which the electrochemical reaction of interest takes place. The solution is generally unstirred and the current is measured throughout the experiment.

Setup Window for Chronoamperometry. *Double-step chronoamperometry may be easily performed with the* ŀgg*CŽkUУ* *The DngŀW9Ylf cWŀa lghmGcŽkUУsets the current range based on the maximum Wŀrrent. The "Default" button resets the default values for all parameters.*

The Setup Window for Chronoamperometry is shown above. The Conditioning Voltage is used to electrochemically treat the electrode prior to the experiment. The current ranging may be automatic or fixed. The user has a choice of iR compensation using current interrupt or positive feedback. A current limit may be specified so that, when exceeded, the experiment is terminated.

The gCŽkUУincludes a decimation feature to maximize the efficiency of the data acquisition. In a Chronoamperometry experiment, data is often acquired very rapidly and for long periods of time, resulting in a large data file. With decimation enabled, the data acquisition rate is reduced with each decade of time. Data are acquired rapidly in the initial stages of the experiment when it is changing rapidly, but at a lower rate in the latter portion of the experiment where the current tends to be relatively stable. Decimation is illustrated in the Chronoamp experiment shown below.

Chronoamperometry analysis techniques in the DngŀW9Ylf cWŀa lghmGcŽkUУinclude Min/Max, Background subtract, Fit Cottrell Equation, Normalize by Area, and Integrate.


Chronoamperometry Display with Decimation. *With Decimation, the rate of data acquisition decreases by a factor of ten with each decade of time. Decimation is also available in Chronocoulometry and Chronopotentiometry.*

Repeating Chronoamperometry

Repeating Chronoamperometry alternates between the application of two different potential steps. The current-versus-time profile is measured as this two-step process is repeated for a user-defined length of time. This experiment has single-use criterion to terminate the test if a current limit is measured. Data are stored in a single file. This experiment finds many applications in the pulse-plating industry.

Data analysis routines of the Repeating Chronoamperometry experiment are similar to that of the standard Chronoamperometry experiment, including Integrate, Min/Max, etc.
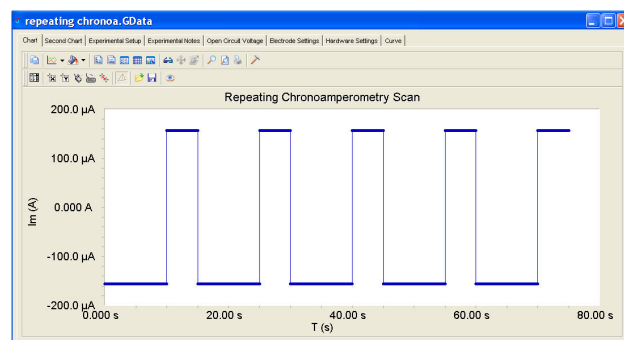
Repeating Techniques Waveform. *This waveform is the same shape for Repeating Chronoamperometry and Repeating Chronopotentiometry. Two steps of individually specified magnitude and length are applied cyclically. Data are stored in a single file.*

Multiple-Step Chronoamperometry

Multiple-Step Chronoamperometry applies up-to-48 potential-steps of individually specified voltage and time. The data from this experiment are conveniently stored in a single data file. This experiment is designed for the experiment in which the potential-steps do not follow a pattern of size or duration. This experiment in combination with Repeating Chronoamperometry and the Sequence Wizard provides ultimate flexibility to create the voltage-step-based signal you need. The ability to create an arbitratry waveform has found applications in several fields, particularly the sensor industry.
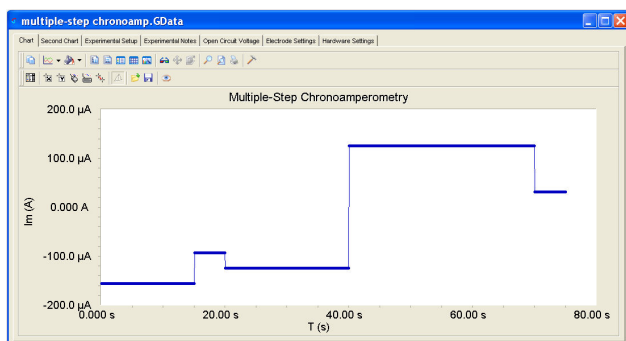
Multiple-Step Chronoamperometry Waveform. The Multi-Step experiment is for users that want to individually specify numerous steps of different sizes and durations. This is an ideal experiment to run for unique signals that do not repeat or differ by any regular increment.

Chronocoulometry

Chronocoulometry is chronoamperometry in which the cell current is integrated to calculate charge. The presentation of the charge allows more convenient access to certain information in the experiment. Chronocoulometry is particularly useful for studying adsorption processes and other surface-constrained reactions, such as modified electrodes. Chronocoulometry also includes decimation. Analyses included for this technique are Min/Max, Background subtract, and Fit Integrated Cottrell Equation.

Chronopotentiometry

Chronopoteniometry is performed by stepping from an initial current, typically zero, to some finite value and monitoring the potential vs. time. The potential at zero current is the Open-Circuit Potential. When the initial electroactive species has been depleted, a transition in potential will occur. The transition time is related to several electrochemical parameters through the Sand Equation. Chronopotentiometry includes decimation on the potential measurement. The Limit V feature enables Chronopotentiometry with current reversal.

Repeating Chronopotentiometry

Repeating Chronopotentiometry alternates between the application of two different current steps. Voltage-versus-time is measured as this two-step process is repeated for a user-defined number of cycles. This experiment has a single-use criterion to terminate the test if a voltage limit is measured. Data are stored in a single file. This experiment finds many applications in the pulse-plating industry.

Controlled Potential Coulometry

Controlled Potential Coulometry is an electrochemical experiment in which an electroactive species is exhaustively oxidized or reduced while measuring and integrating the current. The total coulombs accumulated during the experiment allows the calculation of the number of electrons transferred in the electrochemical reaction or the concentration through Faraday's Law. Since Controlled Potential Coulometry is essentially a long-term chronocoulometry experiment, it utilizes the chronocoulometry analysis procedures for viewing and manipulating the data.

System Information

The Physical Electrochemistry Software requires a

Reference 600, Reference 3000, Series G™, or PCI4™ Gamry Potentiostat to conduct experiments. Microsoft

Windows® XP, Vista or Windows 7 is required for operation of th‌ȷ̏ģ̌ƉzƵȤkUȜ̏

Gamry Instruments can supply complete systems including the Potentiostat and software installed in a desktop or portable computer. Custom computer configurations, software, training, and installation are available by special order. Contact us for further details on these systems.

Specifications

Min. Scan Rate: 0.0175 µV/s
Sampling Period: 3.3 µs-600 s
Min. Step Height: 12.5 µV
Max. Points per Data File: 262,143
iR Compensation: Current Interrupt or Positive Feedback