

PHE200™ Physical Electrochemistry Software

The PHE200 Physical Electrochemistry Software is the electrochemical tool to perform in-depth studies of the structure of the electrode interface and the mechanisms of electrochemical reactions. The PHE200 brings cyclic voltammetry and other recognized electrochemical research techniques to the Gamry product family. Other Gamry software includes electrochemical impedance spectroscopy, DC corrosion techniques, and electrochemical noise.

The PHE200 incorporates the following electrochemical techniques:

- Cyclic Voltammetry
- Linear Sweep Voltammetry
- Chronoamperometry
- Chronocoulometry
- Chronopotentiometry
- Controlled Potential Coulometry

Like most Gamry software, the PHE200 and a PC4 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.

Cyclic Voltammetry

We've re-tooled our acquisition software and written completely new analysis software which brings new flexibility and power to cyclic voltammetry, among the worlds most commonly used electrochemical techniques. 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 next. You can define the potentials as absolute voltages or by their relationship to the Open-Circuit Potential.

The potential staircase is defined by the scan rate (mV/sec) and the Step Size (mV):

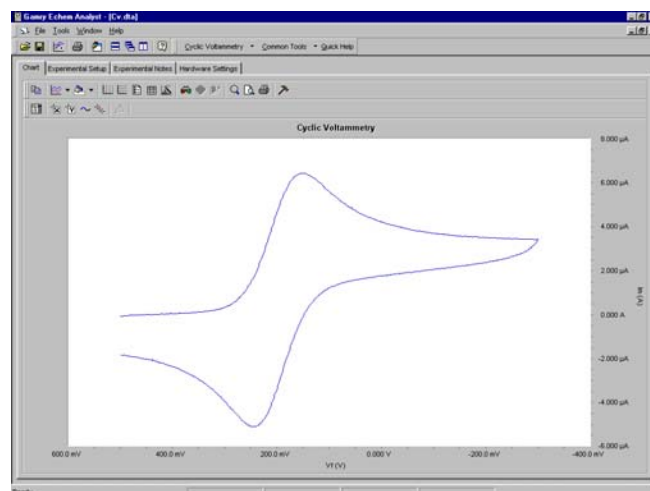
$$\text{Scan Rate} = \text{Step Size} / \text{Sample Period}$$

The minimum sample period is 100 μsec . The maximum scan rate is a function of Step Size. For example, the maximum scan rate with a 2 mV step is 20 V/sec. 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 PHE200 can save, *and display*, up to 65,535 data points! The number of CV cycles that can be displayed is dependent upon the scan parameters:

$$\text{No. of Cycles} = 65,535 \times \text{Step Size (mV)} / \text{Voltage Span of the CV(mV)}$$



Typical Cyclic Voltammogram in the PHE200. 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 50 V/sec 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 "PC4 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 of the 9 to 10 current ranges available. Auto-ranging, however, should only be used for relatively low scan rates (less than 100 mV/sec). Higher scan rates require Fixed mode in which the user enters the maximum current and the PHE200 sets the appropriate current range.

Cyclic Voltammetry

Default Save Restore OK Cancel

Estat 08145

Test Identifier

Output File

Electrode Area (cm²)

Notes...

Initial E (V) vs Eref vs Eoc

Scan Limit 1 (V) vs Eref vs Eoc

Scan Limit 2 (V) vs Eref vs Eoc

Final E (V) vs Eref vs Eoc

Scan Rate (mV/s)

Step Size (mV)

Cycles (#)

I/E Range Mode Auto Fixed

Max Current (mA)

IRComp None PF CI

PF Corr. (ohm)

Equil. Time (s)

Init. Delay Off Time(s) Start (mV/s)

Conditioning Off Time(s) E(V)

Advanced Pstat Setup On

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 the PHE200. (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/sec. Simply turn Current Interrupt on with the radio button and the PHE200 takes it from there.

For higher scan rates, positive feedback is required. 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 number of fairly high frequencies 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. By the way, neither the EIS measurement of Ru nor current interrupt costs you anything – it's standard on every Gamry Potentiostat!

The Advanced Pstat Setup checkbox will open the Hardware Settings window if selected. This feature allows convenient, but 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 scan rate of the experiment and the noise level in the potential and current measurement. The Advanced Pstat Setup is available in all techniques in the PHE200.

Hardware Settings

Default Save Restore OK Cancel

I/E Stability East Norm Slow

CA Speed East Norm Med Slow

I/E Speed East Slow

Ych Filter 100kHz 1kHz 5Hz

Ich Filter 100kHz 1kHz 5Hz

Purge/Stir Cell On Time(s)

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.

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, a freehand baseline can be drawn using the mouse. When Peak Find is selected, the peak is located, then the peak height is measured directly above the 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.

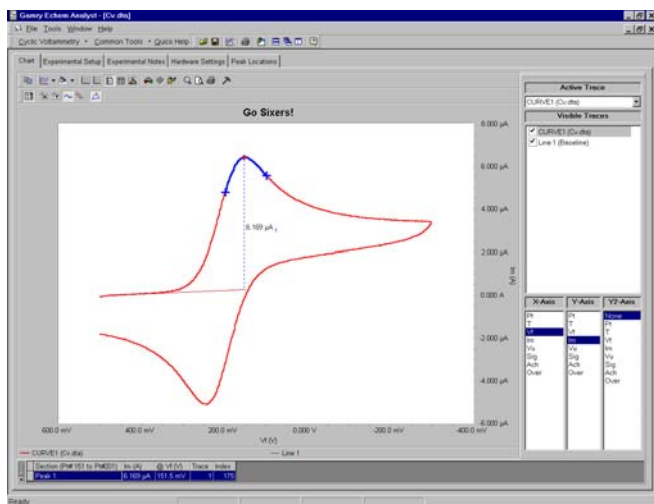
Subtract Background From File: Subtract a background curve from your sample curve. It is not necessary that all the experimental parameters be identical in both curves.

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.

Normalize by Area: Calculate the current density by dividing the current by the electrode area. This allows experiments with different electrode areas to be compared.

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



CV Data Analysis in the PHE200. Peak Find located the peak in the selected portion of the curve and measured the peak height above the Freehand Line. The results are reported below the curve and in the tab labeled "Peak Locations". 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 PHE200 is simple tab-delimited ASCII text. PHE200 data can be easily imported into other data analysis or presentation software. A utility for direct export to DigiSym* is contained within the PHE200.

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 an application!

Linear Sweep Voltammetry

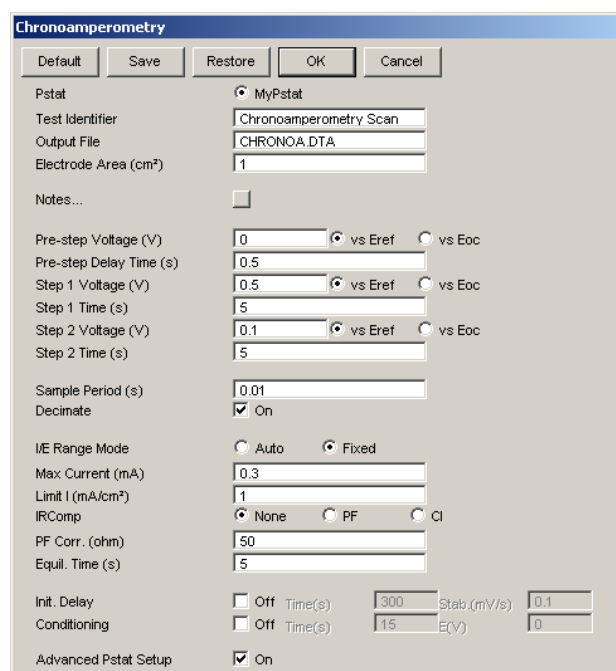
Linear sweep voltammetry is best described as the first portion of a cyclic voltammogram. The Linear Sweep Voltammogram appears exactly as the initial portion of a CV from Initial E to Scan Limit I. Most of the CV parameters of the PHE200 apply in the same fashion to Linear Sweep

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.



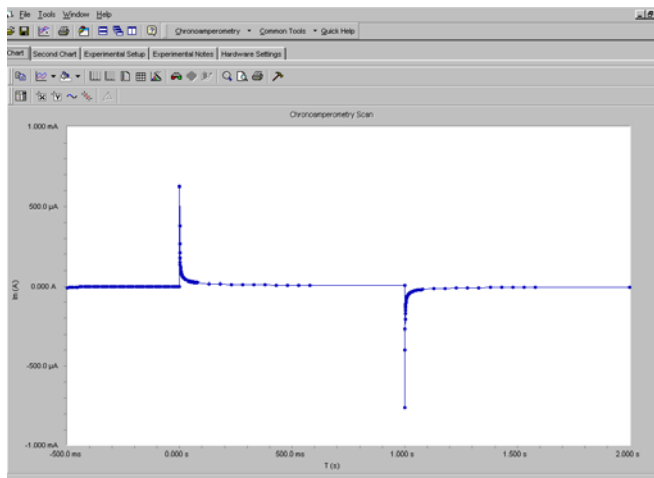
Setup Window for Chronoamperometry. Double-step chronoamperometry may be easily performed with the PHE200. The PHE200 sets the current range based on the maximum current. The "Default" button resets the default values for all parameters.

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 PHE200 includes 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 is 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 PHE200 include 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.*

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, Fit Integrated Cottrell Equation, and Normalize by Area.

Chronopotentiometry

Chronopotentiometry 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. A Limit V feature aborts the experiment if the voltage is exceeded.

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 Faradays 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 PHE200 Physical Electrochemistry Software requires a PC4/300, PC4/750, or FASI Gamry Potentiostat to conduct experiments. Microsoft Windows 98™, Me™, 2000™, or XP™ is required for operation of the PHE200. Gamry recommends a computer with a 450 MHz processor or higher with 64 Mb of RAM or higher. Microsoft Excel is not required.

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

* DigiSym is a product of Bioanalytical Systems, Inc.
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