ARTISAN®
TECHNOLOGY GROUP

Your **definitive** source for quality pre-owned equipment.

**Artisan Technology Group**
(217) 352-9330 | sales@artisantg.com | artisantg.com

**Full-service, independent repair center**
with experienced engineers and technicians on staff.

**We buy your excess, underutilized, and idle equipment**
along with credit for buybacks and trade-ins.

**Custom engineering**
so your equipment works exactly as you specify.

- Critical and expedited services
- In stock / Ready-to-ship
- Leasing / Rentals / Demos
- ITAR-certified secure asset solutions

**Expert team | Trust guarantee | 100% satisfaction**

All trademarks, brand names, and brands appearing herein are the property of their respective owners.

Find the *Princeton Applied Research / EG&G 263* at our website: *Click HERE*

# Software Incompatibilities with IBM ValuePoint 325T Computer

The Install program disks include a batch file that allows you to start the electrochemical software simply by typing ECHEM (if you have installed the Model 250 or 270 software), COOL (for the Model 271), or CORR (for the Model 252 or 352).

If you are using an IBM ValuePoint 325T personal computer to run your software, you must type several additional characters to make the HP ColorPro plotter work properly with it. This is because the BIOS of the IBM 325T computer has been changed from earlier versions and is no longer completely compatible with the GSS HP plotter driver included with the software. As a result, the driver does not properly recognize the hardware handshake on the computer's 9-pin COM1 serial port, causing the plotter to "hang up".

Luckily, there is an easy way around this problem. Install the software in the normal way using the Install disk. Be sure to install the plotter using the "HPGL Compatible" option in the Install program. (The ColorPro plotter works as a "7440".) Complete the installation normally.

Then, when you are ready to start the program, type the normal startup command followed by a space, COM1, and a period. Thus, the complete command you need to type will be one of the following:

| | |
|---|---|
| ECHEM COM1. | (for the Model 250 or 270) |
| COOL COM1. | (for the Model 271) |
| CORR COM1. | (for the Model 252 or 352) |

The plotter will now function normally. Note that the terminal period is part of the command and *must be typed*.

You can make things a bit simpler if you create a new batch file to start the program. This batch file would call the original batch file and append a space and "COM1.". For example, to start Model 250 or 270 software, the batch file might have the file name ECHEMP.BAT and would contain the single line:

```
ECHEM COM1.
```

(Again, the period at the end is part of the command and must be typed.) You would then only have to type ECHEMP to start the program. You could write a batch file using the same idea to start the Model 271, 252, or 352 software.

This fix relies on the capability of the GSS driver for HPGL-compatible plotters to direct the HPGL information to a file. This feature is useful in its own right. Several desktop publishing programs and several popular word processors can read and display HPGL files as part of a document.

If you wish to direct the HPGL plotting instructions to a disk file instead of to a plotter, start the program with one of the following:

| | |
|---|---|
| ECHEM plotfile | (for the Model 250 or 270) |
| COOL plotfile | (for the Model 271) |
| CORR plotfile | (for the Model 252 or 352) |

where plotfile is the file name you wish to use for the HPGL output. Each plot ("page") will be a different file, with the file extension .000 used for the first one, .001 for the second, and so on in sequence.

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

# EQUIVALENT CIRCUIT

*written by*

*Bernard A. Boukamp*

# USERS MANUAL

222537-A-ADD

*Manual Addendum*

*for*

*Version 4.5*

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

**Find Circle**

When an inductive loop is encountered with the Find Circle option the user can choose to interpret this with a negative resistance / negative capacitance combination. When an inductive loop is detected first the inductive result will be displayed followed by the prompt:

**Change to negative CPE (neg. Capacitance)? [y/n]:**

With a Yes response the interpretation with a negative resistance / negative capacitance will be displayed followed by the prompt:

**Change to positive CPE (Inductance)? [y/n]:**

Answering again Yes will return the first interpretation, while a No answer will continue the Find Circle procedure with the prompt for circuit and parameter transfer to Note Pad. Only the currently displayed interpretation will be transferred to Note Pad.

**HP desk & laser jet printers**

To accommodate the printing of screen graphics on HP-jet type printers (Laser Jet / Desk Jet) the program has been modified. In the '***Set System***' sub-program a switch has been added to the '*Config.System*' screen. The default value for the **H)P desk/laser jet printer** is **OFF**. In this mode graphics dumps on the printer (function key **<F9>** and **<F10>**, see manual) are made in the ***EPSON*** format, which is used by most dot matrix printers. In the **ON** position the ***HP desk/laser jet*** format is used. When the printer switch is set from **OFF** to **ON** the printer is reset (partially printed paper will be ejected). Also when the program is started with the HP-jet option **ON** the printer will be reset. The HP-jet option is saved in the **EQUIVCRT.STM** file like all other program parameters.

The current version of ***EQUIVALENT CIRCUIT*** can not use the VGA graphics mode. It will set the VGA card in the EGA mode. Because of this there will be a mismatch between the screen aspect ratio and the printer aspect ratio. The software tries to correct this by adding extra printing lines. For EGA graphics use a plot aspect ratio of 0.75 (***Set System*** sub-program, option 3: '*Plot Aspect*'). Semi-circles will then appear properly on the EGA screen and in the print out. It is the responsibility of the user to ensure that there is enough space left on the paper for the plot. For best results always start on a new sheet by using the **<F9>** function key.

**Plot files (HP-GL)**

In the *Set System* section 2 (*Configure System*) the HP-GL plot device must be selected. Four options are available:

| | |
|---|---|
| COM1: | standard serial port for HP-compatible plotters |
| LPT1: | use a printer selector for switching between printer and plotter |
| HPLJ3/4 | HP laser jet series III en 4, program selects HP-GL print mode |
| Disk file | the HP-GL plot instructions file will be saved on disk |

For the HP lj4 use the '@PJL SET RESOLUTION=300' command to set the plot resolution. This is necessary in order to avoid memory overflow problems in the printer.

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

## EQUIVALENT CIRCUIT, version 4.50, March 1993

A number of improvements have been made to the program. With respect to the version 3.96 these improvements are:

Circuit Description Code;

* The CDC has been improved, a different set of brackets, [ and ], is now used to group elements placed in series, hence ( and ) will now only group parallel elements. Thus ..(RCQ).. designates a *parallel* arrangement of a R, C and a CPE, while ...[RCQ]... now designates a *series* arrangement of a R, C and a CPE. It is not necessary to type the correct ( or [ when entering the CDC, the computer will keep track of the proper sequence. No brackets must be used for the 'ground level' series arrangement (see manual).

Data Cruncher:

* *Find Line*: Repair of error in the transfer of data to the Note Pad in case of inductive effects.
* *Find Circle*: For negative semi-circles (inductive loops) a second interpretation with a negative capacitance / negative resistance pair is possible (see instruction below). Only one set may be transferred to the Note Pad.

NLLS-Fit and Simulation:

* The Gerischer dispersion function has been added, see below for a brief explanation.
* For regular data a function weighting routine has been implemented. When Chi-squared falls below $1x10^{-3}$ then the proportional data modulus weighting is replaced by proportional function modulus weighting.

Screen Plot:

* In the Bode plot mode of the Capacitance magnitude and $\alpha$ versus frequency the presentation of $\alpha$ has been changed to represent the true phase angle ($\alpha_{new}=\pi/2-\alpha_{old}$).
* Screen plots may now be printed on HP laser jet and desk jet printers (see below). For the laser/desk jet printers a cartesian frame is generated.

Hard Copy Plot:

* The error in the text of the left axis of the Capacitance Bode plot has been repaired. Also the phase angle representation has been changed as for the Screen Plot mode.
* In the Nyquist plots (complex plane plots) a precaution has been build in to prevent the plotter pen from damaging the paper when too many points are drawn in a small area. The program requires a minimum distance between the centres of the symbols to be drawn. If the next plot symbol is too close to the previous one it will not be drawn.

HP-GL plot files:

* Plot files may now be directed to the HP laser jet III or 4 printer, when these are connected to the LPT1 parallel port. For the HP lj4 printer it may be necessary to set the resolution to 300 DPI as otherwise a memory overflow error may occur for complex plots (especially 3-D graphs).
* Also a parallel plotter may be added to the LPT1 port (preferably through a printer selector switch). The operator must take care of the proper switch position.

Kramers Kronig transformation:

* A separate program has been added for K-K transforms of the *impedance* data. Results can be read by EQUIVALENT CIRCUIT v4.50 and are stored in the simulation arrays. The K-K program is briefly described below.

*April 5, 1993,* *Bernard A. Boukamp*

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

**Gerischer Impedance**

The general admittance formula for the Gerischer dispersion is represented by:

$$Y(\omega) = Y_0\sqrt{K_a + j\omega} \tag{1}$$

which can be split into a real and imaginary part:

$$Y(\omega) = \frac{Y_0}{\sqrt{2}}\left(\sqrt{\sqrt{\omega^2 + K_a^2} + K_a} + j\sqrt{\sqrt{\omega^2 + K_a^2} - K_a}\right) \tag{2}$$

or alternatively:

$$Y(\omega) = Y_0\sqrt{\omega/2}\left(\sqrt{\sqrt{1+g^2} - g} + j\sqrt{\sqrt{1+g^2} - g}\right) \tag{3}$$

with $g = K_a/\omega$. For the impedance representation one obtains:

$$Z(\omega) = \frac{Z_0}{\sqrt{2}}\left(\sqrt{\frac{\sqrt{\omega^2 + K_a^2} + K_a}{\omega^2 + K_a^2}} - j\sqrt{\frac{\sqrt{\omega^2 + K_a^2} - K_a}{\omega^2 + K_a^2}}\right) \tag{4}$$

with $Z_0 = (Y_0)^{-1}$. Like eq. (3) an alternative expression for eq. (4) can be given:

$$Z(\omega) = \frac{Z_0}{\sqrt{2\omega}}\left(\sqrt{\frac{\sqrt{1+g^2} + g}{1 + g^2}} - j\sqrt{\frac{\sqrt{1+g^2} - g}{1 + g^2}}\right) \tag{5}$$

From eqs (3) and (5) it is obvious that for $g<1$ (high frequencies) these equations change to the Warburg or semi-infinite diffusion dispersion:

$$Y(\omega) = Y_0\sqrt{j\omega} = Y_0(\sqrt{\omega/2} + j\sqrt{\omega/2}) \tag{6}$$

For low frequencies the imaginary part disappears (=0) resulting in a dc-resistance with $R_{dc}=Z_0\,K_a^{-0.5}$

For the representation of the Gerischer dispersion eq. (1) is used in the NLLSF-program. The CDC-symbol is '*G*'. The parameters needed (or fitted) by the program are $Y_0$ (in ohm$^{-1}$s$^{0.5}$) and $K_a$ (in s$^{-1}$). An example of the Gerischer impedance is presented in fig. 1. For display purposes the Gerischer impedance has been offset by a series resistance (CDC: *RG*). Parameter values are: $R$=20 Ω, $Y_0$=0.01 ohm$^{-1}$s$^{0.5}$ and $K_a$=2 s$^{-1}$. Estimates for $Y_0$ can easily be found by using the 'Find Line' option in 'Data Cruncher' for the high frequency (Warburg like) part. The estimate for $K_a$ can be obtained from the resistance value measured between the high frequency and the low frequency intercept, $R_{dc}$, with the real axis:

$$K_a = (Y_0 R_{dc})^{-2} \tag{7}$$

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

the data is expanded over two decades (to $x_{min}=0.01\omega_{min}$ and $x_{max}=100\omega_{max}$) on both sides using a simple extrapolation based on a depressed semi-circle. This semi-circle is modelled with a $R_1(R_2\ Q)$ circuit, which is fitted to the end parts of the dispersion. Next the gap between $x=0$ and $x=x_{min}$, and between $x=x_{max}$ *and* $x=\infty$ is covered by an exponential extrapolation:

$$\int_{-\infty}^{\ln x_{min}} e^{C\ln x + D}\, d\ln x = e^{D} x_{min}^{C}/C \qquad (10)$$

and:

$$\int_{\ln x_{max}}^{\infty} e^{C\ln x + D}\, d\ln x = -e^{D} x_{max}^{C}/C \qquad (11)$$

provided that $C$ is positive in eq. (10) and negative in eq. (11). (If these conditions fail in the Kramers-Kronig program then an error message is displayed on the screen and this specific extrapolation is not included for the current frequency)

The semi-circle (or R CPE) fitting must be performed with the program EQUIVALENT CIRCUIT in the *Data Cruncher* sub-program. Unfortunately the obtained parameters must be written down, there is currently no way to transfer these directly to the K-K program. (In a future major upgrade of EQUIVALENT CIRCUIT the K-K transform procedure will be integrated in the program.) If the data contains a series inductance, this inductance must be removed before the K-K transform can be carried out. If the low frequency end is dominated by a CPE (blocking electrode) then the data extrapolation is carried out with a R Q circuit.

The preparation for the Kramers-Kronig procedure goes as follows. First read the data file with EQUIVALENT CIRCUIT, remove bad data points (if necessary) and remove *any* double frequency data set as the appearance of two identical frequencies will cause a crash during the K-K transform. Then *save the data again from the program.* This is essential as the K-K program will only read '**resaved-ZZ**' data. The importance is that the data must be properly ordered with respect to frequency. Go to *Data Cruncher* and select the *Find Circle* option. First fit a circle to the low frequency part. If sufficient data points are available then perform a partial NLLS-fit for improved values. Write down the resulting circuit parameters. If the low frequency end shows 'open ended' CPE behaviour then chose the *Find Line* option and fit a *R Q* circuit to the low frequency end. If possible improve the results with a partial NLLS-fit.

For the high frequency end extrapolation use again the *Find Circle* option. If appropriate let the circle go through the origin ($R_l = 0$). If an inductive element, in series with the sample, was present then include this in the subsequent partial NLLS-fit (use a **LR(RQ)** circuit). Again write down the circuit parameter values for use in the K-K program. Next quit Equiv.Circt. and go to the Kramers-Kronig program (type: **KRAMKRON**). Below the sequence of the dialogue is given, comments are placed between {}, the program prompts are printed in bold. As an example the test file **IMPLELEC.DAT** is used.

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

For further reading see:

M. Sluyters-Rehbach and J.H. Sluyters in Comprehensive Treatise of Electrochemistry **9**, E. Yeager, J.O.M. Bockris, B.E. Conway, S. Sarangapani eds, Plenum Press, New York (1984)

R.C. Makkus, K. Hemmes and J.H.W. de Wit, Ber. Bunsenges. Phys. Chem. **94** (1990) 960.

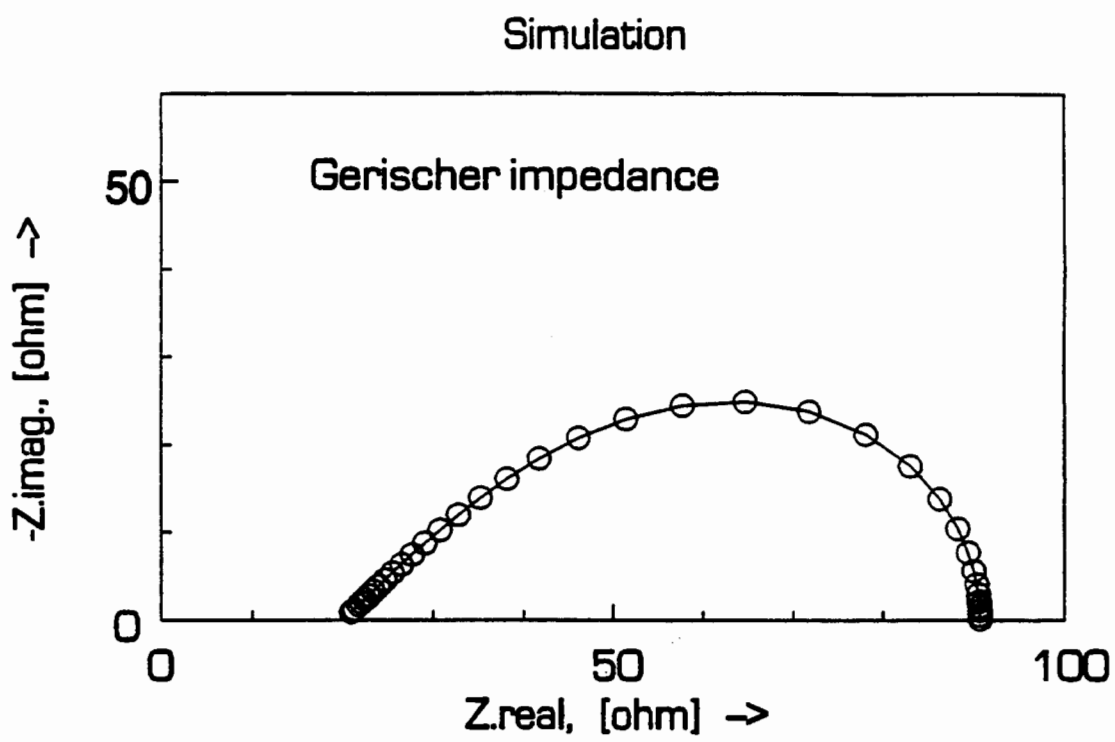



*Fig. 1 Impedance spectrum of the series combination of a resistor and a Gerischer impedance.*

**Kramers Kronig transforms:**

A separate program, KRAMKRON.EXE, is located on the diskette. With this program data files may be transformed according to the K-K relations. For the imaginary to real transform:

$$Z_{re}(\omega) = Z_{re}(\infty) + \frac{2}{\pi}\int_0^\infty \frac{xZ_{im}(x) - \omega Z_{im}(\omega)}{x^2 - \omega^2}\, dx \qquad (8)$$

and real to imaginary transform:

$$Z_{im}(\omega) = \frac{2\omega}{\pi}\int_0^\infty \frac{Z_{re}(x) - Z_{re}(\omega)}{x^2 - \omega^2}\, dx \qquad (9)$$

As the data set has a limited frequency range a special procedure is used for the extrapolation to zero frequency at the low frequency side and to infinite frequency at the high frequency side. First

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

**Kramers-Kronig transform program**

| | |
|---|---|
| **give path and file name:** a:\implelec.dat | {data path and file name} |
| **integration mode: 0 = spline; aabb = polynomial with aa data set length and bb polynomial degree** | |
| **give integration mode:** 0 | {spline integration} |
| **subtract series inductance? [y/n]:** Yes | {series inductance must be subtracted} |
| **Inductance value in Henri:** 2.1536e-5 | {remove series inductance} |
| **low frequency extension** | |
| **Yes = semi-circle, No = CPE? [y/n]:** Yes | {check type of extrapolation model} |
| **give CPE parameters.** | {enter the $R_1(R_2\ Q)$ circt. parameters} |
| **series resistance** = 305.44 | {$R_1$} |
| **parallel resistance** = 57.516 | {$R_2$} |
| **CPE Yo value** = 2.3029e-2 | {Q-$Y_0$} |
| **CPE exponent** = 0.9946 | {Q-n} |
| **high frequency extension? [y/n]:** Yes | |
| **give CPE parameters.** | {now for the high frequency end} |
| **series resistance** = 13.17 | {$R_1$} |
| **parallel resistance** = 373.84 | {$R_2$} |
| **CPE Yo value** = 5.7304e-5 | {Q-$Y_0$} |
| **CPE exponent** = 0.68147 | {Q-n} |
| **calculation time is: 1.37** | {calculation time in seconds} |
| **error sum: 5.70216e-6** | {comparison between data and K-K tr.} |
| **Output for Equivalent Circuit = yes no = for other software (e.g. slide)? [y/n]:** Yes | {special output for Equivalent Circuit} |
| **give path and filename for data out:** a:\implelec.kkt | |

The error sum is defined as follows:

$$S = \frac{1}{N} \sum_{i=1}^{N} \frac{[Z_{re,i} - Z_{re,KK}(\omega_i)]^2 - [Z_{im,i} - Z_{im,KK}(\omega_i)]^2}{|Z_{KK}(\omega_i)|^2} \qquad (12)$$

and is a good indication for the quality of the Kramers-Kronig transform.

The results can be exported in two ways. A special form that can be read directly by EQUIVALENT CIRCUIT (version 4.5 only!) and a general form without any headers or number of data sets. The form of this file is:

| | | | | |
|---|---|---|---|---|
| freq-1 | Zreal-1 | Zreal-KK | Zimag-1 | Zimag-KK |
| freq-2 | Zreal-2 | Zreal-KK | Zimag-2 | Zimag-KK |
| " | " | " | " | " |
| freq-N | Zreal-N | Zreal-KK | Zimag-NN | Zimag-KK |

As an example the comparison of the **IMPLELEC.DAT** data and its K-K transform (done with the sequence above) is presented in the impedance diagram on the next page. This graph was plotted directly from EQUIVALENT CIRCUIT through a network on a HP laser jet 4 printer.

Details of the Kramers-Kronig transform algorithms will be published in Solid State Ionics:

Bernard A. Boukamp, '*Practical application of the Kramers-Kronig transformation on impedance measurements in solid state electrochemistry*', accepted for publication in Solid State Ionics.

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

## Getting EG&G PARC Software Plot Outputs into Word Processing Programs.

Very often is desirable to produce a report or publication with plots from the EG&G PARC M270, M271, M352, or M398 software. This is actually fairly simple to do.

Many modern word processors ( we are familiar with Word™ for Windows ) allow you to import or include a file that is written in 'HPGL' or 'HPL'. This is the standard plotting language used by Hewlett Packard for their plotters. The trick, then, is to have the EG&G PARC software send the plotting commands to a file rather than to the plotter. This is easily done when the software is installed properly.

When the software is installed (or reconfigured) using the INSTALL disk, a DOS Batch file is created. This batch file loads the drivers for the input and output devices you have specified, and then calls the desired program (M270, M271, M352, or M398.) These batch files are ECHEM.BAT, COOL.BAT, CORR.BAT, and EIS.BAT. If you wish to generate HPGL files, you should install (or reconfigure) the program using the INSTALL program on the INSTALL/DRIVERS disk.

When the INSTALL program prompts you for the display, mouse, printer, and GPIB card select the one that is appropriate for your installation. However, when the INSTALL program asks for the plotter type, you should respond with **3**, the choice for HPGL compatible, even if you do not have a plotter! The program then asks for the plotter type. We have found the default '7440' to be satisfactory. Finally, you are asked for the communications port to which it is attached. The default of COM1 is satisfactory.

The INSTALL program will generate a batch file that will look very similar to the ECHEM.BAT shown below.

```
c:
cd\M270
set m270file=c:\M270\
set plotter=hpglpltr
set hpglpltr=COM1
if not (%1)==() set hpglpltr=%1
c:\parc\drivers
m270
c:\parc\drivers /a
set plotter=
set hpglpltr=
set m270file=
cd\
```

The batch files for M271 (COOL.BAT), M352 (CORR.BAT), or M398 (EIS.BAT) will look similar, except that **271** (or **352**, or **398**) will be substituted for **270**.

If the program is initiated normally, by typing

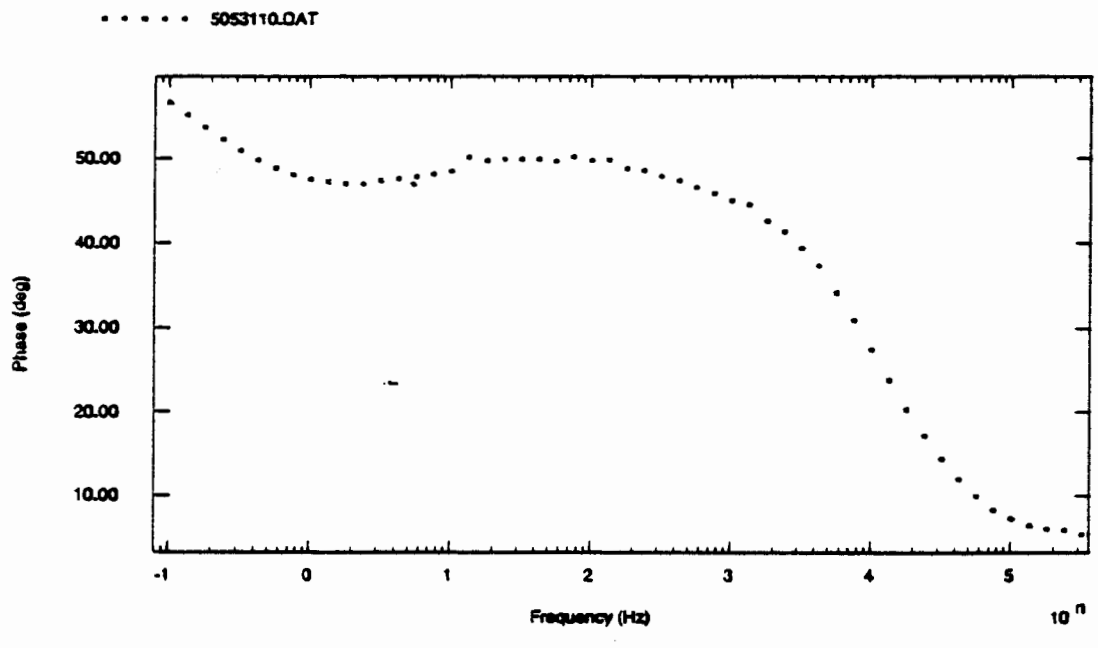
Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

```
ECHEM
```
then the plotter output will go COM1 as it would normally.

If, however, if you begin the program by typing
```
ECHEM diskfile
```
then each plot will be directed to a different file, starting with *diskfile*.000 with the extension being incremented with each "page" of output. It is the line
```
if not (%1)==() set hpglpltr=%1
```
which performs this magic.

To import these files into Word for Windows, you must rename the file. Word uses the extension of the file to determine its type. The extension must be *hgl* for Word to interpret it as an HPGL file. So, if you began the M270 software by typing
```
ECHEM PLOTS
```
then the files will be called PLOTS.000, PLOTS.001, *etc.* You should rename the files to something unique, but ending with the extension *hgl*. In our example, you might choose to rename them PLOTS000.hgl, PLOTS001.hgl, *etc.* Be sure the 8 character file name is unique for each file!

The plots can then be placed in a Word document by simply selecting **Insert** followed by **Picture**. Select ***hgl*** as the file type from the list of supported graphics formats. When you give Word the file name PLOT001.hgl, it will convert that plot from the hgl format, and draw it in your document. This document may be printed out on any supported printer.




This note was written using Word for Windows 6.0 and printed on a postscript printer.

6/95

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

EG&G PRINCETON APPLIED RESEARCH

Electrochemical Instruments Group

# A REVIEW OF TECHNIQUES FOR ELECTROCHEMICAL ANALYSIS

## Introduction

Electrochemistry is the study of the chemical response of a system to an electrical stimulation. The scientist using electrochemistry studies the loss of electrons (oxidation) or gain of electrons (reduction) that a material undergoes during the electrical stimulation. These reduction and oxidation reactions are commonly known as redox reactions and can provide information about the concentration, kinetics, reaction mechanisms, chemical status and other behavior of a species in solution. Similar information can be obtained concerning the electrode surface. Electrochemical techniques can be used to investigate many things – from neurotransmitter behavior in biological situations to brightener concentrations in plating baths to initiator behavior in polymerizations to the speciation of cadmium ions in natural waters.

To the researcher studying chemical systems, electrochemistry offers a different perspective than spectroscopy or other techniques. This is because electrochemical techniques examine different phenomena than those studied with techniques such as spectroscopy. This difference should encourage the researcher to learn and use electrochemistry, since it can often solve research problems that the other approaches cannot.

In an electrochemical experiment, you can measure one or more of four parameters – potential (E), current (i), charge (Q), and time (t) (see the side bar). The response of a system depends on which parameter is used as the excitation signal. By plotting different parameters in different ways the researcher can derive a wealth of information.

In most electrochemical techniques, there are three electrodes – the working electrode, the reference electrode, and the counter (or auxiliary) electrode. The three electrodes are connected to a potentiostat, an instrument which controls the potential of the working electrode and measures the resulting current. In one typical electrochemical experiment, you apply a potential to the working electrode, measure the resulting current, and then plot the current versus time. In another, you vary the potential and then plot the resulting current versus the applied potential.

The different combinations of parameters and working electrode types makes for a long list of techniques, including voltammetry, polarography, cyclic voltammetry, linear sweep techniques, chronoamperometry, chronopotentiometry, pulsed techniques, and others. (For information on pulsed techniques please request EG&G PARC Application Note P-2). Many researchers are uncomfortable with electrochemical techniques because of this seemingly endless list. In fact, since only four parameters are measured, electrochemical techniques are relatively simple and most can be done with one instrument. The remainder of this application note will introduce and define the more commonly used techniques.

### Experimental Parameters

Potential (E) is the amount of electrical force or energy in a system. As the potential increases, more force is available to make a reaction happen. The base unit for potential is the volt (V).

Current (i) is the magnitude of the electron flow in a system. Its base unit is amperes (A) (often shortened to amps), but most electrochemical experiments measure currents on the microamp ($10^{-6}$ amps) or nanoamp ($10^{-9}$ amps) scale. Cathodic i is due to reduction, anodic i is due to oxidation.

Charge (Q) is a measure of the number of electrons used per equivalent. Its base unit is the coulomb (C). You can measure charge directly or calculate it by multiplying the current and the time.

Time (t) is a measurement of duration. Its base unit is the second (s). Electrochemical experiments may require times as short as microseconds or as long as days.

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

## Linear Sweep Voltammetry (LSV)

In linear sweep voltammetry (LSV) you vary the electrode potential at a constant rate throughout the scan and measure the resulting current. Figure 1 illustrates an LSV measurement made at a mercury drop electrode in unstirred, deaerated 0.1 M HCl. In most electrochemical experiments, the studied species must be in a conductive supporting electrolyte, the supporting electrolyte must be purged of oxygen, and the supporting electrolyte must not be stirred. Notice that the applied potential is plotted on the x-axis and the resulting current on the y-axis. All potentials are specified in relation to the reference electrode.

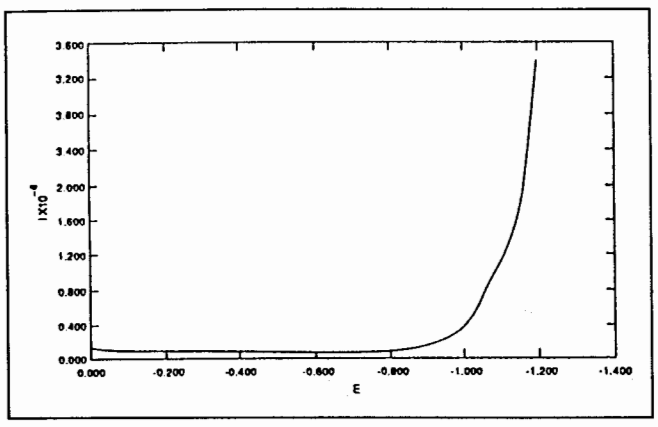



**FIGURE 1. Linear sweep voltammogram of 0.1 M HCl. Scan rate: 100 mV/sec, Working electrode: Hanging Mercury Drop Electrode.**

For potentials from 0 volts to -1.0 volts the current is small and constant. This small current is due to the electron flow necessary to maintain a charged double layer at the electrode surface. This current is often called the charging current. As you vary the potential beyond -1.0 volts, an electrochemical reaction occurs at the surface of the electrode – that is, electrons transfer from the electrode surface to the hydrogen ions in solution, causing a reduction of $H^+$ to $H_2$ and a rapid increase in current.

Notice that with $Cd^{+2}$ added to the HCl solution (Figure 2), the current does not remain constant from 0 to -1.0 volts. As the potential goes more negative, the reductive power of the system increases. Thus, at potentials where $Cd^{+2}$ is reduced, the current increases. As the scan continues in a negative direction, cadmium continues to reduce and the current continues to increase.

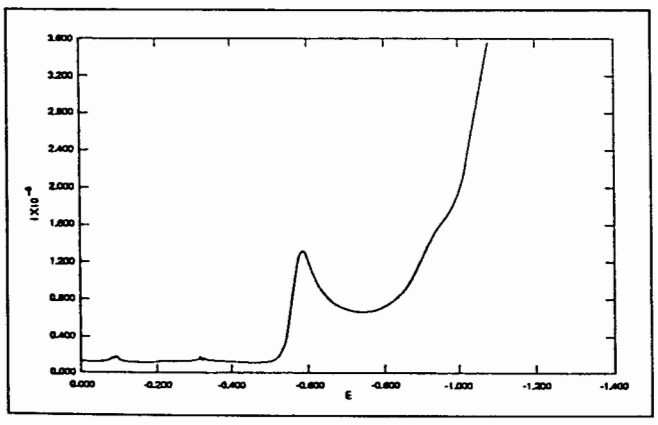



**FIGURE 2. Linear sweep voltammogram of cadmium in 0.1 M HCl. Conditions are the same as figure 1.**

### Electrodes

It is important to note that the working electrode is a critical variable in an electrochemical experiment. The working electrode is where the reactions of interest take place and is usually constructed of an inert material. The potential of the working electrode is measured versus the reference electrode. A typical reference electrode is the familiar saturated calomel electrode commonly used in pH measurements.

By design, the reference electrode is always at a known potential. Since potential is a measurement of the voltage difference between two points, the fixed value of the reference electrode provides a way to measure the working electrode potential.

In an electrochemical measurement system, current flows in the solution between the working and the counter (or auxiliary) electrode. The counter electrode is typically a wire constructed of platinum or another inert material.

The current measured is a function of the concentration of the $Cd^{+2}$ at the surface of the electrode. The current peaks and starts to decrease when the concentration of $Cd^{+2}$ ions in the diffusion layer (the area close to the electrode) starts to decrease. Beginning at that point, the cadmium must diffuse to the electrode from increasingly greater distances. The measured current then becomes a function of the diffusion of the cadmium ions to the electrode – not simply the reduction of the cadmium ions already in the diffusion layer. The system becomes limited by the mass transport of the ion to the electrode surface or is said to be diffusion controlled. So the current peak (or maximum) occurs because the initial concentration of $Cd^{+2}$ ions at the surface of the electrode is higher than the steady-state concentration.

Figure 3 illustrates how the addition of a second electroactive species to the solution (in this case cadmium and lead) produces multiple peaks. Each peak occurs at a potential characteristic of the reacting species, the type of supporting electrolyte, and the working electrode type.

Note that the lead ion continues to reduce at the potential where the cadmium ion starts to reduce. The resulting peak is additive and represents the reductions of both cadmium and lead. You can use LSV for quantitative electrochemical analysis.

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

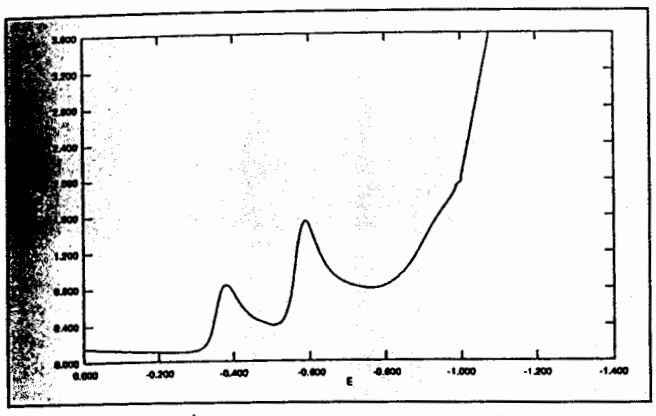


FIGURE 3. Linear sweep voltammogram of cadmium and lead in 0.1 M HCl. Conditions are the same as figure 1.

# Cyclic Voltammetry (CV)

## Overview

Cyclic Voltammetry (CV), one of the more commonly used electroanalytical techniques, is an excellent methods development tool, but is not usually a good technique for quantitative analysis. Its main advantage in electroanalysis is its ability to characterize an electrochemical system.

A single CV experiment only hints at the events that constitute the electrochemical reaction at the electrode. However, multiple CV experiments can be used for a variety of applications, including:

- the determination of Nernstian (reversible) or non-Nernstian (irreversible) behavior of a redox couple.
- the number of electrons transferred in an oxidation or reduction
- formal potentials
- rate constants
- formation constants
- reaction mechanisms
- diffusion coefficients

## Definition

In a CV experiment, the potentiostat applies a potential ramp to the working electrode to gradually change the potential and then reverses the scan, returning to the initial potential (see the triangular waveform in Figure 4).

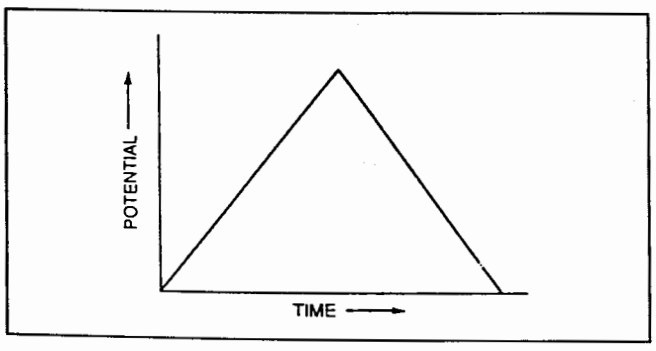



FIGURE 4. Typical excitation waveform for analog cyclic voltammetry.

During the potential sweep, the potentiostat measures the current resulting from the applied potential. These values are then used to plot the CV graph of current versus the applied potential.

You can run single-cycle or multiple cycle CV experiments. The repetition of the potential waveform allows the system to come to a steady-state or allows the buildup of reaction products at the electrode surface.

## Data Interpretation

Figure 5, a typical CV plot, shows the four important pieces of information obtained from a CV experiment – the cathodic peak height ($I_{pc}$), the anodic peak height ($I_{pa}$), the cathodic peak potential ($E_{pc}$), and the anodic peak potential ($E_{pa}$). Note that Figure 5 uses the American convention for plotting electrochemical data – that is, negative potential to the right and cathodic (reductive) current positive (upward).

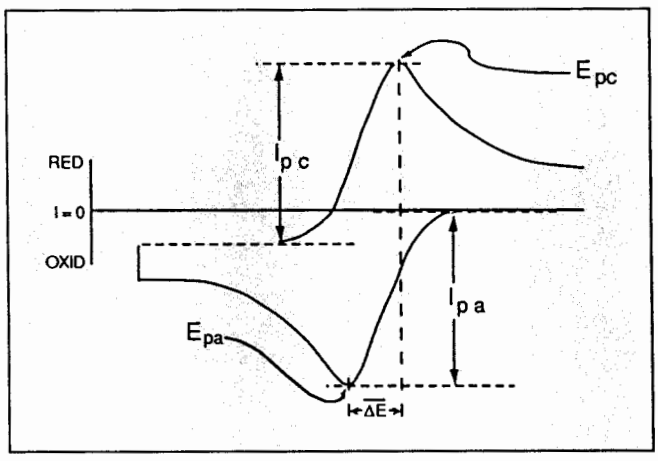



FIGURE 5. Theoretical cyclic voltammogram for a reversible case.

## Single CVs

A single CV is useful for determining whether or not a species is electroactive. A peak current response within a given potential range indicates whether a material has been involved in a reaction.

However, from a single CV plot, you can draw only limited conclusions about the reversibility of a redox couple. One criterion for reversibility is that the $I_{pc}$ should equal the $I_{pa}$, so it may seem that if a single CV shows $I_{pc}$ equal to $I_{pa}$ that the system is reversible. However, if the scan rate is increased the $I_{pc}$ may no longer equal the $I_{pa}$ and the system would appear irreversible. The same can be true of other variables in the experiment. A change of concentration or electrolyte could also affect the results of the experiment. Thus, a single CV is only useful to define reversibility for a very specific set of experimental conditions.

A single CV is also useful in determining the number of electrons transferred in a reaction. If you assume the reaction is reversible (i.e., follows the Nernst equation) you can calculate the number of electrons transferred during the oxidation/reduction.

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

The current maximum for each peak should be 28.5 mV from the formal potential; the potential difference between $E_{pa}$ and $E_{pc}$ should be 57mV(1). These values are good for a one electron transfer. In general the peak separation is expressed by the equation:

$$\Delta E = \frac{(57\text{-}63)\,mV}{n}$$

where n = the number of electrons transferred

## Multiple CVs

Many researchers often find it useful to run multiple CV experiments. This allows the researcher to see chemical changes with time or allows a system to reach equilibrium before measurements are made. In fact, the diagnostic information explained above for a single CV scan is more appropriately used after two or three cycles of the CV are run. Multiple CV experiments also allow the researcher to observe reaction products formed at the surface of the electrode that may not be stable.

## CV Studies

Although the previous examples show that a single CV experiment can yield useful information, you should run a series of CV experiments to fully investigate an electrochemical problem.

In a typical CV study, you run a series of experiments in which you selectively vary the potential scan rate, the experiment temperature, the species concentration, or the ionic strength of the supporting electrolyte.

You can vary the scan rate in a series of experiments to determine the diffusion coefficient of a species. In this approach, you plot the $I_{pc}$ versus the square root of the scan rate (see Figure 6). For a reversible system, the peak

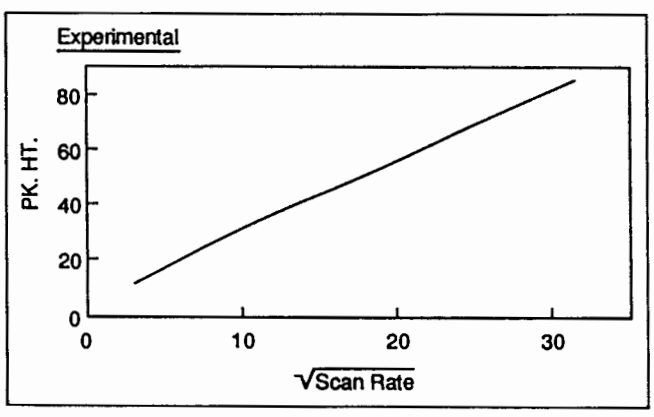



**FIGURE 6. Plot of peak height for cadmium reduction at various scan rates.**

height will increase linearly with the square root of the scan rate. The slope of the resulting line will be proportional to the diffusion coefficient, as shown in the Randles-Sevcik equation(2).

$$i_p = 269n^{3/2}AD^{1/2}v^{1/2}C^b$$

where $i_p$ = peak height (amp)
n = number of electrons
A = area ($cm^2$)
D = Diffusion coefficient ($cm^2sec^{-1}$)
v = scan rate (volts $sec^{-1}$)
$C^b$ = concentration in the bulk of solution (molar)

Another application would be to determine the deviation from reversible behavior of a species in a given environment. Figure 7 represents the data obtained from the same CV experiments as above, but here we have plotted the product of the peak potential difference and the number of electrons transferred versus 1/square root of scan rate. As Figure 7 shows, at high scan rates (where $1/v^{1/2}$ is small) the cadmium redox couple exhibits irreversible behavior. At the more typical scan rates of a few hundred mV/sec, the couple exhibits the more familiar reversible behavior.

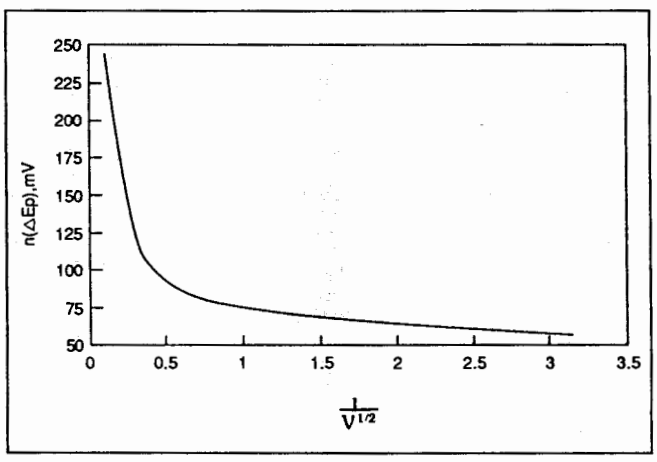



**FIGURE 7. Plot of peak separation at various scan rates for cadmium. Notice that at high scan rates (small values of $\frac{1}{V^{1/2}}$) cadmium does not exhibit reversible behavior.**

The deviation from reversible behavior may be due to coupled chemical reactions, or in this case it may be due to the speed of the charge transfer. The exchange of electrons between an electrode and a species does not happen instantly. You can calculate this charge transfer rate constant (ks) by using the same plot as above. A discussion of the theory of this method and the calculations can be found in a paper by Nicholson(3).

## Analog vs. Digital Measurements

Nicholson and Shain have written many important papers concerning the theory of stationary electrodes(4-10). Their work extended CV theory and single-sweep voltammetry from the reversible case to the more complicated cases of irreversible reactions and electrochemical reactions coupled with chemical reactions.

Nicholson and Shain derived their equations using an analog ramp as the potential waveform in their experiments. However, most modern instruments use computer-generated digital waveforms. Unlike the smoothly

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

changing analog waveform, the digital waveform is made up of small, discrete steps (see Figure 8).

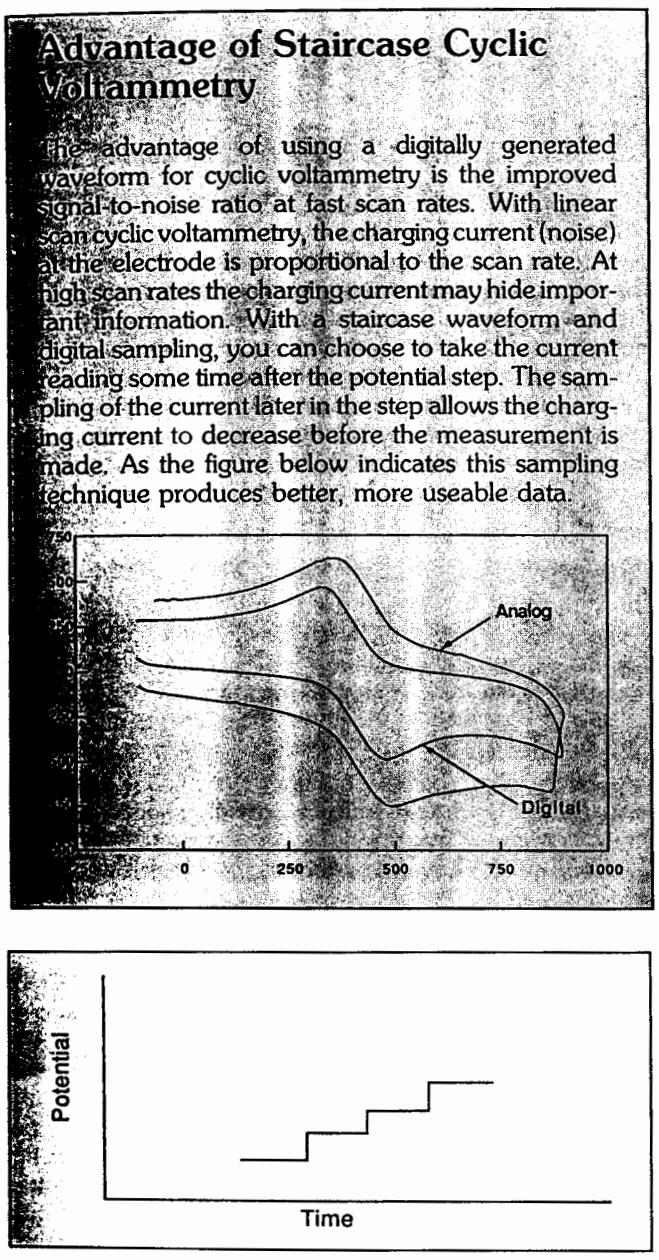



**FIGURE 8. A digital or staircase excitation waveform.**

When a digitally generated waveform is used for cyclic voltammetry, the technique is properly called staircase cyclic voltammetry. Many electrochemists were concerned that the theory developed by Nicholson and Shain would not apply to this non-classical excitation waveform. However, both Perone's(11) empirical work and Osteryoung's(12) rigorous work showed that if you sample the current at the appropriate points during the step, you can expect your results to agree with the Nicholson and Shain theory.

As Figure 9 shows, you can sample the current at 25%, 50%, 75% or 100% of the step time (the time the potential remains the same). Osteryoung(12) has shown that for Abelian (reversible) systems, sampling at 25% of the step time gives results corresponding to those obtained using an analog waveform. However, this is true only if the step height is equal to or less than 8 mV.

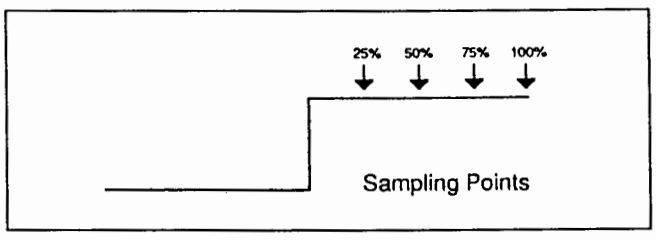



**FIGURE 9. Sampling points along a step time of the excitation staircase.**

The non-Abelian (irreversible) systems best fit the analog theory if you sample the current at 50% of the step time. Figure 10 shows the difference in the voltammograms for Cd at a Hg drop sampled at 25% and 100%. Figure 11 shows the voltammograms for a irreversible system (nickel at a Hg drop) which has been sampled at 50% and 100%.

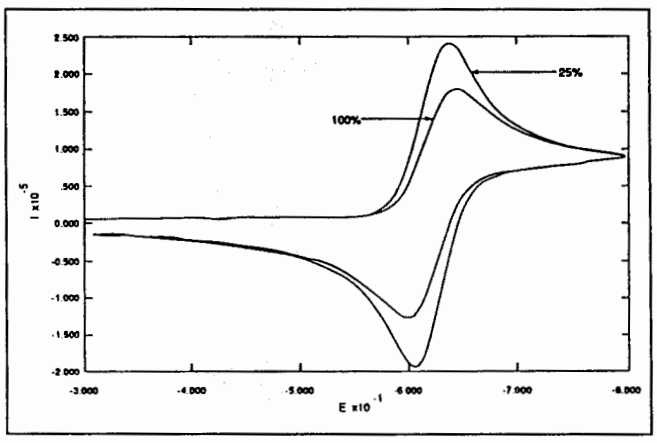



**FIGURE 10. Comparison of results when sampling at 25% and 100% of the step time for a reversible case. Note peak height differences and peak separations.**

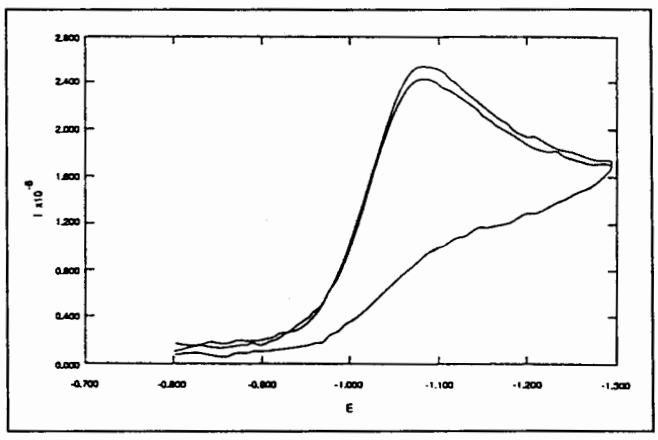



**FIGURE 11. Comparison of results when sampling at 50% and 100% of the step time for an irreversible case. Note that there is little difference.**

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

# Chronoamperometry (CA)

## Overview

Chronoamperometry (CA), another commonly used electroanalytical technique, is a useful tool for determining diffusion coefficients and for investigating kinetics and mechanisms. Unlike the CV technique, CA can yield this information in a single experiment. Moreover, you can run multiple experiments to further characterize the system.

## Definition

When a potential step large enough to cause an electrochemical reaction is applied to an electrode, the current changes with time. The study of this current response as a function of time is called Chronoamperometry (CA).

## Data Interpretation

Figure 12 shows a typical potential excitation waveform and the resulting current response. This response requires semi-infinite linear diffusion (that is, an unstirred solution, linear diffusion to the electrode surface, a planar electrode, and a supporting electrolyte to insure the absence of ion migration) and no other reactions. When these factors govern the system, you can predict the current-versus-time response using the Cottrell equation:

$$i = \frac{nFAD^{1/2}C^b}{(\pi t)^{1/2}}$$

where n = number of electrons
F = Faraday
D = diffusion coefficient
$C^b$ = bulk concentration
A = Area

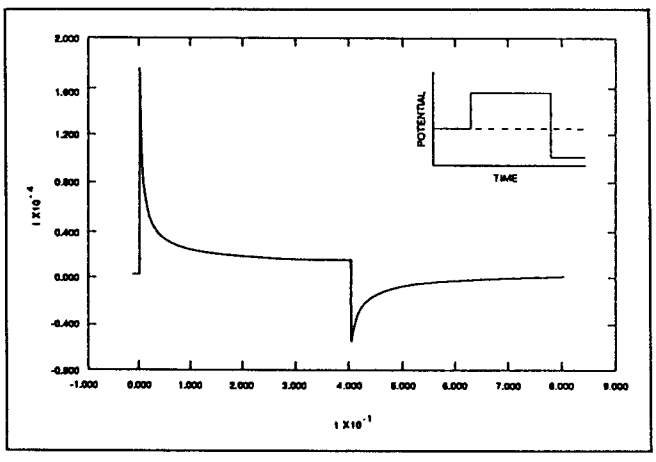



**FIGURE 12. Typical chronoamperogram. Inset is excitation waveform.**

Simply stated, the Cottrell equation shows that the current is proportional to $1/t^{1/2}$ and that a plot of $it^{1/2}$ versus time yields a horizontal line (see Figure 13). Of more interest to the electrochemist, these plots reveal whether or not an electrochemical system deviates from the assumptions of the Cottrell equation.

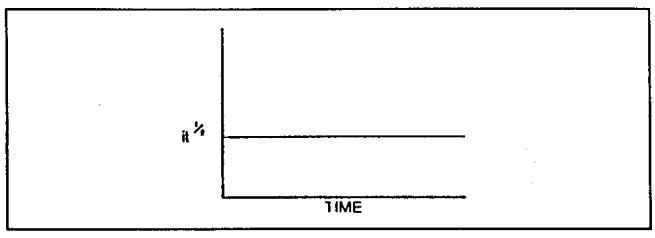



**FIGURE 13. A plot of $it^{1/2}$ versus time for a Cottrellian system.**

Using the Cottrell equation the diffusion coefficient can be calculated by simply rearranging the equation, providing the number of electrons obtained from the CV experiment, and providing values for the other variables. Another useful parameter to calculate is the "true" area of the electrode. In many cases the geometric area of an electrode is not the same as the electrochemically active area. Geometric area calculations assume a smooth surface, but any surface roughness actually increases the available area of the electrode.

## Single CA

In a single experiment, if the measured current does not correspond to that predicted by the Cottrell equation, you can assume either a slow heterogeneous electron transfer or some other slow step in the reaction.

## Multiple CAs

By performing multiple CA experiments, you can tell whether the deviation from the Cottrell equation is caused by slow electron transfer or by a preceding slow chemical reaction. The slow heterogeneous electron transfer will exhibit a strong dependence on the size of the potential step. That is, the shape of the current-versus-time curve will change with the size of the potential step.

In contrast, the preceding chemical reaction will show no dependence on the size of the potential step. However, you should infer a preceding slow chemical reaction only if the potential is stepped to a potential point on the current voltage curve where the reaction is diffusion controlled. All systems will show a potential step dependency if the potential is stepped only to the foot of the peak or only part way up the rising portion of the curve (see Figure 14).

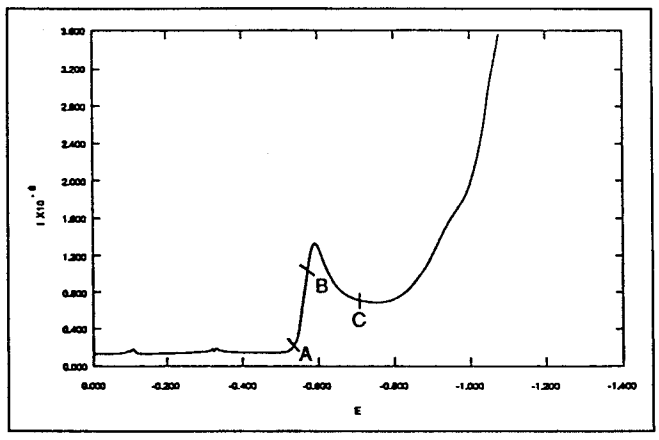



**FIGURE 14. In a CA experiment potential should be stepped to point C, stepping to either A or B will show a potential step dependence for all systems.**

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

## Other Applications

The CA technique is also useful for determining the rate constant of the slow step in a reaction. An example is the ECE mechanism, a reaction in which the first step is an electrochemical reaction (E), the intermediate step is a chemical reaction (C) that forms an electrochemically active species, and the final step is the electrochemical reaction (E) of that species. Alberts and Shain(13) have shown that for the ECE mechanism the apparent value of n can be calculated from the Cottrell equation:

$$n_{apparent} = \frac{i(\pi t)^{1/2}}{FAD^{1/2}C^b}$$

and that from a simple working curve values of the rate constant k can be calculated. Many researchers have used this approach to help determine reaction mechanisms and kinetic constants(14-15).

# Chronocoulometry (CC)

## Overview

Chronocoulometry (CC) is an outgrowth of the Chronoamperometric technique. Although the CC technique is used for many of the same reasons as CA, it has two advantages. First, you can more accurately determine a kinetic rate constant. And second, you can more easily detect adsorption of a species on an electrode surface.

## Definition

In a CC experiment, the charge used in an oxidation or reduction is measured and then plotted with respect to time. The excitation waveform is the same as that used for CA, but the resulting curve shows an increase of charge with time, rather than the decrease of current with time seen in CA.

## Data Interpretation

Like the CA response curve, the CC curve shows that in most reactions, the diffusion of the reacting species to the electrode takes some time (see the theoretical curve in Figure 15). This implies that at the start of the experiment (time zero), the only charge measured is due to the charging of the double layer of the electrode. In cases where a species is adsorbed on the surface of the electrode, the reaction of this material can take place at time zero. This reaction gives rise to current and to a larger value of charge at the initial point than would be expected for a non-adsorbed species (see Figure 15). Many experimenters have used the value of the charge due to adsorption to calculate adsorption layer thickness.

## Measuring Charge

Since CC is based on the same assumptions as CA, the charge at any time can be calculated by simply integrating

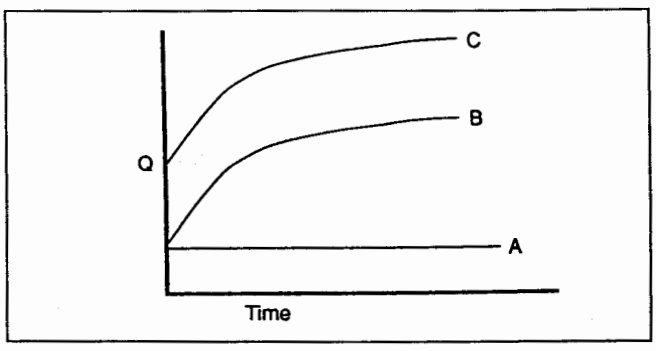



**FIGURE 15. Typical chronocoulogram. A is for a blank solution, B for a system exhibiting redox response, and C for a system exhibiting adsorption effects.**

the Cottrell equation and adding corrections for the charge due to the double layer and any interfacial interactions (for example, adsorption). The resulting equation is:

$$Q = \frac{2nFAC^bD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{d.l.} + Q_i$$

where Q = charge
n = the number of electrons in the reaction
F = Faraday
A = electrode area
$C^b$ = bulk concentration
D = diffusion coefficient
$Q_{dl}$ = charge due to the double layer
$Q_i$ = charge due to interfacial phenomenon

If Q is plotted versus $t^{1/2}$ the result is the Anson plot shown in Figure 16. If we assume that no adsorption occurs, the slope of this line is

$$\frac{2nFAC^bD^{1/2}}{\pi^{1/2}}$$

and the intercept is the double layer charge. If adsorption does occur, the line in Figure 16 would be offset by the charge due to this interfacial phenomenon. It is easy to differentiate between the charge due to the double layer and that due to adsorption. You merely run the same experiment on an electrolyte blank. The blank will not exhibit the adsorption effect but will exhibit the double layer charging current (see Figure 16).

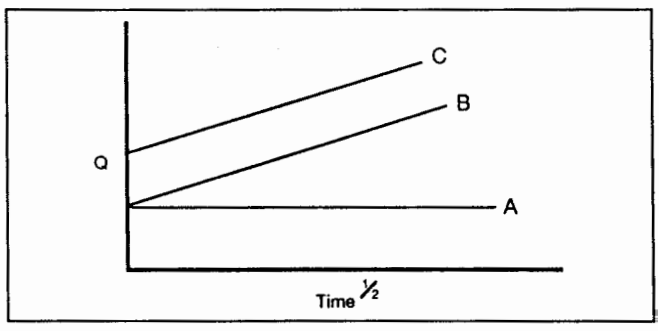



**FIGURE 16. Theoretical Anson plots for a blank (A), a redox system (B), and a system showing adsorbtion (C).**

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

# Chronopotentiometry (CP)

## Overview

Some experimenters use chronopotentiometry for analytical purposes(16). Its major advantage over the more common polarographic/voltammetric methods is its ability to measure higher concentrations. Typical accuracies for the method are 4-5%.

## Definition

Chronopotentiometry (CP) is a technique in which a constant current or a current step is applied to the electrode and the resulting potential change is plotted versus time.

## Data Interpretation

A typical chronopotentiogram is shown in Figure 17. You can understand the curve by considering the events at the electrode surface. In order for current to flow at the electrode, a reaction must take place. The electrode potential is the minimum required to drive a reaction that will support the constant current. If a species is present which is oxidized or reduced more easily than the solvent, the electrode will be driven to the potential appropriate for that reaction. As the concentration of that species at the electrode surface moves toward zero, the potential of the electrode moves toward the next stable potential of the system.

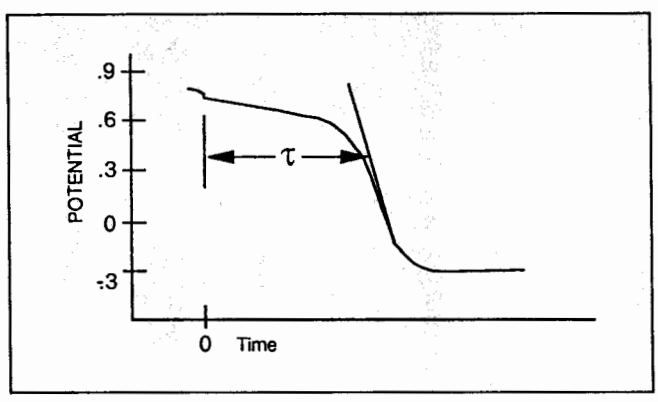



**FIGURE 17. Theoretical chronopotentiogram.**

The chronopotentiogram in Figure 17 is for a single species in an acid solution. The electrode assumes an initial potential required to reduce metal ion $M^{++}$ to metal ion $M^{+}$. As the concentration of $M^{++}$ at the electrode surface decreases, the potential of the electrode gradually moves more negative until the metal ion concentration is depleted at the electrode surface. As soon as no more metal ion exists at the surface, the electrode potential shifts to the potential needed to support a reaction that will give rise to the desired current. In this case that is the reduction of $H^{+}$ to $H_2$ and a potential of $-0.3$ volts versus SCE.

Transition time is the time between cell turn-on and the rapid change in potential. This quantity is related by the Sand equation to the diffusion constant, the area of the electrode, the bulk concentration, and the number of electrons involved in the reaction:

$$\tau^{1/2} = \frac{\pi^{1/2} n FAD^{1/2} C^{b}}{2i}$$

where i = Current
$\tau$ = transition time
F = Faraday
A = Area
D = diffusion constant of species
$C^{b}$ = Concentration of species.

Examination of the Sand equation shows that the transition time is proportional to the concentration since all other values are constant for a given experiment.

## Multiple CPs

In a series of CP experiments, you might vary either the concentration of the species or the applied constant current. If you vary the current, you might want to plot $it^{1/2}$ versus i. For a Nernstian system under diffusion control, this plot should be a horizontal line (see Figure 18). If the system is non-Nernstian, the Sand equation does not apply and you will see deviations from the horizontal line.

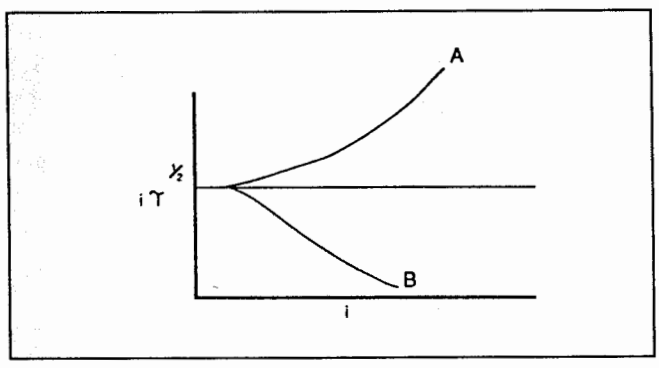



**FIGURE 18. Diagnostic plot of a series of chronopotentiometry experiments. A.—Adsorption. B.—Preceding reaction.**

A positive (upward) deviation is usually due to adsorption effects. The transition time is longer than under diffusion control because of the adsorbed species. As the current is increased, the transition time does not decrease proportionally. It is always larger due to the adsorbed species. At very large currents the adsorbed species makes a more pronounced contribution to the transition time (see Figure 18).

A negative (downward) deviation is usually due to a preceding reaction. This is because the transition time value will be smaller if a preceding reaction limits the concentration of the species at the electrode. The reaction is kinetically controlled and not diffusion controlled. If the concentration of the species is lower it will take less time than the Sand equation predicts for the transition to a different potential. At higher currents the deviation becomes greater as the difference in time required to oxidize or reduce decreases but the time required to produce the electroactive species remains the same.

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

# Square Wave Voltammetry (SWV)

## Overview

Square Wave Voltammetry (SWV), pioneered by Barker (17) in the 1950s, is one of the recent techniques used by electrochemists for analytical, kinetic, and mechanistic work. However, the form of SWV most electrochemists use today, called Osteryoung square wave (18), is based on work done by Ramaley and Krause (19,20) in 1969.

## Definition

Figure 19 shows the excitation waveform used in Osteryoung SWV. With this waveform, you sample the current response to the potential excitation once on each forward pulse and once on each reverse pulse (see Figure 19). Using this technique, you can generate three possible current potential plots – forward current versus potential, reverse current versus potential, or difference current versus potential.

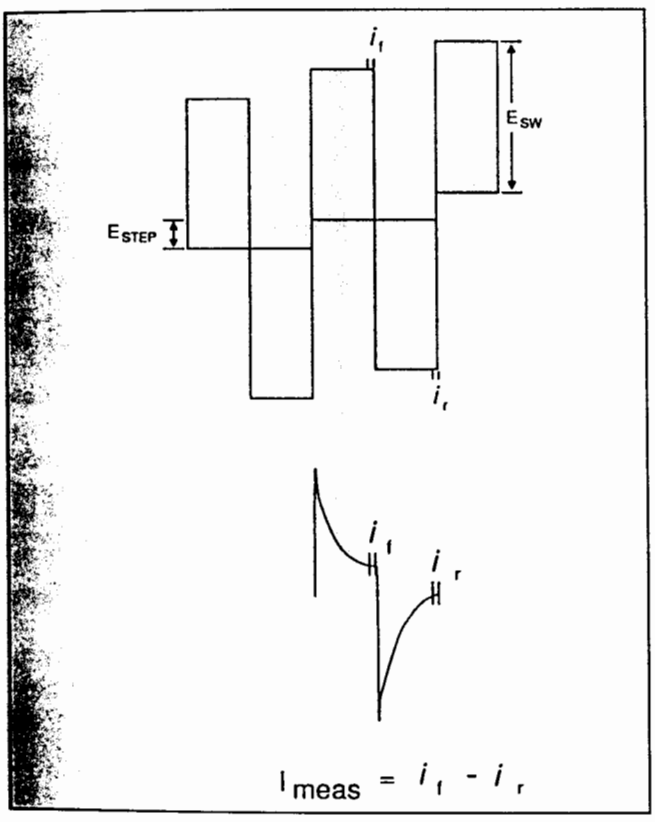



**FIGURE 19. Excitation waveform and current sampling points for Osteryoung squarewave.**

In most analytical applications, you use only the difference plot. The resulting voltammogram yields peaks for each electroactive species present, with the peak height being proportional to the concentration of the species in the bulk of the solution.

The three different plots may also be overlaid. The resulting combination plot has been suggested as the most useful form for investigating kinetics and mechanisms (21).

## Advantages

One of the drawbacks of rapid scanning in CV is that it introduces a large capacitive background current. This background current (or noise) makes it hard to detect the faradaic current, which is the signal of interest, and severely affects the signal-to-noise ratio.

Since SWV is a pulsed technique, it can discriminate against the charging current and eliminate this drawback (see Ref. 18 for a discussion of pulsed techniques). For this reason SWV has an advantage over CV in the following three areas:

**Speed:** Since SWV effectively removes the background current from the measurement, it allows you to program higher scan rates. This lets you make faster measurements and/or investigate faster reactions.

**Sensitivity:** SWV can detect micromolar concentrations of electroactive species. In contrast, cyclic voltammetry can detect only millimolar concentrations. Because of this increased sensitivity, you can run experiments on rare or expensive materials, such as biological materials. You can also detect intermediates that exist at low concentrations.

**Dynamic range:** The dynamic range of a detection system is defined as its ability to respond to both high and low concentrations of electroactive species. Since SWV effectively removes the background current from a measurement, it has a wide dynamic range. This allows you to use concentration as an experimental variable.

## SWV as an Analytical Tool

Square wave voltammetry has become a popular technique for analytical work because of its speed and sensitivity. For more information on square wave voltammetry for analytical purposes, please request EG&G PARC Application Note S-7.

## SWV in Kinetic Studies

SWV has three main advantages in the study of kinetic systems:

You can still obtain reliable data using lower concentrations than in other techniques.

You can use concentration as a parameter in the system under study.

You can study fast reactions.

See O'Dea, et al, (21) for a detailed discussion of SWV theory in kinetic systems.

## The Literature

To date, much of the literature has focused on the theoretical evaluation of SWV as a viable technique. However, given the recent enthusiasm for the technique, upcoming literature will likely reflect the use of SWV in specific applications. Experimenters may begin interpreting SWV data in much the same way as they interpret CV data but without the problems associated with the use of working curves(22).

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

## General References:

A number of good general references for electrochemistry are:


R.N. Adams, *Electrochemistry at Solid Electrodes*, Marcel Dekker, New York, 1969

F.C. Anson, *Electroanalytical Chemistry*, ACS Audio Course, American Chemical Society, Washington, D.C., 1976

A.J. Bard, editor, *Electroanalytical Chemistry*, vol. 1-14, Marcel Dekker, New York

A.J. Bard and L.R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, New York, 1980

P. Delahay and C.N. Reilley, *New Instrumental Methods in Electrochemistry*, Interscience Publishers, New York, 1954

P.T. Kissinger and W.R. Heineman, *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker, New York, 1984

D.T. Sawyer and J.L. Roberts, Jr., *Experimental Electrochemistry for Chemists*, John Wiley & Sons, New York, 1974


## References to text:


1) R.S. Nicholson and I. Shain, *Anal. Chem.* 36:706 (1964)
2) F.C. Anson, *Electroanalytical Chemistry*, page 55, ACS Audio Course Manual, American Chemical Society, Washington, D. C., 1976
3) R.S. Nicholson, *Anal. Chem.* 37:1351 (1965)
4) R.S. Nicholson and I. Shain, *Anal. Chem.* 36:706 (1964)
5) _____, *Anal. Chem.* 37:178 (1965)
6) _____, *Anal. Chem.* 37:190 (1965)
7) M.L. Olmstead and R.S. Nicholson, *Anal. Chem.* 38:150 (1966)
8) D.S. Polcyn and I. Shain, *Anal. Chem.* 38:370 (1966)
9) _____, *Anal. Chem.* 38:376 (1966)
10) R.S. Nicholson, *Anal. Chem.* 38:1406 (1966)
11) S.P. Perone and J.J. Zipper, *Anal. Chem.* 45:452 (1973)
12) J.G. Osteryoung, et al, *J. Electroanal. Chem.* 222:69 (1987)
13) G.S. Alberts and I. Shain, *Anal. Chem.* 35:1859 (1963)
14) M. Kodama and R.W. Murray, *Anal. Chem.* 37:1638 (1965)
15) A.J. Bard, et al, *Anal. Chem.* 35:2210 (1963)
16) D.G. Davis in *Electroanalytical Chemistry* vol. 1, A.J. Bard, Ed., Marcel Dekker, New York, 1966
17) G.C. Barker and I.L. Jenkins, *Analyst* 77:685 (1952)
18) J. Osteryoung and J.J. O'Dea in *Electroanalytical Chemistry* vol. 14 page 212, A.J. Bard, Ed., Marcel Dekker, New York, 1986
19) L. Ramaley and M.S. Krause, Jr., *Anal. Chem.* 41:1362 (1969)
20) _____, *Anal. Chem.* 41:1365 (1969)
21) J.J. O'Dea, et al, *Anal. Chem.* 53:695 (1981)
22) J.J. O'Dea, et al, *J. Phys. Chem.* 90:2761 (1986)


Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

# Glossary

**applied potential** – The potential the potentiostat is forcing the working electrode to assume.

**charge transfer rate constant** – The speed at which an electron is transferred from the one material to another.

**charging current** – The amount of current needed to charge the double layer of the working electrode. It is not due to a redox reaction but is present on all electrochemical measurements. It is typically thought of as noise.

**Cottrell equation** – The mathematical equation which predicts the current measured at any time after a potential step is applied assuming the system under study is governed by semi-infinite linear diffusion.

**counter electrode** – The electrode which provides the current path in an electrochemical cell. It is typically platinum but any inert conductor is useable. In some experiments it should be isolated from the bulk of solution.

**diffusion coefficient** – A measure of how fast an ion migrates in solution using only diffusion as the mode of migration. It is represented by the letter D and its units are $cm^2/sec$.

**diffusion layer** – The area immediately adjacent to the working electrode where the mode of ion transport is governed by diffusion.

**double layer** – The interface between the working electrode and the solution. It is well accepted that this layer behaves as a capacitor would in an electrical circuit. However, the capacitance of this layer changes with potential and this is not typical capacitor behavior.

**ECE mechanism** – A three step reaction mechanism which involves an electrochemical reaction (E) followed by a chemical reaction (C) followed by an electrochemical reaction (E).

**electron transfer** – The movement of an electron from the surface of the working electrode to a species in solution or vice versa.

**faradaic current** – The current in an electrochemical reaction due to an oxidation or reduction.

**formal potential** – The potential at which a given reaction will occur as predicted by thermodynamic equations.

**initial potential** – The starting potential of an experiment.

**ionic strength** – The ionic concentration of a solution as defined by the equation $1/2(m_1Z_1 + m_2Z_2 + m_3Z_3....)$ where m is the molar concentration of each ion and z is the charge.

**mass transport** – The physical movement of an ion or molecule through a solution.

**Nicholson and Shain Theory** – A set of diagnostic criteria used to categorize reactions based on cyclic voltammetry data. The original work was done by Nicholson and Shain in 1964.

**peak separation ($\Delta P$)** – The difference in potential between the forward and reverse peaks.

**potential ramp** – A change in potential at a constant rate. Potential may be ramped up or down.

**potentiostat** – An electrochemical instrument which controls the potential applied to the working electrode.

**purge** – To pass an inert gas through a solution in order to remove oxygen or other unwanted dissolved gases.

**Randles-Sevcik Equation** – A mathematical equation that predicts the current peak height measured for a reversible reaction when a potential ramp is applied to the working electrode.

**reference electrode** – The electrode against which the potential of the working electrode is measured. It is a well-behaved, stable electrochemical half-cell. Typical reference electrodes are Silver/Silver Chloride (Ag/AgCl) and saturated calomel (SCE).

**reversibility** – In electrochemistry the ability for a species to be oxidized (or reduced) to a new species and for that new species to be reduced (or oxidized) back to the original species.

**Sand equation** – A mathematical equation that predicts the transition time of a chronopotentiometry experiment.

**scan rate** – The speed at which the potential is being changed. It is expressed in SI units as volts/second.

**supporting electrolyte** – A conductive solution in which the electrochemical reactions of interest take place. Although usually an aqueous solution of a salt, acid, or base, it can be an organic solvent, molten salt or other conductive media.

**working electrodes** – The electrode where the reaction of interest takes place. It is typically made of an inert material such as Hg, Pt, Ag, Au, or carbon.

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

EG&G PRINCETON APPLIED RESEARCH

**Applied Instruments Group**

**APPLICATION NOTE CORR 1**

# BASICS OF CORROSION MEASUREMENTS

*An introduction to the theory of electrochemical corrosion measurement techniques, including potentiodynamic polarization measurements, polarization resistance, and Tafel plots.*

Table of contents


| | Page |
|---|---|
| Potentiodynamic Polarization Measurements | 2 |
| Polarization Resistance Measurements | 4 |
| Tafel Plots | 6 |
| Corrosion Behavior Diagrams | 11 |
| References | 12 |


Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

# Potentiodynamic polarization measurements

## *Introduction*

Many corrosion phenomena can be explained in terms of electrochemical reactions. It follows, then, that electrochemical techniques can be used to study these phenomena. Measurements of current-potential relations under carefully controlled conditions can yield information on corrosion rates, coatings and films, passivity, pitting tendencies and other important data.

Potentiodynamic anodic polarization is the characterization of a metal specimen by its current-potential relationship. The specimen potential is scanned slowly in the positive-going direction and therefore acts as an anode such that it corrodes or forms an oxide coating. These measurements are used to determine corrosion characteristics of metal specimens in aqueous environments. A complete current-potential plot of a specimen can be measured in a few hours, or in some cases in a few minutes.

Investigations such as passivation tendencies and effects of inhibitors or oxidizers on specimens are easily performed with this technique. With this knowledge the corrosion characteristics of different metals and alloys can be compared on a rational basis and compatible specimen-environment combinations secured for further long-term testing.

## *Electrochemical Principles and Potentiodynamic Polarization Measurements*

When a metal specimen is immersed in a corrosive medium, both reduction and oxidation processes occur on its surface. Typically the specimen oxidizes (corrodes) and the medium (solvent) is reduced. In acidic media hydrogen ions are reduced. The specimen must function as both anode and cathode, and both anodic and cathodic currents occur on the specimen surface. Any corrosion processes that occur are usually a result of anodic currents.

When a specimen is in contact with a corrosive liquid and the specimen is not connected to any instrumentation—as it would be "in service"— the specimen assumes a potential (relative to a reference electrode) termed the *corrosion potential*, $E_{CORR}$. A specimen at $E_{CORR}$ has both anodic and cathodic currents present on its surface. However, these currents are exactly equal in magnitude so there is no net current to be measured. The specimen is at equilibrium with the environment (even though it may be visibly corroding!). $E_{CORR}$ can be defined as the potential at which the rate of oxidation is exactly equal to the rate of reduction.

It is important to stress that when a specimen is at $E_{CORR}$ both polarities of current are present. If the specimen is *polarized** slightly more positive than $E_{CORR}$, then the anodic current predominates at the expense of the cathodic current. As the specimen potential is driven further positive the cathodic current component becomes negligible with respect to the anodic component. A mathematical relationship exists which relates anodic and cathodic currents to the magnitude of the *polarization* (References 2, 3), but a discussion of this relationship is beyond the scope of this application note. Obviously if the specimen is polarized in the negative direction the cathodic current predominates and the anodic component becomes negligible.

Experimentally one measures polarization characteristics by plotting the current response as a function of the applied potential. Since the measured current can vary over several orders of magnitude, usually the log current function is plotted vs. potential on a semi-log chart. This plot is termed a *potentiodynamic polarization plot*. Note that the use of a semi-log display prevents indication of polarity on such plots. Potentials negative of $E_{CORR}$ give rise to cathodic current while potentials positive of $E_{CORR}$ give rise to anodic current.

Figure 1 shows the potentiodynamic anodic polarization plot of a sample of 430 stainless steel. The logarithm of the current is plotted (as the abscissa) as a function of the applied potential (the ordinate). This plot can be described in the following way:

Region A in Figure 1 is the *active* region in which the metal specimen corrodes as the applied potential is made more positive. At B further increase in the rate of corrosion (as measured by the current) ceases and the onset of *passivation* begins. The loss of chemical reactivity under certain environmental conditions, probably due to the formation of a film on the surface of the metal, is referred to as specimen passivation. This point is characterized by two coordinate values, the *primary passive potential* ($E_{PP}$) and the *critical current density* ($i_C$). In region C the current decreases rapidly as the passivating film forms on the specimen. A small secondary peak is observed followed by region D where there is little change in current as the potential is increased. The passivating film begins to break down in region E, the *transpassive* region.

A potentiodynamic anodic polarization plot such as Figure 1 can yield important information such as

(1) The ability of the material to spontaneously passivate in the particular medium;

(2) The potential region over which the specimen remains passive; and

(3) The corrosion rate in the passive region.

* This implies use of a voltage source to force the specimen to assume a potential other than the corrosion potential. The current measured in this case is a net current, representing the difference between anodic and cathodic currents.



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

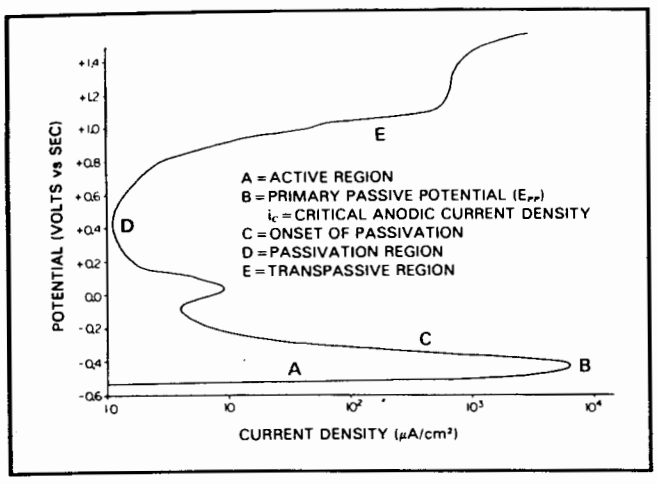



**FIGURE 1. Standard potentiodynamic anodic polarization plot of 430 stainless steel**

The following discussion will deal with a class of metals that can exhibit active to passive behavior. Whether a specimen will or will not passivate depends on the form and intersection of the individual anodic and cathodic polarization plots. A diagrammatic presentation of these concepts in Figure 2 will be helpful.

Figures 2A, 2B, and 2C are "theoretical" examples of an anodic polarization curve (labeled a), upon which are superimposed three "idealized" cathodic polarization curves (diagonals, labeled c). Each cathodic curve represents a single reduction process (such as hydrogen evolution) with different possible exchange current densities. These curves are theoretical in nature because it is not possible to independently measure the *cathodic* curve at potentials positive to the corrosion potential since the specimen has net anodic character in this region. Similarly it is also not possible to independently measure anodic performance at potentials negative to $E_{CORR}$. In these figures $E_{CORR}$ corresponds to the intersection point(s) of the individual anodic and cathodic plots—the point(s) at which the anodic current exactly equals the cathodic current. As previously stated, in the vicinity of $E_{CORR}$ both currents are present in the specimen, but experimentally it is possible to measure only the net current. The net current has a single measurable polarity— either positive or negative. At $E_{CORR}$ the net measured current is exactly zero.

Figures 2D, 2E, and 2F correspond to the experimentally-determined curves for Figure 2A, 2B and 2C, respectively. It is instructive to treat each pair separately.

If the cathodic curve intersects the anodic curve in the passive region only, as in Figure 2C, the material will passivate spontaneously. Such behavior is exhibited by stainless steels and titanium in acid solutions containing oxidizers. This situation is the most desirable from a materials construction point of view and is easiest to facilitate if the critical anodic current density can be made small enough so as not to intersect the reduction polarization curve. Experimentally, Figure 2F does not exhibit the peak-shaped active to passive transition because the

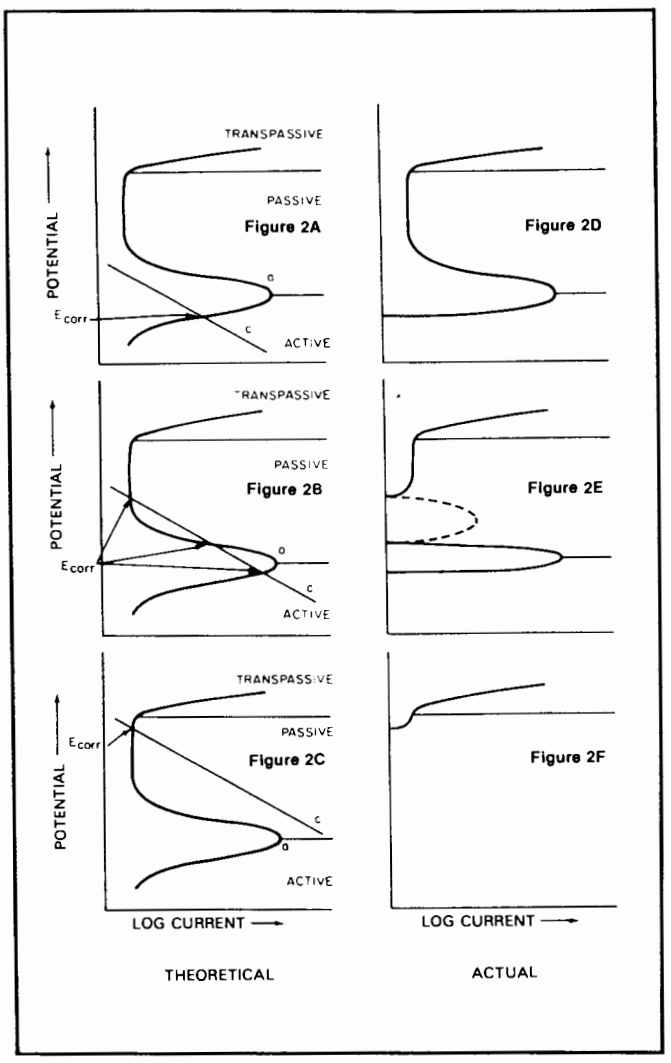



**FIGURE 2. Theoretical and actual potentiodynamic polarization plots of active-passive metals.**

specimen has already been fully passivated. In the Corrosion Behavior Diagram section of this application note a procedure will be described that permits experimental observation of the peak-shaped active to passive transition.

If the cathodic curve intersects the anodic curve in the active region as is in Figure 2A the specimen will corrode rapidly even though it may be passivated under other experimental conditions. This behavior is observed for titanium in dilute, air-free sulfuric or hydrochloric acid. Figure 2D, the experimental counterpart to the theoretical Figure 2A, shows very similar shape to the anodic portion of 2A since the intersection of the polarization curves occurs low in Figure 2A and the anodic portion predominates. Obviously Figure 1 for 430 stainless steel corresponds to the shape of Figure 2D except that 430 stainless exhibits a secondary peak in the passive region.

If the cathodic curve intersects the anodic curve as in Figure 2B the specimen can exhibit either high corrosion rates or low corrosion rates. Such behavior is observed for chromium in air-free sulfuric acid or iron in dilute nitric



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

acid. Figure 2B indicates intersections in each of active, partially passive, and passive regions. Measurement of the polarization curve of the specimen yields Figure 2E in which "cathodic" current loops are observed after the peak-shaped active to passive transition has already occurred. Multiple loops can also be observed if the anodic and cathodic lines become superimposed in the partially passive region. In effect the specimen doesn't know whether to behave as an anode or a cathode—or both. Metals which exhibit this behavior are undesirable since a surface believed to be passive can be rendered active by scratching the passive film or through some other mechanism. Once the surface becomes active it may not passivate again and corrosion can proceed to complete destruction of the material.

At this point it is instructive to consider how the polarization curves can be manipulated to yield the desirable curve in Figure 2F, in which the specimen has spontaneously passivated. This can be achieved by arranging conditions such that the critical anodic current density, $i_C$, lays below the cathodic polarization curve. This in turn is done by:

(1) Choosing alloying materials which have a small critical anodic current density.

(2) Adding a sufficient quantity of oxidizer ($Fe^{3+}$, $Cu^{2+}$, $CrO_4^{2-}$, etc.) so that a specimen exhibiting Figure 2D behavior is converted to Figure 2F behavior.

(3) Taking advantage of velocity effects for metals in contact with flowing streams which corrode under diffusion control (see Reference 2 for more details).

In summary, potentiodynamic polarization measurements are valuable in rapidly identifying desirable materials-environment combinations and in predicting how a material will behave when exposed to a particular environment. The technique quickly indicates the ability of the specimen to protect itself against aggressive attack from the liquid environment. However, it must be recognized that the procedures described in this note correspond to an artificial method for corroding the sample. This approach is similar to the use of elevated temperature studies to artificially accelerate a kinetically-limited or aging process. Accordingly these procedures can aid in predicting how a sample might behave over the long term but they should not be used to replace long term studies where other mechanisms may be operative.

# Polarization resistance

## *Introduction*

The electrochemical technique of polarization resistance is used to measure absolute corrosion rates, usually expressed in milli-inches per year (mpy). Polarization resistance measurements can be made very rapidly, usually in less than ten minutes. Excellent correlation can often be made between corrosion rates obtained by polarization resistance and conventional weight-loss determinations. Polarization resistance is also referred to as "linear polarization".

## *Polarization Resistance*

A polarization resistance measurement is performed by scanning through a potential range which is very close to the corrosion potential, $E_{CORR}$ (see Figure 3). The potential range is generally $\pm 25$ mV about $E_{CORR}$. The resulting current is plotted versus potential, as shown in Figure 4. The corrosion current, $i_{CORR}$*, is related to the slope of the plot through the following equation.

$$\Delta E/\Delta i = \frac{\beta_A \beta_C}{2.3\ (i_{CORR})(\beta_A + \beta_C)} \qquad (1)$$

where

$\Delta E/\Delta i$ = slope of the Polarization Resistance plot, where $\Delta E$ is expressed in volts and $\Delta i$ is expressed in $\mu$A. This slope has units of resistance, hence, Polarization Resistance.

$\beta_A, \beta_C$ = anodic and cathodic Tafel constants (must be determined from a Tafel Plot—see Section III). These constants have units of volts/decade of current.

$i_{CORR}$ = corrosion current, $\mu$A.

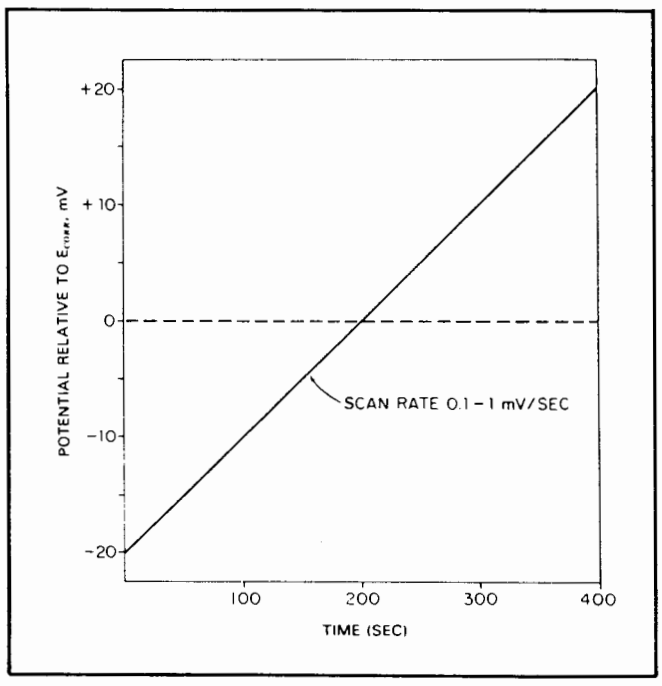



**FIGURE 3. Excitation waveform for polarization resistance.**

* In this application note, "i" will be used to represent current, while "I" will denote current density.



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

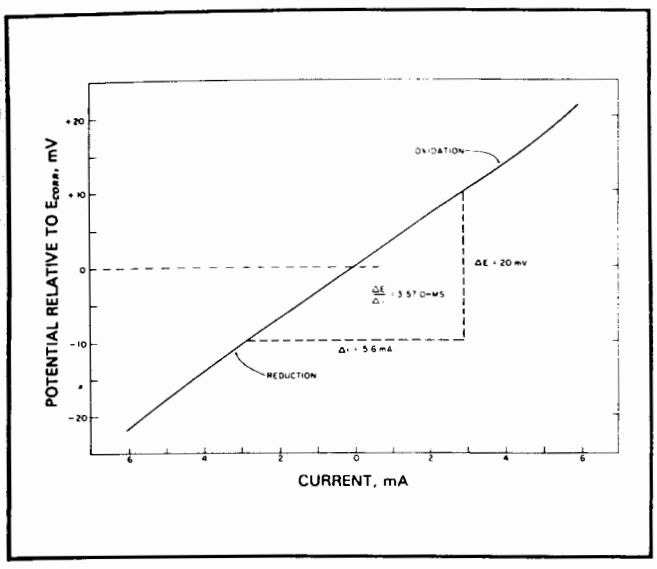



**FIGURE 4. Experimentally measured polarization resistance.**

Rearranging equation (1)

$$i_{CORR} = \frac{\beta_A \beta_C}{2.3(\beta_A + \beta_C)} \quad \frac{\Delta i}{\Delta E} \tag{2}$$

The corrosion current can be related directly to the corrosion rate through the following equation.

$$\text{Corrosion Rate (mpy)} = \frac{0.13\, I_{CORR}(\text{E.W.})}{d} \tag{3}$$

where
E.W. = equivalent weight of the corroding species, g.
d = density of the corroding species, g/cm³
$I_{CORR}$ = corrosion current density, μA/cm²

See Section III of this application note for derivation of equation (3). For a more complete discussion of corrosion potential and corrosion current, see Sections I and III.

## *Electrochemical Corrosion Theory and Polarization Resistance*

Stern and Geary[15] have provided a firm theoretical background for polarization resistance measurements. The derivation is summarized in this section. For more detail, the original reference should be consulted.

In a corroding system, two co-existing electrochemical reactions are present.

$$M^+ + e^- \rightleftharpoons M \tag{4}$$

$$Z^+ + e^- \rightleftharpoons Z \tag{5}$$

where M is the corroding metal and Z is usually a species in solution. The current-potential relationship of such a mixed-couple system is shown in Figure 5[16]. The equilibrium potentials of the couples in equations (4) and (5) are labeled $E_{EQ,M}$ and $E_{EQ,Z}$, respectively, in Figure 5. When the corrosion potential is sufficiently removed from $E_{EQ,M}$ and $E_{EQ,Z}$, the rate of reduction of $M^+$ becomes insignificant compared to the rate of oxidation of M, and the rate of oxidation of Z becomes insignificant with respect to the rate of reduction of $Z^+$. The corrosion potential is the potential at which the rate of oxidation of M (defined by current $i_{O,M}$) is equal to the rate of reduction of $Z^+$ (defined by current $i_{R,Z}$). The terms "rate" and "current" are used interchangeably since, according to equation (3), they are directly proportional. Since the *net* current is the difference between the oxidation and reduction currents, the current measured with an external device will be zero.

$$i_{MEAS} = i_{O,M} - i_{R,Z} = 0 \text{ at } E_{CORR} \tag{6}$$

and

$$i_{CORR} = i_{O,M} = i_{R,Z}.$$

To calculate the corrosion rate, $i_{CORR}$ must be determined.

When a potential is imposed on the metal specimen from an external voltage source, such as a potentiostat, a current will pass according to the following equation.

$$i_{MEAS} = i_{O,M} - i_{R,Z} \tag{7}$$

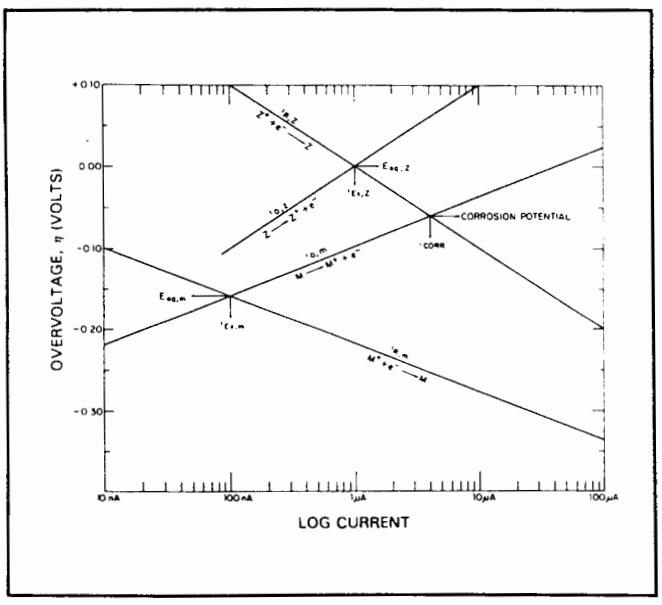



**FIGURE 5. Potential-current relationship for a mixed-electrode system consisting of two electrochemical reactions.**

The anodic and cathodic currents obey the Tafel equations (see Section III).



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

$$\eta = \beta_A \log \frac{i_{o,M}}{i_{CORR}} \quad (8)$$

$$\eta = -\beta_C \log \frac{i_{R,z}}{i_{CORR}} \quad (9)$$

where
$\eta$ = overvoltage, the difference between the potential imposed on the specimen and the corrosion potential, $\eta = E_{APP} - E_{CORR}$.

Equations (8) and (9) may be rearranged to give

$$\log \frac{i_{o,M}}{i_{CORR}} = \eta/\beta_A \quad (10)$$

$$\log \frac{i_{R,z}}{i_{CORR}} = -\eta/\beta_C \quad (11)$$

Since $\log x = y$ is the same as $10^y = x$, equations (10) and (11) may be rewritten as

$$10^{\eta/\beta_A} = \frac{i_{o,M}}{i_{CORR}} \quad (12)$$

$$10^{-\eta/\beta_C} = \frac{i_{R,z}}{i_{CORR}} \quad (13)$$

Substitution of equation (12) and (13) into (7) yields

$$i_{MEAS} = i_{CORR}(10^{\eta/\beta_A} - 10^{-\eta/\beta_C}) \quad (14)$$

$10^x$ can be approximated by the following power series

$$10^x = 1 + 2.3x + \frac{(2.3x)^2}{2!} + \ldots\ldots + \frac{(2.3x)^n}{n!} \quad (15)$$

If x in this series is small, the third and later terms of the series can be neglected without significant error. Substituting $\eta/\beta_A$ and $-\eta/\beta_C$ for x gives

$$10^{\eta/\beta_A} = 1 + 2.3\ \eta/\beta_A \quad (16)$$

$$10^{-\eta/\beta_C} = 1 - 2.3\ \eta/\beta_C \quad (17)$$

Substitution of equations (16) and (17) into equation (14) and simplifying yields

$$i_{MEAS} = 2.3\ i_{CORR}\ \eta\ \frac{\beta_A + \beta_C}{\beta_A \beta_C}$$

Rearrangement to solve for polarization resistance gives

$$\eta/i_{MEAS} = \frac{\beta_A \beta_C}{2.3\ i_{CORR}\ (\beta_A + \beta_C)} \quad (18)$$

which is identical to equation (1).

It is important to realize that equation (18) is valid only if the assumption regarding equation (15) is valid, i.e., $\eta/\beta$ is small. This means that $\eta$ must be small compared to $\beta$. A typical value of $\beta$ is 100 mV/decade. The overvoltage in this case should be less than 10 mV.

### *Remarks*

Polarization resistance is an extremely rapid procedure for determining corrosion rates. At a scan rate of 0.1 mV/sec, a potential range of 50 mV requires less than ten minutes. The rapidity of the measurement also makes polarization resistance useful for less rigorous experiments, such as qualitative evaluation of inhibitors.

Since the applied potential is never far removed from the corrosion potential, the surface of the specimen is not materially affected by the experiment, and the same specimen can often be used in other studies.

For most accurate results, the Tafel constants, $\beta_A$ and $\beta_C$, must be independently determined from a Tafel Plot (see Section III). For a more rapid measurement, values of the Tafel constants may be assumed. Tafel constants are generally found to be in the range of 0.1 V/decade. Pourbaix[17] has found that if $\beta_A$ and $\beta_C$ are assumed to be 0.1 V/decade, the calculated corrosion rate will be correct within a factor of 2.2. In many cases, more accurate Tafel constants can be inferred from the literature for similar chemical systems.

Experimentally, polarization resistance data can exhibit significant curvature within 10-20 mV of the corrosion potential. This deviation from linearity is theoretically recognized. For further discussion on this phenomenon and procedures for calculating the corrosion current, see References 18 through 23 and Reference 34.

## Tafel plots

### *Introduction*

Electrochemical techniques of corrosion measurement are currently experiencing increasing popularity among corrosion engineers, due primarily to the rapidity with which these measurements can be made. Long-term corrosion studies, such as weight-loss determinations, may take days or weeks to complete, while an electrochemical



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

experiment will require, at most, several hours. The speed of electrochemical measurements is especially useful for those metals or alloys which are highly corrosion resistant.

This section describes the use of Tafel Plots to measure corrosion rates. Tafel Plots will be described in terms of electrochemical corrosion theory.

## *Tafel Plots*

A Tafel Plot is performed on a metal specimen by polarizing the specimen about 300 mV anodically (positive-going potential) and cathodically (negative-going potential) from the corrosion potential, $E_{CORR}$, as shown in Figure 6. The potential does not have to be scanned, but can be "stepped" in a staircase waveform, if desired. The resulting current is plotted on a logarithmic scale as shown in Figure 7.

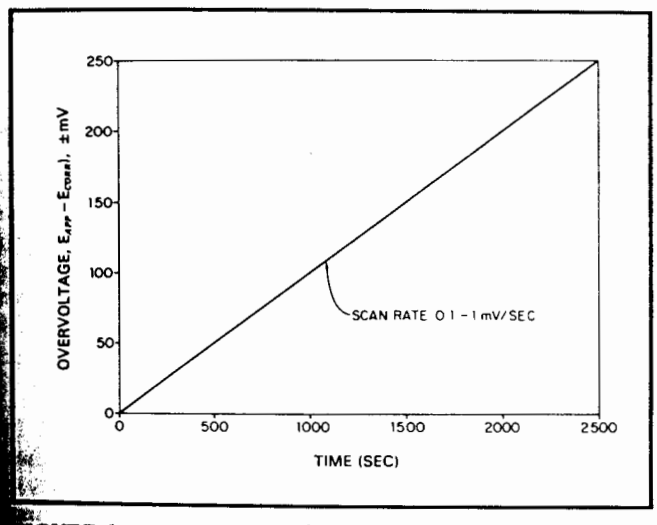
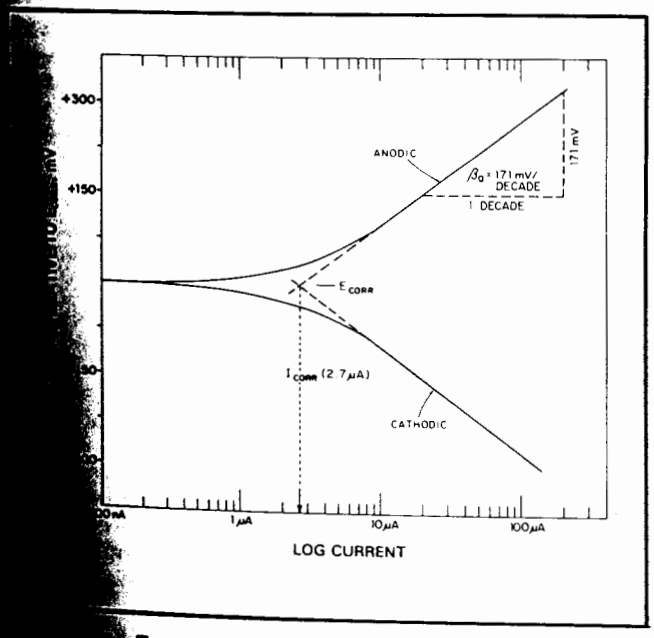



**FIGURE 6. Excitation waveform for Tafel plots.**




**Experimentally measured Tafel plot.**

The corrosion current, $i_{CORR}$, is obtained from a Tafel Plot by extrapolating the linear portion of the curve to $E_{CORR}$, as shown in Figure 7. The corrosion rate can be calculated from $i_{CORR}$ by using Equation 3.

The anodic or cathodic Tafel Plots are described by the Tafel equation.

$$\eta = \beta \log \frac{i}{i_{CORR}} \qquad (19)$$

where

$\eta$ = overvoltage, the difference between the potential of the specimen and the corrosion potential

$\beta$ = Tafel constant

$i_c$ = current at overvoltage $\eta$, $\mu$A

Rearrangement of equation (19) gives

$$\eta = \beta \ (\log i - \log i_{CORR}) \qquad (20)$$

This equation has the form $y = mx + b$, so a plot of $\eta$ vs. log i is a straight line with slope $\beta$. Notice from equation (20) that when $\eta = 0$ ($E_{CORR}$), log $i/i_{CORR} = 0$, or $i/i_{CORR} = 1$, or $i = i_{CORR}$.

Tafel constants, designated $\beta_A$ and $\beta_C$, must be calculated for both the anodic and cathodic portions of the Tafel Plot. The unit of the Tafel constant is either mV/decade or V/decade. A decade of current is one order of magnitude. A Tafel constant calculation is illustrated in Figure 7. Tafel constants are used to calculate corrosion rates from polarization resistance data (see Section II).

## *Calculation of Corrosion Rate from the Corrosion Current*

According to Faraday's Law

$$Q = \frac{nFW}{M} \qquad (21)$$

where

Q = coulombs

n = number of electrons involved in the electrochemical reaction

F = the Faraday, 96,487 coulombs

W = weight of electroactive species

M = molecular weight

From equation (21),

$$W = QM/nF$$

Since equivalent weight = M/n

$$W = \frac{Q \times E.W.}{F}$$



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

and since Q = it from Faraday's Law,

$$W = \frac{i\,t(E.W.)}{F} \qquad (22)$$

W/t is the corrosion rate (C.R.) in grams/second. It is convenient and traditional to express corrosion rate as milli-inches per year (mpy). These units provide an indication of penetration.

Dividing equation (22) by the electrode area and the density gives

$$C.R.\ (cm/sec) = i\ (E.W.)/dFA$$

Convert seconds to years and centimeters to milli-inches. Convert the Faraday (amp-sec/eq) to microamps.

$$C.R.\ (mpy) = \frac{i(E.W.) \times 31.6 \times 10^6 \times 10^3}{dFA \times 2.5 \times 10^6}$$

Express the terms i/A as current density. Combining all the constants gives

$$\text{Corrosion Rate (mpy)} = \frac{0.13\ I_{CORR}(E.W.)}{d} \qquad (23)$$

where
$I_{CORR}$ = corrosion current density, $\mu A/cm^2$
E.W. = equivalent weight of the corroding species,g
d = density of the corroding species, $g/cm^3$

Equation (23) is used to calculate the corrosion rate directly from $I_{CORR}$.

## *Electrochemical Corrosion Theory and Tafel Plots*

According to the mixed potential theory[26], any electrochemical reaction can be divided into two or more oxidation and reduction reactions, and there can be no accumulation of electrical charge during the reaction (to avoid confusion later, note that this electrochemical reaction is taking place in the *absence* of any externally applied potential). In a corroding system, then, oxidation of the metal (corrosion) and reduction of some species in solution is taking place at the same rate, and the net measurable current is zero.

$$i_{MEAS} = i_{RED} - i_{OX} = 0 \qquad (24)$$

When a metal or alloy is placed in contact with a solution, the metal will assume a potential that is dependent upon the metal and the nature of the solution. This "open-circuit" potential, i.e., no external potential is applied to the cell, is referred to as the corrosion potential, $E_{CORR}$. $E_{CORR}$ should be measured with a potentiometer*.

* A potentiometer does not draw any current while making a voltage measurement.

It is essential to the understanding of corrosion phenomena to realize that the oxidation current(s) and the reduction current(s) at the corrosion potential are equal and *nonzero*. Unfortunately, only the total current is measurable, and the net current is zero, in accordance with equation (24).

The mechanism of corrosion is extremely complex in comparison to a homogeneous chemical system. Not only may several different elements be present, but several different compounds of each element may be present or may be formed during the corrosion process. There are also surface effects to consider. For this reason, corrosion rate measurements must be made rather non-specific with regard to the element in the metal or alloy. For example, rate measurement by weight-loss determination requires no presumption of the actual identity of the corroding species.

Electrochemically, corrosion rate measurement is based on the determination of the oxidation current at the corrosion potential. This oxidation current is called the corrosion current, $i_{CORR}$. Equation (19) may now be rewritten as

$$i_{MEAS} = i_{CORR} - i_{RED} = 0 \text{ at } E_{CORR} \qquad (25)$$

Current has the units of coulombs per second. As shown in the last section, coulombs can be equated to the weight of electroactive material through Faraday's Law. The corrosion current, then, is related directly to the corrosion rate. A Tafel Plot is performed to experimentally determine $i_{CORR}$, from which the corrosion rate is calculated.

*Stern-Geary Treatment*

Much of modern corrosion techniques are based on theoretical analyses of the shape of polarization curves by Stern and Geary[15]. The following is a brief description of the derivation. For more details, the original papers should be consulted.

In a simple non-corroding system containing Z and $Z^+$ (such as a copper electrode in contact with a $Cu^{2+}$ solution), at equilibrium

$$Z^+ + e^- \rightleftharpoons Z$$

and

$$i_{R,Z} = i_{O,Z} = i_{EX} \qquad (26)$$

where
$i_{R,Z}$ = current for reduction of $Z^+$
$i_{O,Z}$ = current for oxidation of Z
$i_{EX}$ = the exchange current (analogous to $i_{CORR}$ in a corroding system)

If a potential is imposed on the metal from an external voltage source and the reaction rate is controlled by a slow chemical step that requires an activation energy

$$i_{R,Z} = i_{EX} e^{-\eta/\beta'} \qquad (27)$$



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

$$i_{o,z} = i_{EX} e^{\eta/\beta''} \quad (28)$$

where

$\eta$ = the overvoltage, the difference between the potential imposed on the specimen and the corrosion potential, $\eta = E_{APP} - E_{CORR}$

$\beta'$ and $\beta''$ are constants

Taking the log of equations (27) and (28) and solving for $\eta$ yields

$$\eta = -\beta_C \log \frac{i_{R,z}}{i_{EX}} \quad (29)$$

$$\eta = \beta_A \log \frac{i_{o,z}}{i_{EX}} \quad (30)$$

where $\beta_C = 2.3\beta'$ and $\beta_A = 2.3\beta''$.

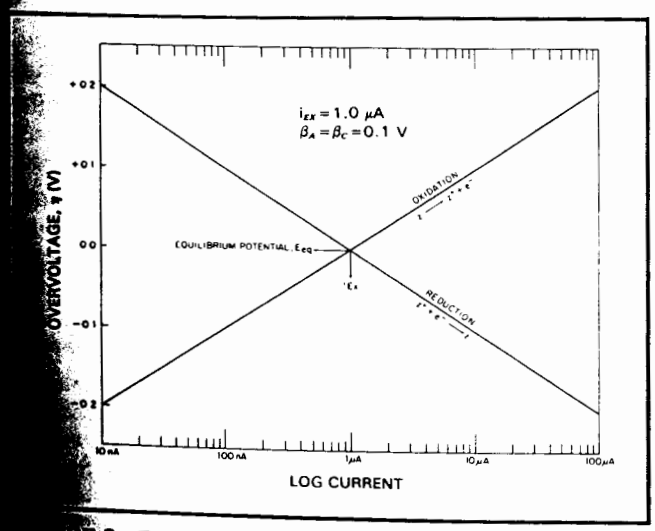
Equations (29) and (30) are called Tafel equations after J. Tafel, who proposed an equation of similar form in 1904 to express hydrogen overvoltage as a function of current density[27].

When the equilibrium of the reaction is disturbed by an externally applied potential, the rates of the forward and reverse rates change as shown in Figure 8[27]. An exchange current of 1 $\mu$A and Tafel Constants of 0.1 V were assumed. Figure 8 was constructed from equations (29) and (30). Experimentally, only the total current is measured. The total current is the difference between the rate of oxidation and the rate of reduction.

$$i_{MEAS} = i_{R,z} - i_{o,z} \quad (31)$$

In Figure 8, if a potential of $-0.10$ V is applied, the rate of reduction is 10 $\mu$A and the rate of oxidation is $-0.1$ $\mu$A. The measured current will therefore be 9.9 $\mu$A.

It is obvious from Figure 8 and equation (31) that as the difference between $E_{APP}$ and $E_{CORR}$ becomes more negative, $i_{MEAS}$ approaches $i_{R,z}$.




**RE 8. Response of a reduction-oxidation system to an lly applied potential.**

Substituting equation (13) into equation (11) gives

$$\eta = -\beta_C \log \frac{i_{MEAS} + i_{o,z}}{i_{EX}} \quad (32)$$

A plot of $\eta$ vs log $i_{MEAS}$ is shown in Figure 9[27]. Deviation from linear Tafel behavior occurs at low current levels. Only when the oxidation current becomes insignificant with respect to the reduction current will a true Tafel relationship be obtained.

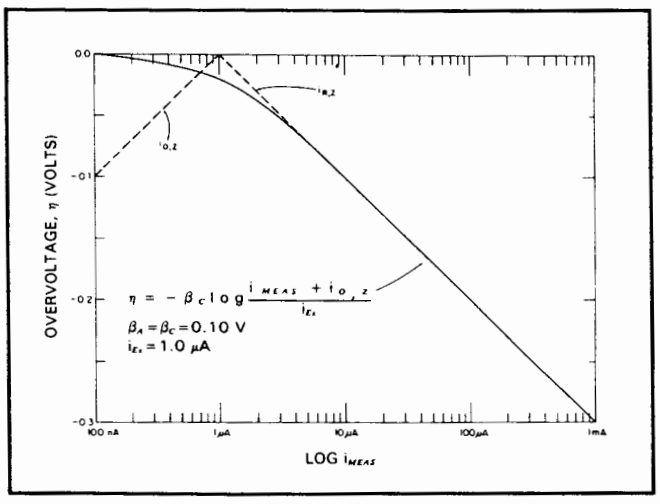



**FIGURE 9. Measured current as a function of externally applied potential.**

The relationships described thus far are dependent only on activation overvoltage. This measurement may be complicated by two interfering phenomena: concentration polarization and resistance drop effects.

Concentration polarization occurs when the reaction rate is so high that the electroactive species cannot reach or be removed from the electrode surface at a sufficiently rapid rate. The reaction rate becomes diffusion controlled. Figure 10[27] illustrates the effect of concentration polarization on the experiment. As $\eta$ increases, the current becomes diffusion limited and the linear current range is truncated. The effect of concentration polarization is minimized by stirring the solution.

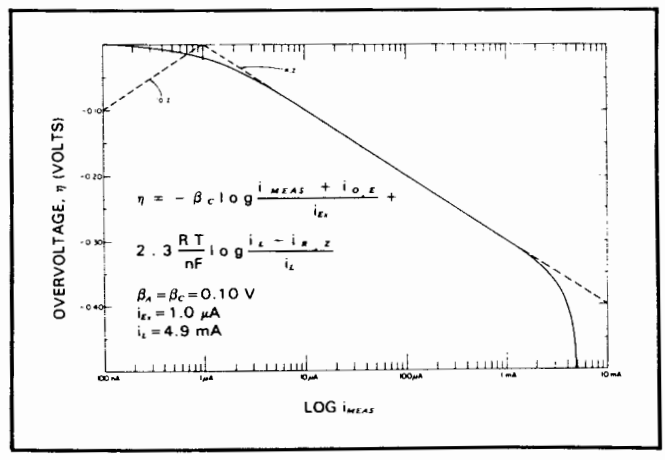



**FIGURE 10. Effect of concentration polarization on measured current as a function of applied potential.**



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Resistance drops across the solution can also cause non-linear Tafel behavior at high currents.

$$E_{IR} = i_{MEAS}\, R_{SOLN}$$

$R_{SOLN}$ is the uncompensated resistance of the solution, i.e., the resistance between the working electrode and the reference electrode bridge tube. It is dependent on the geometry of the electrodes. As $i_{MEAS}$ increases, $E_{IR}$ increases, causing an error in the true potential at the working electrode.

The effects of concentration polarization and resistance drops are most serious when $i_{EX}$ (or $i_{CORR}$) is large and high currents are needed to verify Tafel behavior. As a general rule, linearity over two decades of current is desired. This may require current measurements in the region of 1000 $i_{CORR}$.

*In a corroding system*, the situation is more complicated. In addition to the reaction treated above,

$$Z^+ + e^- \rightleftharpoons Z$$

the corroding metal must also be considered

$$M^+ + e^- \rightleftharpoons M$$

Each of these systems has its own equilibrium potential, exchange current, and Tafel slope. At the corrosion potential,

$$i_{R,Z} + i_{R,M} = i_{O,Z} + i_{O,M} \qquad (33)$$

Figure 5[27] illustrates the potential-current relationships for such a mixed-electrode system. In Figure 5, the Tafel constants for M are assigned a value of 0.06 V and $i_{EX}$ for M is assigned a value of 0.1 $\mu$A. The equilibrium potential for M is arbitrarily assumed to be $-0.160$ V compared to the equilibrium potential of Z.

The corrosion rate by definition is $i_{O,M} - i_{R,M}$. By rearrangement of equation (33) it may also be defined as $i_{R,Z} - i_{O,Z}$. When the corrosion potential of the mixed electrode system is sufficiently different from the equilibrium potentials of the individual reactions, then $i_{R,M}$ and $i_{O,Z}$ become insignificant in comparison to $i_{O,M}$ and $i_{R,Z}$, respectively. The corrosion rate, $i_{CORR}$, then becomes equal to $i_{O,M}$ or $i_{R,Z}$. The corrosion potential is closely approximated by the potential at which $i_{R,Z} = i_{O,M}$ as shown in Figure 5.

The overall effect of the mixed-electrode system, concentration polarization, and resistance effects is shown in Figure 11[27]. Tafel parameters are the same as in Figures 8 and 10. An uncompensated resistance of 10 ohms is assumed. The parameters used to calculate the curve in Figure 11 are completely arbitrary. Actual measurements may be better or worse. A high corrosion current in conjunction with a low diffusion-limited current and a high solution resistance may reduce the linear Tafel region to the extent that extrapolation to $i_{CORR}$ is extremely difficult.

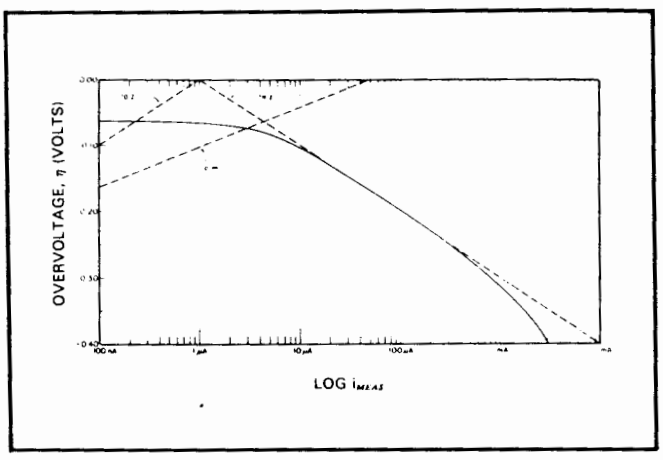



**FIGURE 11. Effect of mixed-electrode system, concentration polarization, and resistance effects on the measured current as a function of potential.**

In most cases, non-linear Tafel behavior can be minimized by stirring the solution and compensating instrumentally for IR effects.

## *Remarks*

Tafel Plots can provide a direct measure of the corrosion current, which can be related to corrosion rate. The technique is extremely rapid compared to weight-loss measurements. The Tafel constants, $\beta_A$ and $\beta_C$, obtained from Tafel Plots can be used with Polarization Resistance data (Section II) to calculate corrosion rates.

The rapid determination of corrosion rates with Tafel Plots can be advantageous for such studies as inhibitor evalutations, oxidizer effects, and alloy comparisons.

However, several experimental disadvantages can be associated with Tafel Plots. Although Tafel Plots are fairly rapid, polarization resistance measurements (Section II) can be made even faster. At a scan rate of 0.1 mV/sec, a Tafel Plot with a scan range of 250 mV requires about 45 minutes. An anodic and cathodic scan would require about 2 hours.

The relatively large potential range associated with the Tafel Plot has the effect of changing the surface of the specimen, so that two specimens are required for a complete Tafel Plot.

As described in Section III-4, concentration polarization and IR drops can combine to reduce the linear region to a point where extrapolation to $i_{CORR}$ is difficult. A linear region over one current decade is generally considered to be the minimum for reliable measurement of $i_{CORR}$.

Experimentally, it can happen that the extrapolations of the anodic and cathodic linear Tafel regions do not intersect at $E_{CORR}$. The true value of the corrosion current will then be subject to interpretation. If this occurs, the inference must be drawn that there is an error in the measurement, since the rate of oxidation must equal the rate of reduction at $E_{CORR}$. In most cases, the error is



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

probably in the anodic measurement. Since the metal specimen is corroding, the surface is changing and the mechanism of corrosion may not be completely described by the equations in Section III-4. The measured Tafel Plot could then reflect the combination of several different Tafel slopes. If this behavior is observed, it is probably safest to measure $i_{CORR}$ at the point where the cathodic Tafel extrapolation intersects $E_{CORR}$.

## Corrosion behavior diagrams

As discussed in Section I Electrochemical Corrosion Theory, an ironic situation is observed for specimen-environment combinations such as Figure 2B which yield a single anodic-cathodic intersection in the passive region. This situation arises because by the time the measurement of the specimen's $E_{CORR}$ is complete, the specimen has already spontaneously passivated and the measurement of the primary passive potential and the critical anodic current density is impossible. All that would be observed in the standard experiment described above is Figure 2F. Knowledge of the shape of the current potential curve during the active to passive transition stage is useful for characterizing the specimen-environment combination, and in order to observe the entire curve it becomes necessary to alter the experimental procedure. Morris and Scarberry[5,6] have described a rapid scan potentiostatic technique to accomplish this objective. The measurement is made immediately after immersion of the specimen without allowing the specimen time to equilibrate—and spontaneously passivate. Also, three polarization curves are run on a single specimen without interruption to gain additional qualitative information on the nature and stability of the passive film. A plot of the three composite polarization curves is termed a *Corrosion Behavior Diagram* (CBD). Figure 12 summarizes the experimental procedure. Figure 13 shows a typical CBD for a sample of Inconel 600 in 10% sulfuric acid at 80°C and Table 1 summarizes the qualitative information available from a CBD. CBDs have been employed by Inco[5,6] for the rapid characterization of more than 2000 alloys of widely varying composition. Corrosion Behavior Diagrams have also been applied to problems in a chemical process situation[35].

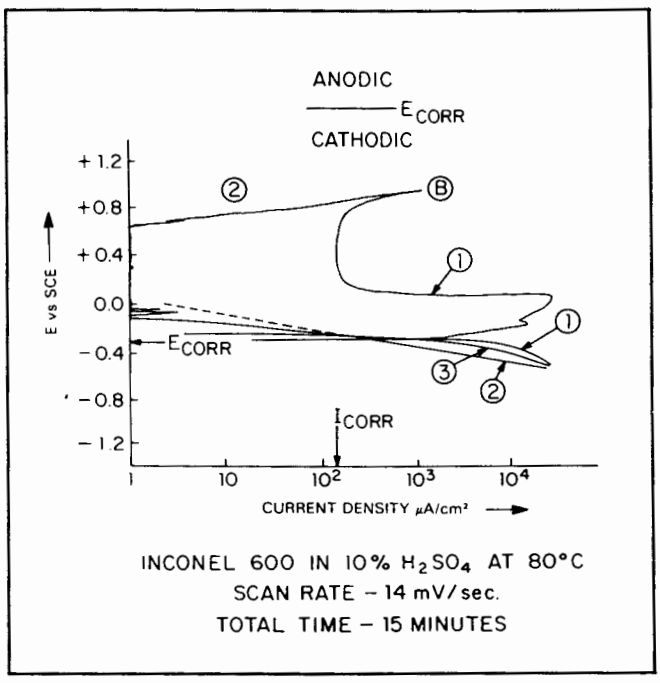



**FIGURE 12. Corrosion behavior diagram.**

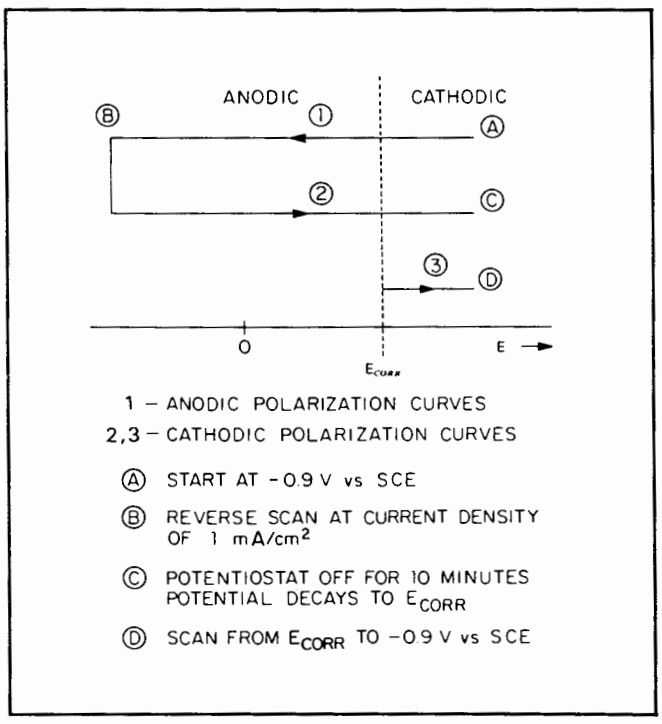



**FIGURE 13. Waveform required for corrosion behavior diagram.**

Application Note CORR 2, "Techniques of Corrosion Measurement", provides owners of EG&G PARC Model 331 Corrosion Measurement Systems with specific applications information. Included in AN CORR 2 are instrument calibration and experimental settings for the experiments described in this application note along with Galvanic Corrosion Measurements, Log Current Density Measurements, and Specimen Preparation.

EG&G PARC Model 350 Corrosion Measurement System owners will find applications information in the Model 350 Owners Manual.

| | |
|---|---|
| **GOOD FILM** | **POOR FILM** |
| Small current during reverse scan | Higher current during reverse scan |
| **RESISTANT ALLOY** | **POOR ALLOY** |
| E linear with Log I over several decades for 2nd scan | Short linear range |
| 3rd scan lies between 1st & 2nd scans | 3rd scan coincides with 1st scan |

**TABLE 1: Passive film stability information.**



Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

## References

Several additional references are included if additional information is required.

Reference 23 is a collection of papers presented at a symposium on Electrochemical Techniques for Corrosion. It is highly recommended for a theoretical and practical background of electrochemical corrosion studies.

Reference 34 gives the ASTM recommended practices for electrochemical corrosion measurements.


1. 1980 Annual Book of ASTM Standards, Part 10, G5, American Society for Testing and Materials, Philadelphia, PA.
2. "Corrosion Engineering," Mars G. Fontana and Norbert D. Greene, McGraw-Hill, New York, 1967.
3. "Electrochemical Polarization. . A Theoretical Analysis of the Shape of Polarization Curves," M. Stern and A. L. Geary, *J. Electrochem. Soc., 104,* 33-63 (1957).
4. "The Second Anodic Current Maximum for Type 430 Stainless Steel in 0.1 *N* $H_2SO_4$," *Corrosion, 31* (11), 413-415 (1975).
5. "Anodic Polarization Measurements of Active-Passive Nickel Alloys by Rapid-Scan Potentiostatic Techniques," P. E. Morris and R. C. Scarberry, *Corrosion, 26* (7), 169 (1970).
6. "Predicting Corrosion Rates with the Potentiostat," P. E. Morris and R. C. Scarberry, *Corrosion, 28* (12), 444 (1972).
7. "Experimental Electrode Kinetics," N. D. Greene, Rensselaer Polytechnic Institute, Troy, New York 1965.
8. "Predicting Behavior of Corrosion Resistant Alloys by Potentiostatic Polarization Methods," N. D. Greene, *Corrosion, 18,* 136 (1962).
9. "Potential—pH Diagrams for 90-10 and 70-30 Cu-Ni in Sea Water," K. D. Efird, *Corrosion 31,* (3) 77-83 (1975).
10. "Corrosivity of Pressurized Liquids in Aerosol Cans," L. S. Su and E. Sheppard, *Corrosion, 31* (6), 192 (1975).
11. "Anodic Polarization Behavior of Low Alloy Steels in Sulfuric Acid Solutions," J. R. Myers and F. K. Saxer, *Corrosion, 22* (22), 346-348 (1966).
12. "Anomalous Effects of Temperature on the Polarization Characteristics of Type 409 Stainless Steel," R. L. Chance, T. P. Schreiber and W. D. France, Jr. *Corrosion, 31* (8), 296 (1975).
13. "Applications of Potentiostats in Corrosion Studies," J. M. West, *Br. Corros, J., 5,* 65 (1970).
14. "Anodic Polarization Behavior of High-Purity 13 and 18% Cr Stainless Steels," E. A. Lizlovs and A. P. Bond, *J. Electrochem. Soc., 122* (6), 719 (1975).
15. M. Stern and A. L. Geary, *J. Electrochem. Soc., 104,* 56 (1957).
16. Adapted from Reference 15.
17. M. Pourbaix, "Lectures on Electrochemical Corrosion," Plenum Press, New York (1973), p. 25.
18. "The Range of Validity of the Linear Polarization Method for Measurement of Corrosion Rate," R. L. Leroy, *Corrosion, 29,* 272 (1973).
19. "Simultaneous Determination of Instantaneous Corrosion Rates and Tafel Slopes from Polarization Resistance Measurements," F. Mansfeld, *J. Electrochem. Soc., 120,* 515 (1973).
20. "Practical Experience with Linear Polarization Measurements," R. H. Hausler, *Corrosion, 33,* 117 (1977).
21. "Analysis of Errors in Measuring Corrosion Rates by Linear Polarization," R. Bandy and D. A. Jones, *Corrosion, 32,* 126 (1976).
22. "Evaluation of Corrosion Rates from Nonlinear Polarization Data," R. L. Leroy, *J. Electrochem. Soc., 124,* 1006 (1977).
23. Electrochemical Techniques for Corrosion. A Publication of the National Association of Corrosion Engineers, 2400 West Loop South, Houston, TX 77027.
24. M. Stern, *Corrosion, 14,* 440t (1958).
25. "The Effect of Uncompensated IR-Drop on Polarization Resistance Measurements," F. Mansfeld, *Corrosion, 32,* 143 (1976).
26. C. Wagner and W. Traud, Zeitschrift fur Electrochemie, ZEELA, *44,* 391 (1938).
27. Adapted from Reference 15.
28. "Corrosion and Corrosion Control," Herbert H. Uhlig, John Wily and Sons, New York (1971), p. 45.
30. M. Stern, *J. Electrochem. Soc., 102,* 609. 663 (1955).
31. M. Stern, *Corrosion, 14,* 440t (1958).
32. "Corrosion Engineering," M. G. Fontana and N. D. Greene, McGraw-Hill, New York (1967).
33. F. Mansfeld, "The Polarization Resistance Technique for Measuring Corrosion Currents," *Advances in Corrosion Science and Technology,* Vol. 6, ed. by M. G. Fontana and R. W. Staehle, Plenum Press, New York (1976).
34. 1980 Annual Book of ASTM Standards, Part 10, American Society for Testing and Materials, Philadelphia, PA.
    1. G1—Rec. Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens.
    2. G3—Rec. Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing.
    3. G5—Rec. Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements.
    4. G15—Def. of Terms Relating to Corrosion and Corrosion Testing.
    5. G46—Rec. Practice for Examination and Evaluation of Pitting Corrosion.
    6. G59—Practice for Conducting Potentiodynamic Polarization Resistance Measurements.
    7. G61—Practice for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion.
35. "Practical Applications of the Corrosion Behavior Diagram; A Critical Evaluation," J. G. Stoecker, O. W. Seibert, and P. E. Morris, Paper No. 76 presented at CORROSION/80. Available from NACE.
36. "Electrochemical Corrosion Testing," Special Technical Publication 727, ed. by F. Mansfeld and U. Bartocci, American Society for Testing and Materials, Philadelphia, PA.


**EG&G PARC Application Notes**

CORR-2—Techniques of Corrosion Measurement with the Model 331 Corrosion Measurement System.

CORR-3—A Microprocessor-Based Corrosion Measurement System.

Electrochemical Corrosion Newsletter.

**CORR-1; 12/82; 10M; MAX**

**Copyright ©1982 EG&G PRINCETON APPLIED RESEARCH**

**Printed in U.S.A.**

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

Artisan Technology Group - Quality Instrumentation ... Guaranteed | (888) 88-SOURCE | www.artisantg.com

**Artisan Technology Group** is an independent supplier of quality pre-owned equipment

## Gold-standard solutions

Extend the life of your critical industrial, commercial, and military systems with our superior service and support.

## We buy equipment

Planning to upgrade your current equipment? Have surplus equipment taking up shelf space? We'll give it a new home.

## Learn more!

Visit us at **artisantg.com** for more info on price quotes, drivers, technical specifications, manuals, and documentation.

Artisan Scientific Corporation dba Artisan Technology Group is not an affiliate, representative, or authorized distributor for any manufacturer listed herein.

We're here to make your life easier. How can we help you today?

(217) 352-9330 | sales@artisantg.com | artisantg.com

ARTISAN® TECHNOLOGY GROUP