

CBP Bipotentiostat User Guide



Pine Research Instrumentation
2741 Campus Walk Avenue
Building 100
Durham, NC 27705
USA

<http://www.pineresearch.com>

Phone: +1 919.782.8320 Fax: +1 919.782.8323

Copyright © 2008 - 2017 Pine Research Instrumentation



Table of Contents

1. Introduction	1
1.1 Features	1
1.1.1 Multi-Purpose Potentiostat and Galvanostat	1
1.1.2 Analog Sweep Generator	1
1.1.3 Flexible Voltage Control	1
1.1.4 Current Conversion	1
1.1.5 Front Panel Voltmeter	1
1.1.6 Overload Indicator	1
1.1.7 Front Panel Connections	2
1.1.8 Dummy Cell	2
1.2 Warranty	2
1.3 Scope of this Manual	2
1.4 Setting Up the System	2
1.4.1 Inspection	2
1.4.2 Installation	2
1.4.3 Setting the Proper Line Input Voltage	3
1.4.4 Testing	3
2. The Front Panel	4
2.1 General Controls	4
2.2 Electrode Connections	4
2.3 Sweep Generator	6
2.3.1 Using the Sweep Output	7
2.3.2 Adjusting the Sweep Limits	7
2.3.3 Adjusting the Sweep Rate	8
2.3.4 Adjusting the Initial Potential	9
2.3.5 Zeroing the Sweep Output	9
2.3.6 Manual Adjustment of the Sweep Output	10
2.3.7 Moving the Sweep Output to a Limit Potential	10
2.3.8 Starting and Stopping the Sweep	10
2.3.9 Setting the Sweep Direction	11
2.3.10 Stopping at a Limit Potential	11
2.4 Electrode Controls	11
2.4.1 Applying an Offset Potential	11
2.4.2 Applying a Potential Sweep	12
2.4.3 The Current Converter	12
2.4.4 Signal Connections	13
2.5 Voltmeter	13

3. Signal Connections	15
3.1 SWEEP GENERATOR	15
3.2 ELECTRODES.....	15
3.3 Grounding Connections.....	15
3.4 K1 Electrode	15
3.5 K2 Electrode	16
3.6 REAR PANEL Connections.....	16
4. Instrument Controls	17
4.1 General Controls.....	17
4.2 Sweep Generator Controls.....	17
4.3 Electrode Controls.....	18
5. Experimental Voltammetry	20
5.1 General Experimental Apparatus.....	20
5.2 Controlled Potential Techniques.....	21
5.2.1 Potential Sweep Methods.....	21
5.3 Experiment (Cyclic Voltammetry).....	22
5.3.1 Apparatus.....	22
5.3.2 Reagents	23
5.3.3 Procedure.....	23
5.3.4 Potential Step Methods	24
5.3.5 Hydrodynamic Methods.....	25
5.4 Controlled Current Methods	26
5.4.1 Constant Current Chronopotentiometry	27
5.4.2 Current Ramp Chronopotentiometry	27
5.4.3 Other Galvanostatic Methods	28
5.5 Open Loop Potentials.....	28
5.6 Four Electrode Arrangements.....	29
5.7 Two Electrode Arrangements.....	31
5.8 Proper Grounding	32
5.8.1 Oscillations.....	32
6. Troubleshooting	34
6.1 Testing the Sweep Generator	34
6.2 Testing an Electrode Unit (K1 or K2)	35
6.3 Further Troubleshooting	36
6.3.1 Symptom: No observed current.....	36
6.3.2 Suggestions: No observed current	36
6.3.3 Symptom: No motion on X axis (voltage)	36
6.3.4 Suggestion: No motion on X axis (voltage).....	36

6.3.5	Symptom: Linear Current Response	36
6.3.6	Suggestion: Linear Current Response	36
6.3.7	Symptom: OVERLOAD Indicator ON.....	37
6.3.8	Suggestions: OVERLOAD Indicator ON.....	37
6.3.9	Symptom: Noise	37
6.3.10	Suggestions: Noise.....	37

7. Technical Information 38

7.1	Bibliography.....	38
7.2	Specifications	38
7.3	Interface Cable Description.....	39

Table of Tables

Table 6-1: CURRENT CONVERTER Setting Expected Voltmeter Reading (I1 or I2).....	35
Table 7-1: AFCBP1 Specifications	38

Table of Figures

Figure 2-1: AFCEP1 Front Panel Illustration	5
Figure 2-2: General Controls.....	6
Figure 2-3: Electrode Connections.....	6
Figure 2-4: The Sweep Limit Controls.....	8
Figure 2-5: The Dual Range Sweep Rate Controls.....	9
Figure 2-6: The Sweep Controls.....	9
Figure 2-7: The Offset Voltage Control.....	12
Figure 2-8: The Sweep Voltage Control.....	12
Figure 2-9: The Current Converter.....	13
Figure 2-10: K1 Electrode Signal Jacks.....	13
Figure 5-1: Cable Connections for Cyclic Voltammetry.....	22
Figure 5-2: Cable Connections for Chronoamperometry.....	25
Figure 5-3: Cable Connections for RRDE Voltammetry.....	26
Figure 5-4: Open Loop Settings.....	28
Figure 5-5: Proper pH Electrode Connections.....	29
Figure 5-6: Voltage Response of a pH Electrode in Various Buffers.....	29
Figure 5-7: Typical Four-Electrode Arrangements	31

1. Introduction

The AFCBP1 bipotentiostat is a general purpose electrochemical instrument with a built-in analog voltage Sweep Generator. It can function as a traditional potentiostat or galvanostat using three electrodes (working, reference, and counter electrodes), and it may also independently control an additional (second) working electrode. While this bipotentiostat feature was originally designed for use in classic ring-disk electrode voltammetry, the instrument has also found use in many other dual working electrode techniques.

1.1 Features

1.1.1 Multi-Purpose Potentiostat and Galvanostat

The AFCBP1 can be operated as either a three or four electrode potentiostat for use in many kinds of electrochemical experiments, including cyclic voltammetry, anodic stripping voltammetry, rotated disk voltammetry, rotated ring-disk voltammetry, and interdigitated array experiments. It can also be operated as a two-electrode device for tracing the current-voltage characteristics of electrochemical systems. One of the working electrodes can be operated in a galvanostatic manner where the current is controlled.

1.1.2 Analog Sweep Generator

The dual range Sweep Generator produces a true analog voltage sweep. The user controls the sweep rate and limits rather than the period or frequency of the sweep. Particular attention has been applied to the circuit design to provide flexibility in adjusting, sweeping, or stopping the sweep at any point in a particular cycle. Its output may also be used independently for non-electrochemical purposes. Sweep rate and limits are set using push button potentiometers.

1.1.3 Flexible Voltage Control

The AFCBP1 offers independent control of the potential at each working electrode. The applied potential may reflect any combination of the Sweep Generator output, an offset voltage adjusted on the front panel, or an external voltage source. Summing circuits add these three inputs and apply the sum to the electrode. The electrode voltage is presented on the front panel. Offset voltages are set using push button potentiometers.

1.1.4 Current Conversion

The current through each working electrode is presented as a proportional voltage on a front panel output. This voltage signal is suitable for driving a $x - y$ recorder or sampling by a digital oscilloscope or computer controlled A-to-D board. Each working electrode has seven decades current-to-voltage conversions, easily selected using push buttons on the front panel.

1.1.5 Front Panel Voltmeter

A 3-1/2 digit voltmeter displays voltages for all principle front panel outputs.

1.1.6 Overload Indicator

Saturation of any internal amplifiers is signaled by a front panel LED.



1.1.7 Front Panel Connections

All connections are made via banana jacks except the reference electrode input, which utilizes a BNC type shielded connector. Signal outputs are protected against short circuits to circuit common.

1.1.8 Dummy Cell

A set of internal resistors can be switched in place of the external electrochemical cell, providing a way to idle the instrument between experiments.

1.2 Warranty

The AFCBP1 manufactured by Pine Instrument Company is warranted to be free from defects in material and workmanship for a 6 month period from date of shipment to original purchaser and used under normal conditions. The obligation under this warranty being limited to replacing or repairing any part or parts which shall upon examination disclose to Pine Instrument's satisfaction to have been defective and shall have been returned freight pre-paid and clear of encumbrances to Pine Instrument Company in Grove City, PA within the warranty period. This warranty being expressly in lieu of all other warranties expressed or implied and all other obligations or liabilities. All specifications are subject to change without notice.

1.3 Scope of this Manual

This manual focuses on the use of the AFCBP1 as a "stand-alone" instrument. The user is assumed to have some type of recording device, such as an $x - y$ plotter or digital oscilloscope, connected to the instrument. Further, it is assumed that the user is familiar with the subject of electrochemistry, especially cyclic voltammetry.

Users who primarily control the AFCBP1 via the AKCBP1 software package may still find this manual useful as it describes the capabilities of the instrument in detail. Those who are interested in upgrading their system to a computer controlled instrument should contact Pine Instrument Company for more information.

1.4 Setting Up the System

1.4.1 Inspection

The AFCBP1 Potentiostat should be inspected for shipping damage immediately after unpacking. If any damage is found, please notify the carrier and Pine Instrument Company as soon as possible.

1.4.2 Installation

The AFCBP1 has a rugged design and is intended for laboratory use. Exposure to corrosive chemicals, however, may damage the exterior finish on the chassis. Special care should also be given to the markings on the non-metal surface of the front panel.

The instrument may be placed on a suitable desk, lab bench, or equipment rack. Access to the rear panel is rarely required in normal use, but the unit should be positioned so that all front panel controls and connections are readily accessible. Connections between the AFCBP1 and external recording devices should be made using shielded coaxial cables whenever possible. If the AFCBP1 is to be connected to a computer, careful thought should be given to the placement of the computer and the cable as well.

1.4.3 Setting the Proper Line Input Voltage

The power entry module located on the rear panel is where AC voltage enters the AFCBP1 bipotentiostat. The module features a power cord receptacle that allows for easy removal or changing of the power cord. There is a line fuse to help protect the bipotentiostat internal circuitry, and there is also an input voltage selection system that allows selection of either 120 and 240 VAC as the input voltage.

The correct operating voltage is set with the voltage selector card inside the module. The "120" setting should be used for line voltages between 100 and 125 VAC. The "240" setting should be used for line voltages between 200 and 250 VAC. To change the factory setting, perform the following operations:

1. Remove the power cord from the module.
2. Slide the clear door to the left.
3. Use a pair of pliers to remove the voltage selector card.
4. Re-insert the card with the desired voltage visible (120 or 240 VAC).
5. Plug the power cord back into the module.

1.4.4 Testing

If the AFCBP1 is not operating properly, always check the fuse first. The fuse is located in the power entry module on the back panel. Remove the power cord, slide the clear door to the left, and use the "PULL FUSE" lever to remove the fuse. If required, replace fuse with a 3 A Slow Blow type fuse after checking for the cause of the blown fuse. If the fuse is in good condition, the operation of the unit can be tested as outlined in the "Troubleshooting" section.

2. The Front Panel

Located within the AFCBP1 are a fully functional bipotentiostat and an independent analog sweep generator. Both of these electronic circuits are controlled by an internal microprocessor which, in turn, is controlled by your choice of settings on the front panel. Adjusting these settings is a simple matter, as all front panel controls (except one) are of the push button type, and forty-one small red indicator lights instantly reflect any adjustments that you make to these settings. In addition, the internal microprocessor is equipped with non-volatile memory so that the AFCBP1 stores all of your front panel settings even when the power is off.

Controls and jacks are grouped according to their function into seven main sections on the front panel (see: Figure 2-1). The three largest sections are labelled Sweep Generator, K1 Electrode, and K2 Electrode. The Voltmeter and other general controls are located on the left side of the panel. Cell connections are made using the four jacks at the right side of the panel. The rear panel has six jacks which allow connection of external frequency compensation circuitry, and there is also a fifty pin connector used to attach the AFCBP1 to a computer.

2.1 General Controls

Located in the lower left hand corner of the front panel are a group of controls that affect the general operation of the AFCBP1 (see: Figure 2-2). When the power switch is switched on, the internal power supply supplies power to all internal circuits. When the power switch is switched off, an internal battery (with a 10-year lifetime) supplies power to the non-volatile memory used to store the front panel settings.

The CONTROL SOURCE push button setting determines whether the bipotentiostat is under the control of the front panel or an external computer. This control must be switched to the "external" setting when using the AFCBP1 with an external computer. For stand-alone use, the control is switched to the "panel" setting. When in the "external" mode, all front panel settings are inactive and/or ignored except for the voltmeter control and the control source button itself. This allows you to switch between modes at any time. Note that this button has a one second delay in order to prevent accidental mode changes.

The two ELECTRODES controls determine how and if the bipotentiostat is connected to the external electrochemical cell. The OPEN control is normally deactivated, but can be activated if you wish to make "open loop potential" measurements using a pH or ion selective electrode (discussed later).

The NORM vs DUMMY control is used to switch the electrode connections between an internal resistor network (the dummy cell) and the (normal) external electrochemical cell. Usually, you switch to "dummy" mode while setting up an experiment and switch back to "normal" mode just before starting an experiment.

2.2 Electrode Connections

There are four jacks located on the far right side of the front panel that are used to make connections to the electrochemical cell (see: Figure 2-3). The upper banana jack is a low impedance output to the auxiliary or counter electrode (CE).

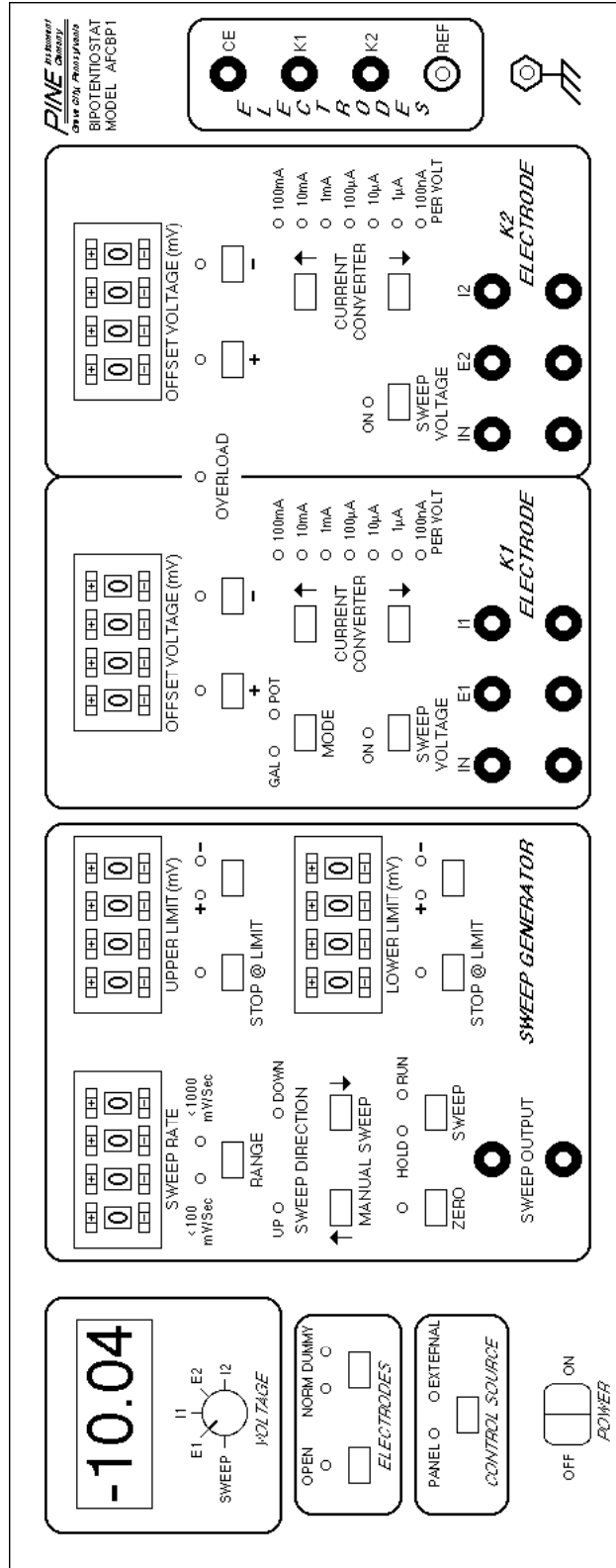


Figure 2-1: AFCBP1 Front Panel Illustration

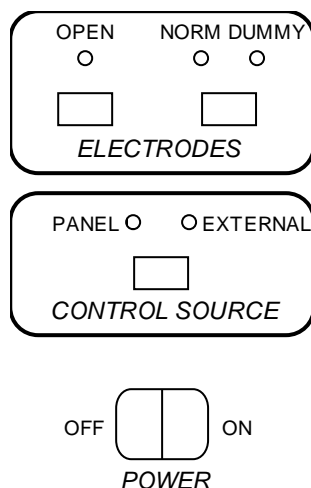


Figure 2-2: General Controls

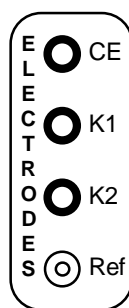


Figure 2-3: Electrode Connections

Below the CE jack are two jacks labelled K1 and K2 which are the connections to the working electrodes. If you are using a conventional three electrode system, the working electrode should be connected to the K1 jack (which is held at virtual DC common by feedback circuitry). If you are using a four electrode system, then connect the working electrode that is physically nearer to the reference electrode to the K1 circuit. For rotated ring-disk electrodes, the disk should be connected to K1 and the ring to K2.

The reference electrode connector (REF) is of the shielded BNC type. The reference electrode should be connected to the central (signal) connection on this jack. This is a high impedance input which measures the reference electrode voltage without loading the system. The cable which connects the AFCBP1 to the reference electrode is susceptible to picking up stray electrical noise.

To help prevent noise problems, a coaxial cable should be used to connect the reference electrode. The outside (shielding) connection on the BNC jack provides a driven shield that should be connected to the sheath of the coaxial cable. No connection should be made to this sheath at the electrochemical cell, and by no means should it be grounded.

2.3 Sweep Generator

The AFCBP1 has a built-in, true analog voltage sweep generator capable of providing the potential sweep signal required for most cyclic voltammetry experiments. The output of this dual range Sweep Generator may be used to supply a sweep signal to either or both working electrodes and is also available at the front panel for other uses. Particular attention has been given to the design of the

Sweep Generator circuit so that there is complete flexibility in adjusting or stopping the sweep at any point in the sweep cycle. All Sweep Generator settings are indicated by over a dozen front panel lights, and easy-to-use push button controls allow these settings to be adjusted at any time.

The Sweep Generator does not operate by controlling the period or frequency of a "triangle" wave, and neither does it generate a digital "stairstep" like other popular sweep generators. The three controlled parameters for this analog sweep are its rate, the upper sweep limit, and the lower sweep limit. All three of these parameters are adjusted using four-digit push button potentiometers. Other push button controls allow the sweep direction to be adjusted "on-the-fly" and control how and at what potential the sweep is stopped.

In a repetitive sweep, the upper and lower limits of sweep are independently adjustable between $+9.999\text{ V}$ and -9.999 V . The output signal sweeps between the high and low limits at the set sweep rate. The sweep can be stopped and held at any point, then started in either direction from the stop point at the discretion of the operator. In a normal operation, the Sweep Generator is free running. If desired, the Sweep Generator can be set to automatically stop at either end of the sweep. The voltage will hold at that point until the sweep circuit is started again.

Each of the Sweep Generator functions is discussed in more detail below. The user is encouraged to spend time experimenting with these controls. The built-in Voltmeter can be used to monitor the sweep output during such experimentation. With a little practice, one can easily become adept at producing just about any desired sweep signal for cyclic voltammetry.

2.3.1 Using the Sweep Output

The Sweep Generator is a self-contained, independent circuit within the AFCBP1, and the sweep output may be used as the signal for a cyclic voltammetry experiment or for some other non-electrochemical application. In the latter case, an external connection can be made to two output jacks on the front panel labelled SWEEP OUTPUT. This output may also find use as a trigger in some applications.

Usually, however, you will want the output of the sweep generator to be applied to the K1 and/or K2 working electrode circuit. This connection is made internally by activating the SWEEP VOLTAGE control in the appropriate electrode control section on the front panel.

2.3.2 Adjusting the Sweep Limits

In most voltammetry experiments, it is desirable to sweep the working electrode potential one or more times between two "limit" potentials. One of these, the upper limit must always be set at a more positive potential than the lower limit. The Sweep Generator has two identical sets of controls for adjusting the upper limit and lower limit. These are shown side-by-side, but on the front panel they are on top of each other (see: Figure 2-4).

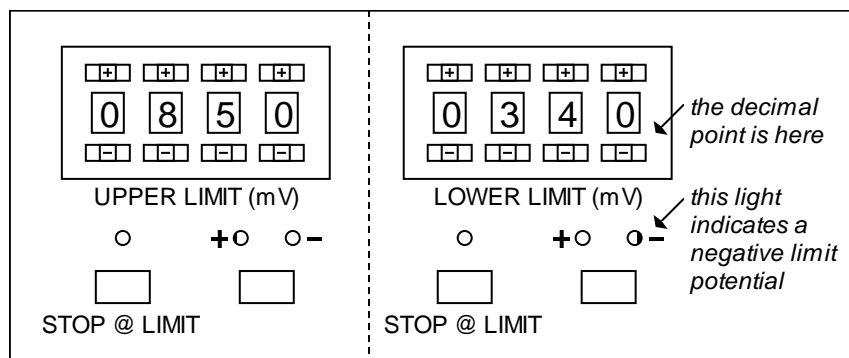


Figure 2-4: The Sweep Limit Controls

The four-digit push button potentiometers permit individual setting of each numeric digit in the limit potential using the small buttons above and below each digit. You can set any number of millivolts between "0000" and "9999". Note that the decimal point is located immediately to the right of the fourth digit.

Just below each push button potentiometer are two push buttons. The one labelled STOP @ LIMIT is discussed later, while the other (unlabeled) push button is used to change the mathematical sign on the limit potential. Two small lights above this push button indicate whether the sign is positive (+) or negative (-). In Figure 4, the upper limit is set at +850 mV, and the lower limit is set at -340 mV. The limit potentials can be set both positive, both negative, or one positive and one negative; however, the upper limit must always be more positive than the lower limit. The absolute difference between the two limits should exceed ten millivolts.

2.3.3 Adjusting the Sweep Rate

There are two sweep rate ranges available using the front panel controls. The slower range operates between 0.00 and 99.99 mV/s while the faster range operates between 000.0 and 999.9 mV/s. (Under external computer control, sweep rates up to 10,000 mV/s are available.) The desired range and sweep rate are adjusted with the front panel controls (see: Figure 2-5).

The four-digit push button potentiometers permit individual setting of each numeric digit in the limit potential using the small buttons above and below each digit. You can set any number between "0000" and "9999", and the sweep rate is read from the panel in millivolts per second. Note that the position of the decimal point depends on the range setting, as illustrated in (see: Figure 2-5). Two small indicator lights show which range setting is presently chosen.

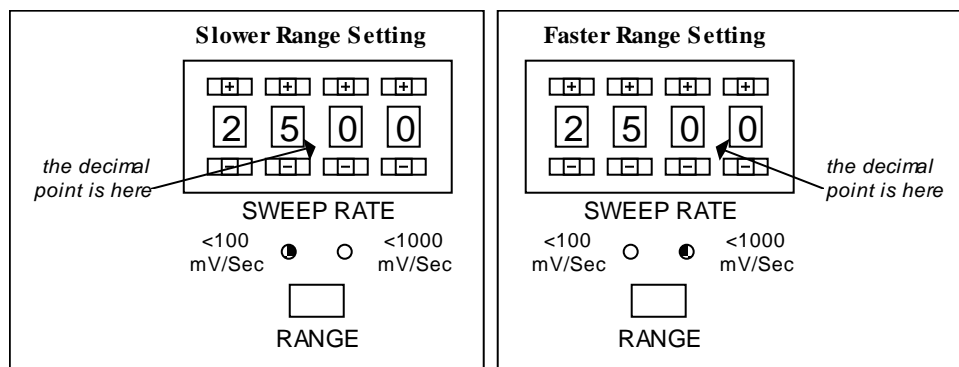


Figure 2-5: The Dual Range Sweep Rate Controls

2.3.4 Adjusting the Initial Potential

The next three sections describe how to adjust the sweep output to just about any initial potential. While you are adjusting the initial potential, however, it is possible that the potential may make an excursion through a range where significant electrochemical activity occurs. To prevent this, it is a very good idea to put the bipotentiostat in "dummy" mode while adjusting the potential, returning it to normal mode only after the desired initial potential has been set up.

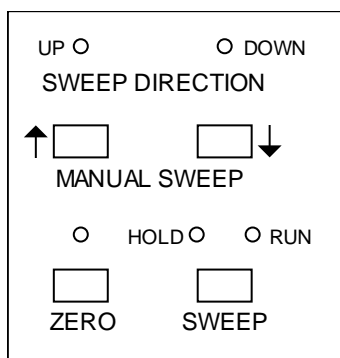


Figure 2-6: The Sweep Controls

2.3.5 Zeroing the Sweep Output

A section of the Sweep Generator control panel containing four push buttons (see: Figure 2-6). These controls are used together to adjust the sweep output to any desired potential. To zero the sweep output, simply activate the ZERO control, which overrides all other settings and sends the sweep output to zero volts and holds it there until deactivated.

At this point, you can switch the Sweep Generator to "hold" mode using the SWEEP control. This allows you to deactivate the zero control while maintaining the sweep output at zero volts. This is the normal starting point for many of the adjustments described below.

2.3.6 Manual Adjustment of the Sweep Output

Once you have set up the sweep limits and the sweep rate, you may wish to adjust the sweep output to some arbitrary potential. You should begin by setting the sweep output to zero volts as described above. Then, you can manually move the sweep output up or down using the MANUAL SWEEP buttons. The SWEEP control should be in "hold" mode while making this kind of adjustment.

When one of the MANUAL SWEEP buttons is pressed, the sweep output moves in the appropriate direction at the present sweep rate. By watching the front panel voltmeter carefully, the sweep output may be adjusted to any desired value. If the value changes too quickly for you to make a precise adjustment, you should temporarily set the sweep rate to a lower value.

Note that pressing either MANUAL SWEEP button usually changes the sweep direction, as indicated by the two small indicator lights located just above the buttons. After making a manual adjustment and before starting the sweep, make certain that the sweep direction is set to the direction you want it to go. Also note that if you adjust the potential to some value outside the range bracketed by the upper and lower limit potentials, the sweep direction is automatically set to head back towards the bracketed range.

2.3.7 Moving the Sweep Output to a Limit Potential

Once you have set up the sweep limits and the sweep rate, you may desire to set the sweep output potential equal to one of the two limit potentials. While this can be done using the manual method described above, the method below is somewhat more convenient.

Begin by setting the sweep output to zero volts as described above, making certain that the SWEEP control is left in "hold" mode after zeroing the potential. Next, you should manually move the sweep output to some value that is in between the upper and lower limit potentials. (In most cases, this step is not actually required because zero will fall between the two limit potentials.)

Once in between the limit potentials, use a MANUAL SWEEP button to set the sweep direction towards the appropriate limit potential, and activate the appropriate STOP @ LIMIT button. If you wish to set the initial potential equal to the lower limit, then set the sweep direction to negative (down) and activate the lower STOP @ LIMIT button. If you wish to set the initial potential equal to the upper limit, then set the sweep direction to positive (up) and activate the upper STOP @ LIMIT button.

Next, turn on the sweep by switching the SWEEP control to "run" mode. The sweep output will move (at the present sweep rate) towards the desired limit potential, and then it will stop at that limit. At this point, switch the SWEEP control to "hold" mode and deactivate the STOP @ LIMIT control. The sweep output will hold at the limit potential until you decide to start the sweep.

2.3.8 Starting and Stopping the Sweep

The SWEEP control allows you to start and stop the sweep "on-the-fly" at any point during the sweep program. This push button switch alternately halts and then restarts the sweep. Two indicator lights associated with this switch indicate whether the sweep is in "hold" or "run" mode. Note that the ZERO control, described above, overrides the setting of the SWEEP control. That is, when the ZERO control is activated, the sweep output is sent to zero regardless of whether the Sweep Generator is in "hold" or "run" mode.

2.3.9 Setting the Sweep Direction

The two MANUAL SWEEP momentary push button controls are usually used to change the direction of a sweep in progress. When the left-hand "up" button is pressed, the voltage sweep proceeds in a positive direction. When the right-hand "down" button is pressed, the sweep proceeds in a negative direction. Sweep direction can be adjusted before or during a sweep, and two indicator lights above these push buttons indicate the present direction of the sweep. These two push buttons can also be used to adjust the Sweep Generator output when it is in "hold" mode.

2.3.10 Stopping at a Limit Potential

If the STOP @ LIMIT control associated with one of the limit potentials is activated, a potential sweep in progress is halted just as soon as it reaches that limit potential. Generally, you will use this control "on-the-fly" to stop the sweep at the end of an experiment. The precise behavior of the STOP @ LIMIT controls can be complex under unusual circumstances. There are three distinct conditions that influence how the upper STOP @ LIMIT control behaves:

- If the sweep output is less than the upper limit and the sweep direction is positive, then the sweep stops as soon as it hits the limit potential. (normal case)
- If the sweep output is less than the upper limit and the sweep direction is negative, then the sweep is halted immediately.
- If the sweep output is already greater than the upper limit potential (an unusual event), then the sweep is halted immediately.

Similar behavior can be expected from the lower stop @ limit switch. Note that if both STOP @ LIMIT controls are activated simultaneously, the sweep halts until one of the two controls is deactivated.

2.4 Electrode Controls

Both working electrodes (K1 and K2) operate independently of each other, and both have independent controls on the front panel. These controls allow you to specify the potential that is applied to a working electrode and its current sensitivity. Because both working electrodes have virtually identical controls, the descriptions given in this section of the manual apply equally to either the K1 or the K2 electrode controls. Note, however, that the K1 electrode has an additional control that permits it to be operated in a galvanostatic rather than a potentiostatic manner.

2.4.1 Applying an Offset Potential

An offset (or baseline) potential can be applied to a working electrode using a four-digit push button potentiometer to set any number of millivolts between "0000" and "9999". Two other controls (located just below the potentiometer) are used to set the mathematical sign, "+" or "-", for the offset potential. If both of these controls are deactivated, then no offset potential is applied to the electrode (see: Figure 2-7).

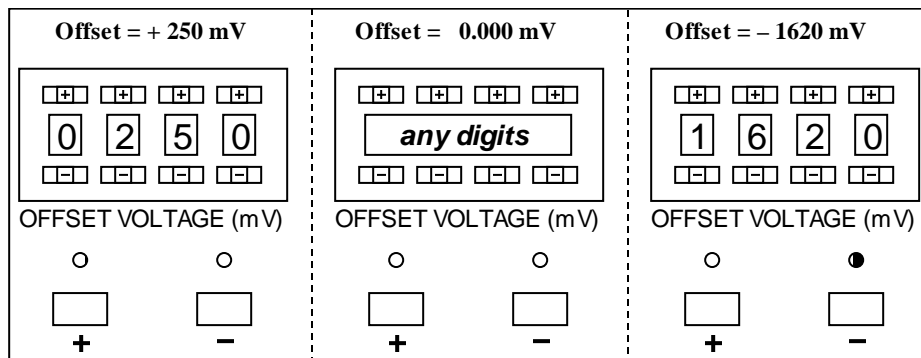


Figure 2-7: The Offset Voltage Control.

Use of the OFFSET VOLTAGE control is a convenient way to hold the potential of a working electrode at some non-zero value. For example, in rotated ring-disk voltammetry, one might sweep the potential of the disk electrode while holding the ring electrode at some fixed potential set using the OFFSET VOLTAGE.

Another possible use for the OFFSET VOLTAGE control is to apply a sudden potential step to a working electrode, such as that required during a chronoamperometry experiment. A step from zero volts to some non-zero potential can be accomplished by starting with the OFFSET VOLTAGE deactivated and then manually depressing either the "+" or "-" push button to initiate the potential step to a non-zero potential.

2.4.2 Applying a Potential Sweep

If you wish to sweep the working electrode potential, you should activate the SWEEP VOLTAGE control. This applies the output of the Sweep Generator to the internal summing circuit for the working electrode. The indicator just above the SWEEP VOLTAGE control turns "on" whenever this control is active (see: Figure 2-8).



Figure 2-8: The Sweep Voltage Control.

2.4.3 The Current Converter

The potentiostat controls the potential of a working electrode and measures the current passing through that electrode. The AFCBP1 features a current-to-voltage converting system that presents the working electrode current as a proportional voltage on a front panel output jack. This allows for easy connection to external recording devices, such as $x - y$ plotters or digital oscilloscopes.

The sensitivity of working electrode current measurements is set using the CURRENT CONVERTER control (see: Figure 2-9). Seven decades of scaling factors, from 100 mA/V down to 100 nA/V , are available. Currents as low as 1 nA can be measured with the 100 nA/V setting and proper electrical shielding.

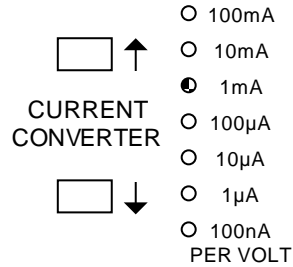


Figure 2-9: The Current Converter.

As an example, assume that the working electrode current is 5.72 mA . With the CURRENT CONVERTER set to 1 mA/V , the signal presented at the front panel jack would be 5.72 V (see: Figure 2-9). Obviously, it is a good idea to set the CURRENT CONVERTER to a range that closely matches the currents you expect to observe in a particular experiment. In general, the largest current that can be measured at any particular setting is about ten times the value listed next to the indicator light for that setting.

2.4.4 Signal Connections

Each working electrode section on the front panel has three pairs of banana jacks (see: Figure 2-10). The E1 and I1 jacks are output signals suitable for driving $x - y$ plotters and digital oscilloscopes. The E1 jack presents the working electrode potential, and the I1 jack presents a voltage signal proportional to the working electrode current (see the discussion of the CURRENT CONVERTER control, above.)

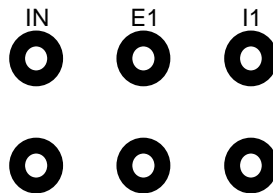


Figure 2-10: K1 Electrode Signal Jacks.

The IN jack is an input that is connected directly to the internal summing circuit for the working electrode. This jack is generally used to apply the output of some external function generator to the working electrode. For example, the AFCBP1 has no built-in provision for providing a pulse sequence for pulse polarography, but a third-party pulse programmer might provide this capability.

2.5 Voltmeter

A voltmeter is provided to help you measure various front panel signal voltages conveniently. The actual reading displayed depends on the setting of the VOLTAGE knob control located under the voltmeter display.

To display the output of the Sweep Generator, turn the knob to the "sweep" position. The voltage presented across the SWEEP OUTPUT jacks is displayed on the voltmeter. Because the voltmeter display is only updated periodically, the display will tend to skip from one reading to the next in a discontinuous fashion during a potential sweep. This effect is most pronounced when using fast sweep rates.

To display the potential of a working electrode, turn the knob to either the "E1" or "E2" position. The voltmeter will display the appropriate potential corresponding to the potential being presented at the "E1" or "E2" output jacks on the front panel.

To monitor the current at a working electrode, put the knob in either the "I1" or "I2" position. The voltmeter will display a voltage which is proportional to the current at the electrode. The voltage is the same voltage which is presented across the front panel output jacks for "I1" or "I2". To convert this voltage to a current, multiply it by the setting of the appropriate CURRENT CONVERTER control.

3. Signal Connections

Most connections to the AFCBP1 are made via standard banana jacks located on the front panel. The reference electrode connection on the front panel, however, is of the BNC type to reduce noise. The only connections on the rear panel are six jacks for frequency compensation and the ribbon cable connector used for external computer control.

3.1 SWEEP GENERATOR

The Sweep Generator output is presented across this pair of jacks. It may be used independently of any other function of the AFCBP1. It is labeled on the front panel of the AFCBP1 as SWEEP OUPUT.

3.2 ELECTRODES

- **CE** This red banana jack provides a low impedance output to the counter or auxiliary electrode.
- **K1** This yellow banana jack provides a low impedance connection to the disk or working electrode. Internal feedback circuitry holds this connection at virtual DC common.
- **K2** This blue banana jack provides a low impedance connection to the ring or second working electrode.
- **REF** The reference electrode should be connected to the central (signal) connection on this BNC jack. This is a high impedance input which measures the reference electrode voltage without loading the system. The outside (shielding) connection connects to the sheath of a coaxial cable running to the reference electrode in the cell. No connection should be made to this sheath at the cell, and it should never be grounded.

3.3 Grounding Connections

All black jacks along the bottom of the front panel present the DC Common for the AFCBP1 circuit. They are not connected to either the chassis frame or the earth ground. It is labeled on the front panel of the AFCBP1 as DC COMMON.

The Binding Post located near the lower right corner of the front panel is the chassis or earth ground. This is a convenient point for connecting the DC Common to the earth ground, if desired. This point represents earth ground only if the 3-prong power cord is connected to a properly grounded outlet. This EARTH GROUND is labeled with a grounding symbol on the front panel of the AFCBP1.

3.4 K1 Electrode

- **IN** This voltage input jack is connected through an internal 10K ohm resistor to the summing point for the K1 electrode circuitry. Usually an external function generator will be connected to this input. When the K1 electrode is operating in "Potentiostat" mode, this external voltage is summed with the OFFSET VOLTAGE and the SWEEP VOLTAGE (if activated) and then applied to the K1 electrode. When the K1 electrode is operated in "Galvanostat" mode, this voltage sum is converted to a current according to the CURRENT CONVERTER setting, and the resulting current is sent through the K1 working electrode.
- **E1** This voltage output jack provides a voltage indication of the actual K1 electrode voltage with respect to the REF electrode. This is a buffered output suitable for driving the input of an X-Y Recorder or for sampling by a digital oscilloscope or a computer controlled A-to-D board.
- **I1** This voltage output jack provides a voltage proportional to the actual K1 working electrode current. The CURRENT CONVERTER setting determines the factor used to convert current to

voltage. For example, if 2 V is presented at this jack, and the CURRENT CONVERTER is set at 10 mA/V, then the actual K1 current is 20 mA. (e.g. $2.0\text{ V} \times 10\text{ mA/V} = 20\text{ mA}$).

3.5 K2 Electrode

- **IN** This voltage input jack is connected through an internal 10K ohm resistor to the summing point for the K2 electrode circuitry. Usually an external function generator will be connected to this input. The K2 electrode always operates in "Potentiostat" mode, and this external voltage is summed with the OFFSET VOLTAGE and the SWEEP VOLTAGE (if activated) and then applied to the K2 electrode.
- **E2** This voltage output jack provides a voltage indication of the actual K2 electrode voltage with respect to the REF electrode. This is a buffered output suitable for driving the input of a $x - y$ recorder or for sampling by a digital oscilloscope or a computer controlled A-to-D board.
- **I2** This voltage output jack provides a voltage proportional to the actual K2 working electrode current. The CURRENT CONVERTER setting determines the factor used to convert current to voltage. See the description of I1, above.

3.6 REAR PANEL Connections

- **K1, K2** These jacks, which operate in pairs, allow capacitors to be inserted into the AFCBP1 circuit to slow its response time. Oscillations, which may occur under certain conditions, can be eliminated in this way. Refer to Section 6 on noise and oscillations for details.
- **GAL** These jacks, which operate in pairs, allow capacitors to be inserted into the AFCBP1 circuit to slow its response time. Oscillations which may occur under certain conditions can be eliminated in this way. Refer to Section 5.8.1 on noise and oscillations for details.
- **EXTERNAL CONTROL** is a fifty pin ribbon cable connector that allows external control of the AFCBP1 by an external computer equipped with an appropriate analog-to-digital interface board. See cable pinout in Section 7.3 for further details.

4. Instrument Controls

There are forty-one (41) small red light emitting diodes (LEDs) on the front panel that indicate the present state of the bipotentiostat. Most of these LEDs are associated with nearby switches and indicate the present setting of a particular switch. There is one LED, however, that is not associated with a particular switch. It is the Overload indicator, located between the K1 and K2 electrode sections. This LED lights up whenever one of the amplifiers in the AFCBP1 is nearing saturation (i.e., an output greater than about 10.0 V). Measurements made during an overload condition are likely to be inaccurate!

4.1 General Controls

- **POWER** The power switch is located in the lower left corner of the panel.
- **CONTROL SOURCE** A push button switch with a one second delay which switches control of the AFCBP1 between the front panel and an external computer. When control is passed to an external computer, all front panel controls are disabled and/or ignored, with the exception of the control source push button itself.
- **ELECTRODES** There are two push button switches that control cell connections to the bipotentiostat. The push button on the right (labelled "norm dummy") determines whether the circuitry of the bipotentiostat is connected to the external cell (normal) or to a set of internal resistors (dummy). The latter provides a convenient way to idle and/or test the instrument.

The push button on the left (labelled "open") is normally turned off when performing any type of voltammetry experiment. When turned on, the potentiostat measures the "open circuit potential" between the working electrode and the reference electrode. This essentially turns the bipotentiostat into a very expensive voltmeter for use with pH or other ion selective electrodes.

- **VOLTAGE** A knob type switch that determines which voltage appears on the voltmeter display. When in the "Sweep" position, the output of the Sweep Generator is displayed. When in the "E1" or "E2" position, the voltage presented at the "E1" or "E2" jack appears on the voltmeter display. When in the "I1" or "I2" position, the voltage presented at the "I1" or "I2" jack appears on the voltmeter display. This voltage reading may be converted to a current value by noting the setting of the appropriate current converter.

4.2 Sweep Generator Controls

- **ZERO** A push button switch which sends the output of the Sweep Generator to zero volts. The indicator light associated with this switch is turned on and the output remains at zero volts until switch is pressed again.
- **SWEEP** A push button switch which alternately halts and then restarts the sweep. Two indicator lights associated with this switch indicate whether the sweep is in a "hold" or "run" condition. The setting of this switch is overridden by the zero switch, described above.
- **MANUAL SWEEP** Two momentary push buttons that are usually used to change the direction of a sweep in progress. When the left-hand "up" button is pressed, the voltage sweep proceeds in a positive direction. When the right-hand "down" button is pressed, the sweep proceeds in a negative direction. Sweep direction can be adjusted before or during a sweep, and two indicator lights above these push buttons indicate the present direction of the sweep. These two push buttons can also be used to adjust the Sweep Generator output when it is in a "hold" condition (see sweep control, above).
- **SWEEP RATE** A four digit push-button potentiometer is used in conjunction with a push button switch to adjust the sweep rate. The push button is labelled "range", and it toggles between

the two available sweep ranges as indicated by the associated indicator light. When the "< 100 mV/s" range is selected, the push-button potentiometer provides reproducible sweep rate settings from 0.00 to 99.99 mV/s in 0.01 mV/s increments. When the "< 1000 mV/s" range is selected, the push-button potentiometer provides reproducible sweep rate settings from 0.0 to 999.9 mV/s in 0.1 mV/s increments.

- **UPPER LIMIT** The four digit push-button potentiometer is used in conjunction a push button switch below it to adjust the upper voltage limit for the sweep. The push button controls the sign ("+" or "-") of the upper limit voltage, and the push-button potentiometer provides reproducible voltage settings from 0000 to 9999 mV in 1 mV increments. An indicator light above the push button switch indicates the sign of the limit potential.
- **LOWER LIMIT** The four digit push-button potentiometer is used in conjunction a push button switch below it to adjust the lower voltage limit for the sweep. The push button controls the sign ("+" or "-") of the lower limit voltage, and the push-button potentiometer provides reproducible voltage settings from 0000 to 9999 mV in 1 mV increments. An indicator light above the push button switch indicates the sign of the limit potential.
- **STOP@LIMIT** In general, when one of these controls is active, the sweep halts when it reaches the corresponding limit potential. More specifically, if the upper "STOP@LIMIT" is activated, a positive going sweep continues until it reaches the upper limit, while a negative going sweep halts immediately. Conversely, if the lower "STOP@LIMIT" is activated, a negative going sweep continues until it reaches the lower limit, but a positive going sweep will halts immediately. Activating both "STOP @ LIMIT" buttons halts the sweep immediately.



INFO:

The limits can be set both positive, both negative, or one positive and one negative; however, the upper limit must always be more positive than the lower limit., and the absolute difference between them should exceed ten millivolts

4.3 Electrode Controls

Both working electrodes (K1 and K2) operate independently of each other, and each has a set of independent, yet virtually identical, controls on the front panel. The only difference is that the K1 electrode can be operated in either "galvanostat" or "potentiostat" mode, depending on whether the K1 current or voltage is controlled, respectively.

- **SWEEP VOLTAGE** When this push button switch is activated the light above it turns "on", and the output of the Sweep Generator is applied to the summing circuit of the working electrode. When turned "off", there is no internal connection between the Sweep Generator and the working electrode circuit.
- **OFFSET VOLTAGE** This four digit push-button potentiometer is used together with two push buttons adjust an offset voltage applied to the summing circuit for the working electrode. The two push buttons control the sign ("+" or "-") of the offset voltage, and the push-button potentiometer provides reproducible voltage settings from 0000 to 9999 mV in 1 mV increments. If both push button switches are "off", then no offset voltage is applied to the working electrode.
- **CURRENT CONVERTER** Two push button switches control the conversion factor used for scaling the working electrode current to a proportional voltage presented on the front panel. Seven decades of conversion factors are available from 100 mA/V to 100 nA/V.

- **MODE** This push button is located in the K1 electrode section of the front panel, and it only applies to the K1 working electrode circuit. Pressing this button toggles the K1 electrode between the "galvanostat" mode and the "potentiostat" mode. The K2 electrode is always in "potentiostat" mode.

5. Experimental Voltammetry

The AFCBP1 may be used in a wide variety of electrochemical experiments, and some of the more popular electroanalytical methods are described in this section. Before using the instrument in any new application, be certain to consult the specifications for the AFCBP1 if there is any question that your experiment will exceed the capabilities of the instrument. Some general guidelines to keep in mind are discussed below.

The bipotentiostat circuit inside the AFCBP1 is designed for use in the "middle range" of currents usually encountered in electrochemical experiments. On the upper end, the maximum current that can be measured is one ampere, while on the lower end, the minimum current that can be measured is about 1 nA . At the low current end, extreme care must be taken to shield the experiment from electrical noise, and a very sensitive recording device should be used.

The circuit inside the AFCBP1 is also designed for use in low to moderate frequency experiments. The operational amplifiers that make up the bipotentiostat feedback circuit have a rise time of 0.5 V per second, and the frequency response of the instrument, measured as the "small signal bandwidth", is at least 10 kHz . Results obtained from experiments using sweep rates exceeding ten volts per second or pulse widths shorter than ten microseconds should be viewed with caution.

When making connections to the AFCBP1, be careful not to short output signals to each other or to the DC common. All output signals are current limited to prevent damage to the potentiostat in the event of a short duration short circuit to DC common.

The AFCBP1 has a compliance voltage of $\pm 10 \text{ V}$ although most typical electrochemical measurements require only a $\pm 2 \text{ V}$ window. On occasion, an experimental situation will result in a very high current or voltage condition which saturates one of the internal operational amplifiers. Whenever one of the amplifiers nears saturation, and the OVERLOAD indicator lights up to let you know that there could be an error in the measurement being made. The circuits continue to function even though the indicator is on.

The AFCBP1 can be used with two, three, or four electrodes. To use the AFCBP1 as a conventional three-electrode potentiostat or galvanostat, it is not necessary to make any connections to the K2 electrode circuit. To use the AFCBP1 for two-electrode current vs. voltage measurements, use the K1 and REF electrode inputs, but also short the CE input to the REF input.

5.1 General Experimental Apparatus

All electrochemical experiments require roughly the same materials and apparatus. After choosing the AFCBP1 bipotentiostat, the next priority is choice of a data recording device. Common choices include a $x - y$ recorder or a digital oscilloscope. Dual electrode experiments generally require a two pen recorder or a dual trace oscilloscope.

Additional instrumentation is required for certain applications. Hydrodynamic methods require an electrode rotator, such as the Pine Research AFMSRCE Rotator. Potential step methods, such as chronoamperometry, require a programmable pulse generator.

Choice of working and reference electrodes is highly dependent on the particular electrochemical system being studied. Common working electrode materials include glassy carbon (GC), platinum (Pt), and gold (Au). Popular reference electrodes include the saturated calomel electrode (SCE) and the

silver-silver chloride (Ag/AgCl) reference. The counter electrode, also called an auxiliary electrode, is typically a piece of platinum wire, but more elaborate designs are available.

Glassware used for electrochemical cells varies widely from one application to another. In general the cell must have provisions for mounting three (or four) electrodes, and for hydrodynamic experiments, the cell must have an opening suitable for the shaft of a rotating working electrode.

If dissolved oxygen is likely to interfere with an electrochemical measurement, the cell design should include appropriate connections for bubbling and blanketing the test solution with an inert gas. A cylinder of compressed nitrogen or argon, a gas regulator, and associated plumbing will also be required in these situations.

Electrolyte solutions suitable for use with electrochemical techniques are somewhat limited. Aqueous electrolyte solutions are easiest to prepare and are quite popular. An inert salt, such as potassium nitrate, dissolved in HPLC grade water works very well. Non-aqueous systems, however, can dissolve a wider range of compounds, including organic and organometallic substances. The most popular non-aqueous solvent systems are based on acetonitrile solutions of tetraalkylammonium salts.

5.2 Controlled Potential Techniques

Most popular electroanalytical techniques require a potentiostat, that is, a device capable of measuring the working electrode current while controlling its potential. These popular techniques include cyclic voltammetry, chronoamperometry, most rotated ring-disk methods, and square wave voltammetry, to name just a few. All of these techniques share the common trait that it is the working electrode potential that is the controlled variable in the experiment, while the working electrode current is the measured variable. Because the AFCBP1 is a bipotentiostat, it can control two working electrodes in this fashion, and the potential applied to one working electrode does not affect the potential or the current at the other electrode.

5.2.1 Potential Sweep Methods

Perhaps the most popular of electroanalytical techniques, both linear sweep voltammetry (LSV) and cyclic voltammetry (CV) produce a quick survey of the electrochemical behavior of a system. Both methods are three electrode potentiometric methods, meaning that a potentiostat controls the potential of a working electrode (versus a reference) while simultaneously measuring the current at the working electrode. Current is essentially prevented from passing through the reference electrode by the use of a counter electrode.

In Linear Sweep Voltammetry, the potential at the working electrode is swept from an initial potential (E1) to a final potential (E2) at some predetermined sweep rate (ν). Usually E1 and E2 are chosen to span a region of electrochemical interest, such as the formal potential, E° , of an electroactive analyte. Experimental results are typically presented as a plot of current versus applied potential, known as a linear sweep voltammogram.

Cyclic Voltammetry is an extension of Linear Sweep Voltammetry that uses a triangle wave rather than a simple potential ramp. The potential at the working electrode is swept at a predetermined rate (ν) from an initial potential (E1) to another potential (E2). Upon reaching this potential limit; however, the direction of the potential sweep is reversed. The potential is swept back to a second potential limit (E3). At this point, one cycle of the experiment is complete, but in many cases, it is desirable to cycle the potential several more times between E3 and E2. Frequently, the initial potential, E1, coincides with one of the potential limits, E2 or E3, but this is not a requirement. Experimental results are typically presented as a plot of current versus applied potential, known as a cyclic voltammogram.

The Model AFCBP1 bipotentiostat is capable of performing either LSV or CV experiments through the use of its internal Sweep Generator. Because the output of the Sweep Generator unit can be applied to either electrode, it does not matter whether K1 or K2 is used as the working electrode. If desired, an external signal generator may be used to provide the voltage sweep. Figure 5-1 shows the connections required to configure the AFCBP1 for cyclic voltammetry using a single pen $x - y$ recorder. A digital oscilloscope may also be used.

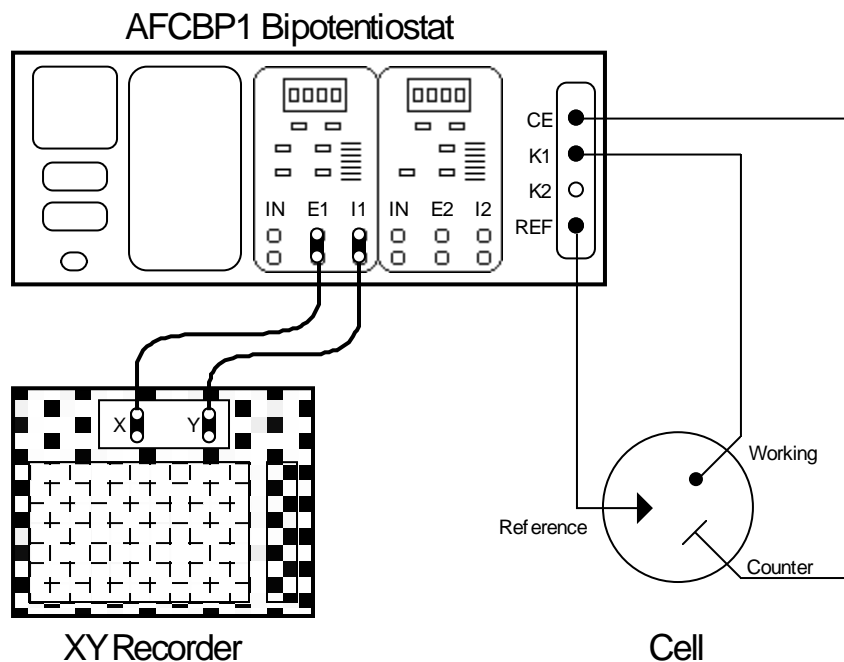


Figure 5-1: Cable Connections for Cyclic Voltammetry

5.3 Experiment (Cyclic Voltammetry)

This procedure illustrates how the AFCBP1 is used in a typical cyclic voltammetry experiment. Details of the procedure will vary according to the particular apparatus actually used.

5.3.1 Apparatus

- Pine Research Model AFCBP1 Bipotentiostat
- $x - y$ Recorder (or PC with National Instruments interface board and controlled by PineChem or Aftermath software)
- Electrochemical cell
- Platinum working electrode, Platinum counter electrode
- Reference electrode (saturated Calomel, SCE, used as a reference in this description)
- Cylinder of compressed, purified nitrogen for deaeration of solutions
- Various electrical cables with BNC, banana and alligator connectors

5.3.2 Reagents

5.0 *mM* potassium ferricyanide in 1.0 *M* potassium nitrate aqueous solution.

5.3.3 Procedure



INFO:

It is usually desirable to place the AFCBP1 in "Dummy" mode and lift the $x - y$ recorder pen while an experiment is being set up. This prevents needless marks on the recorder paper.

1. Assemble the electrochemical cell and fill it with the potassium ferricyanide solution. Mount the three electrodes in the cell. Connect the platinum working electrode to the K1 input. Connect the platinum counter electrode to the CE input. Connect the SCE reference to the REF input. The AFCBP1 should be in "Dummy" mode while electrode connections are being made. Bubble nitrogen through the ferricyanide solution for about 10 minutes to displace dissolved oxygen from the solution. You may perform steps 2 through 7 while bubbling.
2. Connect the E1 output of the AFCBP1 to the x -axis input on the $x - y$ recorder. Connect the I1 output of the AFCBP1 to the y -axis input on the $x - y$ recorder. Suggested settings for the recorder are 100 *mV/cm* sensitivity on both axes and location of the origin near the center of the recorder paper.
3. Set the K1 electrode controls as follows: Turn off the OFFSET VOLTAGE. Turn on the SWEEP VOLTAGE. Set the CURRENT CONVERTER to one of the lower sensitivities (such as 10 *mA/V*) to prevent accidental overload while setting up.
4. Set the voltmeter so that it monitors "E1", the working electrode (K1) potential. Make certain that K1 is in the "potentiostat" mode.



INFO:

Steps 5 and 6 (below) set up the AFCBP1 Sweep Generator to sweep the working electrode potential between +0.800 *V* and -0.200 *V* starting at an initial potential of +0.800 *V*. This range includes the formal potential of the ferricyanide/ferrocyanide redox couple, vs. reference electrode, which in this description, is SCE.

5. Set up the Sweep Generator as follows: Set the UPPER LIMIT to +0800 *mV*. Set the LOWER LIMIT to -0200 *mV*. Set the SWEEP RATE at 100.0 *mV/s*.
6. This step illustrates how to make the initial potential the same as a limit potential.
7. Activate the ZERO push button. The voltmeter display should read "0.00".
8. Push the MANUAL SWEEP button that is labelled with an "up" arrow.
9. Next, press the SWEEP button so that it indicates "Run" mode.
10. Activate the STOP @ LIMIT for the UPPER LIMIT.
11. Deactivate the ZERO push button. Observe the K1 potential ramp to 800 *mV*.
12. Put the SWEEP control in the "hold" mode.

13. Deactivate the STOP @ LIMIT switch.
14. Switch the potentiostat from "dummy" to "normal" and activate the XY plotter pen.
15. To begin the experiment, put the SWEEP control in the "Run" position.
16. A cyclic voltammogram should be traced on the $x - y$ recorder. The Y-axis sensitivity will probably have to be adjusted so that the current signal expands to fill the recorder paper. The CURRENT CONVERTER setting may be adjusted to achieve the desired effect.

**INFO:**

There is an alternate way to perform steps 5 and 6 that uses the Sweep Generator in conjunction with the OFFSET VOLTAGE to produce the desired potential sweep. The K1 OFFSET VOLTAGE is set to the initial potential, +0800 mV, while the Sweep Generator UPPER LIMIT is set to 0000 mV, and the LOWER LIMIT is set to -1000 mV. Because the voltage applied to the working electrode is the sum of the offset voltage and the Sweep Generator output, these settings have the same effect as those in the main procedure above. The advantage to this variation is that moving to the initial potential is easily accomplished by zeroing the Sweep Generator output. The (minor) disadvantage is that the upper and lower sweep limits cannot be directly read off of the front panel of the instrument.

To obtain a Linear Sweep Voltammogram, use the STOP @ LIMIT switch to halt the experiment after the first sweep.

5.3.4 Potential Step Methods

Several electrochemical experiments involve the application of one or more voltage pulses to the working electrode. The most common of these is simple chronoamperometry (CA), but variations of this basic experiment, including chronocoulometry (CC) and double potential step chronoamperometry (DPSCA), are also popular. All of these methods are three electrode potentiometric methods, meaning that a potentiostat controls the potential of a working electrode (versus a reference) while simultaneously measuring the current at the working electrode. Current is essentially prevented from passing through the reference electrode by the use of a third electrode, known as either the counter electrode or the auxiliary electrode.

Chronoamperometry involves a single voltage pulse (or potential step). The working electrode is initially at a potential, E_1 , and it is quickly stepped to another potential, E_2 . The time, t , at which the potential step is applied is taken as $t = 0$. Usually E_1 and E_2 are chosen to span a region of electrochemical interest, such as the formal potential, E° , of an electroactive analyte. A current transient is observed in response to the sudden change in electrode potential as electrons are transferred between the working electrode and the analyte in the adjacent solution. In an unstirred solution, the rate of this transfer is limited by how fast the analyte can physically diffuse to the electrode surface. An equation for this so-called diffusion controlled current, $i(t)$, was developed in 1902 by Cottrell as follows:

$$i(t) = vFAD^{1/2}C(\pi t)^{-1/2}$$

where n is the number of electrons exchanged between an analyte and the electrode, F is Faraday's constant, A is the area of the electrode, D is the diffusion coefficient of the analyte, C is the molar concentration of the analyte in the solution, and t is time since application of the pulse. Experimental results are typically presented as a Cottrell plot, which is a plot of current versus the inverse square root of time (i vs. $t^{-1/2}$). The slope of such a plot yields the quantity $D^{1/2}C$, and in most cases, the value of either D or C is known from previous experiments.

While the AFCBP1 has no built in circuitry for generating voltage pulses, it is possible to connect a third-party pulse generator to a potential input on the AFCBP1. With the instrument set in "potentiostat" mode, pulses from the external pulse generator are applied to the working electrode, and the current at this electrode is presented by the AFCBP1 for recording by either a $x - y$ recorder or digital oscilloscope. If the only recorder available is a $x - y$ recorder, the Sweep Generator on the AFCBP1 can be made to function as a time base for the x -axis on the recorder. With the AFCBP1, a pulse generator, and a digital oscilloscope chronoamperometry can be performed (see: Figure 5-2).

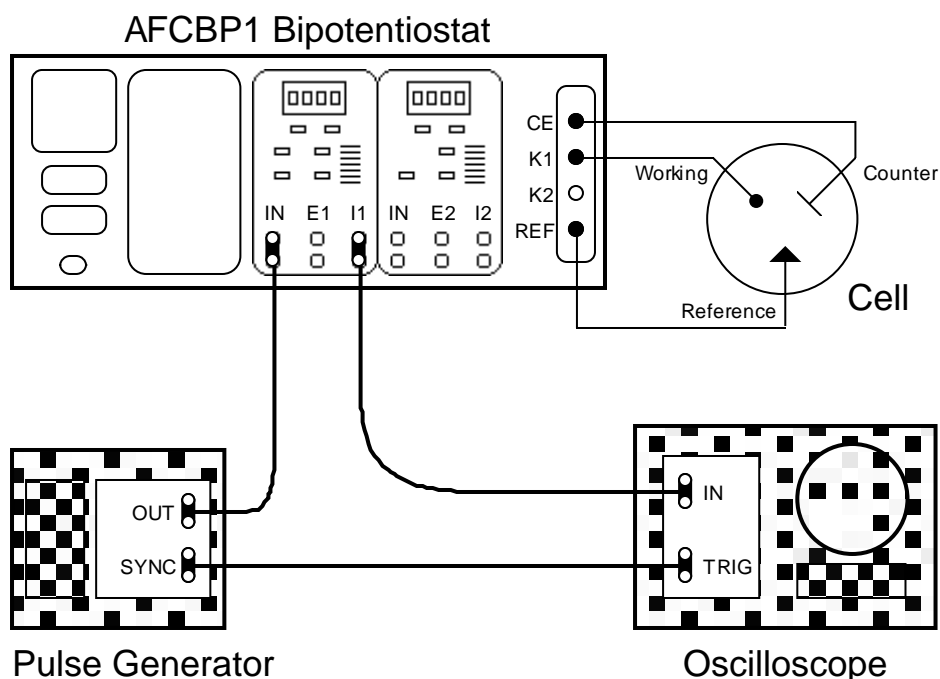


Figure 5-2: Cable Connections for Chronoamperometry.

5.3.5 Hydrodynamic Methods

Electrochemical experiments where the solution is moving with respect to the electrode (or vice versa) are termed hydrodynamic experiments. The most popular of these are the forced convection methods involving either a rotating disk electrode (RDE) or a rotating ring-disk electrode (RRDE). The rotating motion of the electrode sets up an easily characterized solution flow within the electrochemical cell. Using the electrode surface as a frame of reference, the solution immediately adjacent to the surface appears stagnant while the remaining bulk of the solution is being stirred.

Analyte from the bulk of the solution is brought near to the electrode by the convective (stirring) action of the electrode. Once near to the electrode, physical diffusion is responsible for bringing the analyte to the electrode surface. This second process determines how fast analyte reaches the electrode

surface, and this rate of diffusion will be reflected in the observed current at the electrode. Of course, current will only be observed when the electrode potential is suitably poised to either oxidize or reduce the analyte once it arrives at the electrode surface.

The AFCBP1 bipotentiostat was designed for use in both RDE and RRDE voltammetry. In both experiments, the potential of the disk electrode is typically scanned through a region of electrochemical interest using the Sweep Generator, and the disk current is plotted versus the disk potential. A steady state voltammogram with a sigmoidal shape usually results. In RRDE, the current at the ring electrode is also monitored, and a dual pen recorder is required. To set up an RDE experiment, simply omit all connections associated with the K2 electrode (see: Figure 5-3).

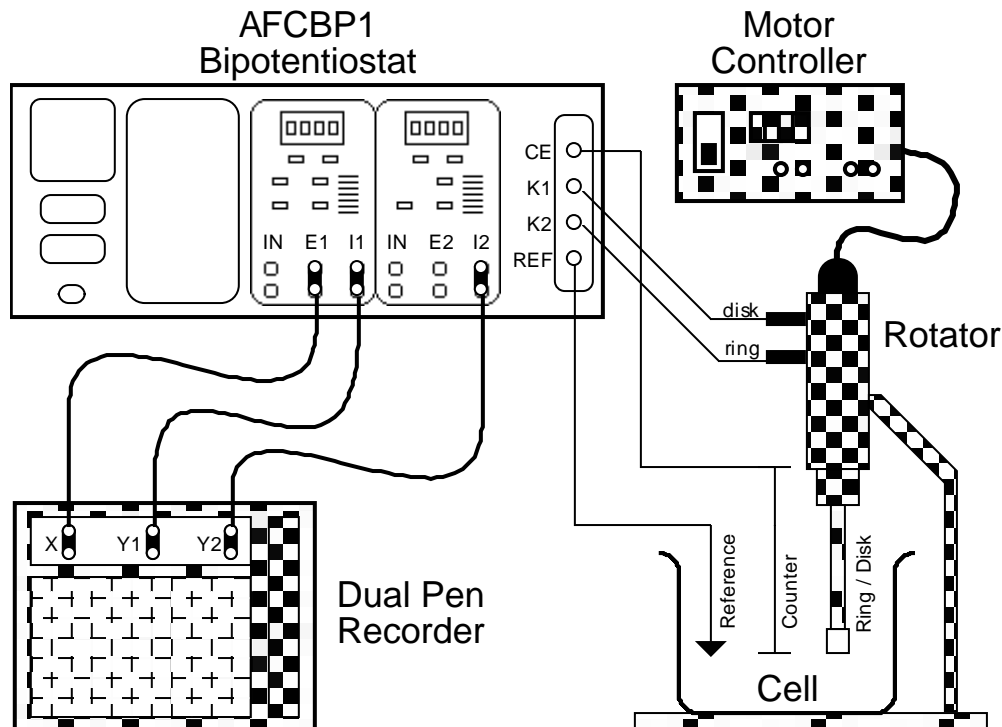


Figure 5-3: Cable Connections for RRDE Voltammetry.

5.4 Controlled Current Methods

Electroanalytical methods in which the working electrode current is the controlled variable, and the working electrode potential is the measured variable, require the use of a galvanostat rather than a potentiostat. These methods are usually referred to as chronopotentiometric methods and involve the use of three electrodes. The galvanostat passes a controlled current between the working and counter electrodes while at the same time monitoring the potential of the working electrode with respect to a reference electrode. Chronopotentiometric methods are classified according to the way in which the current is controlled, and the simplest is constant current chronopotentiometry.

When the MODE push button (in the K1 electrode section) is switched to the "Galvanostat" position, the operation of working electrode K1 is switched from potential control to current control. As always, the potential at the K1 electrode may be monitored at output "E1", and the current at the K1 electrode may be monitored (as a proportional potential) at the "I1" output. The setting of the CURRENT CONVERTER

plays its usual role in determining the proportionality constant for calculating the K1 current from the voltage presented at the "I1" output.

The K1 CURRENT CONVERTER setting also plays a second role when operating in galvanostatic mode. Because the controlled variable is the working electrode current, it is necessary to have some way of specifying just how much current is to be passed through the working electrode. This may be accomplished by using a voltage signal from the OFFSET VOLTAGE, the SWEEP GENERATOR output, an external signal applied to the "IN" input, or any combination of the three. The sum of all three of these voltages is converted (internally) to a current according to the CURRENT CONVERTER setting. It is this resulting current that is then applied to the K1 working electrode.

The types of controlled current experiments that can be performed include (1) constant current chronopotentiometry, (2) current ramp chronopotentiometry, (3) current reversal chronopotentiometry, (4) cyclic chronopotentiometry, and (5) so-called diffusion layer titrations using a rotated ring-disk electrode (RRDE). To perform a chronopotentiometric experiment, the AFCBP1 should be configured as shown in Figure 12, except that the "E1" output should be connected to the recording device. The pulse generator may or may not be required.

5.4.1 Constant Current Chronopotentiometry

In this experiment, the current is simply stepped from zero to some value which is held constant for the duration of the experiment. As the analyte is either oxidized or reduced at the electrode surface, the potential of the electrode changes according to the ratio of oxidized to reduced analytes as described by the Nernst equation. Typically, results are plotted as working electrode potential versus time. Such a plot is called a chronopotentiogram and typically exhibits a sigmoidal shaped curve. The start of the curve is at time zero, and the sigmoid ends at the so-called transition time, t_T . The Sand equation (below) relates the transition time to the current, i , and analyte concentration, C .

$$i = 0.5nFAD^{1/2}\pi^{1/2}Ct_T^{-1/2}$$

where n is the number of electrons exchanged between an analyte and the electrode, F is Faraday's constant, A is the area of the electrode, D is the diffusion coefficient of the analyte, C is the molar concentration of the analyte in the solution.

To produce the sudden current step for constant current chronopotentiometry, use the K1 OFFSET VOLTAGE. The OFFSET VOLTAGE should initially be turned off by deactivating both the "+" and the "-" push button switches (indicator lights off). The magnitude of the desired current step may be set using the four digit push-button potentiometer, noting that this magnitude is scaled by the setting of the CURRENT CONVERTER. The current step can then be applied suddenly at any time simply by pressing either the "+" or the "-" push button. In a typical experiment the potential response would be monitored as a function of time from the moment the current step is applied.

5.4.2 Current Ramp Chronopotentiometry

To produce a smooth analog current sweep, use the SWEEP GENERATOR output. The SWEEP GENERATOR should be set up to provide a voltage sweep that begins at zero volts and ends at some potential corresponding to whatever final current is desired. As always, the proportionality between this final potential and the final current is controlled by the setting of the CURRENT CONVERTER. Similarly, this setting governs the relationship between the rate of the potential sweep and the rate of the current sweep. In a typical experiment the potential response would be monitored as a function of time from the moment the sweep commences.

5.4.3 Other Galvanostatic Methods

Both current reversal chronopotentiometry and cyclic chronopotentiometry require that the current be controlled by a pulse sequence. While the AFCBP1 has no internal circuitry that allows pulse programming, it is possible to connect a third-party pulse generator to the "IN" input for the K1 electrode. The incoming signal should be set up to provide a voltage pulse corresponding to whatever current pulse sequence is required. The proportionality between then incoming voltages and the applied currents is controlled by the setting of the CURRENT CONVERTER. In a typical experiment the potential response would be monitored as a function of time from the moment the pulse sequence commences.

Galvanostatic control of the disk electrode of a RRDE, with potentiostatic control of the ring electrode, can be applied for quantitative analytical determinations of non-electroactive species, by way of so-called diffusion layer titrations, and for the measurement of rate constants for pseudo second-order homogeneous reactions.

5.5 Open Loop Potentials

The AFCBP1 can be used to make simple potentiometric measurements by placing it in "open loop potential" mode. When in this mode, the function of the bipotentiostat is essentially changed to that of a high input impedance digital voltmeter. The potential difference between a working electrode (K1 and/or K2) and the reference electrode is measured at zero current, and this potential is presented at the appropriate front panel output jack (E1 and/or E2). The built-in voltmeter may be used to monitor these potentials, but it may lack the precision required in certain applications.

Most often, the "open loop" feature is used in conjunction with a pH or ion selective electrode together with a reference electrode, such as a standard calomel electrode (SCE). The pH or ion selective electrode is connected to the K1 input jack, and the reference electrode is connected to the REF input jack. It is actually possible to have two pH or ion selective electrodes operating simultaneously by connecting one of the electrodes to K1 and the other to K2. Note that only the (center) signal line on the REF BNC connector should be connected to the reference electrode. The counter electrode (CE) is not used for open loop measurements.

To put the AFCBP1 in "open loop" mode, use the two front panel push buttons (see: Figure 5-4). The left hand button is used to turn on "open loop" mode, and the right hand button is used to select "normal" mode. (If the bipotentiostat is put in "dummy" mode, the open loop potential goes to zero volts.)

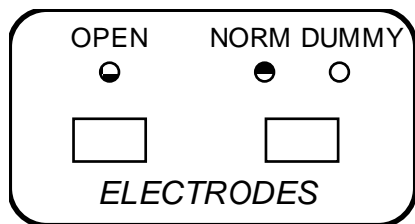


Figure 5-4: Open Loop Settings.

Some pH and ion selective electrodes are equipped with an internal reference electrode. This type of electrode will have two separate leads coming out of it, although many times this fact is disguised by the use of two conductor coaxial cable. When using this type of electrode, it is important to determine which lead connects to the internal reference electrode and which connects to the sensing electrode.

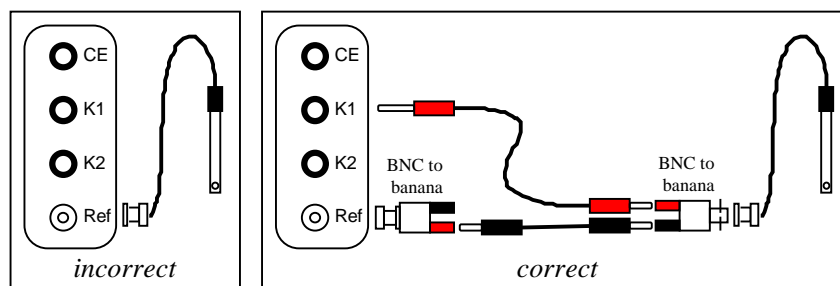


Figure 5-5: Proper pH Electrode Connections.

For example, a typical "combination" pH electrode shown in has a single coaxial cable coming out of it which terminates with a standard BNC connector (see: Figure 5-5). The inner (signal line) part of the BNC connector makes contact with the sensing electrode, while the outer (shield) part makes contact with the internal reference electrode. It is incorrect to directly connect the pH electrode to the REF jack on the AFCBP1; rather, a pair of BNC-to-banana adapters and two jumper cables are used to correctly connect the pH electrode to the bipotentiostat.

Measurements of open loop potential made with a pH electrode immersed in three different buffer solutions is shown (see: Figure 5-6). A linear relationship between potential and pH is observed, as expected, with the slope of the calibration curve being close to the ideal value of 59 mV/pH unit.

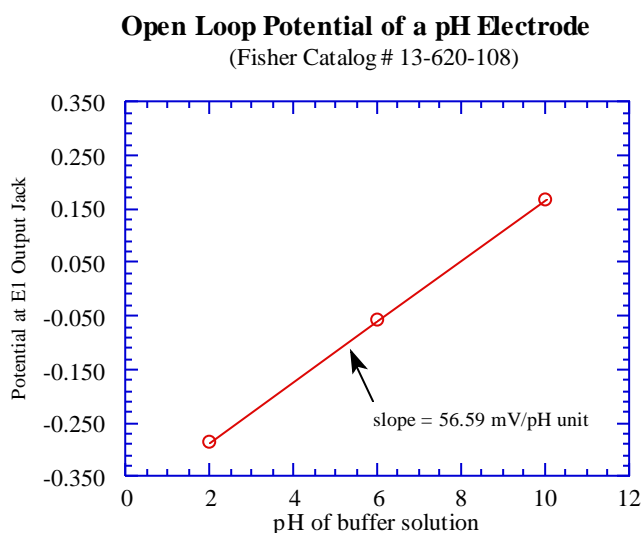


Figure 5-6: Voltage Response of a pH Electrode in Various Buffers.

5.6 Four Electrode Arrangements

Bipotentiostats have found use in several types of four electrode experiments other than the traditional rotated ring-disk variety. Many flow cell designs call for potential control at two working electrodes. This ability to independently control two working electrodes has been used successfully to generate concentration gradients across thin layers of liquid solutions and conducting polymer films (see: Figure 5-7).

A common feature shared by all three cells is that the reference electrode is located close to the K1 working electrode (see: Figure 5-7). While the K1 and K2 circuitry do operate independently and are equivalent in function, the possibility exists for the two electrodes to interact via the uncompensated solution IR drop in a particular electrochemical cell. Error from this interaction is minimized by locating the reference electrode close to the K1 working electrode. Some attention to this matter is required when designing any four electrode arrangement.

The interdigitated array electrode (IDA) is usually fabricated on a silicon substrate as a microlithographically defined array of parallel microband gold or platinum electrodes. Alternating microbands are in electrical contact, and the region of experimental interest is the gap between each alternate finger, which is typically from 1 – 50 μm across. It is across this small gap that a classic "collection" experiment can be performed. An electroactive analyte may be oxidized at the electrode on one side of the gap, allowed to diffuse across the gap, and then reduced at the opposing electrode. These experiments may be conducted in traditional electrolyte solutions or with polymeric electrolyte solvents, such as doped poly(ethylene oxide). See the following articles for more information:

- C.E.D. Chidsey, B.J. Feldman, C. Lundgren, R.W. Murray, *Anal. Chem.* 58 (1986) 601.
- K. Aoki, M. Morita, O. Niwa and H. Tabei, *J. Electroanal. Chem. Soc.* 106 (1984) 7389.

The polymer sandwich electrode arrangement is frequently used to study a special type of conducting polymer called a "redox conducting polymer". Of interest is measuring the mobility of electrons as they "hop" through the thin layer of polymer from one working electrode to the other. Usually, the sandwich is immersed in electrolyte solution along with a reference and a counter electrode. Because of the relatively high resistance of the polymeric film, it is important that the inner (platinum) electrode not be connected to the K1 input. Rather, the outer (gold) electrode should be connected to the K1 input because it is closer to the reference electrode. See the following articles for more information:

- C.E.D. Chidsey and R.W. Murray, *Science* 231 (1986) 25.
- P.G. Pickup and R.W. Murray, *J. Am. Chem. Soc.* 105 (1983) 4510.

Another cell requiring the use of four electrodes is the dual electrode thin layer cell. Two opposing working electrodes, separated by a small gap, are used to generate a concentration gradient across the gap. Typically, one electrode is held at a constant potential while the other is scanned past the formal potential of the redox couple being studied. When the potential difference across the gap becomes large enough, analyte is oxidized at one electrode and reduced at the opposing electrode. A steady-state current response similar to that of a rotated disk electrode is observed. See the following articles for more information:

- L.B. Anderson and C.N. Reilly, *J. Electroanal. Chem.* 10 (1965) 295, 538.
- G.P. Kittlesen, H.S. White, and M.S. Wrighton, *J. Am. Chem. Soc.* 106 (1984) 7389.

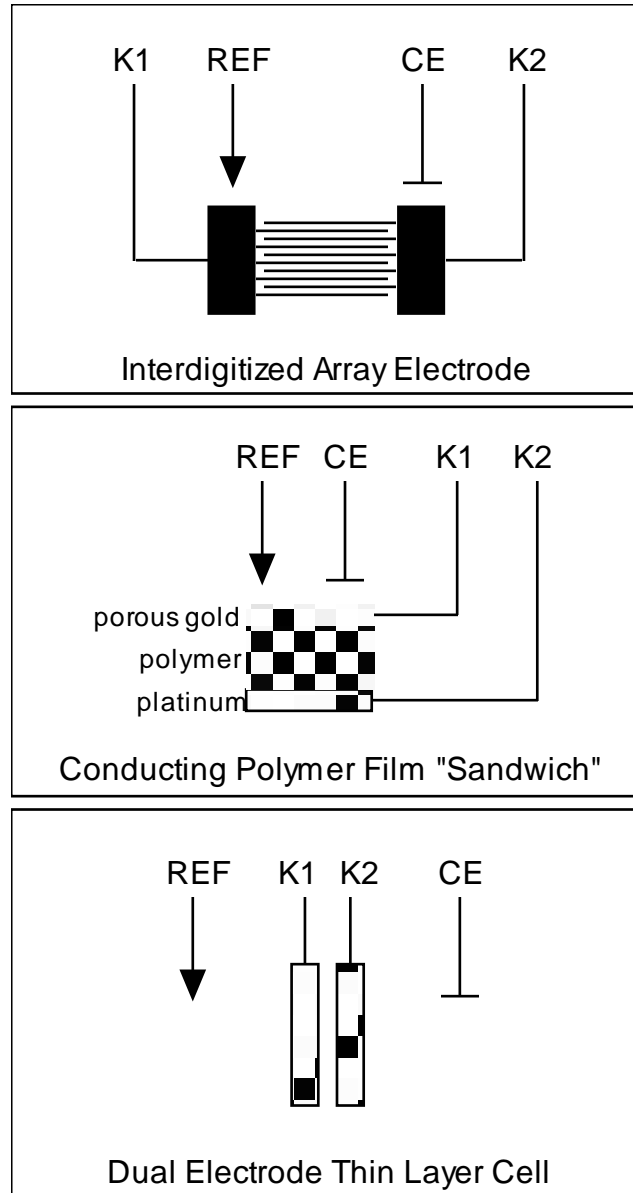


Figure 5-7: Typical Four-Electrode Arrangements

5.7 Two Electrode Arrangements

The AFCBP1 can be used to trace the current vs. voltage response across just two electrodes in an electrochemical cell. This usually results in a measurement of cell conductivity.

In order to use the AFCBP1 in this fashion, one of the cell's electrodes is connected to the K1 jack on the AFCBP1, and the other is connected to the CE jack. Also, the REF and CE inputs are shorted together to prevent overload. (The outer shield on the REF jack is unused).

The Sweep Generator output, the K1 Offset Voltage, and/or any external voltage source are summed and applied as a potential difference across the two electrodes. The current through the cell is

presented at the "I" jack as a proportional voltage according to the setting of the CURRENT CONVERTER.

5.8 Proper Grounding

The electrochemical cell should be placed in a Faraday cage to shield it from laboratory electrical noise. A Faraday cage is simply a small cabinet which is covered with some form of shielding, such as a metal sheet or screen. Typically, this shielding is grounded to a DC Common jack on the AFCBP1. The eight black banana jacks on the front panel provide easy access to the AFCBP1's DC Common.

Recording devices, including $x - y$ recorders and digital oscilloscopes should also be grounded to a DC Common jack. Other items associated with an electrochemical experiment may require grounding. These include the following: support racks, push carts, glove boxes, stir plates, and nearby computers.

The AFCBP1 DC Common floats with respect to the instrument chassis. In some cases it may be necessary to connect one of the black banana jacks to earth ground in order to reduce noise. A binding post (banana type) connected to the instrument's chassis is provided on the front panel for convenience in making this connection. The instrument chassis is also connected to the normal ground pin on the 115 V 3-prong plug. If the instrument is plugged into an outlet with a good quality earth ground, then the front panel binding post will be at earth ground as well.

All cables connected to the AFCBP1 front panel, especially the electrode connections, should be kept as short as possible. Because the REF electrode jack presents a very high input impedance, it is susceptible to picking up unwanted noise. The AFCBP1 incorporates an insulated BNC type connector for the REF electrode connection, allowing complete shielding of the REF input lead. The shield (outer portion of the BNC connector) is driven to the same voltage as the REF signal, and should not be grounded. In addition, the shield should not be connected to any other point at the electrode end, so that no current flows in the shield.

It is suggested that no unusual connections be made to the ELECTRODE jacks as they are intended to connect only to the actual electrodes. The REF jack is particularly sensitive to such connections. It is permissible, however, for the CE and REF jacks to be shorted together when the potentiostat is being used for two electrode measurements.

Keep in mind that some noise is inherent to all measurement systems, although it may not always be apparent. Traditionally, $x - y$ plotters have been used extensively to record the results of electrochemical experiments. These plotters usually have an internal RC circuit that limits the frequency response of the plotter, thus filtering out most noise. When a computerized data acquisition system is used, however, there is usually no such filter between the potentiostat and the computer. This means that raw data acquired by the computer may appear (shockingly) noisy, especially to those who's only past experience has been with $x - y$ recorders. Most electrochemical software, including that offered by Pine Instrument Company, will provide the user with a range of data smoothing options to help eliminate noise.

5.8.1 Oscillations

The AFCBP1 is an analog system which relies on feedback for stable operation. There is the possibility, on certain systems, that the feedback may become phase shifted and cause the unit to oscillate. Symptoms of oscillation include unexplained jumps in potential or current, or when the overload indicator is glowing for no apparent reason. The presence or absence of oscillation is verified by using an oscilloscope to observe the output voltages.

If oscillations are observed, and the grounding techniques discussed above do not eliminate the problem, then you should try slowing the response time of the AFCBP1. Located on the back panel are six jacks to which capacitance may be connected. It is suggested that capacitors in the range of 0.001 to 0.1 microfarads be added across the K1 and/or K2 jacks on the back panel. Various combinations should be tried, as experience will best dictate what should be used. The capacitors should be either film or ceramic type and rated for at least 30 volts.

If problems are experienced in the galvanostatic mode of operation, there are two jacks on the rear panel for external compensation in that mode only. Capacitors in the range of 0.001 to 0.1 μF are recommended.

6. Troubleshooting

When a malfunction or some anomalous behavior is observed during an electrochemical experiment, one must first determine whether the difficulty originates within the potentiostat or is external to the potentiostat. In most cases, proper operation of the AFCBP1 potentiostat can be verified without making any external connections. The following procedures allow general testing using an internal dummy cell resistor network rather than an actual electrochemical cell. These procedures do assume that the internal voltmeter is working properly, but if there is reason to believe that the voltmeter is malfunctioning, an external voltmeter can be used in its place. Testing procedures should be followed in the order they are presented.

6.1 Testing the Sweep Generator

1. Turn on the AFCBP1 bipotentiostat. Several small red indicator lights should light up indicating that the power is on.
2. Set the CONTROL SOURCE to "panel" mode (keep in mind that this control has a one second delay time). Set the NORM vs DUMMY control to "dummy" mode. Make certain that the OPEN control is deactivated. Rotate the VOLTMETER knob to the "sweep" position.
3. Set the upper limit to $+9000\text{ mV}$, and the lower limit to -9000 mV . Set the SWEEP RATE to 500.0 mV/s using the " $< 1000\text{ mV/s}$ " setting on the RANGE control. Deactivate both STOP @ LIMIT controls. Activate the ZERO control. Put the SWEEP control in the "hold" position.
4. Deactivate the SWEEP VOLTAGE switches for both working electrodes. Turn off the OFFSET VOLTAGE controls for both working electrodes. Set the CURRENT CONVERTER controls for both working electrodes to the " 1 mA " position. Set the K1 electrode's mode control to the "pot" setting.
5. At this point, confirm that the Voltmeter display reads 0.00 V .
6. Deactivate the ZERO control. Again, confirm that the Voltmeter display reads 0.00 V .
7. Put the SWEEP control in the "run" position and observe the Voltmeter. The digit immediately to the left of the decimal point (i.e., the ones place) should change by one digit every 2 seconds. Next, change the RANGE control to the " $< 100\text{ mV/sec}$ " position and observe the Voltmeter again. Now, the digit immediately to the right of the decimal point (i.e., the tenths place) should change by one digit every two seconds. Return the RANGE control to the " $< 1000\text{ mV/s}$ " position.
8. Put the SWEEP control in the "hold" position and observe the Voltmeter. The value displayed on the Voltmeter should remain constant (the last digit may fluctuate ± 1 digit). Activate the ZERO control. Confirm that the Voltmeter display reads 0.00 V .
9. Momentarily press the "down arrow" MANUAL SWEEP button to set the sweep direction to "down". Confirm that the Voltmeter display still reads 0.00 V . Deactivate the ZERO control and again confirm that the Voltmeter still reads " 0.00 " volts. Put the SWEEP control in the "run" position and observe the Voltmeter. The reading on the Voltmeter should begin to decrease (becoming more negative). Momentarily press the "up arrow" MANUAL SWEEP button and observe the Voltmeter. The reading on the Voltmeter should begin to increase (becoming more positive).
10. Activate the ZERO control. Momentarily press the "up arrow" MANUAL SWEEP button to set the sweep direction to "up". Activate the STOP @ LIMIT for the UPPER LIMIT. Deactivate the ZERO control. The Voltmeter reading should climb to " 9.00 " and stop. Next, activate the STOP @ LIMIT for the LOWER LIMIT. Then, deactivate STOP @ LIMIT for the UPPER LIMIT. The Voltmeter reading should move to " -9.00 " and stop.

The ten steps above test for proper behavior of the major functions of the Sweep Generator. If no problems are encountered, the Sweep Generator is most likely functioning properly.

6.2 Testing an Electrode Unit (K1 or K2)

1. After testing for proper operation of the Sweep Generator (above), leave the AFCBP1 turned on, and follow these directions:
2. Set the CONTROL SOURCE to "panel" mode (keep in mind that this control has a one second delay time). Set the NORM vs DUMMY control to "dummy" mode. Make certain that the OPEN control is deactivated. Rotate the Voltmeter knob to the "E1" or "E2" position, depending on which electrode unit is being tested.
3. Set the UPPER LIMIT to $+1000\text{ mV}$, and the LOWER LIMIT to -1000 mV . Set the SWEEP RATE to 50.00 mV/s using the " $< 100\text{ mV/s}$ " setting on the RANGE control. Deactivate both STOP @ LIMIT controls. Activate the ZERO control. Put the SWEEP control in the "hold" position.
4. Deactivate the SWEEP VOLTAGE switches for both working electrodes. Turn off the OFFSET VOLTAGE controls for both working electrodes. Set the CURRENT CONVERTER controls for both working electrodes to the " 1 mA " position. Set the K1 electrode's MODE control to the "pot" setting.
5. At this point, confirm that the Voltmeter display reads 0.00 V .
6. Set the OFFSET VOLTAGE for the electrode being tested at -1000 mV . The voltmeter should read " -1.00 ". Now, set the OFFSET VOLTAGE at $+1000\text{ mV}$. The voltmeter should read " 1.00 " volts.
7. Rotate the Voltmeter knob to the "I1" or "I2" position, depending on which electrode is being tested. The voltmeter should read " 1.00 ", but may deviate up to 1% from this value. Next, using the CURRENT CONVERTER control, check every other setting from " 100 mA " down to " 100 nA " to verify the other Voltmeter readings listed in the table:

Current Converter Setting	Expected Voltmeter Reading (I1 or I2)
100 mA	"0.01"
10 mA	"0.10"
1 mA	"1.00"
$100\text{ }\mu\text{A}$	"10.00" (with possible OVERLOAD)
$10\text{ }\mu\text{A}$	"13.50" or higher with OVERLOAD!
$1\text{ }\mu\text{A}$	"13.50" or higher with OVERLOAD!
100 nA	"13.50" or higher with OVERLOAD!

Table 6-1: CURRENT CONVERTER Setting Expected Voltmeter Reading (I1 or I2)

8. Return the CURRENT CONVERTER control to the " 1 mA " position. Deactivate the OFFSET VOLTAGE. Activate the SWEEP VOLTAGE control. Verify that the Voltmeter is still displaying the current ("I1" or "I2"), and that it reads " 0.00 ".
9. Deactivate the ZERO control. Initiate a voltage sweep by changing the setting of the SWEEP control to "run". Observe the voltmeter reading. It should slowly sweep from 0.00 up or down to 1.00 or -1.00 V . (The initial sweep direction may be set "up" or "down" by toggling the MANUAL SWEEP control in the desired direction; otherwise, the initial direction is random). It should not matter whether the potential "E" or the current "I" is displayed on the Voltmeter. In either case, it should display a sweep between " 1.00 " and " -1.00 V ".

10. For electrode K1 only: Change the K1 MODE control to "gal". It should not matter whether the potential "E1" or the current "I1" is displayed on the Voltmeter-in either case it should display a sweep between "1.00" and "-1.00 V".

If no problems are encountered, the electrode unit is most likely functioning properly. The next section describes how to troubleshoot problems outside of the potentiostat itself.

6.3 Further Troubleshooting

If the testing procedures outlined in the previous section indicate that the AFCBP1 is functioning properly, then it is quite likely that there is a problem in the external electrochemical cell or connections. The suggestions below describe common problems encountered during electrochemical experiments. Common mistakes, made even by experienced electrochemists, are included as well. Symptoms are described for scanning experiments, such as cyclic voltammetry, but the suggestions apply to other methods as well.

6.3.1 Symptom: No observed current

The $x - y$ recorder shows no motion on the Y axis (current), but the X axis (voltage) is functioning properly. "I1" (or "I2") voltmeter reading remains at or near zero.

6.3.2 Suggestions: No observed current

1. **Low Current Sensitivity.** The CURRENT CONVERTER setting is too high for a signal to be detected by $x - y$ recorder. The Y axis sensitivity on the recorder may also be too low. If the CURRENT CONVERTER is on the most sensitive setting ("100 nA") and there is still no observed current, then there is probably a discontinuity in the working electrode connection.
2. **Working Electrode Discontinuity.** This is most often caused by the working electrode failing to contact the solution. This happens whenever the surface of the electrode is fouled or when there is a gas bubble trapped on the surface. Also, the cable connecting the working electrode to the AFCBP1 may have an open circuit. This frequently happens near jacks at the cable ends.

6.3.3 Symptom: No motion on X axis (voltage)

6.3.4 Suggestion: No motion on X axis (voltage)

1. **Sweep is not being applied to working electrode.** The sweep is not turned on. The SWEEP VOLTAGE push button for the working electrode in question is deactivated. The $x - y$ recorder may also be on "stand-by".

6.3.5 Symptom: Linear Current Response

During cyclic voltammetry, the $x - y$ recorder draws a smooth diagonal line. During step experiments, such as chronoamperometry, a horizontal line is observed instead of a decay transient.

6.3.6 Suggestion: Linear Current Response

1. **Dummy Cell Electrochemistry.** The potentiostat is in "Dummy" mode. Put it in the "Normal" mode and try again.

6.3.7 Symptom: OVERLOAD Indicator ON

Overload occurs whenever potentiostat is placed in "Normal" mode, regardless of applied potential.

6.3.8 Suggestions: OVERLOAD Indicator ON

1. **Low Current Sensitivity.** The CURRENT CONVERTER is set to too sensitive a setting, and this is saturating an internal amplifier. REF to CE Discontinuity. During normal cell operation, there is always an electrically conductive path between the REF and CE jacks. This path consists of cables running to the reference and counter electrodes, and is completed by both electrodes being immersed in the same conductive electrolyte solution. Overload occurs when this path is broken. Check cables to the reference and counter electrodes. If cables are okay, there could be a problem with the cell. Does the test solution contain enough electrolyte? Have any solutions dried up? Is a glass frit clogged? Is there a bubble in a Luggin capillary? Is the reference electrode defective?
2. **Short Circuit between K1 and K2.** In dual working electrode experiments, a direct short between the two electrodes will result in an overload. Shorted ring-disk electrodes, interdigitated arrays, and thin layer cells will cause an overload.

6.3.9 Symptom: Noise

6.3.10 Suggestions: Noise

1. **Rotating electrode experiments.** Dirty electrode contacts on rotator or electrode shaft. Clean gently with abrasive paper. Dirty rotator belt results in buildup of a large electrostatic charge. Clean belt by soaking for 3 hours in nitric acid (50% or 6M) at room temperature. Dispose of acid properly!
2. **Gas bubbles.** Bubbles are impinging on electrode surface during experiment. The gas may be generated electrochemically or nitrogen deaeration may have been left on accidentally.
3. **Discontinuity.** There may be an intermittent discontinuity in an electrode connection. Wiggle each lead separately to determine source.
4. **Poor Grounding.** See earlier section on noise and also check for ground loops.
5. **Noise Pickup.** When operating the AFCBP1 at a high current sensitivity, a Faraday cage will most likely be required. The reference electrode is very sensitive to external noise sources, and may require more elaborate shielding. Thermostated laboratory ovens, variacs, and hot plates generate considerable power line noise.

7. Technical Information

7.1 Bibliography

The following books are recommended for information about electrochemistry.

1. Kissinger, P.T. and Heineman, W.R. (eds): Laboratory Techniques in Electroanalytical Chemistry (Dekker, New York, 1984). This book presents a more practical side of electroanalytical chemistry, providing information about instrument design, choice of chemicals, and data analysis.
2. Bard, A.J. and Faulkner, L.R.: Electrochemical Methods (Wiley, New York, 1980). Widely considered to be the final authority in modern electroanalytical chemistry, this book presents highly detailed technical discourses on just about every conceivable routine electrochemical experiment. It is very often used as textbook for graduate level courses.
3. Sawyer, D.T., Heineman, W.R., and Beebe, J.M: Chemistry Experiments for Instrumental Methods (Wiley, New York, 1984). The first section of this undergraduate laboratory textbook describes a wide variety of electrochemical experiments suitable for use in college instruction. Proven experiments are presented with detailed instructions on how to conduct them.

7.2 Specifications

Specifications are subject to change without notice.

Power	115 VAC or 230 VAC; 50/60 Hz
Weight	12 pounds
Operating Temperature	10 – 40 °C
Dimensions	17 w × 13 d × 7.5 h in.
Sweep Rate	dual range: 0 to 99.99 mV/s or 0 to 999.9 mV/s
Sweep Range	±9.999 V; set using push-button potentiometers
Electrode Current	1 A maximum
Offset Voltage	±9.999 V; set using push-button potentiometers
Electrode Voltage	±10 V
Current Converters	7 ranges from 100 nA/V to 100 mA/V
Input Impedance	10 ¹² Ω on reference potential follower
Small Signal Bandwidth	> 10 kHz; -3dB typical
Dummy Resistors	REF (100 kΩ), CE (2 kΩ), K1 and K2 (1 kΩ)

Table 7-1: AFCBP1 Specifications

7.3 Interface Cable Description

pin #	A-to-D board signal name	AFCBP1 signal name	direction of signal	description of signal (not all lines are used)
1	AI GND	AGND		analog ground (for board inputs)
2	AI GND	AGND		analog ground (for board inputs)
3	ACH00	SWEEP	CBP->BOARD	output of CBP's internal sweep generator
4	ACH08	AGND		analog ground
5	ACH01	E1 OUT	CBP->BOARD	potential of the K1 working electrode
6	ACH09	AGND		analog ground
7	ACH02	I1 OUT	CBP->BOARD	current at the K1 working electrode
8	ACH10	AGND		analog ground
9	ACH03	E2 OUT	CBP->BOARD	potential of the K2 working electrode
10	ACH11	AGND		analog ground
11	ACH04	I2 OUT	CBP->BOARD	current at the K2 working electrode
12	ACH12	AGND		analog ground
13	ACH05	OL+	CBP->BOARD	positive overload condition if this line higher than +7.5V
14	ACH13	AGND		analog ground
15	ACH06	OL-	CBP->BOARD	negative overload condition if this line is less than -7.5V
16	ACH14	AGND		analog ground
17	ACH07	SW LIMIT	CBP->BOARD	indicates the present target sweep limit (unused)
18	ACH15	AGND		analog ground
19	AI SENSE			
20	DAC0OUT	K1 INPUT	BOARD->CBP	potential offset applied to K1 working electrode
21	DAC1OUT	K2 INPUT	BOARD->CBP	potential offset for K2 or back panel rotator control
22	EXTREF			
23	AO GND	AGND		analog ground (for board outputs)
24	DIG GND	DGND		digital signal ground
25	ADIO0	ED0	BOARD<>CBP	used for encoded digital communication
26	BDIO0	ED4	BOARD<>CBP	used for encoded digital communication
27	ADIO1	ED1	BOARD<>CBP	used for encoded digital communication

28	BDIO1	ED5	BOARD<->CBP	used for encoded digital communication
29	ADIO2	ED2	BOARD<->CBP	used for encoded digital communication
30	BDIO2	ED6	BOARD<->CBP	used for encoded digital communication
31	ADIO3	ED3	BOARD<->CBP	used for encoded digital communication
32	BDIO3	ED7	BOARD<->CBP	used for encoded digital communication
33	DIG GND	DGND		digital signal ground
34	+5V			
35	+5V			
36	SCANCLK			
37	EXTSTRB			
38	STRT TRIG		CBP->BOARD	signal to begin acquisition (sync with sweep start)
39	STOP TRIG		CBP->BOARD	signal to halt acquisition (sync with sweep end)
40	EXTCONV			
41	SOURCE1			
42	GATE1			
43	OUT1	ED8	BOARD->CBP	strokes digital data sent from board to potentiostat
44	SOURCE2			
45	GATE2			
46	OUT2			
47	SOURCE5		CBP->BOARD	strokes digital data sent from potentiostat to board
48	GATE5			
49	OUT5			
50	FOUT			

Note: All digital communication between the board and potentiostat is encoded using an error correction scheme to avoid miscommunication. A message packet sent to the potentiostat contains information regarding all front panel settings, potential limits and sweep rates for the analog sweep generator, and other important internal switch settings. The message returned by the potentiostat indicates the success or failure of the communications attempt and whether or not any message parameters are out of range. A software library written in the "C" language that handles communication with the bipotentiostat is available directly from Pine Instrument Company.