

PC4 Potentiostat/Galvanostat/ZRA

Operator's Manual

includes both the

PC4/300 Potentiostat/Galvanostat/ZRA

and

PC4/750 Potentiostat/Galvanostat/ZRA

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Contact us at your earliest convenience. We can be contacted via:

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If you write to us about a problem, provide as much information as possible.

If you are having problems with installation or use of your PC4 Potentiostat, it would be helpful if you called from a phone near to your computer, where you can type and read the screen while talking to us.

We are happy to provide a reasonable level of free support for registered users of our products. Reasonable support includes telephone assistance covering the normal installation and use of the PC4 in standard computer hardware.

We provide a one year warranty covering both parts and labor. A service contract that extends the warranty is available at an additional charge.

Enhancements to the PC4 that require significant engineering time on our part may be available on a contract basis. Contact us with your requirements.

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Chapter 1 -- Introduction

About This Manual

This manual covers the installation and use of the PC4 Potentiostat/Galvanostat/ZRA. It covers both the PC4/300 Potentiostat/Galvanostat/ZRA and its cousin the PC4/750 Potentiostat/Galvanostat/ZRA. These instruments differ primarily in their output current: 300 mA for the PC4/300 and 750 mA for the PC4/750. Throughout this manual, the term PC4 should be interpreted as a reference to both the PC4/300 and the PC4/750.

This manual describes use of a PC4 with Revision 3.1 of the Gamry Framework software. It is equally useful when setting up a newly purchased potentiostat or modifying the setup of a two-year-old potentiostat for use with new software.

The bulk of Chapter 1 is an overview of the PC4's design and modes of operation. Chapter 2 contains PC4 installation instructions. Chapter 3 describes cell cable connections. Chapter 4 covers the difficult issues of potentiostat stability and approaches to prevent oscillation. Chapter 5 discusses the realities of low current, high impedance measurements.

You will find dry technical material such as specifications, DIP switch settings, and connector pin-outs in the Appendices.

This manual does not discuss software installation or operation.

Software support for the PC4 is described in the Operator's Manual for each of the applications programs. All the Gamry Instruments' applications which run under the Gamry Framework control the PC4 via a PSTAT object. See the Framework's On-line Help for programming information.

CE Compliance Required for Sale in Europe

The European Community has instituted standards limiting radio frequency interference from electronic devices and mandating several safety requirements. Gamry Instruments has modified its instruments to comply with these standards. We are shipping CE compliant instruments to all destinations.

The relevant CE regulations include EN55022 Class B and EN60950.

About the PC4

The PC4 Potentiostat is a research grade electrochemical instrument compact enough to fit inside a computer. It can operate as a potentiostat, a galvanostat, or a ZRA (zero resistance ammeter).

The PC4/300 and PC4/750 are two members of Gamry Instruments' PC4 Potentiostat family. They share a number of characteristics with the other members of this family, especially in the areas of signal generation and signal preconditioning prior to A/D conversion.

PC4 features include 9 decade current autoranging, electrical isolation from earth ground, current interrupt iR compensation, and extensive filtering. A sine wave generator on the PC4 allows its use for impedance measurements to at least 100 kHz.

The PC4 consists of two printed circuit cards that install directly into a computer. Each card requires one expansion slot in an AT compatible computer. The cards are interconnected by one ribbon cable. Depending on the number of available slots, up to four PC4 card sets can be installed in one computer.

The first card is called the Potentiostat Card. It contains the analog potentiostat circuitry and its associated isolated power supply. This card is not directly connected to the computer's AT bus, except for the 5V power and its ground. It communicates with the computer over serial lines isolated by optocouplers on the other card. The Potentiostat card can be switched to act as a high performance Galvanostat or as a ZRA (Zero Resistance Ammeter).

The second printed circuit card will be referred to as the Controller Card. It contains an ISA bus interface, optocoupled serial transfer logic, an isolated power supply, a signal generator, and a high performance measurement system.

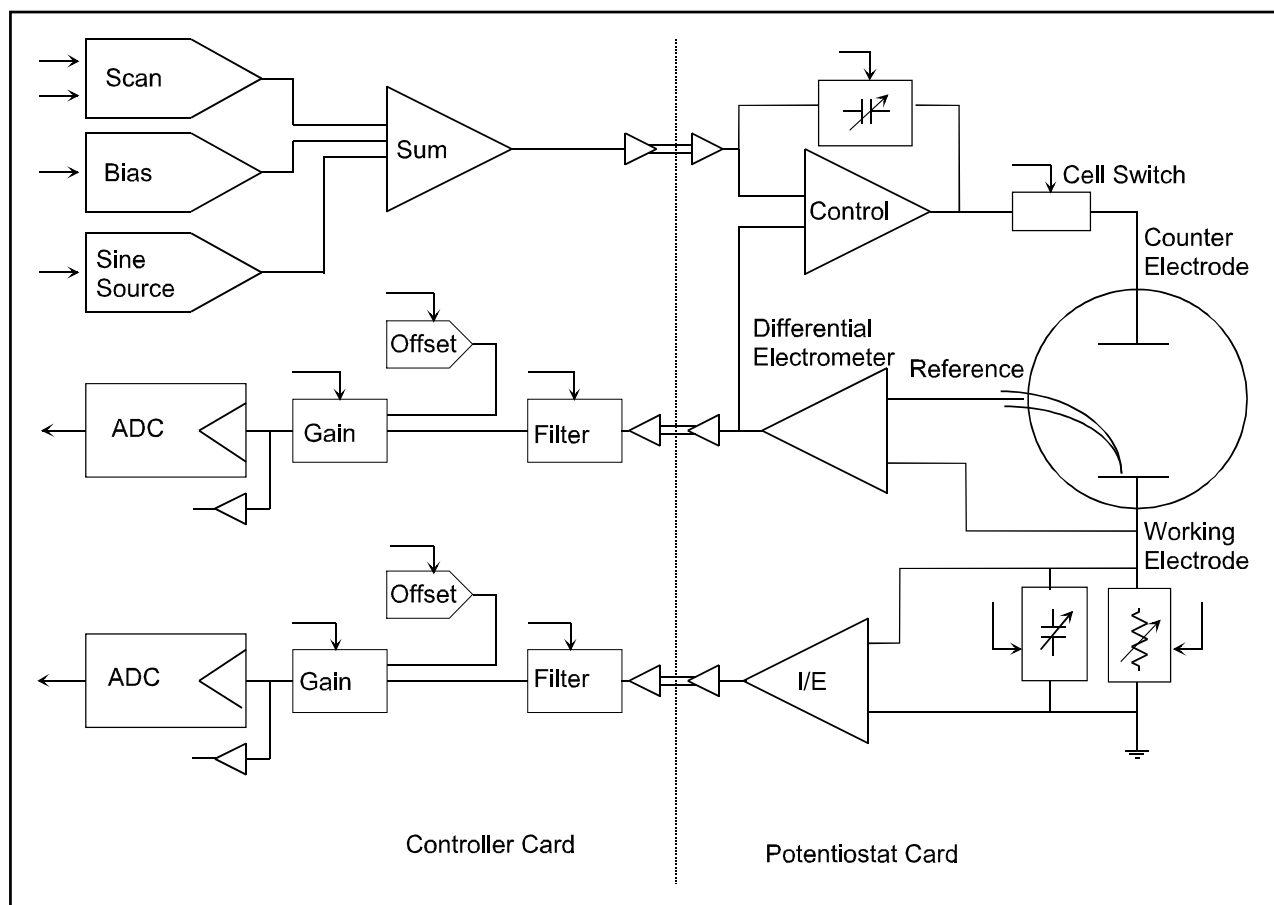
- The ISA bus (also known as the AT bus) interface communicates with the rest of the PC4 over optocoupled serial lines. There is no ground connection between the ISA bus circuitry and the analog circuits in the PC4.
- Each card contains an isolated DC/DC converter. The power supply on the Controller card converts the computer's 12 volt supply into the voltages needed to power its own analog circuitry. The power supply on the Potentiostat card converts the computer's 5 volt supply into a variety of voltages.
- The standard "DC" signal generator on the Controller Card uses two 16 bit D/A converters. A DDS sine wave generator is packaged on a small "piggyback card" that plugs into the Controller card.
- The Controller Card measurement circuitry includes signal filtering, offset, and switchable gain on two independent measurement channels. The output of these channels is measured using a 16 bit A/D converter.

Potentiostat Schematic Diagram

If you are not familiar with electronic schematics or potentiostats, you probably want to skip this section. This information is for expert use only and is not required for routine use of the PC4 Potentiostat.

Figure 1-1 is a highly simplified schematic diagram. It shows the analog portion of the Potentiostat in its potentiostatic control mode.

Figure 1-1
PC4 Analog Circuits in Potentiostat Mode



A few points concerning this schematic:

- The circuits on the right side of the schematic are on the Potentiostat card and those on the left are on the Controller Card. The dotted line shows the separation between the two portions of the instrument. The analog signals sent between the portions are received in differential amplifiers to eliminate grounding problems.
- Arrows pointing into a circuit indicate a computer control input.
- The labels CE , RE and WE stand for counter electrode, reference electrode and working electrode respectively.
- There are two 16 bit D/A converters generating the computer controlled portion of the applied cell voltage.
- The I/E converter uses a series resistor to measure the cell current. The circuit actually uses eight decade resistors that can be switched in under computer control.
- The cell switch is actually two switches in series - a relay for low leakage and an FET switch for fast response.
- The label OLP refers to overload protection.
- Gains and resistor values are not shown.
- Two capacitors can be switched across the I/E converter resistor. These capacitors are used for filtering and stability compensation.
- The control amplifier is shown at the upper right side of the schematic. Compensation capacitors can be switched across the control amplifier to adjust its bandwidth and improve potentiostat stability.
- The A/D converter is a 16 bit successive approximation type converter.
- Some analog circuits, including overload detection circuitry, positive feedback IR compensation, the auxiliary D/A converter, power circuits, and data acquisition controls are not shown.
- All digital circuits, including the AT bus interface, timers, state machines, optocouplers, and digital I/O are not shown.
- Timing for both data acquisition and D/A update in the signal generator is controlled by a state machine working with a crystal oscillator generated clock. A busy processor in the computer cannot create timing jitter.

Notational Conventions

In order to make this manual more readable we have adopted some notational conventions. These are used throughout this manual and all other Gamry Instruments manuals.

- Numbered lists. A numbered list is reserved for step by step procedures, with the steps always performed sequentially.
- Bulleted List. The items in a bulleted list, such as this one, are grouped together because they represent similar items. The order of items in the list is not critical.
- Hexadecimal numbers. Hexadecimal numbers are used for hardware related items such as I/O addresses. The Gamry Framework and this manual use the C programming language convention: all hexadecimal numbers have a prefix of 0x. For example, the default I/O addresses used by a PC4 Potentiostat are 0x120 through 0x13F.
- File names and directories. Inside paragraphs, references to computer files and directories will be in quotes, for example: "WIN.INI" and "\FRAMEWORK\FRAMEWORK.EXE".

Chapter 2 -- Installation

A PC4 Potentiostat is only useful after it has been installed in an AT compatible computer.

If you purchase a PC4 in a system that includes both a computer and an applications software package, Gamry Instruments, Inc. will install the PC4 (and the system software) to produce a "turn-key" system. You may ignore this chapter if you have purchased a turn-key system.

If you buy your own computer, add a PC4 to an existing system, or move an old PC4 to a new computer, you need to know how to install a PC4 into a computer. Read on.

Software installation is discussed in the Installation Manual for each software package. It will not be discussed here.

Computer Requirements

Before you install a PC4 into your own computer you must make sure that your computer meets these simple requirements.

- A computer based on one of the following Intel microprocessors : 486, Pentium™ or Pentium II™, or a 100% compatible processor from another vendor.
- Two full length, full AT height expansion slots for each cardset. These slots must have a 16 bit ISA or EISA bus interface. The ISA bus interface is commonly referred to as the "AT Compatible" bus.
- Up to 30 watts of power supply capacity for each PC4 Card Set. This is in addition to the power normally drawn by your computer and its expansion cards.

Most of the power is drawn from the computer's +12 volt and +5 volt supplies. However, all four power supplies found in a PC (± 5 and ± 12 volts) are required for PC4 operation.

Gamry's Windows application software packages may impose additional, more stringent requirements.

Card Identification

A PC4 Potentiostat consists of two full height, full length AT compatible printed circuit boards. When you look at your PC4 cards, you will notice that a large portion of one card is covered with a large black shield. This card is the PC4 Potentiostat Card. The card without the shield is referred to as the PC4 Controller Card.

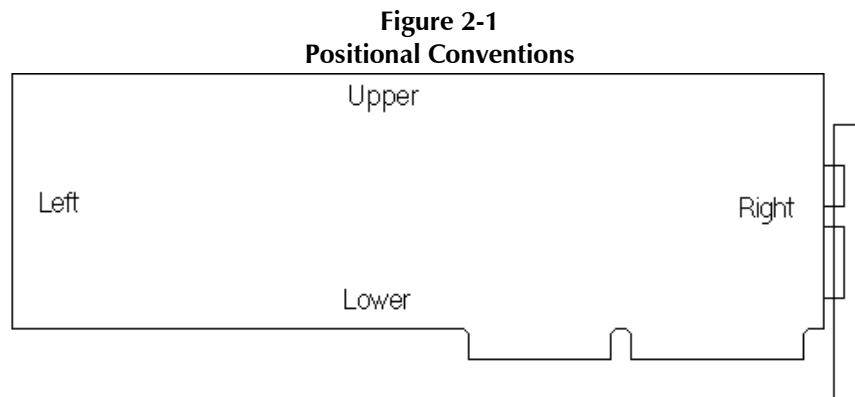
Positional Conventions

Throughout this manual, reference will be made to positions on the PC4 cards. In order to avoid confusion, we will define some conventions that describe positions on these cards.

Assume:

- The card in question is lying on a table in front of you.
- The component side of the card is up.
- The card edge (where the card plugs into the computer) is facing you.

Under these assumptions, Figure 2-1 illustrates our positional convention.



Handling the Cards

The PC4 cards, like most electronic components, are susceptible to damage from static discharges and connection to live circuits. Some elementary precautions should be taken when handling and installing these cards.

- The cards are shipped in anti-static bags. Leave them in these bags until you need to install or reconfigure them.
- Always turn off your computer before plugging in any card.
- If you need to leave a card out of its anti-static bag, such as when you change a configuration DIP switch, lay the anti-static bag on a flat surface, then lay the card on top of the bag.
- Prior to handling the cards, you should momentarily ground yourself to eliminate any static charges on your body. A good way to accomplish this is to turn off your computer, then lightly touch your finger to an unpainted portion of the computer's metal chassis.
- Save the anti-static bags. You must use them if the cards are shipped while not installed in a computer. This includes occasions when the cards must be returned to Gamry Instruments, Inc. for repair.

Dip Switches for System Configuration

The PC4 Controller Card has one 4-pole DIP switch on it. You can use this switch to configure the card for use in a specific computer system.

In most cases you leave the switch in its factory set position and forget it is there. The factory settings should work for all single potentiostat systems where the computer contains only "common" expansion cards. Common is defined for purposes of this discussion as devices such as standard video cards, GPIB adapters, serial & parallel ports, disk controllers, etc.

You only have to set this DIP switch if you have an I/O address or interrupt level conflict between your PC4 Controller Card and another expansion card. You normally discover these conflicts when the newly installed PC4 doesn't work or causes failures in other cards that used to work.

The default factory settings for a PC4 Controller Card are:

- Board I/O address range = 0x120-0x13F (hexadecimal). This range is not used by common AT compatible expansion cards.
- Board number = 1. This is the correct setting for systems containing a single PC4 Potentiostat. This setting must be changed on the second, third and fourth PC4 added to a computer.

If you have questions about what the term I/O Address Range means, or think you may need to change the settings, consult **Appendix C**.

The interrupt level used by the PC4 can also conflict with the level used by other cards in your computer. This level is set via software settings, not via DIP switch changes, so it will not be discussed further here. It is discussed in **Appendix C**.

Installing the Cards in Your Computer

NOTE: Please review the discussion on **Handling the Cards** earlier in this chapter prior to proceeding.

The following procedure is used to install the PC4 cards in your computer. It assumes that you are using the default configuration for the installed card set or that you have already configured the card for a non-standard configuration.

1. Turn off your computer.
2. Following your computer manufacturer's instructions, open up the computer to expose its expansion card slots.
3. Locate an empty full length expansion slot that has an AT (16 bit) interface. If necessary, remove the retaining screw and slot cover (the 'L' shaped metal bracket). Save the screw for use later.
4. Locate a second empty slot that is within 20 cm of the first. You may have to move some of your existing cards to get two suitable slots. Again, remove the retaining screw and slot cover, saving the screw for use later.
5. Remove one card from its anti-static bag.
6. Plug this card into one slot. Make sure the card seats securely in the edge card connector on the motherboard. Secure the card in the slot using the screw from Step 3.

NOTE: All the gold fingers on the lower edge on this card must be in a motherboard edge connector.

7. Repeat steps 5 and 6 with the second card, locating it in the second slot.
8. Do not close up the computer yet.

Connecting the Interconnection Cable Between the Cards

1. Locate the 26 pin headers (group of 26 pins) on both the Controller and Potentiostat cards. They are in the upper middle of each card.
2. Examine the ribbon cable that came with the PC4 Potentiostat. Each end of this cable has a 26 pin connector on it. The two ends of the cable are identical and therefore interchangeable.
3. Plug one end of this ribbon cable into the 26 pin header on the Controller card.
4. Repeat step 5 using the other end of the cable and the header on the Potentiostat card.
5. Carefully double check your work.
6. Once this step is completed you may close up the computer.

Cell Cable Installation

The Cell Connector is a 9 pin female D connector on the Potentiostat card.

The standard cell cable has a 9 pin D connector on one end and a number of leads terminated with banana plugs on the other. The D connector end of the cable is connected to the Cell Connector on the Potentiostat card. The screws on this cable should always be used to hold the cable in place.

Caution: Other PC functions can use female 9 pin D connectors. Make sure that your cell cable is plugged into the correct connector before making any connection to your cell.

Application Software Installation and System Checkout

Software installation is slightly different for each Gamry Instruments, Inc. application package. Refer to the software installation instructions in the Installation Manual for each application package in your system.

You should also perform the system checkout procedures for each application. Follow the instructions in each application's Installation Manual. The system checkout procedures check for correct hardware and software installation. They are not a comprehensive test of each facet of system operation.

Calibration

After you have run the system checkout procedure(s), you should calibrate each PC4 Potentiostat installed in your system. A calibration script is provided with the Gamry Framework. The Installation Manual for every major application package contains instructions for calibration using this script.

CAUTION: PC4 calibration calls for an external resistive dummy cell. A suitable resistor was shipped with the PC4. This resistor is a 100 Ω 1% accurate resistor. Please place this resistor in a safe place where you can find it if your unit requires recalibration.

If you do need to recalibrate and you cannot find the resistor shipped to you, you can substitute another 100 Ω resistor. Its wattage and tolerance are unimportant.

Potentiostat calibration is only required infrequently. You should recalibrate under the following circumstances:

- You are installing a PC4 Potentiostat into a new computer or moving a PC4 into a different computer. The PC4 should be calibrated in the new machine.
- It has been about one year since your last calibration.
- Your potentiostat has been serviced.
- You notice breaks or discontinuities in the data curves recorded with your system.
- You have lost or replaced your "GAMRY.INI" file.

Chapter 3 -- Cell Cable Connections

Normal Cell Connections

Each PC4 in your system was shipped with a standard cell cable.

One end of the cable ends in a 9 pin male D type connector. This end connects to the PC4 Potentiostat Card. Make sure you connect the cable to the correct 9 pin connector on the computer; older video cards, among others, often include 9 pin D female connectors.

You should always screw the cell cable into place, since this cable comes off the card easily otherwise.

The other end of the cell cable terminates in a number of banana plugs and one pin jack. Each termination comes with a removable alligator clip. All PC4 Potentiostats should be shipped with a new cable that includes an Orange Counter Sense lead. If you also own an older PC3 Potentiostat or an older ECM8 Multiplexer, it was supplied with similar cables that do not include this orange lead. Consult the factory before using an older cable with your PC4.

Table 3-1 identifies each terminal of the cable.

**Table 3-1
Cell Cable Terminations - Potentiostat and Galvanostat Modes**

Color	Type	Name	Normal Connection
Blue	Banana Plug	Working Sense	Connect to working electrode
Green	Banana Plug	Working Electrode	Connect to working electrode
White	Pin Jack	Reference	Connect to reference electrode
Red	Banana Plug	Counter Electrode	Connect to counter electrode
Orange	Banana Plug	Counter Sense	Used in ZRA mode - connect to counter electrode
Long Black	Banana Plug	Floating Ground	Leave open or connect to a Faraday shield
Short Black	Banana Plug	Chassis Ground	Connect to Faraday Shield to reduce EMI

Connect both the blue and green cell leads to the working electrode. The working electrode is the specimen being tested. The blue banana jack connection senses the voltage of the working electrode. The green working electrode connection carries the cell current. The working electrode may be as much as 1.5 volts above the circuit ground.

Connect the white pin jack to the cell's reference electrode, such as an SCE or Ag/AgCl reference electrode. The measured cell potential is the potential difference between the blue and white cell connectors.

Connect the red banana plug to the counter or auxiliary electrode. The counter electrode is usually a large inert metal or graphite electrode. The counter electrode terminal is the output of the PC4's power amplifier.

The orange lead is only used in ZRA mode where it senses the counter electrode potential (see following section). Automatic switching to ZRA mode is possible if this lead is connected to the counter electrode. If you

will not be using ZRA mode, this lead can be left open as long as you insure that it will not short against any other electrode.

The longer black banana plug is connected on the PC4 end to Floating Ground. This is the circuitry ground for the analog circuits in the PC4. In most cases, this terminal should be left disconnected at the cell end. When you do so, take care that it does not touch any of the other cell connections.

The shorter black lead is connected to the computer's chassis (earth) ground.

If your cell is a typical glass laboratory cell, all of the electrodes are isolated from earth ground. In this case, you may be able to lower noise in your data by connecting the longer black cell lead to a source of earth ground. The short black lead or a water pipe can be suitable sources of earth ground.

Caution: If any electrode is at earth ground, you must not connect the long black cell lead to earth ground. Autoclaves, stress apparatus, and field measurements may involve earth grounded electrodes.

When you are measuring very small currents, you may find that a metal enclosure completely surrounding your cell (a Faraday shield) will significantly lower the measured current noise. This Faraday shield should be connected to the short black cell connector. If your electrodes are all isolated from ground, you should also connect the shield to the longer black lead.

The alligator clip on a cell connection can be removed to access the underlying banana plug or pin jack. If you need to permanently change the terminations on your cell cable, feel free to remove the banana plugs and replace them with your new termination. Gamry Instruments can provide additional standard or special cell cables.

ZRA Mode Cell Connections

The PC4 can function as a precision Zero Resistance Ammeter (ZRA). It maintains two metal samples at the same potential and measures the current flow between the samples. It can also measure the potential of the samples versus a reference electrode.

The cell cable connections for ZRA mode are shown in Table 3-2. Note that the connections are very similar to those for the potentiostat and galvanostat modes. A second working electrode is substituted for the counter electrode and the orange counter sense lead must be connected.

Table 3-2
Cell Cable Connections for ZRA Mode

Color	Type	Name	Normal Connection
Blue	Banana Plug	Working Sense	Connect to metal sample #1
Green	Banana Plug	Working Electrode	Connect to metal sample #1
White	Pin Jack	Reference	Connect to a reference electrode
Red	Banana Plug	Counter Electrode	Connect to metal sample #2
Orange	Banana Plug	Counter Sense	Connect to metal sample #2
Long Black	Banana Plug	Floating Ground	Leave open or connect to a Faraday shield
Short Black	Banana Plug	Chassis Ground	Connect to Faraday Shield to reduce EMI

The counter sense and the working sense lead are each connected to different metal samples. In the ZRA mode the PC4 is programmed to maintain zero volts between these leads. It therefore maintains the two metal samples at the same voltage.

The white pin jack on the cell cable is normally connected to a reference electrode. The potential between this lead and the working sense lead is reported as the cell potential.

If you don't have a reference electrode in your cell, we recommend that you connect the white reference lead to the working electrode. In theory, the measured potential will be exactly zero when this is done. In practice, A/D noise and offset will create a small, slightly noisy signal very close to zero.

Membrane Cell Connections

The PC4 can be used with membrane cells. In this type of cell, a membrane separates two electrolyte solutions. Two reference electrodes are used - one in each electrolyte. Each electrolyte also contains a counter electrode. The PC4 controls the potential across the membrane. Table 3-3 shows the cell connections used with a membrane type cell.

Table 3-3
Cell Cable Connections for a Membrane Cell

Color	Type	Name	Normal Connection
Blue	Banana Plug	Working Sense	Connect to reference electrode #1
Green	Banana Plug	Working Electrode	Connect to counter electrode #1
White	Pin Jack	Reference	Connect to reference electrode #2
Red	Banana Plug	Counter Electrode	Connect to counter electrode #2
Orange	Banana Plug	Counter Sense	Leave open (only needed in ZRA mode)
Long Black	Banana Plug	Floating Ground	Leave open or connect to a Faraday shield
Short Black	Banana Plug	Chassis Ground	Connect to Faraday Shield to reduce EMI

Note that reference electrode #1 and counter electrode #1 must be on one side of the membrane and reference electrode #2 and counter electrode #2 must be on the other side.

Chapter 4 -- Stability in Potentiostat Mode

Capacitive Cells and Stability

All potentiostats can become unstable when connected to capacitive cells. The capacitive cell adds phase shift to the potentiostat's already phase shifted feedback signal. The additional phase shift can convert the potentiostat's power amplifier into a power oscillator.

To make matters worse, almost all electrochemical cells are capacitive because an electrical double layer forms next to a conductor immersed in a solution.

Potentiostat oscillation is an AC phenomenon. However, it can affect both AC and DC measurements. Oscillation often causes excessive noise or sharp DC shifts in the system's graphical output. The PC4 Potentiostat is often stable on less sensitive current ranges and unstable on more sensitive current ranges. Whenever you see sharp breaks in the current recorded on the system, you should suspect oscillation.

The PC4 has been tested for stability with cell capacitors between 10 pF and 750 F. In all but its fastest control amp speed setting, it is stable on any capacitor in this range -- as long as the impedance in the reference electrode lead does not exceed 20 k Ω . With reference electrode impedances greater than 20 k Ω , the PC4 may oscillate. The RC filter formed by the reference electrode impedance and the reference terminal's input capacitance filters out the high frequency feedback needed for potentiostat stability.

Longer cell cables make the problem worse by increasing the reference terminal's effective input capacitance.

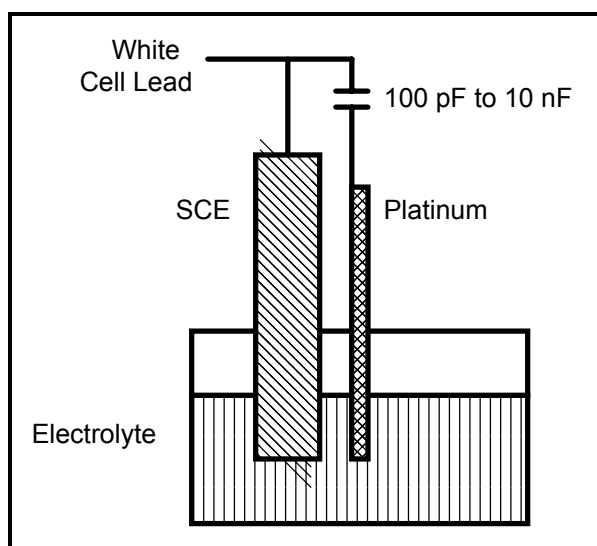
Even when the system is stable (not oscillating), it may exhibit ringing whenever there is a voltage step applied to the cell. The PC4's D/A converters routinely apply steps, even when making a pseudo-linear ramp. While this ringing is not a problem with slow DC measurements, it can interfere with faster measurements. The steps taken to eliminate potentiostat oscillation also help to minimize ringing.

Improving Potentiostat Stability

There are a number of things that you can do to improve an unstable or marginally stable PC4 potentiostat/cell system. This list is not in any particular order. Any or all of these steps may help.

- Slow down the potentiostat. The PC4 has 4 control amplifier speed settings which can be selected in software. Slower settings are generally more stable.
- Increase the PC4's I/E stability setting. The PC4 includes 2 capacitors that can be paralleled with its I/E converter resistors. These capacitors are connected to relays that are under software control. Contact your local Gamry Instruments' representative for more information concerning changes in these settings.
- Lower the reference electrode impedance. Make sure that you don't have a clogged reference electrode junction. Avoid asbestos fiber reference electrodes and double junction electrodes. Avoid small diameter Lugin capillaries. If you do have a Lugin capillary, make sure that the capillaries' contents are as conductive as possible.
- Add a capacitively coupled low impedance reference element in parallel with your existing reference electrode. The classic fast combination reference electrode is a platinum wire and a junction isolated SCE. See Figure 4-1. The capacitor insures that DC potential comes from the SCE and AC potential from the platinum wire. The capacitor value is generally determined by trial and error.

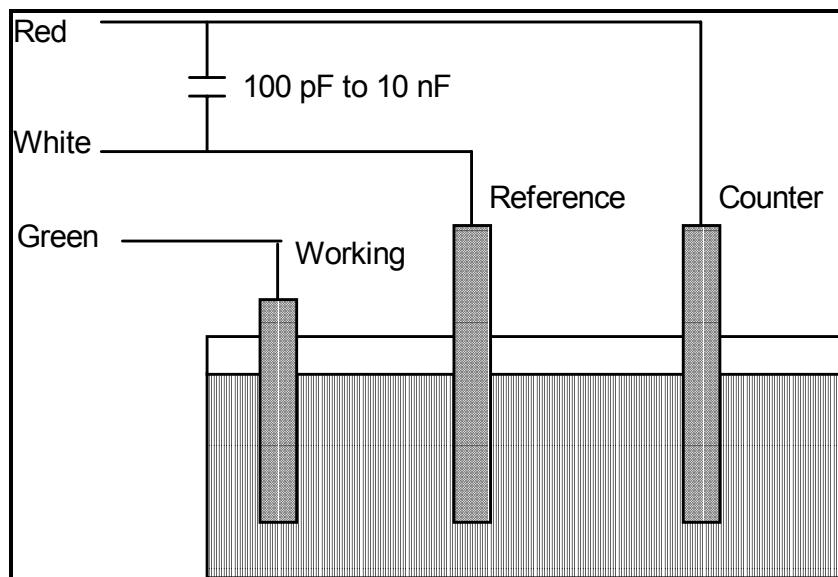
Figure 4-1
Fast Combination Reference Electrode



- Provide a high frequency shunt around the cell. A small capacitor between the red and white cell leads allows high frequency feedback to bypass the cell. See Figure 4-2. The capacitor value is generally determined by trial and error. One nanofarad is a good starting point.

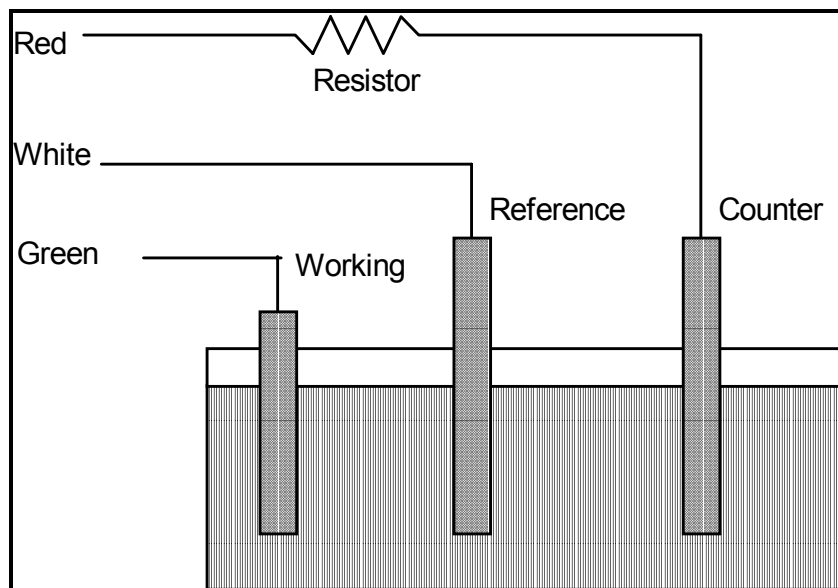
In a sense, this is another form of an AC coupled low impedance reference electrode. The counter electrode is the low impedance electrode, eliminating the need for an additional electrode in the solution.

Figure 4-2
High Frequency Shunt



- Add resistance to the counter electrode lead. See Figure 4-3. This change lowers the effective gain bandwidth product of the control amplifier. As a rule of thumb, the resistor should be selected to give one volt of drop at the highest current expected in the test being run. For example, if you expect your highest current to be around 1 mA, you can add a 1 k Ω resistor.

Figure 4-3
Resistor Added for Stability



Chapter 5 -- Measurement of Small Signals

Overview

The PC4 is a sensitive scientific instrument. It can resolve current changes as small as 0.1 picoamps (10^{-13} amps). To place this current in perspective, 0.1 pA represents the flow of about 600,000 electrons per second!

The small currents measured by the PC4 place demands on the instrument, the cell, the cables and the experimenter. Many of the techniques used in higher current electrochemistry must be modified when used to measure pA currents. In many cases, the basic physics of the measurement must be considered.

This chapter will discuss the limiting factors controlling low current measurements. It will include hints on cell and system design. The emphasis will be on EIS (Electrochemical Impedance Spectroscopy), a highly demanding application for the PC4.

Measurement System Model and Physical Limitations

To get a feel for the physical limits implied by picoamp measurements, consider the equivalent circuit shown in Figure 5-1. We are attempting to measure a cell impedance given by Z_{cell} .

This model is valid for analysis purposes even though the real PC4 circuit topology differs significantly.

In Figure 5-1:

E_s	Is an ideal signal source
Z_{cell}	Is the unknown cell impedance
R_m	Is the current measurement circuit's current measurement resistance
R_{shunt}	Is an unwanted resistance across the cell
C_{shunt}	Is an unwanted capacitance across the cell
C_{in}	Is the current measurement circuit's stray input capacitance
R_{in}	Is the current measurement circuit's stray input resistance
I_{in}	Is the measurement circuit's input current

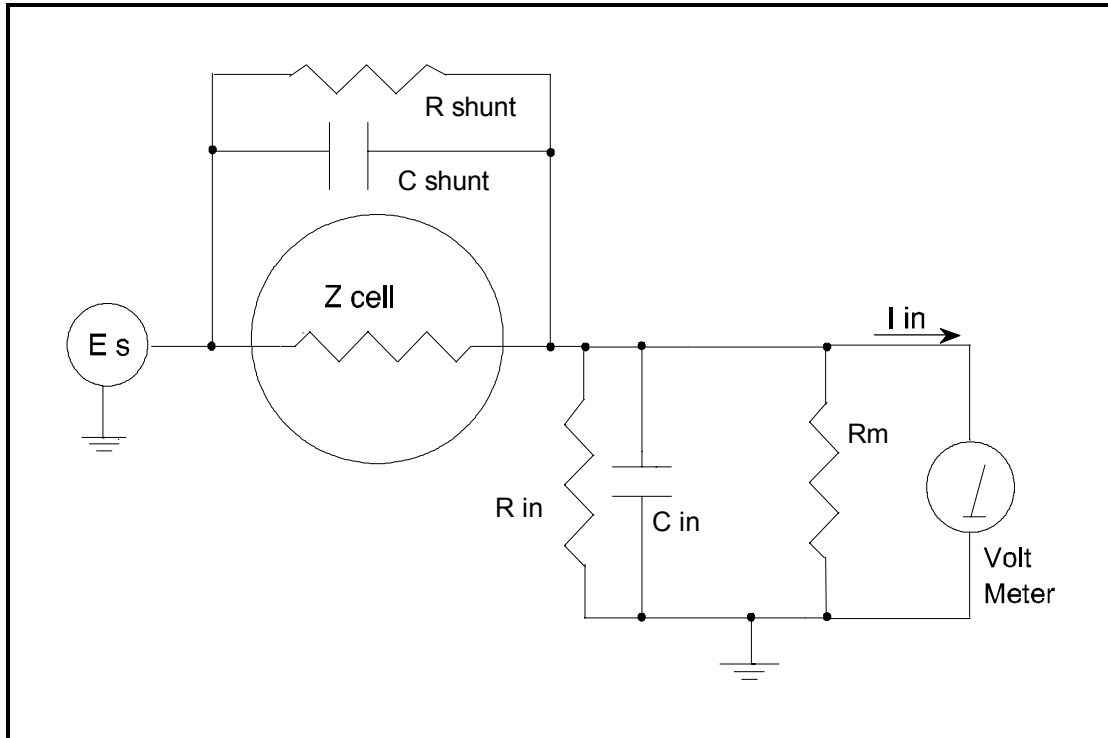
In the ideal current measurement circuit R_{in} is infinite while C_{in} and I_{in} are zero. All the cell current, Z_{cell} , flows through R_m .

With an ideal cell and voltage source, R_{shunt} is infinite and C_{shunt} is zero. All the current flowing into the current measurement circuit is due to Z_{cell} .

The voltage developed across R_m is measured by the meter as V_m . Given the idealities discussed above, one can use Kirchoff's and Ohm's law to calculate Z_{cell} :

$$Z_{\text{cell}} = E_s * R_m / V_m$$

Figure 5-1
Equivalent Measurement Circuit



Unfortunately technology limits high impedance measurements because:

- Current measurement circuits always have non-zero input capacitance, i.e. $C_{in} > 0$
- Infinite R_{in} cannot be achieved with real circuits and materials
- Amplifiers used in the meter have input currents, i.e. $I_{in} > 0$
- The cell and the potentiostat create both a non-zero C_{shunt} and a finite R_{shunt}

Additionally, basic physics limits high impedance measurements via Johnson noise, which is the inherent noise in a resistance.

Johnson Noise in Z_{cell}

Johnson noise across a resistor represents a fundamental physical limitation. Resistors, regardless of composition, demonstrate a minimum noise for both current and voltage, per the following equation:

$$E = (4 k T R \delta F)^{1/2}$$

$$I = (4 k T \delta F / R)^{1/2}$$

where:

k = Boltzman's constant 1.38×10^{-23} J/°K

T = temperature in °K

δF = noise bandwidth in Hz

R = resistance in ohms.

For purposes of approximation, the Noise bandwidth, δF , is equal to the measurement frequency. Assume a 10^{11} ohm resistor as Z_{cell} . At 300°K and a measurement frequency of 1 Hz this gives a voltage noise of 41 μV rms. The peak to peak noise is about 5 times the rms noise. Under these conditions, you can make a voltage measurement of ± 10 mV across Z_{cell} with an error of about $\pm 2\%$. Fortunately, an AC measurement can reduce the bandwidth by integrating the measured value at the expense of additional measurement time. With a noise bandwidth of 1 mHz, the voltage noise falls to about 1.3 μV rms.

Current noise on the same resistor under the same conditions is 0.41 fA. To place this number in perspective, a ± 10 mV signal across this same resistor will generate a current of ± 100 fA, or again an error of up to $\pm 2\%$. Again, reducing the bandwidth helps. At a noise bandwidth of 1 mHz, the current noise falls to 0.012 fA.

With E_s at 10 mV, an EIS system that measures 10^{11} ohms at 1mHz is about 3 decades away from the Johnson noise limits. At 0.1 Hz, the system is close enough to the Johnson noise limits to make accurate measurements impossible. Between these limits, readings get progressively less accurate as the frequency increases.

In practice, EIS measurements usually cannot be made at high enough frequencies that Johnson noise is the dominant noise source. If Johnson noise is a problem, averaging reduces the noise bandwidth, thereby reducing the noise at a cost of lengthening the experiment.

Finite Input Capacitance

C_{in} in Figure 5-1 represents unavoidable capacitances that always arise in real circuits. C_{in} shunts R_m , draining off higher frequency signals, limiting the bandwidth that can be achieved for a given value of R_m . This calculation shows at which frequencies the effect becomes significant. The frequency limit of a current measurement (defined by the frequency where the phase error hits 45°) can be calculated from:

$$f_{\text{RC}} = 1 / (2 \omega R_m C_{\text{in}})$$

Decreasing R_m increases this frequency. However, large R_m values are desirable to minimize voltage drift and voltage noise.

A reasonable value for C_{in} in a practical, computer controllable low current measurement circuit is 20 pF. For a 3 nA full scale current range, a practical estimate for R_m is 10^7 ohms.

$$f_{\text{RC}} = 1 / 6.28 (1 \times 10^7) (2 \times 10^{-12}) \approx 8000 \text{ Hz}$$

In general, one should stay two decades below f_{RC} to keep phase shift below one degree. The uncorrected upper frequency limit on a 30 nA range is therefore around 80 Hz.

One can measure higher frequencies using the higher current ranges (i.e. lower impedance ranges) but this would reduce the total available signal below the resolution limits of the "voltmeter". This then forms one basis of statement that high frequency and high impedance measurements are mutually exclusive.

Software correction of the measured response can also be used to improve the useable bandwidth, but not by more than an order of magnitude in frequency.

Leakage Currents and Input Impedance

In Figure 5-1, both R_{in} and I_{in} affect the accuracy of current measurements. The magnitude error due to R_{in} is calculated by:

$$\text{Error} = 1 - R_{\text{in}} / (R_m + R_{\text{in}})$$

For an R_m of 10^7 ohms, an error $< 1\%$ demands that R_{in} must be $> 10^9$ ohms. PC board leakage, relay leakage, and measurement device characteristics lower R_{in} below the desired value of infinity.

A similar problem is the finite input leakage current I_{in} into the voltage measuring circuit. It can be leakage directly into the input of the voltage meter, or leakage from a voltage source (such as a power supply) through an insulation resistance into the input. If an insulator connected to the input has a 10^{12} ohm resistance between +15 volts and the input, the leakage current is 15 pA. Fortunately, most sources of leakage current are DC and can be tuned out in impedance measurements. As a rule of thumb, the DC leakage should not exceed the measured signal by more than a factor of 10.

The PC4 uses an input amplifier with an input current of around 5 pA. Other circuit components may also contribute leakage currents. You therefore cannot make absolute current measurements of very low pA currents with the PC4. In practice, the input current is approximately constant, so current differences or AC current levels of less than one pA can often be measured.

Voltage Noise and DC Measurements

Often the current signal measured by a potentiostat shows noise that is not the fault of the current measurement circuits. This is especially true when you are making DC measurements. The cause of the current noise is noise in the voltage applied to the cell.

Assume that you have a working electrode with a capacitance of 1 μ F. This could represent a passive layer on a metal specimen. The impedance of this electrode, assuming ideal capacitive behavior, is given by

$$Z = 1/j\omega C$$

At sixty Hertz, the impedance value is about 2.5 k Ω .

Apply an ideal DC potential across this ideal capacitor and you get no DC current.

Unfortunately, all potentiostats have noise in the applied voltage. This noise comes from the instrument itself and from external sources. In many cases, the predominant noise frequency is the AC power line frequency.

Assume a reasonable noise voltage, V_n , of 10 μ V. Further, assume that this noise voltage is at the US power line frequency of 60 Hz. It will create a current across the cell capacitance:

$$I = V_n/Z \approx 4 \text{ nA}$$

This rather large noise current will prevent accurate DC current measurement in the pA ranges.

In an EIS measurement, you apply an AC excitation voltage that is much bigger than the typical noise voltage, so this is not a factor.

Shunt Resistance and Capacitance

Non-ideal shunt resistance and capacitance arise in both the cell and the potentiostat. Both can cause significant measurement errors.

Parallel metal surfaces form a capacitor. The capacitance rises as either metal area increases and as the separation distance between the metals decreases.

Wire and electrode placement have a large effect on shunt capacitance. If the clip leads connecting to the working and reference electrodes are close together, they can form a significant shunt capacitor. Values of 10

pF are common. This shunt capacitance cannot be distinguished from "real" capacitance in the cell. If you are measuring a paint film with a 100 pF capacitance, 10 pF of shunt capacitance is a very significant error.

Shunt resistance in the cell arises because of imperfect insulators. No material is a perfect insulator (one with infinite resistance). Even PTFE, which is one of the best insulators known, has a bulk resistivity of about 10^{14} ohms. Worse yet, surface contamination often lowers the effective resistivity of good insulators. Water films can be a real problem, especially on glass.

Shunt capacitance and resistance also occur in the potentiostat itself. The PC4 Potentiostat Mode specifications in Appendix A contain equivalent values for the potentiostat's R_{shunt} and C_{shunt} . These values can be measured by an impedance measurement with no cell.

In most cases, the cell's shunt resistance and capacitance errors are larger than those from the potentiostat.

Hints for System and Cell Design

The following hints may prove helpful.

Faraday Shield

A Faraday shield surrounding your cell is mandatory for very low level measurements. It reduces both current noise picked up directly on the working electrode and voltage noise picked up by the reference electrode.

A Faraday shield is a conductive enclosure that surrounds the cell. The shield can be constructed from sheet metal, fine mesh wire screen, or even conductive plastic. It must be continuous and completely surround the cell. Don't forget the areas above and below the cell. All parts of the shield must be electrically connected. You will need an opening in the shield large enough to allow the PC4 cell cable to enter the shield.

The shield must be electrically connected to the PC4's floating ground terminal.

An additional connection of both the shield and the PC4 floating ground to an earth ground may also prove helpful.

NOTE: Only connect the PC4 ground to earth ground if all conductive cell components are well isolated from earth ground. A glass cell is usually well isolated. An autoclave is generally not well isolated.

Avoid External Noise Sources

Try to keep your system away from electrical noise sources. Some of the worst are:

- Fluorescent lights
- Motors
- Radio transmitters
- Computers and computer monitors

Try to avoid AC powered or computerized apparatus within your Faraday shield.

Cell Cable Length and Construction

The PC4 is shipped with a 1.5 meter cell cable. We also offer extended length cables as extra cost options.

Cell cables longer than 3 meters may result in degraded instrument performance. Increased noise and decreased stability both can occur. However, with most cells, the instrument will work acceptably with an extended cell cable, so our advice is go ahead and try it. As a rule, you should not attempt to use current interrupt IR compensation with cell cables longer than 5 meters.

We do not recommend that you use the PC4 with any cables not supplied by Gamry Instruments. The PC4 cable is not a simple cable like a typical computer cable. The PC4 cable includes a number of individually shielded wires contained within an overall shield. We pay careful attention to issues such as shield isolation, isolation resistance, and capacitance.

If you do need a special cable, contact us with your requirements.

Lead Placement

Many experiments with the PC4 involve cells with small capacitances, the value of which may be important.

In these cases, the capacitance between the PC4's cell leads can result in an error. The PC4 alligator clips can have 10 pF or more of mutual capacitance if they are run alongside each other.

If you wish to avoid excessive capacitance.

- Place the leads as far apart as possible. Pay special attention to the working electrode lead.
- Have the leads approach the cell from different directions.
- Remove the alligator clips from the leads. In extreme cases you can replace the banana plugs and pin jack with smaller connectors. If you do so, be careful not to compromise the center conductor to shield isolation.

The cell leads must not be moved during an experiment which measures small currents. Both microphonic and triboelectric effects can create spurious results when the cell cables are moved.

Cell Construction

If you need to measure small currents or high impedances, make sure that your cell construction does not limit your response.

A cell where the resistance between the electrodes is only 10^{10} ohms cannot be used to measure 10^{13} ohm impedances. In general, glass and PTFE are the preferred cell construction materials. Even glass may be a problem if it is wet.

You also must worry about C_{shunt} . Make the "inactive" portion of your electrodes as small as possible. Avoid placing electrodes close together or parallel with each other.

Reference Electrode

Keep your reference electrode impedance as low as possible. High impedance reference electrodes can cause potentiostat instability and excessive voltage noise pickup.

Try to avoid:

- Narrow bore or Vycor tipped Lugin capillaries.
- Poorly conductive solutions - especially in Lugin capillaries.
- Asbestos thread and double junction reference electrodes.

Instrument Settings

There are several things to remember in setting up a very sensitive experiment.

- In EIS, use the largest practical excitation. Don't use a 10 mV excitation on a coated specimen that can handle 100 mV without damage.
- Avoid potentials where large DC currents flow. You cannot measure 1pA of AC current on top of 1 mA of DC current.

EIS Speed

In EIS, do not expect the PC4 to measure 10^{10} ohm impedances at 1 kHz. Many of the factors listed above limit the performance.

As a rule of thumb, the product of Impedance, Z , times frequency, f , must be less than $10^9 \Omega\text{Hz}$ for good EIS measurements with a PC4.

$$Z \cdot f < 10^9 \Omega\text{Hz}$$

Ancillary Apparatus

Do not use the PC4 with ancillary apparatus connected directly to any of the cell leads. Ammeters and voltmeters, regardless of their specifications, almost always create problems when connected to the PC4 cell leads.

Floating Operation

The PC4 is capable of operation with cells where one of the electrodes or a cell surface is at earth ground. Examples of earth grounded cells include: autoclaves, stress apparatus, pipelines, storage tanks and battleships. The PC4's internal ground is allowed to float with respect to earth ground when it works with these cells, hence the name floating operation.

Instrument performance can be substantially degraded when the PC4 is operated in a floating mode. The instrument specifications only apply on isolated cells with the PC4 earth ground referenced (not floating).

Special precautions must be taken with the cell connections when the PC4 must float. Make sure that all the cell connections are isolated from earth ground. In this case, even the floating ground terminal of the PC4 must be kept isolated.

Finally, most ancillary apparatus connected to the cell of the PC4 must be isolated. External voltmeters, ammeters, FRA's etc. must be isolated. This includes devices connected to the monitor connectors located on the PC4 controller board minipanel.

Appendix A -- PC4/300 Specifications

Control Amplifier

Compliance Voltage	> ± 20 volts @ 150 mA
Output Current	> ± 300 mA
Unity Gain Bandwidth (software selectable)	>1 MHz, > 200 kHz, > 90 kHz, > 20 kHz
Slew Rate (software selectable)	>50 V/ μ sec, > 10 V/ μ sec, > 5 V/ μ sec, > 1 V/ μ sec

Differential Electrometer

Input Impedance	> 10^{12} Ω in parallel with 5 pF
Input Current	< 10 pA
Bandwidth (-3dB)	> 4 MHz
CMRR	> 100 dB (DC to 2 kHz), >60 dB @ 100 kHz

Voltage Measurement

Full Scale Ranges	± 30 V (± 12 V usable), ± 3 V, ± 300 mV, ± 30 mV
Resolution(16 Bits)	1 mV/bit, 100 μ V/bit, 10 μ V/bit, 1 μ V/bit
DC Accuracy	$\pm 0.3\%$ Range ± 1 mV
Offset Range	± 12 V with 1.5 mV resolution

Current Measurement

Analog Full Scale Ranges	± 3 nA to ± 300 mA in decades
Controller Board Gains	1, 10, 100
Resolution (16 bits)	0.1 pA/bit to 10 μ A/bit
Offset Range	± 4 X full scale (only 2X full scale is useful)
DC Accuracy (with 1X Controller Board Gain)	$\pm 0.3\%$ range ± 50 pA
Bandwidth (-3 dB)	> 500 kHz (300 μ A—300 mA full scale)
	> 100 kHz (30 μ A full scale)
	> 10 Hz (3nA full scale)

Auxiliary A/D Input (see Appendix E)

Range	± 3 volts differential
Bandwidth	20 Hz
Input Impedance	100 k Ω

NOTES:

1. All specifications subject to change without notice
2. Offset specifications apply after software calibration

Auxiliary D/A Output

Range	± 5 volts or 0 to 10 volts
Resolution	2.5 mV

Environmental

Operating Temperature	0-70 °C (inside computer)
Specification Temperature	25 °C

Potentiostat Mode

Applied E Range	± 11 volts
Accuracy	± 2 mV $\pm 0.3\%$ of setting
DC Bias	± 8 V
Scan Ranges	± 6.4 V, ± 1.6 V, and ± 0.4 V
Resolution	200 μ V/bit, 50 μ V/bit, 12.5 μ V/bit
Drift	< 30 μ V/C
Noise and Ripple	< 20 μ V rms (1Hz - 10 kHz)

Galvanostat Mode

Applied i range	\pm full scale current (no 3 nA range)
DC accuracy	$\pm 0.3\%$ full scale
Scan Ranges	$\pm 2X$ full scale current

Current Interrupt

Measurement Type	(sample 2 points on decay, extrapolate)
Cell Switching Time	< 1 μ sec (1 k Ω cell)
Minimum Interrupt Time	15 μ sec
Maximum Interrupt Time	64 msec

A/D converter

Resolution	16 bits
Accuracy	0.1% of full scale
Timing	50 μ sec to 600 sec

General

Power	27 W maximum < 1 A at +12 V < 3 A at +5 V < 0.08 A at -5 V < 0.02 A at -12 V
Leakage i (floating, earthed Working Electrode)	< 3 nA @ DC

Appendix B -- PC4/750 Specifications

Control Amplifier

Compliance Voltage	> $\pm 15\text{V}$ @ 15 mA, > $\pm 12\text{ volts}$ @ 500 mA
Output Current	> $\pm 750\text{ mA}$
Unity Gain Bandwidth (software selectable)	>1 MHz, > 200 kHz, > 90 kHz, > 20 kHz
Slew Rate (software selectable)	>50 V/ μsec , > 10 V/ μsec , > 5 V/ μsec , > 1 V/ μsec

Differential Electrometer

Input Impedance	> $4 \times 10^{11} \Omega$ in parallel with 5 pF
Input Current	< 10 pA
Bandwidth (-3dB)	> 4 MHz
CMRR	> 100 dB (DC to 2 kHz), >60 dB @ 100 kHz

Voltage Measurement

Full Scale Ranges	$\pm 30\text{V}$ ($\pm 9\text{ V}$ usable), $\pm 3\text{V}$, $\pm 300\text{ mV}$, $\pm 30\text{ mV}$
Resolution(16 Bits)	1 mV/bit, 100 μV /bit, 10 μV /bit,, 1 μV /bit
DC Accuracy	$\pm 0.3\%$ Range $\pm 1\text{mV}$
Offset Range	$\pm 12\text{ V}$ with 1.5 mV resolution

Current Measurement

Analog Full Scale Ranges	$\pm 7.5\text{ nA}$ to $\pm 750\text{ mA}$ in decades
Controller Board Gains	1, 10, 100
Resolution (16 bits)	0.25 pA/bit to 25 μA /bit
Offset Range	$\pm 4\text{X}$ full scale (only 2X full scale is useful)
DC Accuracy (with 1X Controller Board Gain)	$\pm 0.3\%$ range $\pm 50\text{ pA}$
Bandwidth (-3 dB)	> 500 kHz (75 μA —750 mA full scale)
	> 20 kHz (7.5 μA full scale)
	> 20 Hz (7.5 nA full scale)

Auxiliary A/D Input (see Appendix E)

Range	$\pm 3\text{ volts}$ differential
Bandwidth	20 Hz
Input Impedance	100 k Ω

NOTES:

1. All specifications subject to change without notice
2. Offset specifications apply after software calibration

Auxiliary D/A Output

Range	± 5 volts or 0 to 10 volts
Resolution	2.5 mV

Environmental

Operating Temperature	0-70 °C (inside computer)
Specification Temperature	25 °C

Potentiostat Mode

Applied E Range	± 11 volts
Accuracy	± 2 mV $\pm 0.3\%$ of setting
DC Bias	± 8 V
Scan Ranges	± 6.4 V, ± 1.6 V, and ± 0.4 V
Resolution	200 μ V/bit, 50 μ V/bit, 12.5 μ V/bit
Drift	< 30 μ V/C
Noise and Ripple	< 20 μ V rms (1Hz - 10 kHz)

Galvanostat Mode

Applied i range	\pm full scale current (no 3 nA range)
DC accuracy	$\pm 0.3\%$ full scale
Scan Ranges	$\pm 2X$ full scale current

Current Interrupt

Measurement Type	(sample 2 points on decay, extrapolate)
Cell Switching Time	< 1 μ sec (1 k Ω cell)
Minimum Interrupt Time	15 μ sec
Maximum Interrupt Time	64 msec

A/D converter

Resolution	16 bits
Accuracy	0.1% of full scale
Timing	50 μ sec to 600 sec

General

Power	34 W maximum < 1 A at 12 volts < 4.4 A at +5 V < 0.08 A at -5 V < 0.02 A at -12 V
Leakage i (floating, earthed Working Electrode)	< 1 nA @ DC

Appendix C -- Changing The Default PC4 Settings

Overview

Your PC4 Potentiostat can be configured for the specific needs of your computer system. DIP switches on the PC4 allow you to:

- Choose the I/O addresses used by the PC4.
- Reconfigure the PC4 as Pstat 1 through Pstat 4 in a multiple potentiostat system.

Whenever a PC4 setting is changed, the software controlling that PC4 must be made aware of the change.

Gamry Instruments' software reads the PC4's settings from an initialization file called "GAMRY.INI". This file lists the hardware configuration for any Gamry potentiostats in the system.

The "GAMRY.INI" file does not merely record DIP switch settings. It also contains software information and information about the software setup of hardware. This includes:

- Interrupt level
- Auxiliary D/A range
- Software calibration data

The "GAMRY.INI" file is located in the Windows directory. It is an ASCII text file that is divided into sections identified by a section name in square brackets (e.g. [EIS300]). Each section contains setting for a specific aspect of the system.

Turnkey systems are provided with a "GAMRY.INI" file appropriate for the items you have purchased with that system. The "GAMRY.INI" file in user installed systems is usually created by the Setup programs that come with Gamry Instruments' Windows based application software. Most configuration information should be changed by rerunning the Setup programs.

Use this appendix when you need to change the system configuration via changes to your DIP switch settings or via manual changes in your "GAMRY.INI" file.

About the "GAMRY.INI" File

Gamry Instruments' Windows based software is configured by means of the "GAMRY.INI" file. The information in this file is used to:

- Identify each potentiostat in the system.
- Determine the I/O address and interrupt level used by the system's potentiostats.
- Authorize use of a specific potentiostat by specific software packages.
- Store calibration data for each potentiostat.
- Store scaling factors for system D/A and A/D converters.
- Store software configuration information.

The "GAMRY.INI" file is an ASCII file. You can modify the file using an ASCII editor or a word processor in a non-document mode (a mode with no formatting codes in the text). The Windows Notepad accessory is a convenient ASCII editor.

The copy of "GAMRY.INI" actually used by the software must be located in the Windows directory (normally C:\WINDOWS). The Setup programs provided with Gamry Instruments' software either install "GAMRY.INI" in the correct directory or modify an existing file in this location.

A portion of a typical "GAMRY.INI" file is shown in Figure C-1. Only some of the information required for PC4 configuration is shown. A complete "GAMRY.INI" file is longer than this example.

In Figure C-1, the 1st line is called a section identifier. The name of the section is enclosed in square brackets, e.g. [Framework]. The [Framework] section extends to the next section identifier [InterruptList]. The [Framework] section contains configuration information for the Gamry Framework program. This section is required in all "GAMRY.INI" files that configure a Gamry Framework System.

The section labeled [DeviceList] contains a list of all the potentiostats in the system. Each entry in this section corresponds to a potentiostat in the system. The entry name is the name of the "GAMRY.INI" section that describes this potentiostat. In the sample file, the [DeviceList] contains only one entry (for Pstat0).

"GAMRY.INI" also contains potentiostat calibration information. Each potentiostat's data is in its section. You do not normally have to edit the calibration data which is automatically created and updated by the calibration routine built into the software.

The [Pstat#] section also contains the AUXDACRES field which you may need to change. See below for details.

Figure C-1
Portion of a Typical "GAMRY.INI" File

```
[Framework]
LineFreq=60
PACKAGE0=DC105

[InterruptList]
IRQ10=

[DeviceList]
Pstat0=

[Pstat0]
;This is a PC4 Potentiostat Section
Label=PC4_1
CMSDriver=PC4.DLL
IRQLevel=10
BaseAddress=0x120
PstatClass=PC4
BoardNo=1
FraCurveClass=FRACURVE4
AuthDC105=1234567890
```

Changing "GAMRY.INI" using Setup

The Setup program that comes with Gamry Instruments' software can automatically make changes in the "GAMRY.INI" file. You can use this program to change the base address, the interrupt level, and PStat identifier information in "GAMRY.INI".

The Setup program for each Gamry Instruments' application software package can generally be used to alter the sections of the "GAMRY.INI" file that apply to that application.

Using Notepad to alter "GAMRY.INI"

It is often convenient to use an ASCII editor to make small changes in the "GAMRY.INI" file. The Notepad accessory included with Windows is a useful ASCII editor. Please read the Microsoft documentation for full instructions about using Notepad.

Adding a New PC4 to an Existing System

To add a new PC4 to a system that already contains one or more PC4s, you need to do the following:

- Set the board number switches for the PC4 Potentiostat to be added.
- Add the potentiostat card set to the computer.
- Add potentiostat information to "GAMRY.INI".

Setting the Board Number Switches on an PC4 Potentiostat

Each potentiostat in a multiple potentiostat system must be set for a unique board number. The board number is set using a DIP switch on the Controller Card.

To change the board number switch settings on a PC4 proceed as follows:

1. Determine the desired board number for this PC4. Board numbers should be sequential starting with board number 1. For example, a two potentiostat system has its cards configured as board numbers 1 and 2.
2. Locate S101, the four pole DIP switch in the middle right side of the Controller Card.
3. The ON position of the switches is marked on the body of the switch.
4. The order of the switches is S101-1 on the left, S101-4 on the right. This also is marked on the body of the switch.
5. Set the switches S101-1 and S101-2 from Table C-1. The switch settings are read across the row labeled with the desired board number. Do not change the settings of S101-3 and S101-4!
6. Double check that the change has been made correctly.
7. Label the outside of the metal bracket with the new board number.

Table C-1
Switch Setting for Different Board Numbers

Board Number	S101-	
	1	2
1	ON	ON
2	OFF	ON
3	ON	OFF
4	OFF	OFF

Installing the PC4 in the Computer

Please follow the instructions in Chapter 2 to install the new card set in the computer. You will need two card slots for each additional PC4 to be installed.

Adding Potentiostat Information to "GAMRY.INI" using Setup

The easiest way to add the new information to "GAMRY.INI" is to rerun the Gamry Instruments Setup program. You can skip over the file copy portion of Setup. Enter the new information in the dialog box that asks for potentiostat information.

Manually Adding Potentiostat Information to "GAMRY.INI"

Before you can add potentiostat information to "GAMRY.INI", you need to understand how potentiostats are identified in the file. We will use the sample "GAMRY.INI" file in Figure C-1 as an aid in our discussion.

Look at the [DeviceList] section in Figure C-1. The line "Pstat0=" declares that there is a potentiostat in the system that is further described in a [Pstat0] section. A field labeled "Pstat1=" would identify a second potentiostat, "Pstat2" the third potentiostat, and so on.

Suppose you are adding another PC4 Potentiostat to this system. You must add the line:

```
Pstat1=
```

to the [DeviceList] section of your "GAMRY.INI" file.

You also must add a [Pstat1] section to the file. In general, you can copy the information in an existing section. Make sure that you change the BoardNo= field to match the setting on the board.

You also have to add one or more authorization codes to the new [Pstat1] section of "GAMRY.INI". Each Gamry Instruments program requires a unique 10 digit authorization code before it will use a specific potentiostat. If the Framework does not find a valid authorization code, it will not take data. See the Gamry Framework Installation Manual for more information on this topic.

Your original shipping documentation should contain all the authorization codes that you need to operate your system.

If you do use Notepad to alter "GAMRY.INI", you must restart Windows before you can be sure the change to "GAMRY.INI" is effective.

Removing a Potentiostat from an Existing System

To remove a potentiostat from a system you need to do two things. The first is to physically remove the card set from the computer. The second is to remove the potentiostat's PstatX= field from the [DeviceList] section in the "GAMRY.INI" file (where X stands for the zero based board number of the potentiostat you are removing).

Interrupt Level Setting

Most peripheral devices in an AT compatible computer coordinate I/O (input/output) operations with the microprocessor by means of hardware interrupts. An interrupt is a request by a device that the computer suspend the program it's currently running, and perform an I/O operation. The PC4 Potentiostat generates an interrupt at the end of each data point.

An IBM AT compatible computer allows for 16 levels of hardware interrupts. In a Gamry Instruments system, all the potentiostats use the same interrupt level. This interrupt level cannot be used by other system functions or expansion cards.

Unfortunately, very few of the 16 interrupt levels are not used by AT compatible system functions or the "common" expansion cards (e.g. video cards, serial ports, disk controllers, etc.). The interrupt levels available to the PC4 card set were chosen as those most likely to be free for PC4 use in a normal computer configuration. Table C-2 lists these levels along with any conflicts with levels assigned in the IBM AT Technical Reference Manual.

**Table C-2
Interrupt Level Selection**

Interrupt Level	Also used for
IRQ5	LPT2
IRQ10	--
IRQ11	--
IRQ15	--

NOTE: All the Gamry potentiostats in a computer are generally set for the same interrupt level.

To change the interrupt level used by the potentiostats in your system, you simply change a setting in the "GAMRY.INI" software initialization file.

If you have any uncommon expansion cards in your computer, you should consult their documentation to determine if they can generate system interrupts. If they can, you should determine their interrupt level setting(s), and select an Interrupt Level for your PC4(s) that does not conflict with these cards.

For example, if you determine that your computer contains a ethernet card that generates interrupts on level 10 , the interrupt level you choose for your PC4(s) cannot be 10. Assume that you choose interrupt level 11. Follow these instructions to change the level.

1. Edit "GAMRY.INI" in the Windows directory. Windows Notepad is a convenient ASCII editor.
2. In this file, locate the [InterruptList] section.
3. Add an entry for the new level (if its not already present). The entry has the form "IRQXX=" where XX is the level to be used. For the default IRQ setting the entry is "IRQ10=".
4. Make sure that every [PstatN] section in the "GAMRY.INI" file has its IRQLevel field set to the new value. In the default file, each [PstatN] section should contain the line "IRQLevel=10".
5. Save the edited file.

The information in the altered "GAMRY.INI" file is not effective until you exit and restart the Framework. If you have unsuccessfully attempted to run an experiment on the wrong level, you may have to power down and restart your computer before interrupts will occur normally.

Changing your I/O Register Address

The PC4 Potentiostat card set, like virtually all IBM compatible expansion cards, has hardware registers that the computer must be able to access. These registers are located at a specific address in the I/O (input/output) address space of the computer's microprocessor. Addresses are expressed in the hexadecimal numbering system where the digits are 1,2,3,4...8,9,A,B,C,D,E,F. We will always precede a hexadecimal number with the prefix 0x, e.g. 0x22F.

The PC4 requires 32 I/O register addresses. Unlike most expansion cards, which cannot share I/O addresses, all of the PC4's in a system normally are set up to use the same I/O register addresses. The board number assigned to each PC4 prevents harmful address clashes among PC4s. However, the I/O address range used by the PC4(s) still must not overlap with the I/O addresses used by any other device in your computer.

The 32 I/O addresses of the PC4 card can be selected to appear at a variety of locations in the I/O address space of the computer. Table C-3 is a list of the locations that can be set using the DIP switch on the Controller Card. Addresses are given as a base (starting) address of the 32 byte I/O address range.

**Table C-3
I/O Address Selection**

Base Address	S101-3	S101-4	Address Range	
			hex	decimal
0x220	ON	ON	0x220-0x23F	544-575
0x120	ON	OFF	0x120-0x13F	288-319
0x240	OFF	ON	0x240-0x25F	576-607
0x140	OFF	OFF	0x140-0x15F	320-351

If you have any uncommon expansion cards in your computer, you should consult their documentation to determine the location of their I/O registers. If their register locations conflict with the default address range of 0x120-0x13F, determine a new base address from Table C-3 that does not conflict with any of your cards.

For example, suppose you determine that your computer contains a tape backup controller that uses I/O registers at addresses 0x130-0x13F. These clash with the default PC4 I/O addresses 0x120-0x13F. Therefore, the PC4 base I/O address must be changed. Assume that you choose a new base I/O address of 0x140. This base I/O address level and its associated S101 switch settings should be entered into the PC4 DIP switches and the "GAMRY.INI" file.

To change the I/O Address on your PC4s, proceed as follows:

1. Determine the desired I/O address. See above discussion.
2. Locate S101, the four pole DIP switch in the middle right side of the Controller Card.
3. The ON position of the switches is marked on the body of the switch.
4. The order of the switches is S101-1 on the left, S101-4 on the right. This also is marked on the body of the switch.
5. Set the switches S101-3 and S101-4 from Table C-3. The switch settings are read across the row labeled with the desired I/O address. Do not change the settings of S101-1 and S101-2!
6. Double check that the change has been made correctly.
7. Repeat 1-6 for any other PC4s Potentiostats in your system.

The procedure for manually changing "GAMRY.INI" to reflect the new I/O address setting is:

1. Edit "GAMRY.INI" in the Windows directory. Windows Notepad is a convenient ASCII editor.
2. In each [PstatN] section, locate the line BaseAddress=0xYYY, where YYY is the old I/O base address. For the default "GAMRY.INI" YYY is 120.
3. Enter the new base address in place of the YYY in this line. For example, if the new base address is 0x140, the line should read BaseAddress=0x140.
4. Save the edited file.

The information in the altered "GAMRY.INI" file is not effective until you exit and restart the Framework.

Changing the Auxiliary Analog Output Scaling

A setting in the "GAMRY.INI" file allows you to change the scaling of the D/A converter used to generate the auxiliary analog output.

The default setting configures this D/A converter for a bipolar output of ± 5 volts with a bit resolution of 2.5 mV/bit. You can switch to a unipolar output of 0 to 10 volts, still with a bit resolution of 2.5 mV/bit.

The D/A scaling is controlled by a field in the [PStat#] section of the "GAMRY.INI" file. This field has the form:

```
AUXDACRES=2.5E-3,0
```

The final 0 indicates that the scaling is bipolar. If this digit was a 1, the scaling would be unipolar.

Appendix D -- I/O Connections for the PC4

The PC4 Potentiostat has a number of connectors that allow it to communicate electronically with the world outside of the computer. This appendix describes these connectors and the signals available on their pins.

CE Compliance, EMI and Cable Shielding

The European Community has instituted standards limiting radio frequency interference (EMI) from electronic devices. Compliance with these standards requires that special shielded cell cable connections are used in all CE compliant systems.

The PC4 is electrically floating. Its connections to the electrochemical cell under test are not connected in any way to earth ground. While this is advantageous for testing many types of electrochemical systems, it can result in significant radio frequency (RF) interference.

The interior of a personal computer is filled with RF energy. The computer's earth grounded enclosure prevents the escape of this energy.

Now consider the case of the PC4. It is a floating potentiostat built on a board that mounts inside the computer. The floating circuits inside the computer act as an antenna, picking up RF energy. The potentiostat's cables can then radiate this energy outside of the enclosure, generating RF emissions.

The cell cable supplied with your PC4 has an overall shield that is connected to the computer's chassis ground. This shield acts as an extension of the computer's chassis, keeping the RF emission level lower than the limits in the regulations. Note that use of cell cables not designed and sold by Gamry Instruments can result in excessive RF radiation.

Grounds and the PC4 Potentiostat

The PC4 has been specially designed for operation with cells in which one of the electrodes is connected to earth ground. Earthed electrodes often occur in field experiments, because metal pipelines and structures are generally earth grounded. In the lab, experiments involving either autoclaves or stress apparatus often have earth grounded electrodes. Conventional potentiostats do not work properly or safely in these experiments. In the typical glass or plastic test cell, none of the electrodes are earth grounded, so no grounding problems arise.

The PC4 analog circuits are electrically isolated from the computer's chassis which is at earth ground. Another name for circuits that are isolated is "floating". The isolation is accomplished by means of optical isolators and transformers.

Extraordinary measures were taken in the design of the PC4 to maximize the degree of isolation. However, you can still measure higher impedances and smaller currents on cells that are not earth grounded than you can on earth grounded cells.

If you are working with earth grounded electrodes, ground connections for your potentiostat are critical. You must be careful that the floating ground connection on all PC4 connectors does not get connected to earth ground.

We strongly recommend that you use an earth grounded Faraday shield whenever you are measuring small currents. See Chapter 5 for a discussion of Faraday shields.

The Cell Connector

The Cell Connector is a 9 pin female D shaped connector on the Potentiostat Card. This connector is used to connect the PC4 to the electrochemical cell being tested. Normally you make your cell connections using the cell cable that Gamry provides you. See Chapter 3 for a description of how the cell connections are made using the standard cell cable.

The metal shell of this D connector is connected to the computer's chassis (earth) ground. This is the source of the chassis ground (earth ground) contact in the cable.

In a few cases, you will find the standard cell cable is inadequate for your needs. You may find that you need to modify a cell cable or make a special purpose cable. By far, the easiest changes involve modifying a standard cell cable. We can sell you an extra cell cable for this purpose. If you do need to make a completely new cable, the pin out of the cell connector is given in Table D-1. We recommend that you use shielded cables for all the cell connections. Coax cable is preferred. Connect the shield of the coax to the pin shown in Table D-1 on the PC4 end, and leave the shield open on the cell end. Make sure that all pins are isolated from each other.

Cell cables longer than 3 meters may result in degraded instrument performance. Increased noise and decreased stability both can occur. However, with most cells, the instrument will work acceptably with an extended cell cable, so our advice is go ahead and try it. As a rule, you should not attempt to use current interrupt IR compensation with cell cables longer than 5 meters.

**Table D-1
Cell Connector**

Pin	Signal Name	Use
1	Working Sense	Normally connected to the working electrode. This is the high impedance negative input of the differential electrometer.
2	WS Shield	A driven shield for the working sense input. Normally connected to the outer shield of a coax cable on pin 1. Do not ground this pin!
3	Working Electrode	The input to the PC4 current measurement circuit. The voltage on this point can be ± 1.5 volt with respect to floating ground.
4	WE Shield	A driven shield for the working electrode input. Normally connected to the outer shield of a coax cable on pin 3. Do not ground this pin!
5	Ground	The PC4's floating ground. Should also be used to provide a shield for the counter electrode if one is used.
6	Ref Electrode	Normally connected to the reference electrode. High impedance positive input of the differential electrometer.
7	Ref Shield	A driven shield for the reference electrode input. Normally connected to the outer shield of a coax cable on pin 6. Do not ground this pin!
8	Counter Sense	Input to a voltage follower. Normally connected to the cell's counter electrode. Used in ZRA mode to develop a feedback signal.
9	Counter Electrode	The output of the PC4 control amplifier. Normally connected to the counter electrode of the electrochemical cell being tested.

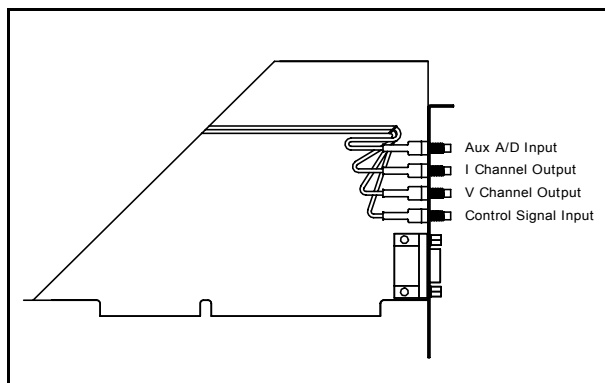
Control Signal Input

The Control Signal Input allows you to inject a signal into the PC4's potential or current control circuits. One use for this input is modulation of the applied voltage or current.

This input is the lowest SMC connector on the Controller Card minipanel. See Figure D-1 for the identity of all the SMC connectors on this minipanel.

Note that the shell of this SMC connector is connected to the PC4's floating ground. Connecting an earth ground referenced signal source to this input will cause problems if you are using the PC4 with a cell that has an earth grounded electrode.

Figure D-1
SMC Connectors on the PC4 Controller Card Minipanel



In controlled potential mode (and ZRA mode), the potential applied to the cell is the sum of the applied potential and the control input voltage. For example, if the programmed voltage is +2 volts, and +1 volt is applied to the control input, the cell voltage ($E_{\text{work}} - E_{\text{ref}}$) will be +3 volt. The input impedance of this input is 10 k Ω . Adding a control resistor, R_{ext} in series with the input allows you to alter the scaling factors. The equation describing the relationship is:

$$V_{\text{cell}} = V_{\text{sig}} \times 10 \text{ k}\Omega / (R_{\text{ext}} + 10 \text{ k}\Omega)$$

V_{sig} is the signal applied to the resistor and V_{cell} is the resulting cell voltage. If 90 k Ω is added in series, a 1 volt signal will be attenuated to cause only a 100 mV cell voltage.

In controlled current mode, you will get full scale current for 3 volts applied to this connector. The current will vary with the current range. For example, on the 30 mA range, 1.5 volts will give you 15 mA of cell current. The sign is such that a positive input gives you a cathodic current.

Aux A/D Input

This input allows you to measure an externally generated voltage signal. The Aux A/D input is the upper of the SMC connectors on the PC4 Controller Card's minipanel. See Figure D-1 for the identity of all the SMC connectors on this minipanel.

Uses of this input include the measurement of temperature, strain, or other non-electrochemical parameters. This input is fully differential, with about 80 dB of common mode rejection. Be careful though, the allowed common mode voltage range is only ± 11 volts with respect to the floating ground. Voltages outside this range should not damage the instrument but they cannot be measured.

The scaling on this signal is ± 3 volts full scale, resulting in $\pm 30,000$ counts on the A/D converter.

The signal conditioning circuitry on this input changed significantly between revision E and revision F of the PC4 Controller Card. The circuitry on revision E and lower had a fixed 25 k Ω input impedance and did not allow for input filtering. Higher revision boards include jumpers to select both input impedance and bandwidth.

See Appendix E for a description of these changes.

V Channel Output

This output reflects the cell voltage signal as seen by the PC4 A/D converter. The V Channel output is the lower-middle SMC connector on the PC4 Controller Card's minipanel. See Figure D-1 for the identity of all the SMC connectors on this minipanel.

The signal on this connector has been through a long and complex analog signal processing chain. It may have been filtered, offset by a DC voltage, and gained. All of these functions are under computer control. The meaning of the signal on this connector is therefore highly dependent on the program controlling the PC4 and cannot be described simply here. The one thing that can be said concerns polarity. If this signal becomes more positive as a result of changes in the cell potential, the cell voltage has become more anodic.

Note that the shell of this SMC connector is connected to the PC4's floating ground. Connecting an earth ground referenced measurement device to this output can cause problems if you are using the PC4 with a cell that has an earth grounded electrode.

I Channel Output

This output reflects the cell current signal as seen by the PC4 A/D converter. The I Channel output is the upper-middle SMC connector on the PC4 Controller Card's minipanel. See Figure D-1 for the identity of all the SMC connectors on this minipanel.

The signal on this connector has been through a long and complex analog signal processing chain. It may have been filtered, offset by a DC voltage, and gained. All of these functions are under computer control. The meaning of the signal on this connector is therefore highly dependent on the program controlling the PC4 and cannot be described simply here. The one thing that can be said concerns polarity. If this signal becomes more positive as a result of changes in the cell potential, the cell current has become more cathodic.

Note that the shell of this SMC connector is connected to the PC4's floating ground. Connecting an earth ground referenced measurement device to this output can cause problems if you are using the PC4 with a cell that has an earth grounded electrode.

Miscellaneous I/O Connector

This connector contains a number of chassis ground related signals. It is the miniature 15 pin female D shaped connector on the PC4 Controller Card. Be careful, the ground on this connector is not the PC4 floating ground. Connecting the two grounds may lead to problems if you are using the PC4 in a floating mode.

The auxiliary analog output, derived from a D/A converter, is on this connector. The scaling is normally 2.5 mV per bit, for a ± 5 volt full scale range. These ranges can be altered via the AUXDACRES field in the "GAMRY.INI" file.

The pin out of this connector is shown in Table D-3.

Table D-3
Miscellaneous I/O Connector

Pin	Name	Use
1	Analog Output Low	The auxiliary output ground connection.
2	Analog Output High	The auxiliary output signal.
3	no connection	
4	Start of Point	A TTL pulse before the start of a data point
5	End Of Point	A 1 μ sec TTL pulse at the end of each data point
6	Ground	Digital ground
7	Digital Out 0	A CMOS digital output- 330 Ω output impedance
8	Digital Out 1	A CMOS digital output- 330 Ω output impedance
9	Digital Out 2	A CMOS digital output- 330 Ω output impedance
10	Digital Out 3	A CMOS digital output- 330 Ω output impedance
11	Digital In 0	A TTL digital input- 2.2 k Ω input impedance
12	Digital In 1	A TTL digital input- 2.2 k Ω input impedance
13	Digital In 2	A TTL digital input- 2.2 k Ω input impedance
14	Digital In 3	A TTL digital input- 2.2 k Ω input impedance
15	+5 Volts	Power- 100 mA maximum current

Appendix E – Auxiliary A/D Input Characteristics

Overview

The Controller Card used in the Gamry Instruments PC4 Potentiostat and the FAS1 Femtostat has undergone a number of changes over its lifetime.

One of the changes was a major modification of the input circuitry used for the Aux A/D function. Early revisions of the Controller Card only allowed connection of low impedance, quiet signals to this input. Revision F (and higher) cards allow for connection of higher impedance signals and for filtering of noisy input signals prior to A/D conversion. Three new jumpers added to the board control access to these features.

Identifying Your Controller Card Revision

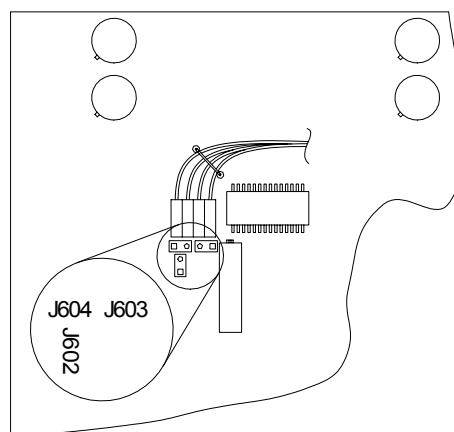
A label on the lower left side of your Controller Card will identify the revision of the card. The revision generally consists of a capital letter followed by a number. The letter identifies the printed circuit board revision. For example, revision F1 uses a revision F printed circuit board. The bulk of the descriptions in this document do not apply if you have a board revision lower than Rev F.

Revision E and Lower – Characteristics

Revision E (and lower) boards have an Aux A/D input with fixed characteristics. The input impedance is 25 k Ω and the bandwidth is not limited by a filter. If your board is earlier than revision F, disregard the rest of this appendix because it does not apply to your instrument.

Jumper Identification

The three jumpers that configure the Aux A/D input are in a cluster located at the left side of the Controller Card. The four coax cables that route analog I/O to the card enter the card just above these jumpers. J603 and J604 are located immediately below the cables. J602 is lower and perpendicular to J603 and J604. See the figure to the right for jumper locations.



Input Impedance Selection

Two jumpers are associated with the input impedance – J603 and J604. With J603 and J604 installed, the Aux A/D inputs have a 100 k Ω input impedance. This is the default setting. With the jumpers installed, the potentiostat can be calibrated without a cable on the input SMC connector.

With both J603 and J604 removed, the Aux A/D input impedance is 10 G Ω (typically). This setting is suitable for use with a high impedance source such as a reference electrode. If you have removed these jumpers, do not calibrate the potentiostat unless you have a cable connecting both Aux A/D inputs to floating ground.

Filter Selection

J602 controls filtering of the Aux A/D input. With J602 removed, there is no filtering on this input. With J602 in place (the default setting), a single pole RC filter is used to limit noise into the A/D. The nominal cutoff frequency of this filter is 20 Hz.

Note that source impedances greater than 1 k Ω will appreciably lower this cutoff frequency. When the Aux A/D input is driven by a source with an output impedance of 1 M Ω , the frequency cutoff will be less than 0.25 Hz.

Revision F or Higher- Aux A/D Specifications

These specifications for the Aux A/D apply to revision F or higher boards:

Range	± 3.276 volts	
Input Impedance	100 k Ω (approx)	J603 & J604 installed
	or 10 G Ω (typical)	J603 & J604 removed
Input Bias Current	< 10 nA	J603 & J604 removed
Filter Cutoff	20 Hz \pm 20%	J602 in place with Z _{source} < 1 k Ω

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