PCI4 Potentiostat/Galvanostat/ZRA

Operator's Manual

includes both the

PCI4/300 Potentiostat/Galvanostat/ZRA

and

PCI4/750 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 PCI4 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 PCI4 in standard computer hardware.

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

Enhancements to the PCI4 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 PCI4 Potentiostat/Galvanostat/ZRA. It covers both the PCI4/300 Potentiostat/Galvanostat/ZRA and its cousin the PCI4/750 Potentiostat/Galvanostat/ZRA. These instruments differ primarily in their output current: 300 mA for the PCI4/300 and 750 mA for the PCI4/750. Throughout this manual, the term PCI4 should be interpreted as a reference to both the PCI4/300 and the PCI4/750.

NOTE: The Gamry Instruments PCI4 interfaces to a computer using the industry standard PCI bus. This manual does not discuss the older Gamry Instruments PC4 family of potentiostats, which used the ISA bus. The PC4 and PCI4 perform similarly, but the installation procedures and specifications between the older and newer instruments are different enough to make this document a poor reference for the PC4. Consult an earlier revision of this manual for PC4 information.

This manual describes use of a PCI4 with Revision 5.0 (and later revisions) of the Gamry Framework software. It is equally useful when setting up a newly purchased potentiostat or modifying the setup of a four-year-old potentiostat for use with new software.

The bulk of Chapter 1 is an overview of the PCI4's design and modes of operation. Chapter 2 contains PCI4 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 and connector pin-outs in the Appendices.

This manual does not discuss software installation or operation.

Software support for the PCI4 is described in the Gamry's On-line Help system. All the Gamry Instruments' applications which run under the Gamry Framework control the PCI4 via a PSTAT object. See the Framework's On-line Help for information concerning PSTAT objects and their functions.

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 EN 61010 and EN 61326..

About the PCI4

The PCI4 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 PCI4/300 and PCI4/750 are two members of Gamry Instruments' PCI4 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.

PCI4 features include 9 decade current auto-ranging, electrical isolation from earth ground, current interrupt iR compensation, and extensive filtering. A sine wave generator on the PCI4 allows its use for impedance measurements at frequencies up to 300 kHz.

The PCI4 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 PCI4 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 opto-couplers 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 a PCI bus interface, optocoupled serial transfer logic, an isolated power supply, a signal generator, and a high performance measurement system.

- The PCI bus interface communicates with the rest of the PCI4 over opto-coupled serial lines. There is no ground connection between the PCI bus circuitry and the analog circuits in the PCI4.
- 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 PCI4 Potentiostat.

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

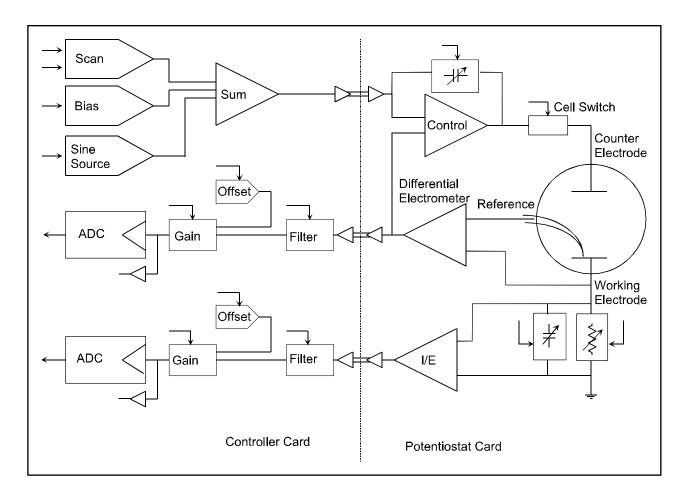


Figure 1-1 PCI4 Analog Circuits in Potentiostat Mode

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, opto-couplers, 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.
- File names and folders. Inside paragraphs, references to computer files and Windows folders will be capitalized and placed within quotes, for example: and "C:\FRAMEWORK\FRAMEWORK.EXE" and "WIN.INI".

Chapter 1 -- Introduction -- Notational Conventions

Chapter 2 -- Installation

A PCI4 Potentiostat is only useful after it has been installed in a Windows™ compatible computer.

If you purchase a PCI4 in a system that includes both a computer and an applications software package, Gamry Instruments, Inc. will install the PCI4 (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 PCI4 to an existing system, or move an old PCI4 to a new computer, you need to know how to install a PCI4 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 PCI4 into your own computer you must make sure that your computer meets these simple requirements.

- A computer based on one of the Pentium[™] family of Intel microprocessors or a 100% compatible processor from another vendor.
- One of the following Operating Systems: Windows 2000, or Windows XP.
- Two unobstructed, full height (11 cm) PCI expansion slots for each PCI4 card set. Each slot must be capable of accepting a 26 cm long (10 inch) card.
- Up to 50 watts of power supply capacity for each PCI4 Card Set. This is in addition to the power normally drawn by your computer and its standard peripherals.
- One unused disk drive power connector. This connector is used to power the PCI4 Controller card.

Most of the PCI4's power is drawn from the computer's +12 volt and +5 volt supplies. However, the PCI4 also requires a small amount (< 50 mA) of current taken from the computer's -12 volt supply.

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

PCI Compatibility

The PCI4 has been designed for compatibility with Revision 2.2 of the PCI Specification. As described in that specification, it is a universal card, able to operate with either 3.3 volt and 5.0 volt PCI signaling levels.

The PCI4 does not draw power from the 3.3 volt supply pins on the PCI bus connector. It can therefore operate with older computers that did not provide 3.3 volts on the PCI bus. It should operate with all PCI computers compliant with Revision 2.0 and higher of the PCI Specification.

Multiple Potentiostat Systems

Gamry's current Framework software (Revision 4.2) allows a computer to operate several Gamry Instruments potentiostats simultaneously. These can include both PCI4 and older PC4 family devices in the same computer. Contact our home office or your local sales representative if you need assistance configuring a system contain both PCI4 and PC4 hardware.

Gamry's Framework contains a utility script to identify PCI4 Family potentiostats in a multiple potentiostat system. See Appendix C of the *Getting Started Guide* for instructions concerning the use of this program.

Card Identification

A PCI4 Potentiostat consists of two full height, 26 cm long PCI compatible printed circuit boards. When you look at your PCI4 cards, you will notice that a large portion of one card is covered with a large black shield. This card is the PCI4 Potentiostat Card. The card without the shield is referred to as the PCI4 Controller Card.

Positional Conventions

Throughout this manual, reference will be made to positions on the PCI4 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 conventions.

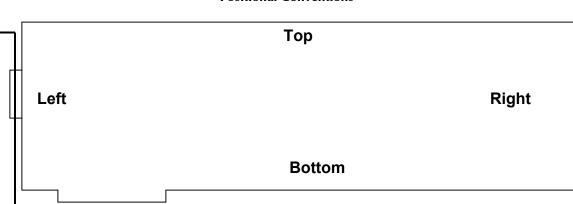


Figure 2-1 Positional Conventions

Handling the Cards

The PCI4 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, 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.

Plug & Play System Configuration

The PCI4 Controller Card is completely compatible with the Windows Plug & Play configuration system. Unlike Gamry's older potentiostats, you don't need DIP switches to configure the card. Like most Plug & Play hardware, it is best if you install the software for the PCI4 <u>before</u> you install the potentiostat hardware.

A Setup program will normally startup automatically when you place the Gamry Instrument's Software CD into the CD drive on your computer. Consult Gamry's software installation manual if you need assistance accessing the Setup program or choosing options in its menus.

Installing the Cards in Your Computer

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

As discussed above, it is best if you install Gamry's Framework software before you install the PCI4 hardware.

The following procedure is used to install the PCI4 cards in your computer.

- 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 expansion slot that has a PCI interface. The slot must be at least 26 cm long.

If necessary, remove the retaining screw and slot cover (the 'L' shaped metal bracket) for this slot. Save the screw for use later.

4. Locate a second empty slot that is within 15 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. <u>Do not</u> close up the computer yet.

Connecting the Internal Cables

- 1. Locate the 26 pin headers (group of 26 pins) on both the Controller and Potentiostat cards. They are in the upper right hand side of each card.
- 2. Examine the ribbon cable that came with the PCI4 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. We recommend that the colored stripe on the cable faces the left side of both cards (nearest the metal bracket).
- 5. Locate the power input connector on the upper left side on the PCI4 Controller card. This mates with a "disk drive" power cable from the PC's power supply. Locate an unused power cable and connect it to the PCI4 power input connector. A power cable extender was supplied with the PCI4, in case the computer's disk drive power cable is too short.

Note that the power cables can only mate in one direction. If the power cable will not plug into the PCI4 card, rotate the cable 180° .

- 6. Carefully double check your work.
- 7. Onc e 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 knurled 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.

1st Time Device Installation in Windows

When a PCI4 is first connected to a computer running Windows, the Windows Plug and Play Manager will see the new device, but will be uncertain what device it is. The message that will appear is something like "New device found" or "Unknown PCI Bridge device Detected".

When this occurs after you've plugged in a PCI4 instrument, tell Windows that you would like to install the new device.

Windows 7 Users: The following windows will not be displayed. Please skip to page 2-7 to continue the installation process.

All other users should see a screen that looks something like this:

Found New Hardware Wizard		
	Welcome to the Found New Hardware Wizard	
	Windows will search for current and updated software by looking on your computer, on the hardware installation CD, or on the Windows Update Web site (with your permission). <u>Read our privacy policy</u>	
	Can Windows connect to Windows Update to search for software?	
	\bigcirc Yes, this time only	
	Yes, now and every time I connect a device	
	O, not this time	
	Click Next to continue.	
	< <u>Back</u> Next > Cancel	

Figure 2 - 2 Welcome to the Found New Hardware Wizard

As shown in this Figure, do <u>not</u> choose to let Windows Update find the device driver that you need. The Windows Update web site has no knowledge of the Gamry Instruments PCI4 family of devices.

Make sure you select **No, not this time**. After you select, <u>Next</u>, you should see a screen that looks like this:

Install the Software Automatically				
Found New Hardw	Found New Hardware Wizard			
	This wizard helps you install software for: PCI4 Family Instrument If your hardware came with an installation CD or floppy disk, insert it now. What do you want the wizard to do? Install the software automatically [Recommended] Install from a list or specific location (Advanced) Click Next to continue.			
	< <u>B</u> ack <u>N</u> ext > Cancel			

Figure 2-3 Install the Software Automatically

All Gamry device drivers are pre-installed to your machine during the software installation process. Select **Install the software automatically**, then select **Next**.

These messages will also be seen when a PCI4 family instrument is moved to a new PCI slot. In this case, you can select **Install the software automatically** even if you do not have the Gamry Instruments CD. The driver that was previously installed on your computer's hard drive will be used

The Windows Device Manger will locate and install the required files, which are already on your system.

Your Gamry Software CD is not required at this point. However, if you do not have your Gamry Software CD or lose the CD at any point, contact Gamry Instruments, or your local Gamry Sales representative for assistance.

Once the drivers and associated support files have to copied to your system, you should see another screen that looks like this:

	Software Automatically	
)evice Settings		
Device PCI4750-39065 Enter a label for your device and corresponding authorization codes.		
Label MyPCI4 Authorization Codes DC105=1234567890 EIS300=2345678901	Add Edit Delete	
Device Section: PCI4750-39065		
	< <u>B</u> ack Finish Cancel	

Figure 2-4 Install the Software Automatically

As displayed in Figure 2-4, you enter a friendly name for your PCI4, as well as any authorization codes you received with your instrumentation. The authorization codes are 10 digit codes that allow different Gamry application software to be used with your PCI4. If you cannot locate your authorization codes, please contact Gamry Instruments or your local Gamry Sales representative for assistance.

To enter an authorization code, simply click on the <u>A</u>dd button. A dialog box will appear as shown in Figure 2-5. You enter the package name, like "EIS300", followed by the 10 digit authorization code.

Figure 2-5 Enter an Authorization Code				
Authoriza	tion Code I	Entry		
<u>P</u> ackage	EIS300	Authorization <u>C</u> ode	2345678901	
			OK	Cancel

Press **OK** when you are finished.

Multiple Potentiostat Systems

Gamry's current Framework software (Revision 5.1) allows a computer to operate up to 16 Gamry Instruments potentiostats simultaneously. The 16 potentiostats can include both PCI4 family devices and the newer PC5 family devices.

A system with multiple PCI4s just needs them all plugged into the computer.

Contact our home office or your local Gamry Instruments representative if you need assistance configuring a system containing both PCI4 and Reference 600 hardware.

Device Manager

If you wish to make changes to the configuration of your PCI4 after it has already been installed, you must use the Windows Device Manager. Steps for getting to the Device Manager can vary by operating system, so check your operating system's online help for more specific information on how to get to the Windows Device Manager.

Under Windows XP, right clicking on the **My Computer** icon and selecting **Properties** brings up the **System Properties** dialog box. Select the **Hardware** Tab and then click on the **Device Manager** button. This should bring up the Device Manager screen. Clicking on the + sign next to Gamry Instruments, should expand the tree view to give you a screen that looks similar to the following figure:

Figure 2-6 Device Manager Window		
🗏 Device Manager		
<u>E</u> ile <u>A</u> ction ⊻iew <u>H</u> elp		
	<u>^</u>	
🗄 😼 Computer		
⊡ Sk drives		
🗄 🧕 Display adapters		
DVD/CD-ROM drives		
Floppy disk controllers		
🗉 😃 Floppy disk drives		
🖻 🔝 Gamry Instruments Devices		
Gamry PCI4 Device 03		
Gamry PCI4 Device 05		
🗉 😁 IDE ATA/ATAPI controllers		
🗉 🥪 IEEE 1394 Bus host controllers	~	

You can now right click on any of the Devices listed under Gamry Instruments and select **Properties** to look at or change its configuration.

Authorization Codes and Label

If you purchase additional Gamry application software, did not enter your authorization codes upon initial device installation, or simply need to make a correction to your authorization codes, you can do so using the Windows Device Manager. You can also change the Label you use for your device. The Gamry Framework Application Software must first be closed before you can use the Device Manager to make changes. Next, you must select the appropriate device, as discussed in the Device Manager section. Once you have selected the appropriate device, right click and select **Properties**. Next, select **Device Settings** and you will see a screen that looks like Figure 2-7:

Device Settings Tab			
Gamry PCI4 Device 05 Properties 🔹 🔹 👔			
General Device Settings Driver Details Resources			
Label MyPCI4			
Authorization Codes			
DC105=1234567890			
<u><u>El3300=2343678301</u></u>			
<u>D</u> elete			
Davies Castient, DCI4750 20005			
Device Section: PCI4750-39065			
OK Cancel			

Figure 2-7

You can enter or edit any of the authorization codes or Label for the device by clicking on the appropriate edit box and entering the information. When you are finished making changes press **OK** to store the changes.

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 PCI4 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.

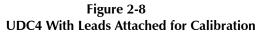
CAUTION: PCI4 calibration calls for an external resistive dummy cell. PCI4s are provided with a Universal Dummy Cell 4 which includes a 2 k Ω , 0.05% accurate resistor in the position marked "Calibration". After calibration, please place this dummy cell in a safe place where you can find it if your unit requires recalibration.

If you do need to recalibrate and you cannot find the resistor shipped to you, you can substitute another 2 k Ω resistor. Its wattage is unimportant. Some performance checks in the calibration process may fail if the resistors inaccuracy exceeds 0.1% (2 Ohms).

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

- You are installing a PCI4 Potentiostat into a new computer or moving a PCI4 into a different computer. The PCI4 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 "GAMRY5.INI" file.





Chapter 3 -- Cell Cable Connections

Cell Indicator

The PCI4 is equipped with four LED indicators, located on the Potentiostat card mini-panel. The uppermost, yellow, LED functions as a Cell Indication. It lights whenever the PCI4 cell switch is on and goes dark whenever the cell is at open circuit. **Figure D-1** in the appendices is a picture of the rear panel of a computer demonstrating the location of this indicator.

The other three LEDs are reserved for future use.

The Cell Indicator is also used in the identification of potentiostats in a multiple potentiostat system, using a special "Identify Potentiostats" script. Appendix C of Gamry's **Getting Started Guide** describes the use of this script.

Normal Cell Connections

Each PCI4 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 PCI4 Potentiostat Card. Make sure you connect the cable to the correct 9 pin connector on the computer.

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 PCI4 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 PCI4.

Table 3-1 identifies each terminal of the cable.

Color	Туре	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

 Table 3-1

 Cell Cable Terminations - Potentiostat and Galvanostat Modes

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 PCI4'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 PCI4 end to Floating Ground. This is the circuitry ground for the analog circuits in the PCI4. 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 <u>must not</u> connect the long black cell lead to earth ground. Autoclaves, stress apparatus, and field measurements may involve earth grounded electrodes.

If you are measuring very small currents, you will probably find that a metal enclosure completely surrounding your cell (a Faraday shield) significantly lowers 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.

In either potentiostatic or galvanostatic mode, if you do not have a reference electrode in your cell, the reference lead can be connected to the counter electrode for a two electrode experiment. The potential reading will be the difference between the counter electrode and the working electrode.

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.

Color	Туре	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

Table 3-2Cell Cable Connections for ZRA Mode

The counter sense and the working sense lead are each connected to different metal samples. In the ZRA mode the PCI4 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.

In ZRA mode, 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, almost noiseless signal very close to zero.

Membrane Cell Connections

The PCI4 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 PCI4 controls the potential across the membrane. Table 3-3 shows the cell connections used with a membrane type cell.

Color	Туре	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

Table 3-3Cell Cable Connections for a Membrane Cell

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 feedback signal (which is already phase shifted). 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 PCI4 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 PCI4 has been tested for stability with cell capacitors between 10 pF and 0.1 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 PCI4 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 PCI4'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 PCI4 potentiostat/cell system. This list is not in any particular order. Any or all of these steps may help.

- Slow down the potentiostat. The PCI4 has 4 control amplifier speed settings which can be selected in software. Slower settings are generally more stable.
- Increase the PCI4's I/E stability setting. The PCI4 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.

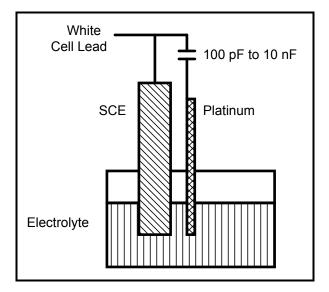


Figure 4-1 Fast Combination Reference Electrode

• 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.

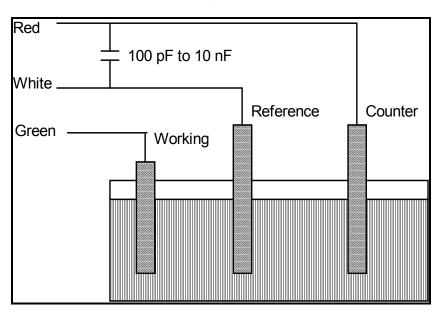


Figure 4-2 High Frequency Shunt

• 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.

This resistor has no effect on the DC accuracy of the potentiostat. It can create problems in high speed experiments such as fast CV scans or EIS, which need high bandwidth.

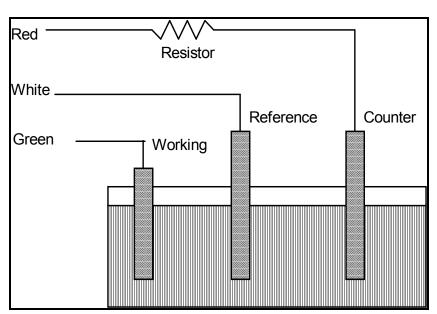


Figure 4-3 Resistor Added for Stability

Chapter 5 -- Measurement of Small Signals

Overview

The PCI4 is a sensitive scientific instrument. It can resolve current changes as small as 0.01 picoamps (10⁻¹⁴ amps). To place this current in perspective, 0.01 pA represents the flow of about 60,000 electrons per second!

The small currents measured by the PCI4 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 PCI4.

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 PCI4 circuit topology differs significantly.

In Figure 5-1:

Es	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, I_{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 Ohms law to calculate Z_{cell} :

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

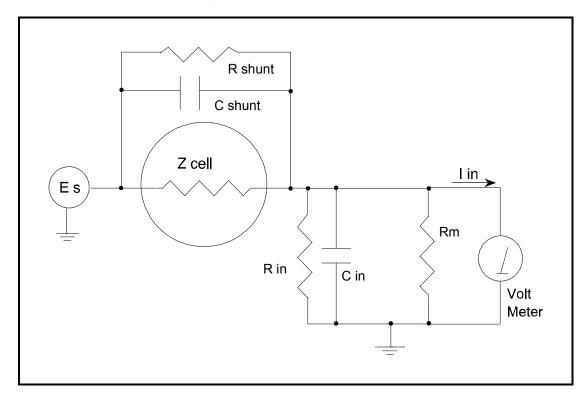


Figure 5-1 Equivalent Measurement Circuit

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:

$$\begin{split} E &= (4 \text{ k T R } \delta F)^{1/2} \\ I &= (4 \text{ k T } \delta F / R)^{1/2} \\ \text{where:} \\ k &= \text{Boltzman's constant } 1.38 \text{x } 10^{-23} \text{ J/oK} \\ T &= \text{temperature in } ^{\circ}\text{K} \\ \delta F &= \text{noise bandwidth in } \text{Hz} \\ R &= \text{resistance in ohms.} \end{split}$$

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 μ V 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 ± 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 μ V rms.

Current noise on the same resistor under the same conditions is 0.41 fA. To place this number in perspective, a \pm 10 mV signal across this same resistor will generate a current of \pm 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:

$$f_{RC} = 1/(2 \omega R_{m}C_{in})$$

Decreasing R_m increases this frequency. However, large R_m values are desirable to minimize the effects of voltage drift and voltage noise in the I/E converter's amplifiers.

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.

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

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:

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

For an R_m of 10⁷ ohms, an error < 1% demands that R_{in} must be > 10⁹ 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 PCI4 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 PCI4. 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 magnitude 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 realistic noise voltage, Vn, of 10 μ V (this is lower than the noise level of most commercial potentiostats). 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:

 $I = Vn/Z \approx 4 nA$

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 5 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, 5 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 10¹⁴ 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 PCI4 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 PCI4 cell cable to enter the shield.

The shield must be electrically connected to the PCI4's floating ground terminal.

An additional connection of both the shield and the PCI4 floating ground to an earth ground may also prove helpful.

NOTE: Only connect the PCI4 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 PCI4 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 <u>may</u> 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 PCI4 with any cables not supplied by Gamry Instruments. The PCI4 cable is not a simple cable like a typical computer cable. The PCI4 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 PCI4 involve cells with small capacitances, the value of which may be important.

In these cases, the capacitance between the PCI4's cell leads can result in an error. The PCI4 alligator clips can have 5 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 isolation between the center conductor and the shield.

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 10¹⁰ ohms cannot be used to measure 10¹³ 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.

Reference electrodes often develop high impedances as they see use. Anything that can clog the isolation frit can raise the electrode impedance. Avoid using saturated KCL based references in perchlorate ion solutions

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 PCI4 to measure 10¹⁰ 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 $10^9 \Omega$ Hz for good EIS measurements with a PCI4.

$$Z \cdot f ~<~ 10^9 \, \Omega Hz$$

Ancillary Apparatus

Do not use the PCI4 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 PCI4 cell leads.

Floating Operation

The PCI4 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 PCI4'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 PCI4 is operated in a floating mode. The instrument specifications only apply on isolated cells with the PCI4 earth ground referenced (not floating).

Special precautions must be taken with the cell connections when the PCI4 must float. Make sure that all the cell connections are isolated from earth ground. In this case, even the floating ground terminal of the PCI4 must be kept isolated.

Finally, most ancillary apparatus connected to the cell of the PCI4 must be isolated. External voltmeters, ammeters, FRA's etc. must be isolated. This includes devices connected to the monitor connectors located on the PCI4 Controller board mini-panel.

Chapter 5 -- Measurement of Small Signals -- Floating Operation

Appendix A -- PCI4/300 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/µsec, > 10 V/µsec, > 5 V/µsec, > 1 V/µsec	

Differential Electrometer

Input Impedance	$> 10^{12} \Omega$ 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 30V (\pm 12 V usable), \pm 3V, \pm 300 mV, \pm 30 mV	
Resolution(16 Bits)	1 mV/bit, 100 μV/bit, 10 μV/bit,, 1 μV/bit	
DC Accuracy	± 0.3% Range ± 1mV	
Offset Range	\pm 12 V with 1.5 mV resolution	

Current Measurement

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

NOTES:

1. All specifications subject to change without notice

2. Offset specifications apply after software calibration

Auxiliary D/A Output

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

Galvanostat Mode

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

Current Interrupt

Measurement Type	(sample 2 points on decay, extrapolate)	
Cell Switching Time	$< 1 \ \mu sec (1 \ k\Omega \ cell)$	
Minimum Interrupt Time	15 µsec	
Maximum Interrupt Time	64 msec	

A/D converter

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

General

Power	40 W maximum	
	< 1 A at +12 V	< 5.5 A at +5 V
	< 0.08 A at -5 V	< 0.02A at -12 V
Leakage i (floating, earthed Working Electrode)	< 3 nA @ DC	

Appendix B -- PCI4/750 Specifications

Control Amplifier

Compliance Voltage	> ± 15V @ 15 mA, > ± 12 volts @ 500 mA
Output Current	> ± 750 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	± 30V (±9 V usable), ± 3V, ± 300 mV, ± 30 mV
Resolution(16 Bits)	1 mV/bit, 100 μV/bit, 10 μV/bit,, 1 μV/bit
DC Accuracy	± 0.3% Range ± 1mV
Offset Range	\pm 12 V with 1.5 mV resolution

Current Measurement

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

Auxiliary A/D Input (see Appendix E)

Range	± 3 volts differential
Bandwidth	20 Hz
Input Impedance	100 kΩ

NOTES:

1. All specifications subject to change without notice

2. Offset specifications apply after software calibration

Auxiliary D/A Output

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

Galvanostat Mode

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

Current Interrupt

Measurement Type	(sample 2 points on decay, extrapolate)
Cell Switching Time	$< 1 \ \mu sec (1 \ k\Omega \ cell)$
Minimum Interrupt Time	15 µsec
Maximum Interrupt Time	64 msec

A/D converter

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

General

Power	45 W maximum
	< 1 A at 12 volts < 6.5 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 PCI4 Settings

Overview

Your PCI4 Potentiostat is fully compliant with the Windows Plug & Play system. PCI4 resources (interrupt settings, register addresses) are not assigned hardware switches or jumpers. Instead, the Windows Device Manager chooses resource assignments. The settings chosen by the Device Manager can be reviewed by selecting Windows Control Panel, Device Manager from the Windows Start Menu.

NOTE: The Device Manager will only show a PCI4 if the hardware is actually installed in the computer and is minimally functional. In the time period after installing the software but prior to hardware installation, a PCI4 will not be seen in the Windows Device Manager, even though its driver has been installed.

The Gamry Framework requires a "GAMRY5.INI" file. This file is used to name the potentiostats in the system.

Turnkey systems are configured appropriately for the items you have purchased with that system. User installed systems should be configured using the Setup programs that come with Gamry Instruments' Windows based application software.

This appendix is used when manual configuration is convenient or required. It includes:

- A description of the "GAMRY5.INI file
- Instructions for changing the Auxiliary D/A ranges.
- Instructions for changing settings for the Auxiliary A/D input

About the "GAMRY5.INI" File

The "GAMRY5.INI" file contain system configuration information. This file is used to:

- Store Potentiostat names.
- Store auxiliary equipment configurations (multiplexers and temperature controllers).
- 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 "GAMRY5.INI" file is an ASCII 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.

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 "GAMRY5.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 "GAMRY5.INI" in the correct directory or modify an existing file in this location.

A portion of a typical "GAMRY5.INI" file is shown in Figure C-1. Only some of the information required for PCI4 configuration is shown. A complete "GAMRY5.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. [Framework5]. The [Framework5] section extends to the next section identifier [PCI4750-12345]. The [Framework5] section contains configuration information for the Gamry Framework program. This section is required in all "GAMRY5.INI" files that configure a Gamry Framework System.

"GAMRY5.INI" normally contains potentiostat calibration information (not shown). 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 [PCI4yyy-xxxx] section also contains the AUXDACRES field which you may need to change. See below for details. In your installation, the "yyy" will be replaced with either "300" or "750" for the model of your potentiostat. The "xxxxx" will be replaced with your controller board's serial number.

[Framework5]
Version=5.0
SystemDir=C:\Program Files\Gamry Instruments\Framework 5\
ScriptDir=C:\Program Files\Gamry Instruments\Framework 5\Scripts\
PACKAGE0=DC105
[PCl4750-12345]
CMSDriver=PCI4.DLL
LABVIEWDriver=PCI4LV.DLL
BaseAddress =
PstatClass=PCI4
FraCurveClass=FRACURVE4
BoardNo=1
SerialNo=12345
Label=My PCI4
AuthDC105=1234567890
AUXDACRES = 2.5E-3,0
AOADACKES = 2.3E-3,0
[ECM8_1]
TYPE=ECM 8
LABEL=My ECM8
PORT=2
MODE=COM2:9600,N,8,1
SerialNo=12345
[DC105]
NAME=DC Corrosion
EXPT1=Corrosion Behavior Diagram,Corrosion Behavior Diagram.exp
EXPT2=Corrosion Potential,Corrosion Potential.exp

Figure C-1 Portion of a Typical "GAMRY5.INI" File

Using Notepad to alter "GAMRY5.INI"

It is often convenient to use an ASCII editor to make small changes in the "GAMRY5.INI" file. The Notepad accessory included with Windows is a useful ASCII editor. Please read the Microsoft documentation for full instructions about using Notepad.

Removing a Potentiostat from an Existing System

To remove a potentiostat from a system you need to physically remove the card set from the computer. You do not need to make changes to the "GAMRY5.INI" file.

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 **PCI4** Potentiostat generates an interrupt at the end of each data point.

All PCI devices in a computer generally share one interrupt level.

Register Address

The PCI4 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 memory 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 PCI4 requires a 64 byte memory space for it's hardware control registers. The Windows Device Manager will show several address spaces for a PCI4 device. The third space is the I/O registers for the PCI4. The other memory spaces are used in PCI configuration.

Changing the Auxiliary Analog Output Scaling

A setting in the "GAMRY5.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 \pm 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 [PCI4yyy-xxxx] section of the "GAMRY5.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 PCI4

The PCI4 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 PCI4 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 PCI4. 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 PCI4 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 PCI4 Potentiostat

The PCI4 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 PCI4 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 PCI4 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 PCI4 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 PCI4 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 PCI4 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 <u>may</u> 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.

Pin	Signal Name	Use	
1	Working Sense	Normally connected to the working electrode. This is the high impedance negative input of the differential electrometer. A 260 Ω series resistor at the cell end of the coax cable on this input is required for system stability.	
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 PCI4 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 PCI4'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. A 260 Ω series resistor at the cell end of the coax cable on this input is required for system stability.	
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 PCI4 control amplifier. Normally connected to the counter electrode of the electrochemical cell being tested.	

Table D-1 Cell Connector

Aux A/D Input

This input allows you to measure an externally generated voltage signal. The Aux A/D input is the top SMC connector on the PCI4 Controller Card's mini-panel. See Figure D-1 for the identity of all the SMC connectors on this mini-panel.

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 \pm 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 \pm 3 volts full scale, resulting in \pm 30,000 counts on the A/D converter.

The signal conditioning circuitry on this input includes jumpers to select both input impedance and bandwidth. See Appendix E for a description of these jumpers.

Control Signal Input

The Control Signal Input allows you to inject a signal into the PCI4's potential or current control circuits. One use for this input is modulation of the applied voltage or current.

This input is the upper-middle SMC connector on the Controller Card mini-panel. See Figure D-1 for the identity of all the SMC connectors on this mini-panel.

Note that the shell of this SMC connector is connected to the PCI4's floating ground. Connecting an earth ground referenced signal source to this input will cause problems if you are using the PCI4 with a cell that has an earth grounded electrode.

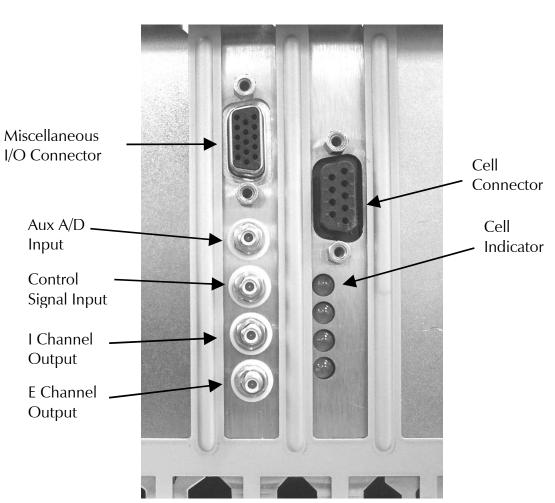


Figure D-1 SMC Connectors on the PCI4 Controller Card Mini-panel Rear View of PCI4 Cards in a Computer

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 ($E_{work} - E_{ref}$) 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:

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

 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.

I Channel Output

This output reflects the cell current signal as seen by the PCI4 A/D converter. The I Channel output is the lower-middle SMC connector on the PCI4 Controller Card's mini-panel. See Figure D-1 for the identity of all the SMC connectors on this mini-panel.

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 PCI4 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 PCI4's floating ground. Connecting an earth ground referenced measurement device to this output can cause problems if you are using the PCI4 with a cell that has an earth grounded electrode.

V Channel Output

This output reflects the cell voltage signal as seen by the PCI4 A/D converter. The V Channel output is the bottom SMC connector on the PCI4 Controller Card's mini-panel. See Figure D-1 for the identity of all the SMC connectors on this mini-panel.

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 PCI4 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 PCI4's floating ground. Connecting an earth ground referenced measurement device to this output can cause problems if you are using the PCI4 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 PCI4 Controller Card. Be careful, the ground on this connector is not the PCI4 floating ground. Connecting the two grounds may lead to problems if you are using the PCI4 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 \pm 5 volt full scale range. These ranges can be altered via the AUXDACRES field in the "GAMRY5.INI" file.

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

Pin	Name	Use	
1	Analog Output Low	The auxiliary output ground connection.	
2	Analog Output High	The auxiliary output signal.	
3	Sync In	Used in slave mode – starts data acquisition	
		2.2 k Ω input impedance	
4	Sync Out	A 125 nsec TTL pulse output before the start of a data poi	
		330 Ω output impedance	
5	No connection	No connection	
6	Ground	Digital ground	
7	Digital Out 0	A TTL digital output- 330 Ω output impedance	
8	Digital Out 1	A TTL digital output- 330 Ω output impedance	
9	Digital Out 2	A TTL digital output- 330 Ω output impedance	
10	Digital Out 3	A TTL 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	

Table D-3 Miscellaneous I/O Connector

Appendix E – Auxiliary A/D Input Characteristics

Overview

The Controller Card used in the Gamry Instruments PCI4 Potentiostat has jumpers that configure the input circuitry used for the Aux A/D function.

Jumper Identification

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

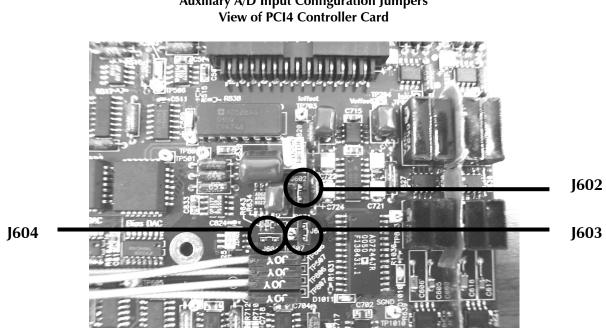


Figure E-1 Auxiliary A/D Input Configuration Jumpers

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.

Aux A/D Specifications

These specifications apply to all PCI4 boards:

Range	±3.276 volts	
Input Impedance	100 kΩ (approx) or	J603 & J604 installed
	10 G Ω (typical)	J603 & J604 removed
Input Bias Current	< 10 nA	J603 & J604 removed
Filter Cutoff	20 Hz ± 20%	J602 in place with Zsource < 1 kΩ

Appendix F – CE Certificate

Certificate of Conformance

CERTIFICATE OF CONFO	JRMANCE	REDITED 36.01
Applicant:	Gamry Instruments, Inc. 734 Louis Drive Warminster, PA 18974	
Equipment Under Test:	Model PCI4-300/750	
Model No.: S/N: PO# Test Report No.: RADIATION SCIENCES INC. CERTIFIES EC 61326 specification as detailed below.		
est report. Emission Specification(s)		Test Result
CISPR 16 - Power Line Conducted B CISPR 16 - Electric Field Radiated B		PASS PASS
mmunity Specification(s)		
EC 61000-4-2 - ElectroStatic Discharge EC 61000-4-3 - Radiated Field Immunity EC 61000-4-4 - Electrical Fast Transient EC 61000-4-5 - Surge Immunity EC 61000-4-6 - Power Line Conducted I EC 61000-4-11 – Voltage Dips and Interru	: Immunity (AC Power) mmunity	PASS Criteria A PASS Criteria A PASS Criteria A PASS Criteria A PASS Criteria A PASS Criteria A
Daniel J. Signore President Radiation Sciences Inc.	<u>4 Дже /</u> Date	<u>c 5</u>
Radiation Sciences Inc., 3131 Detv	viler Rd, Harleysville, PA. 19/	478 (215) 256-4133

Appendix F – CE Certificate -- Certificate of Conformance

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