Reference 3000™

Potentiostat/Galvanostat/ZRA

Operator's Manual

Revision 5.8.1
May 17, 2011

If You Have Problems

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

Telephone	(215) 682-9330 8:30 AM - 6:00 PM US Eastern Standard Time
	(877) 367-4267 Toll Free US & Canada Only
Fax	(215) 682-9331
Email	techsupport@gamry.com
Mail	Gamry Instruments, Inc. 734 Louis Drive Warminster, PA 18974 USA

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

If you have problems in installation or use of a system containing a Reference 3000, it would be helpful if you called from a phone next to your computer, where you can type and read the screen while talking to us.

We will be happy to provide a reasonable level of free support for registered users of the Reference 3000 Potentiostat/Galvanostat/ZRA. Reasonable support includes telephone assistance covering the normal installation, use and simple customization of a computerized system containing a Reference 3000 connected to a Windows™ compatible computer hardware.

A service contract that extends both the hardware warranty and software update period is available at an additional charge. Software updates do not include software enhancements offered to our customers at additional cost.

Enhancements to the Reference 3000 and Gamry's standard applications software that require significant engineering time on our part can be performed on a contract basis. Contact us with your requirements.

Limited Warranty

Gamry Instruments, Inc. warrants to the original user of this product that it shall be free of defects resulting from faulty manufacture of the product or its components for a period of two years from the original shipment date of your purchase.

Gamry Instruments, Inc. makes no warranties regarding either the satisfactory performance of the Reference 3000 Potentiostat/Galvanostat/ZRA including the software provided with this product or the fitness of the product for any particular purpose. The remedy for breach of this Limited Warranty shall be limited solely to repair or replacement, as determined by Gamry Instruments, Inc., and shall not include other damages.

Gamry Instruments, Inc. reserves the right to make revisions to the system at any time without incurring any obligation to install same on systems previously purchased. All system specifications are subject to change without notice.

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Disclaimers

Gamry Instruments, Inc. cannot guarantee that the Reference 3000 Potentiostat/Galvanostat/ZRA will work with all computer systems, operating systems, and third party software applications hardware/software.

The information in this manual has been carefully checked and is believed to be accurate as of the time of printing. However, Gamry Instruments, Inc. assumes no responsibility for errors that might appear.

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Chapter 1 -- Safety Considerations

Your Reference 3000 Potentiostat/Galvanostat/ZRA has been supplied in a safe condition. This chapter of the Reference 3000 Operator's Manual contains some information and warnings that you must follow to insure continued safe operation of the Reference 3000.

The safety information in this chapter applies to both the Reference 3000 and the Reference 3000 equipped with its AE Auxiliary Electrometer.

Inspection

When you receive your Reference 3000 Potentiostat/Galvanostat/ZRA you should inspect it for evidence of shipping damage. If any damage is noted, please notify Gamry Instruments Inc. and the shipping carrier immediately. Save the shipping container for possible inspection by the carrier.

WARNING

A Reference 3000 that has been damaged in shipment can be a safety hazard. Do not operate damaged apparatus until a qualified service technician has verified its safety. Tag a damaged Reference 3000 to indicate that it could be a safety hazard.

Product Safety

The Reference 3000 has been designed, tested and certified to meet the requirements of an international standard, EN 61010, *Safety requirements for **electrical equipment** for measurement, control, and laboratory use*. As defined in this standard, it is a Category I apparatus, designed for connection to circuits other than the power mains.

The Reference 3000 contains a limited amount of internal circuitry that is at “hazardous live” voltages as defined in EN 61010 (the standard mentioned above). “Reinforced insulation” (again defined in EN 61010) is used to reduce the risk of electrical shock due to this “hazardous live” voltage.

The majority of the Reference 3000’s circuitry does not contain voltages higher than 42 Volts DC. As a generalization, input and output voltages in the Reference 3000 are limited to 36 volts. This voltage level is considered safe.

The “AC Adapter” supplied with the Reference 3000 is certified under EN 60950. The AC Adapter converts the AC mains voltage to 24 volts DC, which is used to power the Reference 3000.

You should always use the AC adapter (power brick) supplied with your Reference 3000 to supply DC power to the instrument.

WARNING

Do not use a DC power source other than the AC adapter model provided with your Reference 3000. Other replacements may void the performance and/or safety characteristics of the Reference 3000.

AC Mains Connection to the Power Brick

The Reference 3000 does not connect directly to an AC Mains supply. Instead, the mains are connected to desktop AC adapter (power brick), which outputs 24 volts DC, which in turn powers the Reference 3000.

NOTE

The Reference 3000's AC Adapter is rated for operation from 100 to 240 volts AC, 47 to 63 Hz. It should therefore be useful throughout the world.

The Reference 3000 is normally provided with an AC line cord suitable for your location. This AC line cord connects the AC mains to the AC power adapter. If your Reference 3000 has been provided without an AC line cord, or a cord that is not compatible with your local AC mains socket, obtain a line cord certified for use in your country. Contact your local Gamry Representative or Email to techsupport@gamry.com if you are uncertain what AC line cord to use.

Grounding in the Reference 3000

The circuitry and the metal case of the Reference 3000 are not connected to an earth ground. If they were connected to earth ground, it would compromise the Reference 3000's ability to make measurements in electrochemical cells that contain earth grounded conductors. A few examples of such cells include autoclaves, metallographic stress apparatus, chemical storage tanks, and most large fuel cell stacks.

Most electrochemical cells are isolated from earth ground, so isolation of the Reference 3000 from earth is not required. In these cases, connection of the Reference 3000 chassis to an earth ground may lower noise seen in electrochemical tests. A **Chassis Ground** binding post on the rear panel of the Reference 3000 makes for easy implementation of this connection. Simply run a wire from this binding post to a suitable source of earth ground. A black 1.2-meter wire is provided with the Reference 3000 to facilitate this connection.

NOTE

Sources of earth ground include;

- **Most metal water pipes,**
- **the chassis of most electronic apparatus (which are generally earth grounded), and**
- **the protective ground terminal of an AC Mains power plug.**

We recommend that you discuss grounding with an electrical or electronics professional prior to making this earth ground connection.

Note this connection of the Reference 3000 to an earth ground is not a "Protective Earth Ground" as defined in EN 61010. The Reference 3000 is safe in the absence of this connection.

This binding post is not intended for any use other than connecting the Reference 3000 to an earth ground to improve shielding against noise. Connecting this binding post to a hazardous voltage can create a significant safety hazard.

WARNING

Do not connect the chassis ground binding post to any voltage other than earth ground. An improper connection can create a safety hazard, which could result in personal injury or death.

An earth ground connection can cause problems when testing batteries, fuel cells, or capacitors. Many of these devices can source huge currents, often 10's or 100's of amps. If the Reference 3000 chassis is earth grounded and another location in the stack is accidentally (or intentionally) connected to earth ground, a portion of the stack is shorted through the Reference 3000's cell cable. Very large current flow when this occurs. Fuses in the cell cable will open up to prevent damage to the instrument. When this happens, the failed fuses must be replaced before the instrument can be used again. The fuses in the cell cable are not essential for operator safety. A section in Chapter 5 describes the fuses and their replacement in detail.

NOTE

The fuses in the Reference 3000 cell cable do not protect against a safety hazard. They are needed to prevent damage to the instrument if it is improperly connected.

Temperature and Ventilation

Your Reference 3000 Potentiostat/Galvanostat/ZRA was designed for indoor use at ambient temperatures between 0°C and 45°C.

The Reference 3000 uses forced air-cooling to keep the components within the Reference 3000 within their recommended operating temperature range. Three fans on the rear panel of the Reference 3000 draw air into the chassis. The air exits from slots located on the sides of the chassis near the front panel.

CAUTION

Do not block the airflow into or out of the Reference 3000 chassis. While the circuitry should shut down before it is damaged from excessive heat, the Reference 3000 enclosure may become uncomfortably hot to the touch if insufficient air flows through the chassis. Running the Reference 3000 without adequate cooling could shorten the time to failure of some of the circuitry.

Be careful when operating the Reference 3000 in an enclosed space (such as an enclosed relay rack or NEMA enclosure). The temperature within the enclosure must not exceed 45°C. You may need to provide ventilation holes or even forced air-cooling for the enclosed space if you determine that there is an excessive temperature rise within the space.

Defects and Abnormal Stresses

You should treat your Reference 3000 as potentially hazardous if any of the following is true of the unit:

- it shows visible damage,
- it does not operate properly,
- it has been stored for a long period of time under unfavorable conditions,
- it has been dropped or subjected to severe transport stress,
- it has been subjected to environmental stress (corrosive atmosphere, fire, etc.).

Do not use your Reference 3000 or any other apparatus if you think it could be hazardous. Have it checked by qualified service personnel.

Environmental Limits

Note that there are environmental limit conditions on the storage, shipping and operation of this equipment. The Reference 3000 has not been designed for outdoor use.

Storage

Ambient Temperature	-40 °C to 75 °C
Relative Humidity	Maximum 90% non-condensing

Shipping

Same as storage plus	
Acceleration	Maximum 30 G

Operation

Ambient Temperature	0 °C to 45 °C
Relative Humidity	Maximum 90% non-condensing

WARNING

The Reference 3000 is not designed for operation in conditions where liquid water may enter the chassis, or water vapor may condense within the chassis. Operation of a Reference 3000 that has water within the chassis can create a safety hazard, which in extreme cases could result in personal injury.

Cleaning

Disconnect the Reference 3000 from all power sources prior to cleaning.

Use a cloth lightly dampened with either clean water or water containing a mild detergent to clean the outside of the Reference 3000 enclosure. Alternatively, you can use isopropyl alcohol. Do not use a wet rag or allow fluid to enter the Reference 3000 enclosure. Do not immerse the Reference 3000 in any type of cleaning fluid (including water). Do not use any abrasive cleaners.

Service

Your Reference 3000 Potentiostat/Galvanostat/ZRA has no user serviceable parts inside. You should refer all service to a qualified service technician.

WARNING

The Reference 3000 must not be operated with any cover or panel on the chassis open. Dangerous voltages may present at several points within the Reference 3000 chassis, including PC board traces. Always remove the power connection before opening the Reference 3000 case.

RFI Warning

Your Reference 3000 Potentiostat/Galvanostat/ZRA generates, uses, and can radiate radio frequency energy. The radiated levels are low enough that the Reference 3000 should not create an interference problem in most industrial laboratory environments.

The Reference 3000 has been tested for both radiated and conducted RF interference and has been found to be in compliance with FCC Part 18 and EN 61326:1998—*Electrical equipment for measurement, control, and laboratory use— EMC Requirements.*

Electrical Transient Sensitivity

Your Reference 3000 Potentiostat/Galvanostat/ZRA was designed to offer reasonable immunity from electrical transients, including transients on the incoming AC Mains supply and Electrostatic Discharge. It has been tested for compliance with EN 61326:1998—*Electrical equipment for measurement, control, and laboratory use— EMC Requirements* describing acceptable limits for Electrical Transient susceptibility in Laboratory Test equipment. The Reference 3000 is not rated for continuous use when subject to ESD events. It should suffer no permanent damage when subject to the standard ESD events defined in EN61326, but may cease normal operation until it is powered down and restarted.

In severe cases, the Reference 3000 could malfunction as a result of electrical transients such as a static discharge. If you are having problems in this regard, the following steps may help:

If the problem is static electricity (sparks are apparent when you touch the Reference 3000 or it's cables):

- Placing your Reference 3000 on a static control work surface may help. Static control work surfaces are now generally available from computer supply houses and electronics tool suppliers. An antistatic floor mat may also help, particularly if a carpet is involved in generating the static electricity.
- Air ionizers or even simple air humidifiers can reduce the voltage available in static discharges.

If the problem is AC power line transients (often from large electrical motors near the Reference 3000):

- Try plugging your Reference 3000 into a different AC power branch circuit.
- Plug your Reference into a power line surge suppressor. Inexpensive surge suppressors designed for use with computer equipment are now generally available.

Contact Gamry Instruments, Inc. if these measures do not solve the problem.

CE Compliance

The European Community has instituted standards limiting radio frequency interference emitted by electronic devices, setting limits for susceptibility of apparatus to RF energy and transient events, and mandating safety requirements. Gamry Instruments, Inc. has designed and tested the Reference 3000 to comply with these standards.

The relevant CE regulations include EN 61010 and EN 61326.

RoHS Compliance

The Reference 3000 has been built using lead free components and lead free solder. It is in compliance with the European RoHS initiative.

Chapter 2 -- Introduction

About this Manual

This manual covers the installation, safety, and use of the Gamry Instruments Reference 3000 Potentiostat/Galvanostat/ZRA. It also includes information about the Reference 3000's AE Auxiliary Electrometer option.

This manual describes use of a Reference 3000 with Revision 5.55 (and later revisions) of the Gamry Framework software. It is equally useful when setting up a newly purchased potentiostat or modifying the setup of an older potentiostat for use with new software.

Chapter 1 was an in-depth discussion of safety issues. This chapter describes this manual and gives a brief overview of the Reference 3000 features. Chapter 3 is a description of the electronics circuitry in the Reference 3000. Chapter 4 contains Reference 3000 installation instructions. Chapter 5 describes cell cable connections and Chapter 6 describes the Reference 3000's Front and Rear Panels. Chapter 7 discusses the AE Auxiliary Electrometers option. Chapter 8 covers the difficult issues of potentiostat stability and approaches to prevent oscillation. Chapter 9 discusses the realities of low current, high impedance measurements while Chapter 10 does the same for low impedance EIS.

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

This manual does not discuss software installation or software operation in any detail.

Software support for the Reference 3000 is described in the Gamry's On-line Help system.

All the Gamry Instruments' applications running under the Gamry Framework, control the Reference 3000 via a PSTAT object. See the Framework's On-line Help for information concerning PSTAT objects and their functions.

About the Reference 3000

The Reference 3000 Potentiostat is a research grade electrochemical instrument packaged in a small, easy to handle case. It is the larger, higher current brother of Gamry's extremely popular Reference 600 Potentiostat. It is especially useful when currents higher than the 600 mA current limit of the Reference 600 are required.

Typical applications for the Reference 3000 include research regarding batteries, fuel cells and super-capacitors. It should also prove useful in studies involving electrochemical synthesis, electroplating and corrosion. While it can apply and measure ampere level currents, it is also an excellent small signal potentiostat that can work with picoamp and sometimes even femtoamp current levels.

The Reference 3000 offers measurement capabilities similar to instruments many times larger in size, weight and price. The Reference 3000 can operate as a potentiostat, a galvanostat, or a ZRA (zero resistance ammeter). A new stack mode allows precision control and/or measurement of battery stack voltages as large as ± 36 volts.

The Reference 3000 offers two different compliance voltage and compliance current settings. A user can choose to operate the Reference 3000 set for compliance of ± 1.5 Amperes and voltages up to ± 30 Volts or he/she can chose to operate at ± 3 Amperes and voltages up to ± 15 Volts. This setting cannot be changed in the middle of an experimental run.

Reference 3000 features include:

- 11 decade current auto-ranging,
- electrical isolation from earth ground,
- switchable compliance current and compliance voltage settings,
- current interrupt iR compensation, and
- both analog and digital filtering.

A sine wave generator on the Reference 3000 allows its use for impedance measurements at frequencies up to 1 MHz. Data can be acquired at frequencies up to 300,000 points per second, allowing Cyclic Voltammetry at scan rates of 1500 V/sec with 5 mV per point resolution.

A unique DSP (Digital Signal Processing) data acquisition mode allows the Reference 3000 to reject noise, from the instrument itself, from the electrochemical cell, and from the lab environment. In many cases where other instruments require a cell in a Faraday shield to make quiet measurements, the Reference 3000 can be used with the cell exposed on a bench top.

The Reference 3000 offers an unprecedented combination of high speed, high sensitivity, and low noise. State-of-the-art analog components were used throughout the design. In all design decisions, performance weighed more heavily than product cost.

The Reference 3000, like all Gamry potentiostats, requires a computer for its use. Unlike most of Gamry's older potentiostats, the Reference 3000 interfaces to the computer through a USB connection. The USB connection has become truly universal, with USB ports found on all modern computers. Gamry's software currently supports up to 16 Reference 3000 Potentiostats connected to one computer.

The Reference 3000 is isolated from earth ground. It can therefore be used to make measurements on cells that contain an earth grounded metal. A few of examples of such systems include are autoclaves, large metal storage tanks, stress apparatus, and capillary electrophoresis detectors.

About the Auxiliary Electrometer Option

The Reference 3000 Potentiostat can be equipped with a unique Auxiliary Electrometer option. This factory installed option is especially useful when you need to measure the performance of individual cells in a multi-cell fuel cell or battery stack.

Up to eight completely independent voltages can be measured using this option. The measurements are fully differential, so cell voltages at any point in a stack can be measured. Each input can measure a ±5 volt signal superimposed on a common mode voltage that can be as large as ± 36 volts! The input impedance is greater than $10^{11}\ \Omega$, so the inputs can even be connected to small diameter Lugin probes.

This option can be used to simultaneously measure electrochemical impedance on up to eight cells in a cell stack. This is often of great interest since cells in a fuel cell or battery stack are not identical.

The AE is not restricted to energy conversion and storage applications. The electrometer inputs can measure virtually any voltage. You can measure voltages from temperature, pressure or strain transducers or voltages of multiple reference electrodes in a cell.

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: “C:\MYGAMRYDATA\CV.DTA" and “GAMRY5.INI".

Chapter 3 -- Instrument Circuitry

Reference 3000 Schematic/Block Diagrams

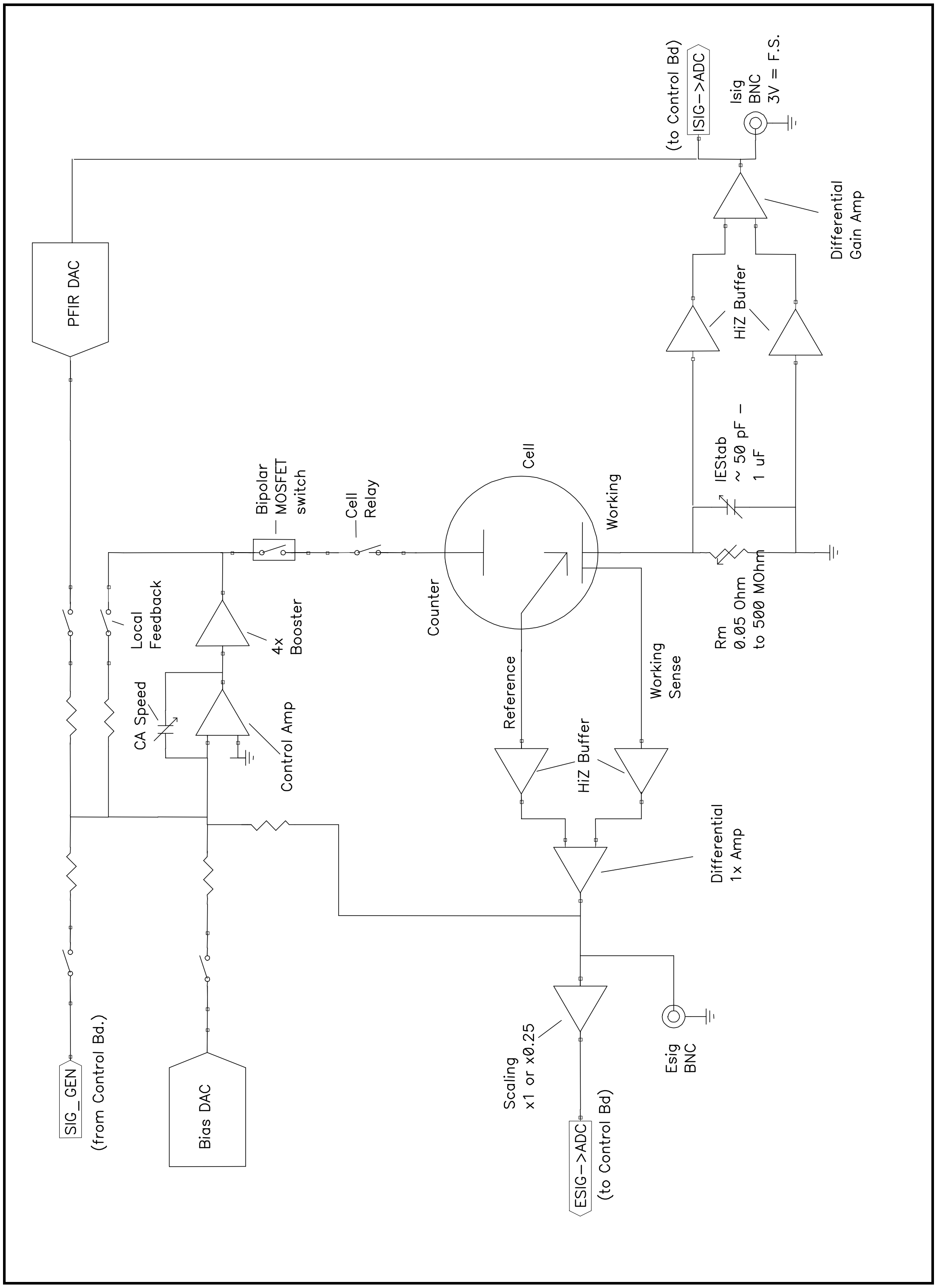
If you are not familiar with electronic schematics or potentiostats, you probably want to skip this chapter. This information is for expert use only and is not required for routine use of the Reference 3000.

The following figures are partly schematic diagrams and partly block diagrams. They are intended to show the basic principles of the Reference 3000 circuitry without the confusion of the full circuitry details. The complexity of the Reference 3000 can be quite daunting – the Reference 3000 circuit boards contain more than 3000 components connected by almost 2500 circuit nets!

The schematic/block diagram figures show:

- the potentiostat board and heat sink board in a potentiostatic control mode,
- the control board circuits for signal generation,
- the control board circuits for signal conditioning and A/D conversion,
- the Auxiliary ADC channel input switching,
- the microprocessors in the Reference 3000,
- DC-DC power conversion,
- The optional Multi Channel (MCE) circuitry.

Figure 3-1
Reference 3000 Potentiostat Board in Potentiostat Mode
Simplified Schematic/Block Diagram



Notes for Figure 3-1

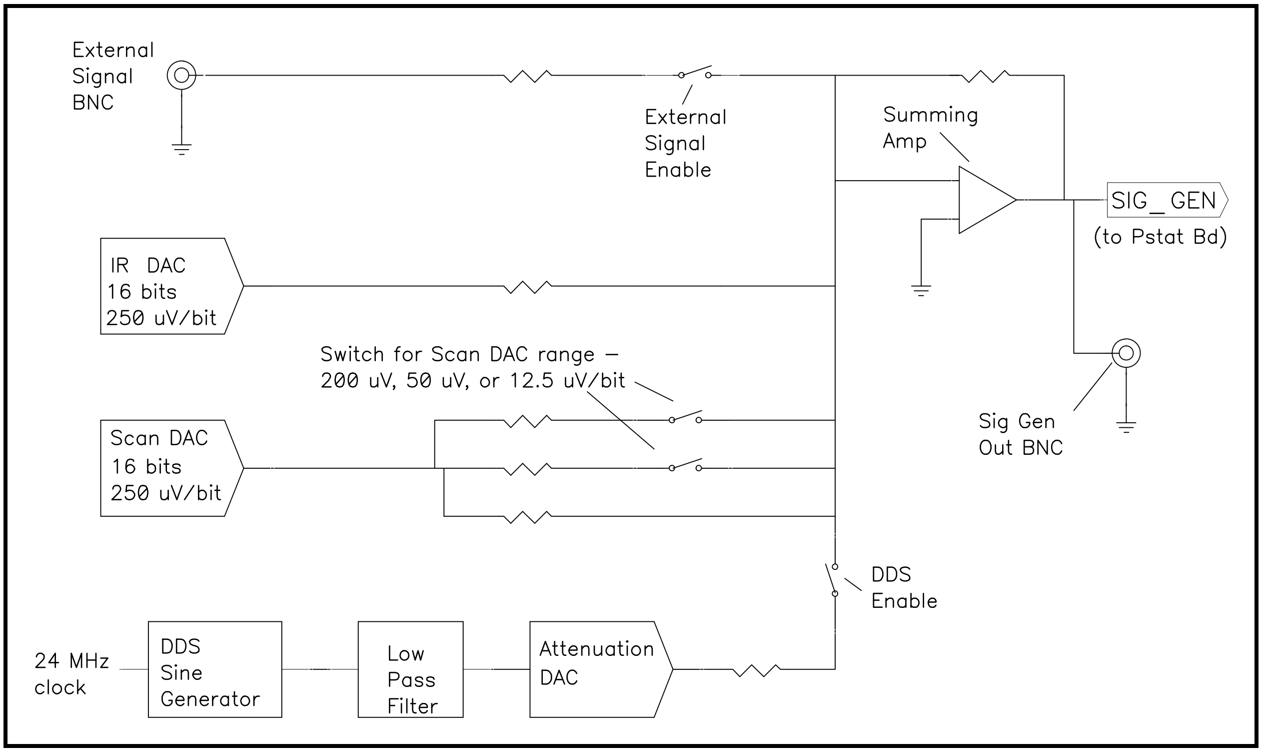
- The 4x booster following the Control Amp can operate with two combinations of compliance current and compliance voltage. One is ± 1.5 amps at ± 30 volts, the other is ± 3 amps at ± 15 volts.
- Only Potentiostat Mode circuitry is shown in this figure. In this mode the voltage difference between the Reference and Working Sense leads (called Esig) is feedback into the control amplifier.

  In Galvanostat Mode, the feedback is from Isig.

  In the ZRA and stack modes, the feedback is from a differential amplifier measuring the difference between the Counter Sense and Working Sense leads of the cell cable. The counter sense circuitry is not shown. It is conceptually similar to the voltage sensing circuit that generates Esig, except that it can measure voltage differences as large as ± 36 volts.
- The Bias DAC and PFIR (Positive Feedback IR compensation) DAC are set using a computer bus that is not shown.
- Switches are either reed relays or MOS switches as appropriate. All switches are under computer control (obviously, since the Reference 3000 does not have a knob and dial front panel).
- The variable current measurement resistor, Rm, is one of eleven fixed value resistors selected using relays. The resistor's values vary by decades: 50 mΩ, 500 mΩ, 5Ω, 50 Ω …500 MΩ. The lower value resistors require software gain corrections. Correction values are measured at Gamry's test facility and stored in an EEPROM on the Reference 3000 potentiostat board. Software calibration of the instrument by a customer does <u>not</u> change these Rm gain corrections.
- Other components shown as being variable (IEStab capacitor and CASpeed capacitor) are actually several fixed value components switched into the circuit, not continuously variable .
- The monitor BNC connectors for Isig and Esig are lightly filtered using an RLC circuit.
- The ADC channel for Esig is actually switchable between Esig (the reference voltage minus the working sense voltage) and Zsig (the counter sense voltage minus the working sense voltage). The Zsig connection allows the Reference 3000 to measure the voltage of battery or fuel cell stacks.
- The programmable attenuator on Esig prior to the ADC channel scales the Esig voltage to make it compatible with the A/D channel's ± 3 volt input range. The 0.25 gain setting allows the Reference 3000 to measure potential signals slightly in excess of 10 volts (on a 12 volt full scale range). Isig is gained to be 3 volts full-scale so it does not require a similar attenuation function.
- All the resistors summing voltages into the Control Amplifier input do not have values shown on the diagram – their values depend on scaling factors too complex to discuss in this chapter.
- Calibration components are not shown.
- Gamry's software can disconnect the signal generator from the Potentiostat. Once disconnected it can be used for other experimental control tasks.
- Overload protection and overload detection are not shown. Good engineering practice demands that any possible misconnection of the cell leads will not damage the instrument. This practice has been followed in the Reference 3000 design.

  The overload protection can handle overloads of up to 30 amps for very short times. Fuses in the Working and Counter Sense leads always open up before overload conditions can damage the instrument. Misconnection of a battery, fuel cell, or super-capacitor stack can open the fuse, but will not cause hardware failures.

Figure 3-2
Reference 3000 Signal Generation Circuitry



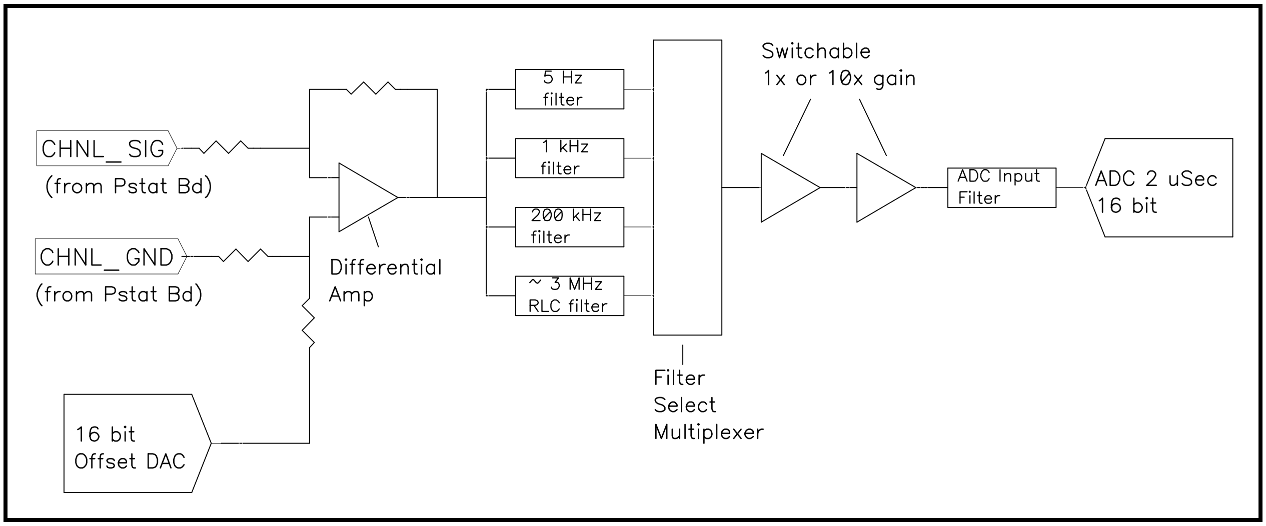
Notes on Figure 3-2:

- All the resistors summing voltages into the Summing Amplifier input do not have values shown on the diagram. Their values depend on scaling factors too complex for this simplified diagram.
- The IR DAC has a ± 8 volt full-scale range.
- Calibration components are not shown.
- The DDS can generate fixed amplitude sine waves with frequencies between 1 MHz and 1 mHz. In practice, Gamry's EIS300 software uses the Scan DAC to generate sine signals if frequency is below 1 Hz.

  The low pass filter removes high frequency distortion in the "raw" DDS output.

  The attenuator scales the DDS. The maximum output signal is 5.979 volts peak-to-peak and the minimum is approximately 11 µV peak-to-peak.
- The BNC connector for Sig Gen out is lightly filtered using an RLC circuit.

Figure 3-3
One A/D Signal Chain in the Reference 3000



Notes for Figure 3-3:

- This diagram shows one of three identical ADC channels. One channel is dedicated to measurement of the potentiostat's current signal, another is used to measure the cell or stack voltage, and the third is switched between a wide selection of possible signals. See Figure 3-4

- All three A/D converters are triggered simultaneously to start a conversion. This trigger and the pulse updating the Scan DAC voltage are under the control of a hardware state-machine. This insures that all waveform and data acquisition timing is tightly controlled and reproducible point-to-point.

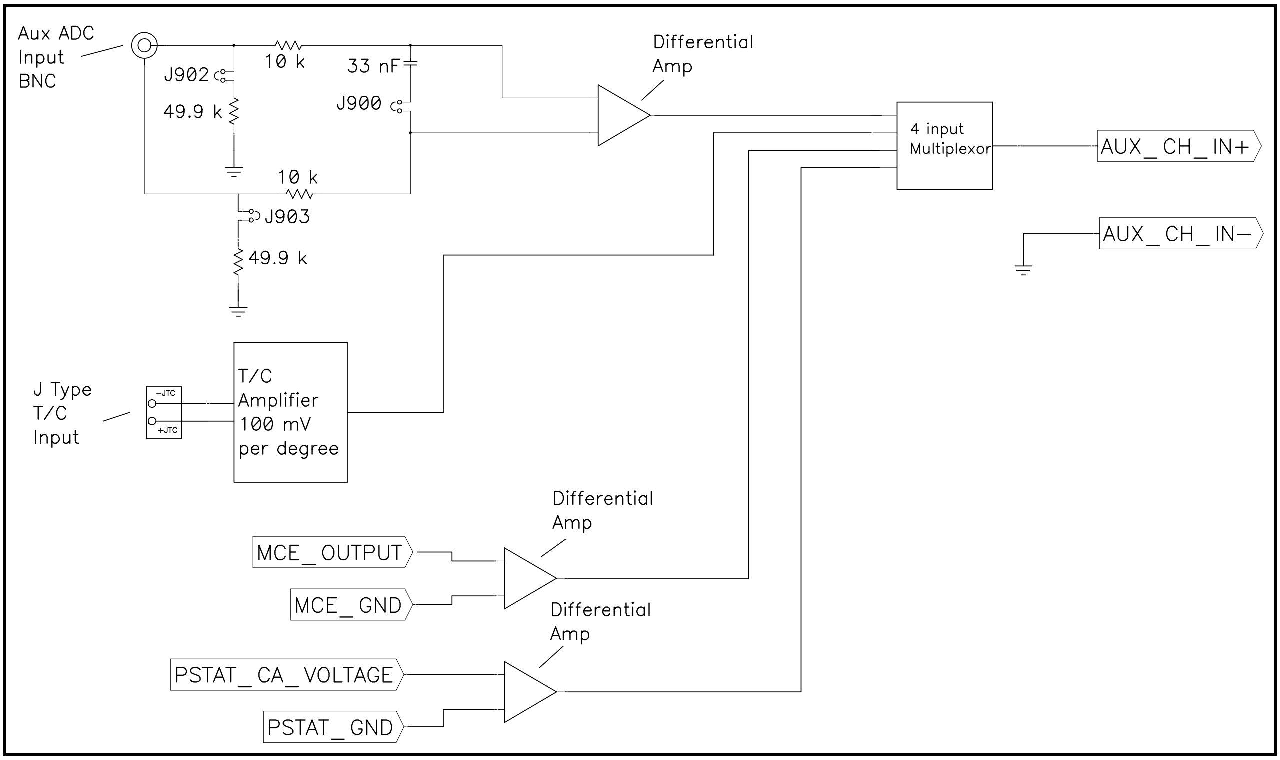
  By default, the data acquisition is synchronized with the 300 kHz power supply switching frequency, to reduce noise due to the power supply. Data acquisition times that are a multiple of 3.333 µSec will maintain this synchronization.

- All analog signals that cross from the Potentiostat Board to the Control Board or vise versa are received differentially as shown here.

- The 5 Hz, 1 kHz, and 200 kHz filters are 2-pole Butterworth filters. The 3 MHz RLC filter has an arbitrary transfer function.

- All signal channel components are selected for optimal DC accuracy, low noise, and high bandwidth.

Figure 3-4
Aux Channel Input Switching

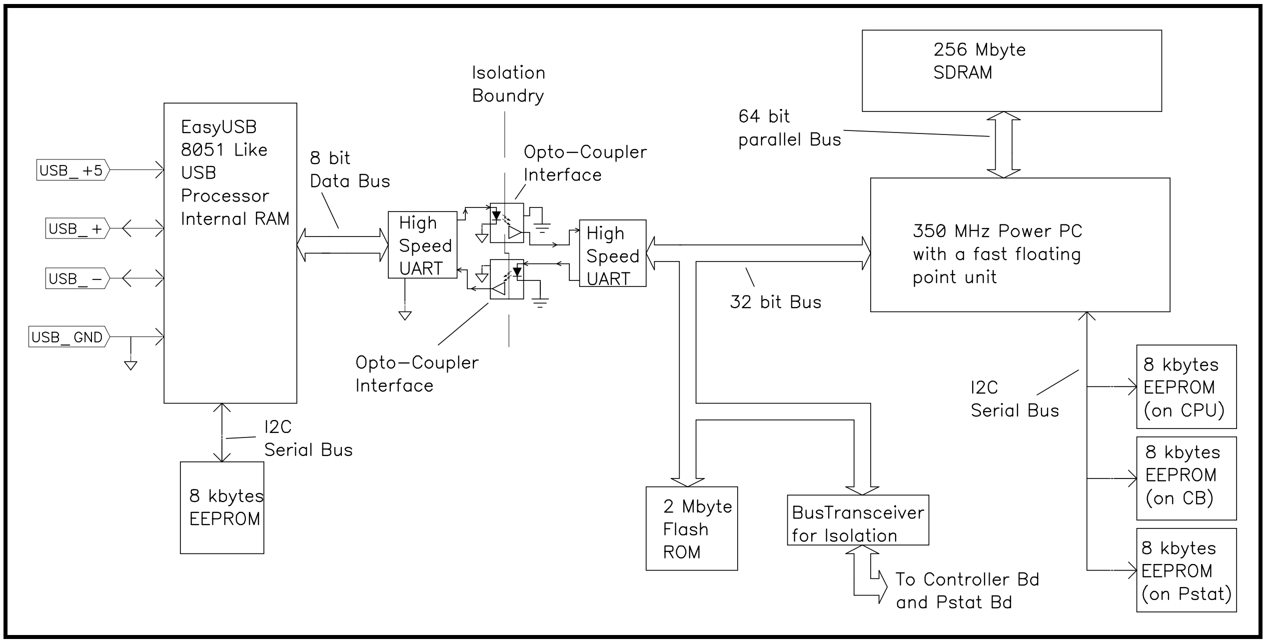


Notes for Figure 3-4:

- Two ADC Channels are dedicated to the potentiostat's voltage and current signals. This diagram shows the signals that can be connected to the third channel.
- The Aux ADC BNC input is a differential input. Some of this input's characteristics can be changed by either jumpers or CMOS switches. Early Reference 3000's use jumpers to change the characteristics, while later units (shipped after the middle of 2009) will use CMOS switches under software control to change the characteristics. Contact Technical Support at Gamry.com if you are uncertain which type of unit you have.

  Jumper configured Reference 3000's are shipped configured for input impedance of 100 kΩ and unfiltered operation. The jumpers shown in this diagram allow it to be configured for high input impedance and/or input filtering.
- The thermocouple input allows for connection of a K Type thermocouple. Note that this circuit must be calibrated to obtain reasonable accuracy. A section of the Reference 3000 calibration procedure allows for user calibration of this input.
- The other two inputs to the Aux channel can be used to measure the AE (Auxiliary Electrometer) signal or a Control Amp voltage signal.

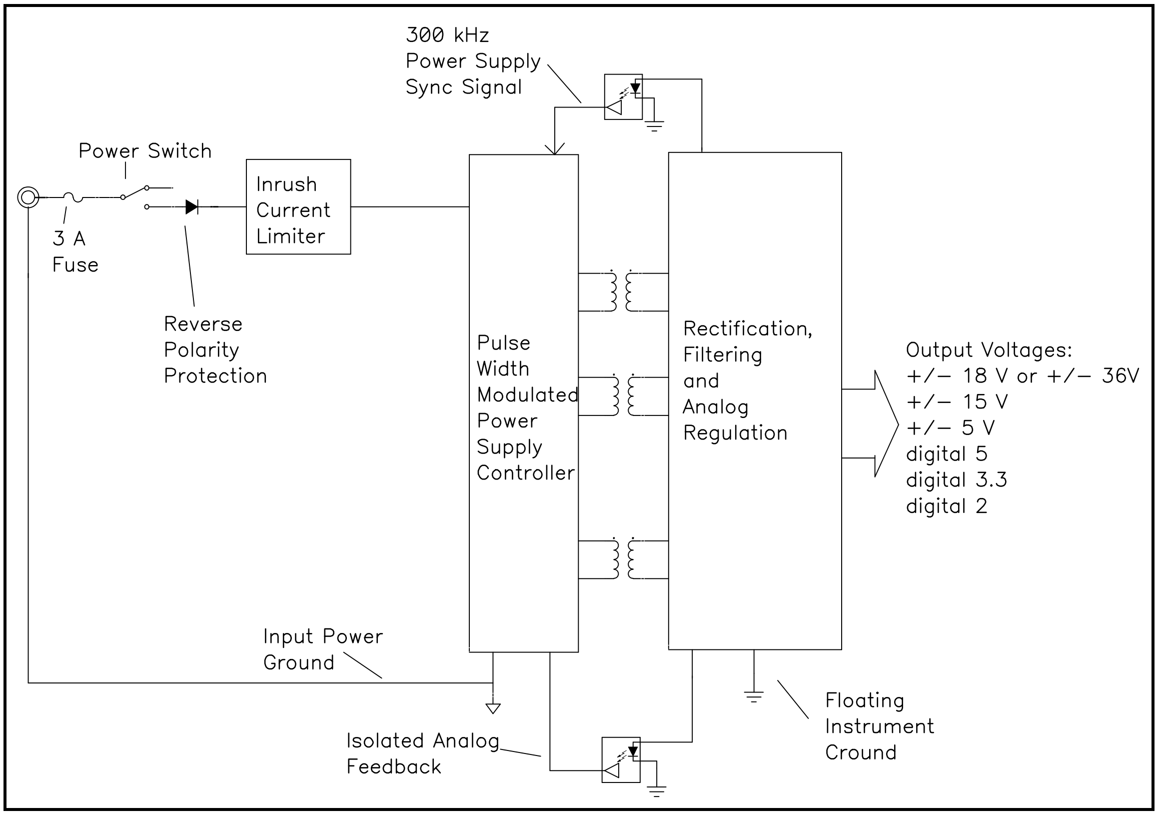
Figure 3-5
Microprocessors in the Reference 3000



Notes for Figure 3-5:

- Note the lack of a ground connection between the USB bus and the Reference 3000 circuitry.
- The EasyUSB firmware is loaded into EasyUSB RAM on power-up. The USB firmware can be updated over the USB via a selection in the Reference 3000 section in the Windows Device Manager.
- The Power PC firmware is also transferred from ROM into RAM on power-up. The Power PC firmware can also be updated over the USB via a selection in the Reference 3000 section of the Windows Device Manager. Time critical sections of the Power PC code are kept in the processor's fast cache memory.
- The term UART refers to a Universal Asynchronous Receiver Transmitter. It converts parallel data to a self-clocking serial bit stream. The UARTs send data at 6 Mbits/second.
- The Bus Transceiver isolates bus activity on the Controller and Potentiostat boards. Only reads and write to locations on these boards generate bus activity. This reduces noise pick-up.
- Each board in a Reference 3000 has local non-volatile data storage. This is used to save calibration data and board revision information. Unlike previous Gamry Instruments Potentiostats, the Reference 3000 calibration data stored in the instrument, not in a data file. When a Reference 3000 is moved from one computer to another, its calibration remains valid.

Figure 3-6
DC-DC Power Conversion



Notes for Figure 3-6:

- Note the ground isolation between the input power and the Reference 3000 circuitry. The Reference 3000 chassis is connected to the Floating Instrument Ground. Transformers and isolators are the only components connected between the grounds.
- The 300 kHz power supply sync signal is derived from the same clock used to control data acquisition. Data points taken at an integer multiple of 3.333 µSec/point will be synchronized with the power supply, minimizing the effect of power supply noise on the data.
- Additional circuitry that is not shown protects the Reference 3000 against ESD (electrostatic discharge) and electrical surges. Not that the Reference 3000 is also protected against damage if an incorrect polarity power input is connected to the unit.
- The incoming DC voltage must be between 22 and 26 volts. With inputs below 22 volts, the PWM (Pulse Width Modulator) may be unable to regulate the supply. Above 26 volts, the PWM may not start-up.

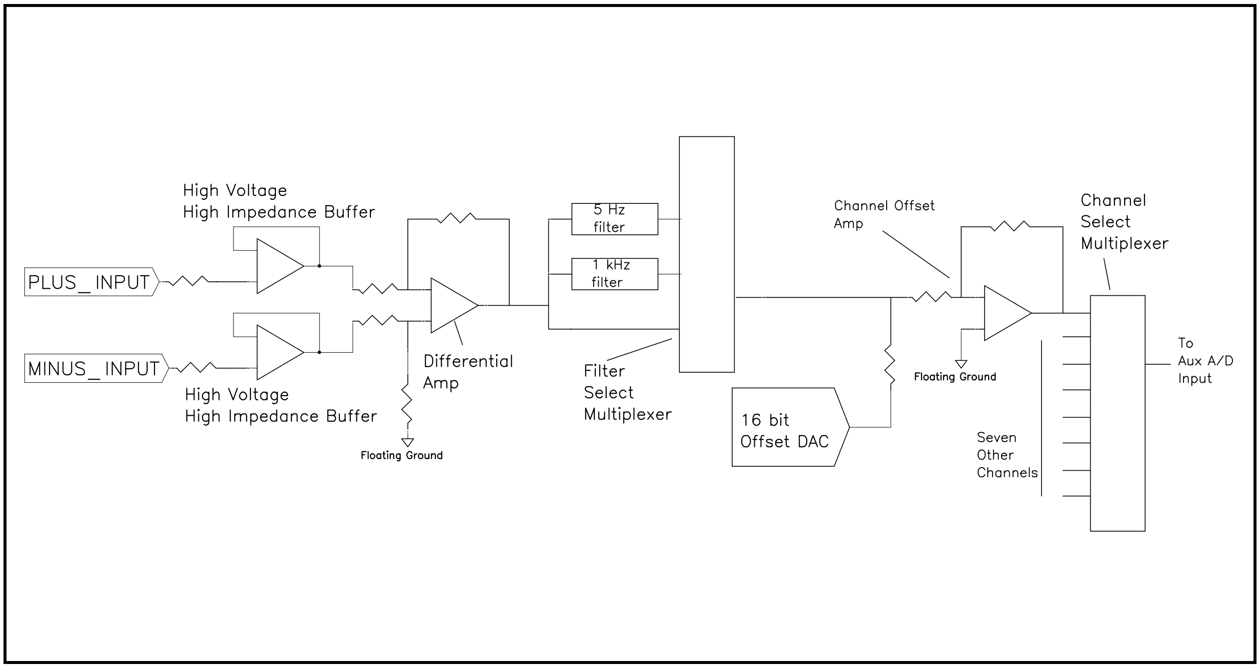
WARNING

Do not use a DC power source other than the AC adapter model provided with your Reference 3000. Other replacements may void the performance and/or safety characteristics of the Reference 3000.

CAUTION

Power input voltages less than 20 volts or greater than 26 volts can damage the Reference 3000's power supply.

Figure 3-7
One AE Channel



Notes for Figure 3-7:

- One of eight identical channels is shown
- The input buffers work over the entire Reference 3000 compliance voltage range.
- The maximum useable differential voltage between the two inputs on a channel is ± 5 volts.
- Each channel has its own filtering. The Aux A/D Channel filter is not useful for switched inputs.
- The x10 and x100 gains in the Aux A/D channel can be used to improve A/D resolution.
- The inputs have an input impedance of greater than 10^{11} Ohms as long as the product is powered.
- The inputs will not be damaged by connection to voltages as large as ± 36 volts versus the Reference 3000's ground, regardless of the compliance voltage setting. This is true even when the Reference 3000 is not powered up. They cannot measure voltages larger than the compliance voltage.

Chapter 4 -- Installation

This chapter of the Gamry Instruments Inc. Reference 3000 Operator's Manual covers normal installation of the Reference 3000. We assume the Reference 3000 is installed as part of a Gamry Framework based electrochemical measurement system containing a Microsoft Windows™ compatible computer.

Figure 4 - 1
Front View of a Reference 3000 without AE Option

Initial Visual Inspection

After you remove your Reference 3000 from its shipping carton, you should check it for any signs of shipping damage. If any damage is noted, please notify Gamry Instruments, Inc. and the shipping carrier immediately. Save the shipping container for possible inspection by the carrier.

WARNING

The "reinforced insulation" that keeps the operator from accessing the "hazardous live" voltages in the Reference 3000 can be rendered ineffective if the Reference 3000 is damaged in shipment. See Chapter 1 for more details. Do not operate damaged apparatus until a qualified service technician has verified its safety. Tag a damaged Reference 3000 to indicate that it could be a safety hazard.

WARNING

If the Reference 3000 is taken from a cold location (for example outdoors in winter conditions) to a warm humid location, water vapor could condense on the cold surfaces inside the Reference 3000, possibly creating a hazardous condition. The "reinforced insulation" that keeps the operator from accessing the "hazardous live" voltages in the Reference 3000 can be rendered ineffective if the Reference 3000 has condensed water inside its case. Before connecting power to a "cold" Reference 3000, allow at least two hours for the Reference 3000 to warm at room temperature.

Physical Location

You normally locate your Reference 3000 on a flat workbench surface. You will want to have access to the rear of the instrument because some cable connections are made from the rear. The Reference 3000 is generally operated in an up-right position (see Figure 4-1). Operation in other positions is possible as long as you insure that air movement through the chassis is not restricted.

CAUTION

Do not block the airflow into or out of the Reference 3000 chassis. While the circuitry should shut down if subjected to excessive heat, the Reference 3000 enclosure may become uncomfortably hot to the touch if no air flows through the chassis. Running the Reference 3000 without adequate cooling could shorten the time-to-failure of some of the circuitry.

If you do place your Reference 3000 within an enclosed space, make sure that the internal temperature within that space does not exceed the 45°C ambient temperature limit of the Reference 3000. Be particularly careful if a computer or other heat dissipating equipment is mounted in the same enclosure as the Reference 3000.

The Reference 3000 has not been designed for outdoor use.

Computer Requirements

Before you connect a Reference 3000 to a computer you must make sure that your computer meets these simple requirements.

- One of the following Operating Systems: Windows XP™ Service Pack 2 or higher, Windows Vista™ 32- or 64-bit, or Windows 7™32- or 64-bit.
- A USB port that supports high speed (480 Mbits/second) USB 2.0 transfers.

Gamry's Windows-based application software packages may impose additional, more stringent requirements. See the software documentation or contact a Gamry representative for details.

Plug & Play System Configuration

The Reference 3000 is completely compatible with the Windows Plug & Play configuration system. Like most Plug & Play hardware, it is best if you install the software for the Reference 3000 before you install the potentiostat hardware.

A Setup program should 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.

Figure 4 - 2
Rear Panel of the Reference 3000

Power Cord and Power Connection

The Reference 3000 does not plug directly in the AC mains supply. Instead, the mains are connected to an external power supply, which supplies a regulated 24-volt DC output. This regulated DC is then connected to the DC power input jack on the rear of the Reference 3000 (see Figure 4 - 2).

The external power supply provided with the Reference 3000 is rated for operation from 100 to 240 Vac, at frequencies from 47 to 63 Hz. It should be useable worldwide.

CAUTION

If you facility owns both Reference 600's and Reference 3000's, you must insure that the smaller power adapter from the Reference 600 is not used to power a Reference 3000. The Reference 3000 will not power up with the smaller adapter. Fortunately, neither the Reference 3000 nor the small power adapter will be damaged if connected in error.

The power adapter for the Reference 3000 is almost 22 cm long. All dimensions on the Reference 600 power adapter are below 11 cm.

The Reference 3000 external supply is supplied with a line cord suitable for use in the United States. In other countries, you may have to replace the line cord with one suitable for your electrical outlet type. You must always use a line cord with a CEE 22 Standard V female connector on the apparatus end of the cable. This is the same connector used on the US standard line cord supplied with your Reference 3000. See Chapter 1 for specific safety information regarding line cord selection.

Power Up Test

Before you make any other connections to your Reference 3000 you should check that the Reference 3000 is at least nominally functional.

One quick test is to power up the Reference 3000 and watch the blue power LED indicator on the front panel of the Reference 3000 (see Figure 4 - 1). After connecting DC power to the Reference 3000, turn on its rear panel Power switch (see Figure 4 - 2). The Power LED should go on for a second or so, flash three times, then remain on.

The status of the other LED indicators is not important at this time.

Each flash of the power LED flashes corresponds to successful conclusion of one portion of the Power PC's power-up self-test.

If the power LED goes on, then turns off and stays off, the Reference 3000 is not working properly! Contact Gamry Instruments or your local Gamry Instruments representative as soon as possible if this power up test fails.

USB Cabling

The Reference 3000 connects to the computer using a standard High Speed USB A/B cable. A suitable cable was shipped with your Reference 3000. If this cable has been lost, you can get a replacement at almost any computer retailer. The replacement cable should be rated for USB 2.0 high speed USB operation.

An A/B USB cable has different connectors on each end. The end with a wider, rectangular shaped connector plugs into a USB port on your computer (or a similar port on a USB hub). The end with a nearly square connector plugs into the USB port on the Reference 3000 (see Figure 4 - 2).

The USB connection can be "hot-plugged". This means, both the computer and the Reference 3000 can be powered-up before the USB cable is plugged in. Unlike many other instrument system connections, you need not power down the system before plugging in the USB.

You can also safely remove the USB cable without powering down the Reference 3000 and your computer. Be aware however, that this may have undesirable consequences if the system is currently taking data or performing an electrochemical experiment.

Front Panel USB LED

The front panel USB LED provides a simple test of two aspects of normal Reference 3000 USB operation. It has three normal states:

- Unlighted - indicating that the USB cable is disconnected or the USB connection is disabled by the host computer,
- Solid Green- indicating that a valid cable connection has been made and the Reference 3000 USB processor is receiving power from the USB cable,
- Flashing Yellow - indicating that valid USB messages are being transferred between the computer and the Reference 3000.

The flashing state will only be seen when Gamry Instruments application software is running.

One additional USB LED indication is possible. A solid red indication occurs during a firmware update. The firmware update process is described later in this chapter.

1st Time Device Installation in Windows

When a Reference 3000 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 may be "New device found" or "Unknown USB device Detected".

When this occurs after you've connected a Reference 3000, select Ok to tell Windows that you would like to install the new device.

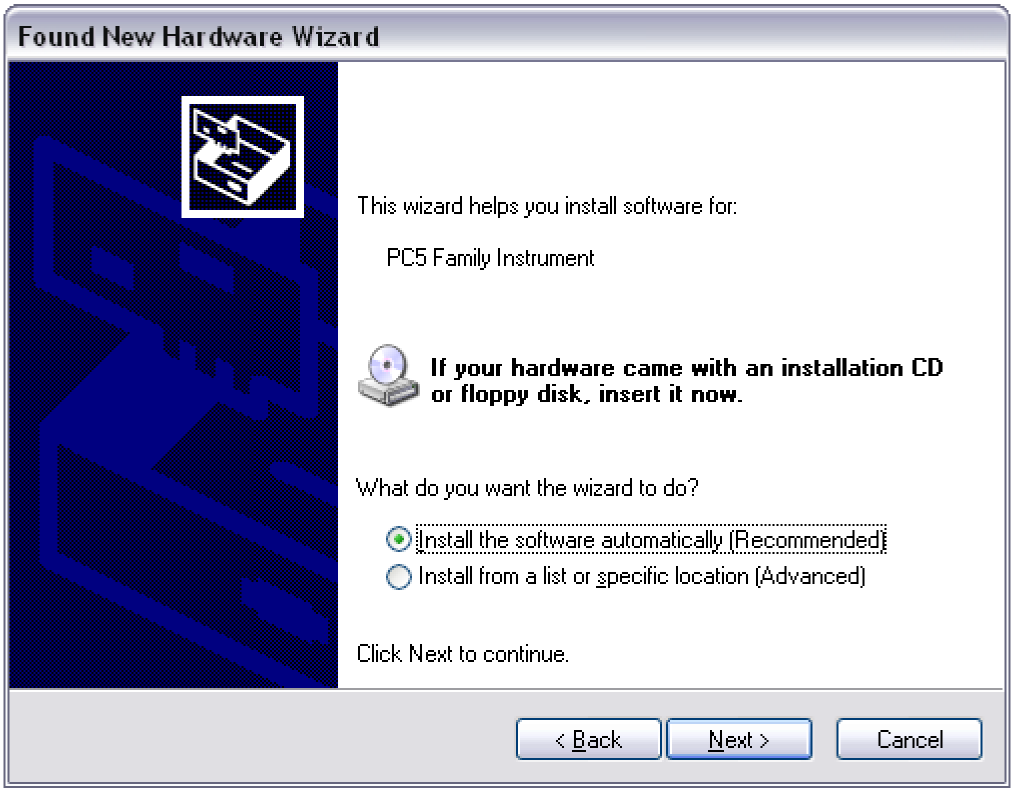
You should see a screen that looks something like this:

Figure 4 - 3
Welcome to the Found New Hardware Wizard

As shown in this Figure, do not choose to let Windows Update find the device driver that you need. The Windows Update web site has no knowledge of the Gamry Instruments Reference 3000.

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

Figure 4-4
Install the Software Automatically



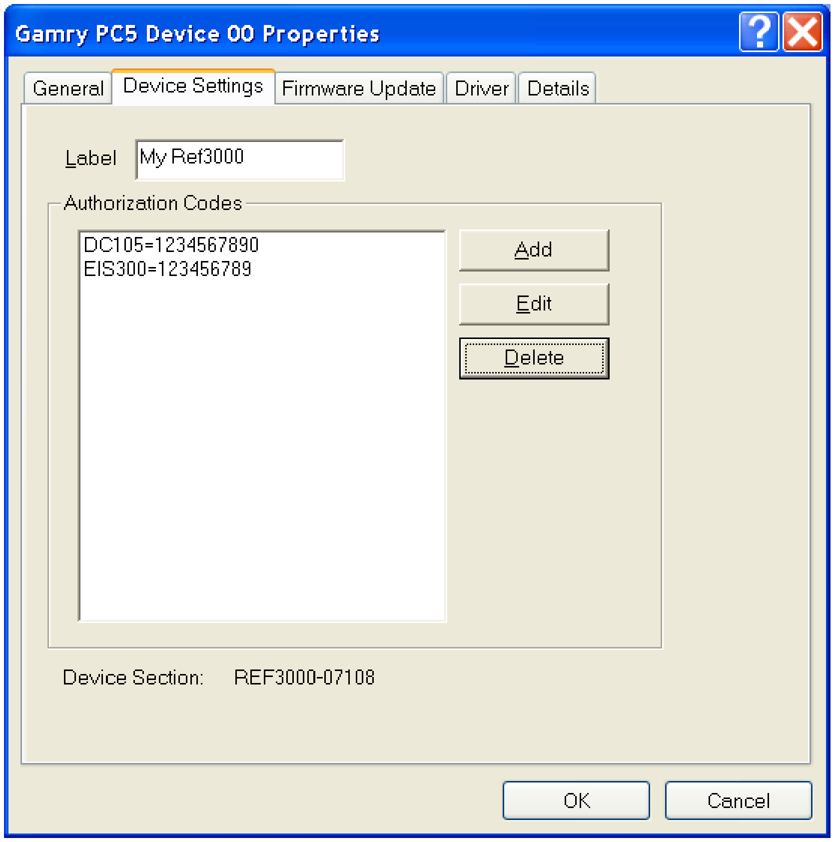
If you have already installed the Gamry Framework software, you can select **Install the software automatically** then select **Next**.

If you have not installed the Framework yet, find your Gamry Instruments software CD (or DVD), insert it in your computers CD (or DVD) drive, select **Install the software automatically**, then select **Next**.

The Windows Device Manger will install the required files from your hard drive or from the CD.

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

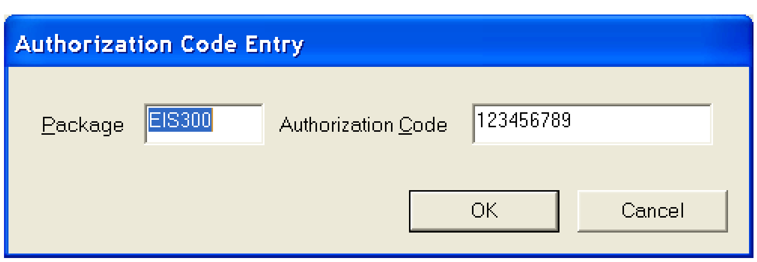
Figure 4-5
Enter New Device Information



As displayed in Figure 4-5, you enter a friendly name for your Reference 3000, 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 Reference 3000. 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 **Add** button. A dialog box will appear as shown in Figure 4-6. You enter the package name, like "EIS300", followed by the 10-digit authorization code.

Figure 4-6
Enter an Authorization Code



Press **OK** when you are finished.

If you need to connect the Reference 3000 to a different USB port, you must repeat the "Found New Hardware" procedure discussed above. Once the Reference 3000 has been connected to a port, removing it and reconnecting to that port should not re-trigger the "Found New Hardware" process.

MultEchem Multichannel Potentiostat Systems

Gamry's current Framework software (Revision 5.61) allows a computer to operate up to 16 Gamry Instruments potentiostats simultaneously. The 16 potentiostats can include both Reference 600's and Reference 3000's and also older PCI4 family devices.

A system with multiple Reference 3000s just needs them all plugged into the computer. We do not recommend using bus-powered hubs to expand your USB network. Externally powered USB hubs are commonly available.

Contact our home office or your local Gamry Instruments representative if you need assistance configuring a system containing both Reference 3000 and PC4 family hardware.

Cell Cable Installation

The Cell Connectors are two 15-pin D-connectors on the front of the Reference 3000 (see Figure 4 - 1).

The upper (female) connector is labeled Counter/Working. It carries the cell current between the Counter electrode wire and the Working electrode wires.

The lower male connector is labeled Sense Inputs. It contains only high impedance inputs used to sense potentials in the cell.

Gamry's standard cell cables always come in pairs. Each cable has a D-connector on one end and a number of leads to connect to electrodes in an electrochemical cell. The D-connector end of the cable is connected to the appropriate D-Connector on the front of the Reference 3000. The male and female cables cannot be interchanged.

Each cable has knurled screws that hold the cable in place. Gamry recommends that you always use these screws, since loss of a cable in the middle of an experiment can be catastrophic.

A wide variety of cell cables are available for the Reference 3000. These include:

- short cables designed for maximum AC performance,
- longer cables in various lengths, and

The Reference 3000 can automatically detect which Gamry Instruments cable is connected and the Gamry Framework software can then adjust the system performance for the characteristics of that cable.

Device Manager

If you wish to make changes to the configuration of your Reference 3000 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 specific information.

In the case of 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 4-7
Device Manager Window

You can now right click on any of the **Devices** listed under Gamry Instruments and select **Properties** to look at or change its configuration. The Reference 3000 is a PC5 Family device.

Authorization Codes and Label

If you purchase additional Gamry application software, you 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 make changes with the Device Manager. 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 4-5:

Firmware Update

Your Reference 3000 was shipped with the latest version of its firmware. From time to time, Gamry may make changes in the instrument code. You must perform a firmware update to load the new code into your Reference 3000.

Different revisions of Gamry's Framework software generally require different firmware revisions. You will get a "Version Mismatch" error if the Framework and firmware do not have compatible revisions.

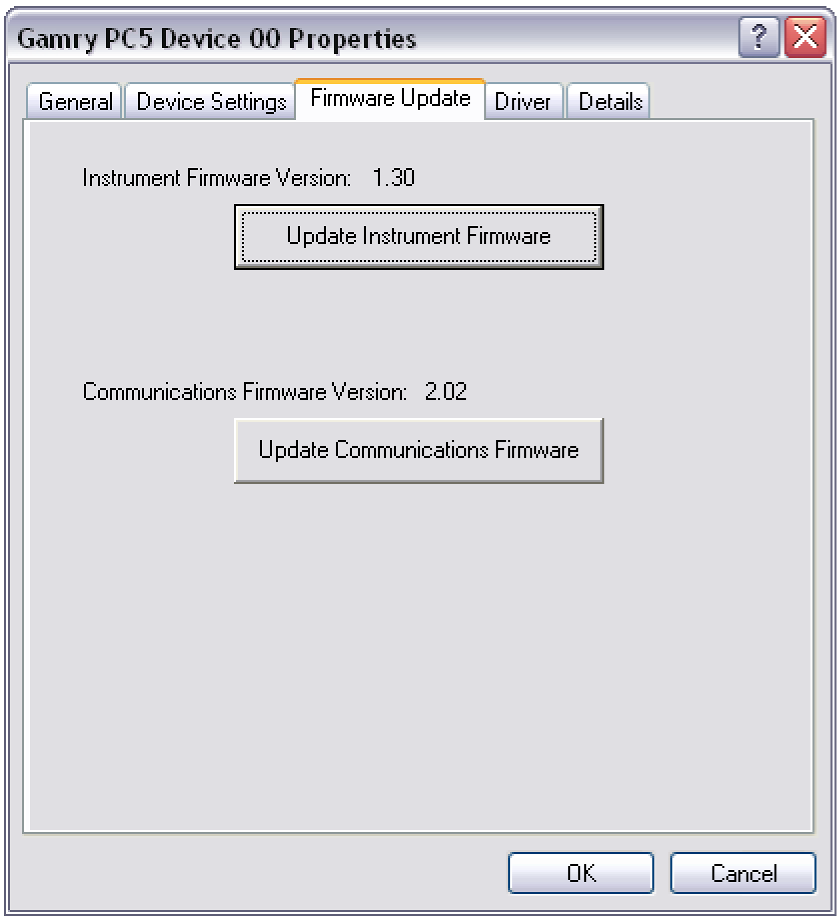
There are two separate code images (firmware files) that can be field updated on your Reference 3000. The first is the Instrument Code. This is the code that handles most of the functionality of the Reference 3000. The second is the Communications Code. This code handles the USB communications between your Reference 3000 and the host computer.

Appropriate update files (code images) can be obtained from the Gamry Instruments website at www.gamry.com. Download the file containing the new code and save it onto your computer's hard disk.

Alternatively, Gamry's software CD contains a firmware folder that contains firmware files compatible with that CD's Framework revision.

You must close the Gamry Framework Software before updating firmware in your Reference 3000. Once the Framework is closed, you select the appropriate Gamry Device in the Device Manager. Once you have selected your device, right click its entry and select **Properties**. Next, select the **Firmware Update** tab and you will see a screen that looks like Figure 4-8:

Figure 4-8
Firmware Update Tab



Depending upon which code you wish to update, click on either **Update Instrument Firmware**, or **Update Communications Firmware.** You will then be prompted for a file. Navigate to the location firmware file's location (on the Gamry software CD or on your computer's hard drive) and then press **Open**. The update procedure will begin. You should see a status bar that shows the progress of the update. The USB indicator on the Reference 3000 should turn red during the procedure.

Press **OK,** once the update is successful, . Your Reference 3000 is once again ready for use.

Should you encounter a problem updating the firmware in your Reference 3000, immediately contact Gamry Instruments for assistance.

Interrupting a firmware download can cause a catastrophic failure of your system. Do not turn off the Reference 3000, do not unplug the USB cable, and do not stop the host computer operation when the USB LED is a steady red color.

CAUTION

Do not interrupt a firmware download that is in progress. An incomplete download can render a Reference 3000 inoperable until it is returned to Gamry for reprogramming.

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 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.

The calibration for the Reference 3000 has been divided into three sections: DC Calibration, AC Calibration, and Low I DC Cal. All three calibration procedures are accessed via the **Utility** selection on the Framework's **Experiment** pull down menu.

Separate Calibration for Each Reference 3000 Cable Type

The Reference 3000 recognizes the type of cable connected to its cell connectors. It maintains a separate AC calibration table for each type of cable. The Gamry Framework will not let you use AC calibration data recorded using a 60 cm shielded cable for experiments run using a longer cable.

DC and AC Calibration

These two procedures use an external resistive dummy cell.

CAUTION

Reference 3000 calibration calls for an external resistive dummy cell. Your Reference 3000 was shipped with a Universal Dummy Cell 4, which includes a 2 kΩ, 0.02% 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 your Universal Dummy Cell 4, you can perform DC Calibration using a different 2 kΩ resistor. Its wattage is unimportant. Some performance checks in the calibration process may fail if the resistors inaccuracy exceeds 0.2% (4 Ω).

We do not recommend AC Calibration with any resistor other than the one on the Universal Dummy Cell 4. The Universal Dummy Cell 4 was designed to separate the working electrode leads from the counter and reference electrode leads. If you perform AC Calibration without adequate separation between these leads, you will see phase shift in your high frequency EIS data. 1.4 pF of stray capacitance across a 2 kΩ resistor causes a 1° phase shift at 1 MHz.

The resistor used for calibration should be enclosed in a Faraday shield during the calibration process. The Faraday shield should be connected to the black lead on the standard cell cable. A Faraday shield suitable for calibration is included in every Reference 3000 shipment.

Earth grounding the Reference 3000 is also recommended during calibration, but is not essential.

Potentiostat calibration is only required infrequently. You should recalibrate your Reference 3000 under the following circumstances:

- 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 are running the system in a very different environment than what you used when the unit was last calibrated. For example, if the Reference 3000 was calibrated at 15 °C and you are now operating it at 30 °C, you should recalibrate.

Low I Range DC Calibration

The standard Reference 3000 calibration is performed with the cell leads connected to a 2 kΩ resistor. During the calibration procedure, DC current range offsets are recorded with the cell switch turned off. A DC current measurement is made on each of the 11 current ranges in the Reference 3000. The measured current on each range is the sum of current contributions from:

- The input current of the I/E Converter input amplifier,
- the input current of the Working sense input amplifier,
- the input current of the Reference input amplifier,
- the input current of a Counter Sense input amplifier,
- current leakage in the cell switch.

In most real-world experiments, the cell is turned on, and the I/E converter does not measure the last three terms listed above. These currents still exist, but they are generally sourced by the low impedance counter electrode lead. Only the first two terms are still in the cell current as measured by the I/E Converter.

The current contributions from each source on the above list are (at most) a few pA, so they are insignificant on all but the most sensitive Reference 3000 current range – the 300 pA range.

This effect can cause differences of up to 8 pA between DC current measured with the cell turned off and current measured with the cell turned on. In most cases the difference is smaller – one or two pA.

Only two Reference 3000 applications are sensitive enough that this current measurement offset causes problems. One is Physical Electrochemistry (Cyclic Voltammetry for example) with small electrodes and the second is EIS on high impedance samples such as barrier coatings. Incorrect DC current readings in EIS can slow the experiment, since the automatic ranging algorithms in the EIS300 software can make poor range choices given incorrect data. This can significantly lengthen the time needed to measure an EIS spectrum.

Most corrosion experiments or macro-electrode measurements involve currents much too large to be affected by this difference.

The Gamry Framework now includes a special "Low I DC Current" calibration procedure that corrects the Reference 3000 offsets to minimize this problem. The procedure uses a script that:

- asks you to disconnect the reference, counter, and counter sense leads from the calibration cell,
- measures the I/E input and Working sense amp input currents on the 300 pA range,

- replaces the 300 pA current range offset measured in the full DC calibration with the improved value.

The error sources listed above are both time and temperature dependent, so we recommend frequent “Low I DC Calibration” - if you need accurate measurement of absolute currents at pA levels. The procedure runs fairly quickly, so daily or weekly calibration should not be too inconvenient.

NOTE

The Low I DC Calibration is not a full calibration. You must run a full DC Calibration on your Reference 3000 before you first run the “Low I DC calibration”. Remember that the Reference 3000 must have a full DC calibration on the same type of cable you are using for the Low I DC Calibration.

Chapter 5 -- Cell Connections

Cell Cable Overview

The Cell Connectors are two 15-pin D-connectors on the front of the Reference 3000.

The upper (female) connector is labeled Counter/Working. It carries the cell current between the Counter electrode wire and the Working electrode wires and the instrument

The lower male connector is labeled Sense Inputs. It contains only high impedance inputs used to sense potentials in the cell.

Gamry's standard cell cables always come in pairs. Each cable has a D-connector on one end and a number of leads to connect to electrodes in an electrochemical cell. The D-connector end of the cable is connected to the appropriate D-Connector on the front of the Reference 3000. The male and female cables cannot be interchanged.

Every Reference 3000 is shipped with a pair of standard shielded cell cables. The Gamry part numbers for these cables are 985-85 and 985-90. They are both 60 cm complex cables, with D-connectors on one end a color coded banana plugs and/or pin sockets on the other end.

In some cases, your system may also include special purpose cell cables. The special purpose cell cables will include documentation describing their use.

You should always screw both cell cables into place since cables can fall off the unit. This can be disastrous if it occurs during an experiment.

Ancillary Apparatus

Do not use the Reference 3000 with ancillary apparatus connected directly to any of the cell leads. Examples of ancillary apparatus include DVMs, oscilloscopes, chart records, and data loggers. Ammeters and voltmeters, regardless of their specifications, almost always create problems when connected to the Reference 3000 cell leads. Ancillary measurement devices can be connected to monitor points on the rear panel of the Reference 3000.

AE Connections

The AE (Auxiliary Electrometers) is an option for the Reference 3000. Its inputs often connect to an electrochemical device, such as a battery or fuel cell stack. The inputs can also connect to external measurement devices, such as a pressure sensor.

AE connections are not described here. See Chapter 7 for AE connection information.

Fuses in the Cell Cable

The Reference 3000 could be damaged if currents much larger than 3 amps were to flow into or out of the Counter electrode or Working electrode leads. Improper connection to a battery, fuel cell, or super capacitor could cause this type of damaging current to flow. All Reference 3000 Counter/Working cell cables contain fuses in the cable that will protect the instrument if it is misconnected. A later section of this manual discusses the fuses and their replacement.

Normal Cell Connections

This section assumes that you are using standard, shielded cell cables. This information does not depend of the length of the cables.

The cell end of the standard cell cables terminates in a number of banana plugs and two pin jacks. Each termination comes with a removable alligator clip. Table 5-1 identifies the terminals of the cables.

Table 5-1
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
Black	Pin Jack	Floating Ground	Leave open or connect to a Faraday shield

Connect both the blue and green cell leads to the working electrode. The working electrode is the electrode being tested. The blue pin 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 250 mV above the circuitry ground (floating 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.

If the instrument is connected in stack mode and the reference input is not used, it should be connected to the floating ground wire. A pin plug shorting bar is provided for this purpose.

You may need to connect the Reference 3000 to a two terminal device (such as a commercial battery). In this case, you connect both the white cell and red cell leads to one side of the device and the blue and green cell leads to the other side. Try to connect the white and blue leads as close to the device as possible.

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 Reference 3000's power amplifier.

The orange lead is only used in ZRA mode and Stack 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 or Stack mode, this lead can be left open or connected to the Counter electrode.

The black pin jack is connected on the Reference 3000 end to Floating Ground. This is the circuitry ground for the analog circuits in the Reference 3000. In most cases, this terminal should be left disconnected at the cell end. When you do so, take care that its metal contact does not touch any of the other cell connections.

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 Reference 3000’s Floating Ground to an earth ground.

A binding post on the rear panel of the Reference 3000 is provided for this purpose. A water pipe can be suitable sources of earth ground.

CAUTION

If any electrode in your cell is at earth ground, you must not connect the Reference 3000 chassis to earth ground. Autoclaves, stress apparatus, and field measurements may involve earth grounded electrodes.

WARNING

Make sure that your earth ground connection is made to a legitimate source of earth ground. Consult a qualified electrician if you are uncertain how to obtain an earth ground. Connecting the Reference 3000 to an incorrect and unsafe voltage can create a safety hazard (see Chapter 1 for details).

If you are measuring very small currents, you may find that a metal enclosure completely surrounding your cell (a Faraday shield) significantly lowers measured current noise. This Faraday shield should usually be connected to both earth ground and Floating Ground. The Floating ground on the black cell lead is a convenient source of ground.

If any electrode in your cell is connected to earth ground, you should only connect your Faraday shield to the black cell lead (Floating Ground).

The alligator clip on any 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 also provide additional standard or special cell cables.

ZRA Mode Cell Connections

The Reference 3000 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 5-2. 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 5-2
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
Black	Pin Jack	Floating Ground	Leave open or connect to a Faraday shield

The counter sense and the working sense lead are each connected to different metal samples. In the ZRA mode the Reference 3000 is normally 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 the instrument is connected in stack mode and the reference input is not used, it should be connected to the floating ground wire. A pin plug shorting bar is provided for this purpose.

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 potential signal with a value very close to zero.

Stack Mode Cell Connections

Batteries, fuel cells, and super-capacitors are often connected with several individual cells connected in series to allow higher voltage operation. This type of connection will be referred to as a Stack connection . Special experiment scripts allow the Reference 3000 to control and measure stack voltages as large as its compliance voltage (±15 volts or ±30 volts). These scripts will refer to Stack Mode cell connections. The cell connections in Stack Mode differ from those in Potentiostatic and Galvanostatic modes.

Voltages in Stack mode are measured as the voltage difference between the Counter Sense input and the Working Sense Input. A special high-voltage electrometer allows the orange lead to operate at high voltage and still draw minimal current from the system under test.

Connections in Stack mode are very similar to ZRA mode. The cell cable connections for Stack mode are shown in Table 5-3.

Table 5-3
Cell Cable Connections for ZRA Mode

Color	Type	Name	Normal Connection
Blue	Banana Plug	Working Sense	Connect to first end of a stack.
Green	Banana Plug	Working Electrode	Connect to first end of a stack.
White	Pin Jack	Reference	Can be connected to a reference electrode
Red	Banana Plug	Counter Electrode	Connect to the second end of a stack
Orange	Banana Plug	Counter Sense	Connect to the second end of a stack
Black	Pin Jack	Floating Ground	Leave open or connect to a Faraday shield

The Counter Sense and the Counter leads are connected to one end of a stack. The Working and the Working Sense leads are connected to opposite ends of a Stack.

The white pin jack on the cell cable can be connected to a low voltage point in the stack. Some Gamry scripts allow the voltage difference between the white and blue leads to be read, even though the Reference 3000 is in Stack Mode.

If the instrument is connected in stack mode and the reference input is not used, it should be connected to the floating ground wire. A pin plug shorting bar is provided for this purpose.

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 potential signal with a value very close to zero.

Membrane Cell Connections

The Reference 3000 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 Reference 3000 controls the potential across the membrane. Table 5-4 shows the cell connections used with a membrane type cell.

Table 5-4
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)
Black	Pin Jack	Floating Ground	Leave open or connect to a Faraday shield

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.

Fuses in the Cell Cable

All standard Reference 3000 Counter/Working cell cables include fuses in the current carrying leads. These fuses protect the instrument from the extremely large currents that can flow through an improperly connected electrochemical energy generation or storage device (including batteries, fuel cells, and capacitors). For convenience, the term battery will be used here to refer to all single-cell or stacked electrochemical devices that can source energy.

Grounding errors on a battery can be particularly dangerous, since they can result in the battery being shorted through the instrument. During the development of the Reference 3000 several prototype instruments, without fuses, were damaged when connected to a Li-Ion battery stack.

NOTE

The fuses in the Reference 3000 Counter/Working cell cable do not protect against a safety hazard. They are needed to prevent damage to the instrument if it is improperly connected.

Both the counter electrode lead and the working electrode lead must be fused. Two different cell cable fuse arrangement have been built or are planned.

In-line Fuse-Holders and Fuses

The In-line fuse design is provided with Counter/Working cable supplied with early Reference 3000 shipments. The fuses in the cable are located plastic and brass fuse-holders located in-line with the current carrying leads, as shown in Figure 5-1. The photograph in this Figure shows the Working and Counter electrode leads with in-line fuse-holders. The Counter electrode fuse-holder has been opened to show the fuse. The fuse-holder contains a hidden spring that keeps the fuse in contact with the cell lead.

NOTE

Always turn off the Reference 3000 and disconnect both ends of the Counter/Working cable before checking or replacing the fuses in the cable.

In this fuse arrangement, the fuse can be removed from the cable by unscrewing the brass knurled nut on the fuse holder, just below the banana plug. Once a fuse has been removed, it can be checked using an ohmmeter, such as that found on modern digital voltmeters. Do not trust a visual inspection of the fuse. A blown (open) fuse should always have a resistance of greater than 100 Ohms. The resistance of a good fuse is very small.

Figure 5-1
Open Fuse-holder Showing Fuse

Four replacement fuses should accompany every cell cable shipped by Gamry Instruments. The Gamry Instruments Part Number for the in-line fuses is 630-00019. If you need to source replacement fuses locally, we currently only recommend Fast Acting (FF), 3.15 amp, 5x20mm cylindrical fuses from the Bussman Corporation. The Bussman Part Number is BK/GMA-3.15-R. Fuses with similar ratings from other manufacturers have not been tested, so we cannot recommend their use.

CAUTION

Always replace the fuses in a Reference 3000 cable with the recommended fuse. Use of improper fuse, especially a fuse with a higher current rating, could cause instrument failure if a battery cell is improperly connected. Use of a non-approved fuse will void Gamry's factory warranty.

Fuses Located in the Cable Hood

The in-line fuses in the Counter/Working are expensive and large enough to be awkward, especially when low impedances connections are required. Newer Counter/Working cables use a simple design with fuses located within the cable hood. This approach is less expensive and allows for lower inductance cell connections

NOTE

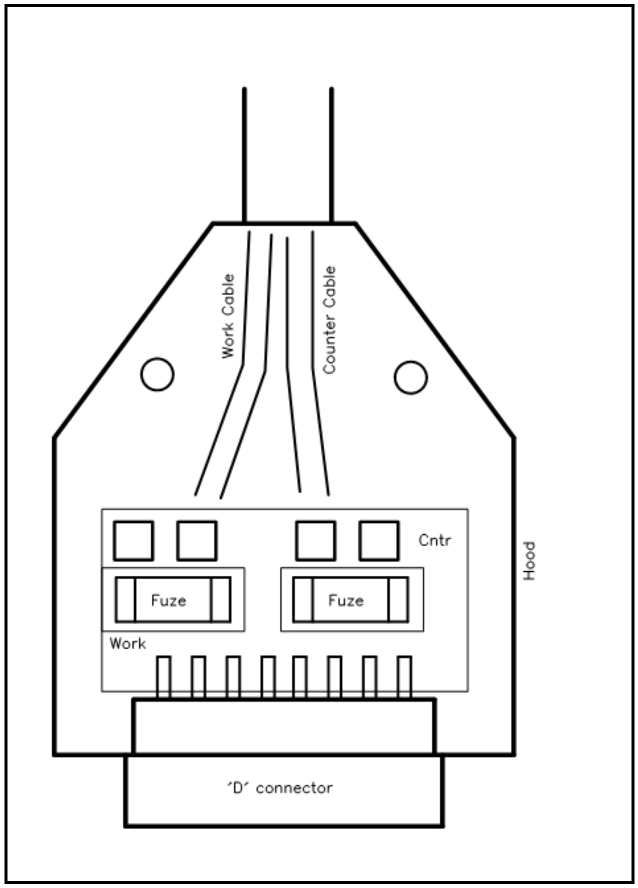
Always turn off the Reference 3000 and disconnect both ends of the Counter/Working cable before checking or replacing the fuses in the cable.

Access to the fuses requires removal of two screws located on opposite sides of the hood covering the D-connector end of the Counter/Working cable. A drawing of the D-connector end of a cable with the hood opened is seen in Figure 5-2. The small rectangular fuses snap into fuse-holders labeled **Work** and **Cntr**. To remove the fuse, either grip it with small pliers and gently lift the fuse out of the fuse-holder, or pry the fuse out of the fuse-holder using a small screwdriver or knife blade.

Once a fuse has been removed, it can be checked using an ohmmeter, such as that found on modern digital voltmeters. A blown (open) fuse should always have a resistance of greater than 100 Ohms. The resistance of a good fuse is very small.

Don't forget the jackscrews when you reassemble the hood.

Figure 5-2
Drawing of Fuse-holder in the D-Connector Hood



Four replacement fuses should accompany every Counter/Working cell cable shipped by Gamry Instruments. The Gamry Part Number for the small rectangular fuses is 630-00021. If you need to source replacement fuses locally, we currently only recommend Very Fast Acting, 3.15 amp, Nano Fuses from the Littelfuse corporation. The Littelfuse Part Number is 04513.15MRL. Fuses with similar ratings from other manufacturers have not been tested, so we cannot recommend their use.

CAUTION

Always replace the fuses in a Reference 3000 cable with the recommended fuse. Use of improper fuse, especially a fuse with a higher current rating, could cause instrument failure if a battery cell is improperly connected. Use of a non-approved fuse will void Gamry's factory warranty.

Testing For Open Fuses

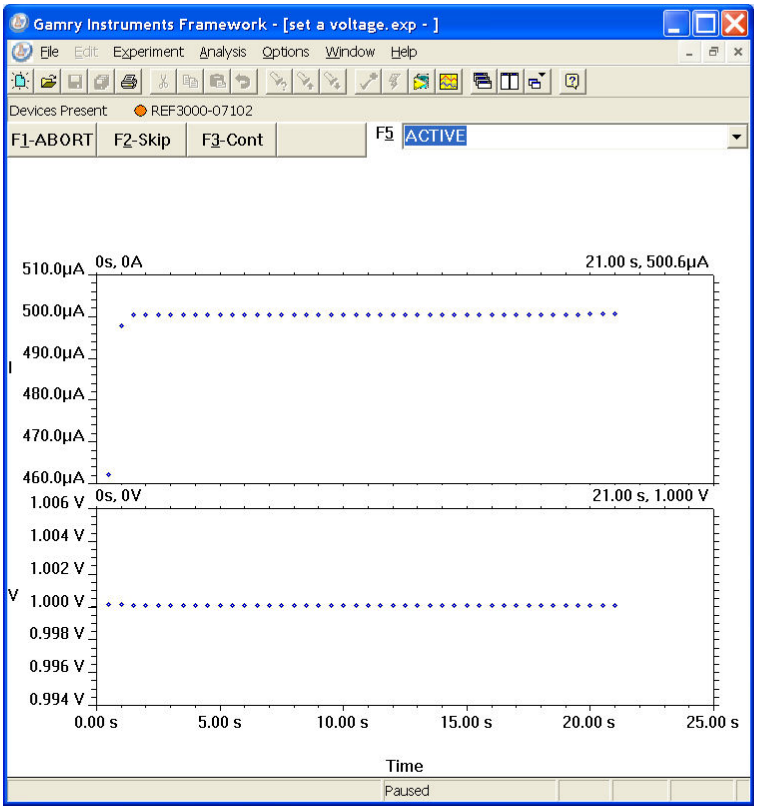
A Gamry Framework test checks for blown fuses without having you removing the fuses. A simple Potentiostatic test is run on the Calibration Cell on the Gamry UDC4 Dummy Cell. The test is run using the "Set a Voltage.exp" script in the Framework's Utilities Package. Utility Package scripts do not require a Authorization Code, so every Framework installation can run this test.

Connect the cell leads to the Calibration side of the UDC4. You do not need to place the UDC4 within a Faraday cage.   Select the command Experiment, Utilities, Set a Voltage on the Framework's menu bar. You will see a dialog box similar to this:

Figure 5-3
Setup Dialog Box for the "Set a Voltage" Script

Enter a **Voltage** of 1 volt as shown above, then press **Ok**. The Framework will open a Runner window and a graph of current versus time should appear.

Figure 5-4
Typical Runner Window with Good Fuses



We expect you will see one of two very different results:

- If the instrument is working properly and the fuses in the cable are good, the measured current will be around 500 µA as seen above. No overloads are seen.
- If the one or both fuses are open, all the current readings will be near zero, and a red CA Overload indication will be seen at the bottom of the runner window.

If this test indicates an open fuse, use the procedures described above to check both fuses. This test cannot tell which fuse is blown. Both fuses can blow at the same time.

If the fuse test indicates an open fuse, and the fuses both check out a good with an ohmmeter, some other problem has occurred in the cables or the instrument. Contact Technical Support at Gamry Instruments at your earliest convenience.

Chapter 6 -- Panel Indicators and Connectors

Front Panel

The Reference 3000 front panel includes two connectors and four backlighted LED indicators. Each of these will be discussed in turn. A picture of the Reference 3000 front panel can be seen in Figure 4 - 1.

The cell connections are discussed at great length in Chapter 5. A pin-out of the two cell cable connectors can be found in Appendix B.

Counter/Working Connector

The **Counter/Working** connector is a 15-pin female D-type connector. It contains the high current connections between a Reference 3000 and an electrochemical test cell.

The **Counter/Working** connector is normally connected to a Gamry Instruments supplied cell cable. Gamry's **Counter/Working** cables always include fuses that prevent instrument failure when a battery of other energy source is improperly connected to the cable.

In addition to the pins used for cell connections, the Reference 3000 **Counter/Working** Connector also uses five pins to read a cell cable ID. Gamry's software can compensate for the cell cable characteristics for optimal system performance, especially in EIS (Electrochemical Impedance Spectroscopy).

Sense Inputs Connector

The **Sense Inputs** connector is a 15-pin male D-type connector. It contains high impedance voltage sense inputs. These inputs are used to measure voltages in electrochemical test cell.

The **Sense Inputs** connector is normally connected to a Gamry Instruments supplied cell cable.

In addition to the pins used for cell connections, the Reference 3000 **Sense Inputs** connector also uses five pins to read a cell cable ID. Gamry's software can compensate for the cell cable characteristics for optimal system performance, especially in EIS (Electrochemical Impedance Spectroscopy).

The Power LED

The Power LED is located on the lower left of the Reference 3000 front panel. It normally glows a steady blue, when the Reference 3000 is turned on and has passed some simple self-tests.

When the Reference 3000 is first turned on, the Power LED will glow steadily for a second or two, blink three times, and then go to its normal steady blue output. Each blink in this sequence indicates successful completion of a portion of the Power PC's power-up self-test routine.

When the Power LED is off, either:

- The rear panel power switch is off.
- There is no DC +24 volt supply connected to the rear panel DC Power In connector.
- The external DC power supply has no input power or is malfunctioning.
- One part of the Power PC's power-up self-test has failed.

CAUTION

The Power LED is used both to indicate power status and to indicate that power-up tests have passed. It therefore cannot be relied on as a true power status indicator. Always unplug the DC Power In connection if you suspect your Reference 3000 is malfunctioning.

The USB LED

The USB LED is located just above the Power LED. It is a tri-color LED, capable of glowing green, orange, or red.

The USB LED will be unlighted when:

- The Reference 3000 is not powered.
- The Reference 3000 does not have a USB cable plugged into its rear panel USB port.
- The computer end of the USB cable is not plugged into a USB port on a computer or hub.
- The USB cable is not supplying USB power to the Reference 3000.
- The computer has disabled the USB port going to the Reference 3000.

The USB LED will glow a steady green if a valid USB connection has been made and the Reference 3000's communication processor is receiving power down the USB cable.

The USB LED will flash orange whenever the Reference 3000 is receiving or transmitting valid USB messages to or from the host computer. It will not flash if there is USB traffic addressed to other devices on the USB bus, including messages aimed at a different Reference 3000.

The USB LED will indicate a solid RED in one special condition. It will be red when a firmware download is taking place. Interrupting a firmware download can cause a catastrophic failure of your system. Do not turn off the Reference 3000, do not unplug the USB cable, and do not stop the host computer operation when the USB LED is a steady red color.

CAUTION

Do not interrupt a firmware download while it is in progress. An incomplete download can render a Reference 3000 inoperable until it is returned to Gamry for reprogramming.

Cell LED

The Cell LED glows yellow whenever the Reference 3000 is actively applying voltage or current to the electrochemical cell attached to the Cell Cable. You should avoid touching the cell cable leads whenever the Cell LED is lighted, because the quality of the data being collected in your experiment may be compromised.

CAUTION

The Cell LED does not indicate a dangerous condition when it is lighted. The voltages output by the Reference 3000 are generally considered to be safe. Still, you should avoid touching the cell leads when the cell is on.

If you need to make changes to your cell leads, you normally do so between experiments, when the Cell LED is off and the potentiostat is inactive.

In a typical experimental sequence, the Cell LED will be off between experiments and during any open circuit potential measurements. It will glow yellow whenever the cell is polarized.

Overload LED

The Overload LED is normally unlighted. When it glows red, this indicates that some circuit in the Reference 3000 has exceeded its normal operating limit. Conditions that generate Overloads include:

- The absolute value of the differential electrometer output voltage (the difference in voltage between the Working and Reference leads) exceeds 10 volts. This condition is known as an E Overload.
- The control amplifier has lost control of the cell.

  Remember that the Reference 3000 can be operating with compliance limits of ± 1.5 Amps at ± 30 Volts or with compliance limits of ± 3.0 Amps at ± 15 Volts.

  The absolute value of the cell current may be trying to exceed the compliance current or the absolute value of the counter electrode voltage may be trying to exceed the compliance voltage setting. Either condition will be called a Control Overload.
- The absolute value of the cell current has exceeded full scale on the current range presently in use. This condition is known as an I Overload.

An Overload indication does not indicate an instrument failure or system malfunction. Many normal conditions can light the Overload indicator.

For example, transient (temporary) overloads <u>during</u> an experiment in which the cell voltage or current is being stepped or swept are often normal. Consider the case of an infinitely fast voltage step into a perfect capacitor. In theory, charging the capacitor requires an infinite current. The current spike seen at each step in a stepped voltage waveform can easily light the Overload LED. The current spike will normally decay to near zero before the actual current and voltage readings are taken.

Overload indications when the cell is being connected or disconnected are also common and usually do not indicate a problem. Overloads can also be seen when one of the cell leads is disconnected from the other cell leads, even though the cell is off. Again, this does not indicate a problem.

A steadily glowing Overload LED <u>during</u> an experiment most likely indicates a problem is occurring. Possible causes include:

- One of the cell leads is disconnected (this is the most common cause),
- a gas bubble in the cell is blocking one of the electrodes,
- the potentiostat could be oscillating (see the next chapter).

NOTE

As described above, a glowing red Overload LED does not necessarily indicate a system malfunction. The Overload LED can light when one or more cell leads are disconnected, without indicating a problem with the system. The Overload LED can often light momentarily during a swept or stepped experiment. The only Overload LED indication that definitely points towards a problem is a <u>continuously</u> glowing Overload LED during an experiment.

Rear Panel

The rear panel contains one switch and a large number of connectors. A picture of the Reference 3000 rear panel can be seen in Figure 4 - 2.

Power In Jack

The Reference 3000 derives all its power from a +24 volts DC supply connected to the Power In jack on the lower right side of the rear panel. The input current is less than 5 amps.

We recommend that you always use the power adapter (power brick) supplied with your Reference 3000 to power to the instrument.

Input power from the power adapter comes from your AC power main. The power adapter supply is rated for operation from 100 to 240 volts AC, at frequencies from 47 to 63 Hz. It should therefore be useable worldwide.

CAUTION

If you facility owns both Gamry Reference 600's and Reference 3000's, you must insure that the smaller power adapter from the Reference 600 is not used to power a Reference 3000. The Reference 3000 will not power up with the smaller adapter. Fortunately, neither the Reference 3000 nor the small power adapter will be damaged if connected in error.

The power adapter for the Reference 3000 is almost 22 cm long. The largest dimension on the Reference 600 power adapter is 11 cm.

While a Reference 3000 may work with other power sources, we cannot guarantee it will work to its full specifications. If you have to use the Reference 3000 with a different supply, make sure that the supply is regulated, has an output between 22 and 26 volts, and supplies at least 5 amps of load current. Inrush current drawn by the Reference 3000 at "power on" has been known to cause improper operation of an external power supply, even though the supply is rated for more than 5 amps of output current.

WARNING

Power input voltages less than 20 volts or greater than 32 volts can damage the Reference 3000's DC-DC power supply.

Power Switch

The Power switch is located just below the Power In jack. It switches the power from this jack to the input of the Reference 3000's DC-DC converter.

Normally, the DC Power is connected before the Power Switch is turned ON. However, no damage will occur if this switch is already in the ON position when the DC Power is connected, or when the AC power input is connected to the external power supply.

Chassis Ground

The rear panel Chassis Ground is intended for one use only. When the Reference 3000 is used with cells isolated from earth ground, connecting the chassis ground to earth ground may lower the noise measured in the system. Note that the chassis of the Reference 3000 is connected to Floating Ground. See Chapter 1, for safety information concerning this connection.

Either a banana plug or the stripped end of a wire can be connected to the Chassis Ground binding post. The other end of the wire is then connected to earth ground.

A black banana-plug to banana-plug lead has been provided with your Reference 3000. You may find it useful when making this earth ground connection.

USB Port

The USB port on the rear panel of the Reference 3000 is a Type B connector as defined in Revision 1.1 and 2.0 of the USB Specification. You use a standard, shielded, Type A/B cable to connect this port to a computer's USB port or a USB hub (preferably an externally powered hub). The two ends of a Type A/B cable are different. The more-rectangular end plugs into the computer and the more-square end plugs into the Reference 3000.

A suitable USB cable was included with your Reference 3000 shipment. If this cable is lost, you can replace it with a cable from your local computer retailer.

The Reference 3000 is a High Speed USB 2.0 peripheral, capable of data transfer at 480 Mbits/second. If it is plugged into a computer port incapable of High Speed operation it will downgrade to USB 1.1 full speed operation (12 Mbits/second). Obviously data transfer speed will be slower if this occurs.

The Reference 3000 USB port is compatible with Revision 1.1 and 2.0 of the USB specification. It supports the Windows Plug-n-Play mechanism, including dynamic connect/reconnect.

The front panel USB LED should be green whenever a valid computer to Reference 3000 connection has been made and both the computer and Reference 3000 are fully powered.

Thermocouple Input

The Reference 3000 has an input jack for a K Type thermocouple. The ISO standard calls for color-coded mini-thermocouple connections. Yellow is the color assigned to K Type thermocouples. The mating connector on your thermocouple should therefore be yellow.

Possible uses for temperature measurement in an electrochemical test include:

- Looking for a temperature rise at end-of-charge on a battery.
- Measuring ambient temperature prior to a corrosion measurement.
- Measuring temperature in a cell before making a CV measurement that will be used to calculate reaction kinetics.

Gamry Instruments chose not to provide a thermocouple with the Reference 3000. There is simply too much variety in the mechanical design of thermocouple probes. Commercial thermocouples designed for measurement in air, on solid surfaces, and in immersion service are available from a variety of vendors. Make sure you get a K type thermocouple.

The Reference 3000 uses a temperature measurement IC to convert the thermocouple output to a useable voltage. It outputs a voltage that is nominally 10 mV per degree Celsius. The IC used, the Analog Device AD594A, is rated for an accuracy of 3°C. Even this accuracy is only achieved when the Reference 3000 is calibrated. The scaling at the A/D converter is ± 3 volts full scale, or ± 300°C full scale.

The Reference 3000 calibration script has an optional section for thermocouple calibration. An ice-water bath and a beaker of boiling water provide convenient standards for a two-point calibration.

CAUTION

One side of the thermocouple is connected to the Reference 3000's Floating Ground. An improper connection to the thermocouple input can compromise the Reference 3000's ability to float and invalidate data collected on earth grounded cells. A connection to an non-insulated thermocouple immersed in your electrochemical cell can also cause erroneous readings.

Misc I/O Connector

The Misc (Miscellaneous) I/O connector is a multipurpose connector. It contains both digital and analog signals used to interface external devices to the Reference 3000.

All of its signals are isolated from both earth ground and the Reference 3000's Floating Ground. The device connected to this connector establishes a ground reference. This isolation allows the Misc I/O connector to be connected to earth grounded apparatus, without compromising the Reference 3000's ground isolation.

A full description of this connector can be found in Appendix C of this manual. This appendix includes details such as connector pin-out, output and input voltage levels and full signal descriptions.

The following list is a short description of the signals in the Misc I/O Connector and their uses:

- Sync Out and Sync In signal allow two or more Reference 3000s to use one data acquisition clock.
- Four digital outputs can be used to turn on external devices under control of an Explain experimental control script.
- Some of Gamry applications assign three of the digital output to control stirring, flow of deaeration gas, and formation of mercury drops on a mercury drop electrode.
- Four digital inputs that can be read in an Explain experimental control script.
- A 12-bit D/A converter used to set "continuously variable" settings, such as electrode rotation rate on a rotating disk electrode.
- A 5 volt isolated power supply that can provide up to 50 mA of current for external circuitry.

I Monitor BNC

The I Monitor BNC connector represents the output of the Reference 3000's current measurement circuit. With the exception of the filtering described below, it is the raw signal. It will be high bandwidth on the less sensitive current ranges. The effective bandwidth of the current signal falls as you reach the nA and pA current ranges. IE Stability capacitors further slow the response.

The outer shell of this BNC connector is connected to the Reference 3000's floating ground.

CAUTION

The shell of the I Monitor BNC is connected to the Reference 3000's Floating Ground. Connection of this BNC to earth ground referenced equipment can compromise the Reference 3000's ability to float and invalidate data collected on earth grounded cells.

Scaling on this signal is ±3 volts for ± the nominal full scale current on the selected current range. Cathodic currents will cause a positive output voltage. If the software is auto-ranging the current-range selection, this signal will be discontinuous at each range change.

The I Monitor BNC connector is lightly filtered using an RLC circuit. It has a bandwidth of approximately 3 MHz when connected to a high impedance input. This bandwidth will be further reduced if a coaxial cable is connected to the BNC. Its output impedance is approximately 200 Ohms in parallel with 220 pF.

E Monitor BNC

The E Monitor BNC connector is the output of the Reference 3000's differential electrometer circuit. With the exception of the filtering described below, it is buffered representation of the voltage difference between the white and blue cell cable leads. It has a high bandwidth.

The outer shell of the BNC connector is connected to the Reference 3000's floating ground.

CAUTION
The shell of the E Monitor BNC is connected to the Reference 3000's Floating Ground. Connection of this BNC to earth ground referenced equipment can compromise the Reference 3000's ability to float and invalidate data collected on earth grounded cells.

The E Monitor BNC connector is lightly filtered using an RLC circuit. It has a bandwidth of approximately 3 MHz when connected to a high impedance input. This bandwidth will be further reduced if a coaxial cable is connected to the BNC. Its output impedance is approximately 200 Ohms in parallel with 220 pF.

Ext. Sig. In BNC

The External Signal In BNC connector allows you to add a voltage to the Reverence 600's Signal Generator. This signal will be summed with the other signal generator sources including the IR DAC, the Scan DAC, and the DDS output.

The outer shell of the BNC is connected to the Reference 3000's floating ground.

CAUTION
The shell of the Ext Sig In BNC is connected to the Reference 3000's Floating Ground. Connection of this BNC to earth ground referenced equipment can compromise the Reference 3000's ability to float and invalidate data collected on earth grounded cells.

The signal generator output is usually directly connected to the potentiostat's input. When the cell is turned on in potentiostat mode, the feedback is such that a negative signal generator output creates a positive differential electrometer signal, which corresponds to a negative working electrode versus reference electrode voltage.

The polarity of the External Signal In signal is inverted at the signal generator's output. As described above, a negative input signal on this BNC will create a positive change in the working electrode versus reference electrode voltage. The input impedance of this signal is 3 kΩ in parallel with 15 pF.

Sig Gen Out BNC

The Sig Gen Out BNC connector allows you to monitor the "signal generator" signal being sent from the Reference 3000's controller board to the potentiostat board. This signal has a high bandwidth. The signal output range is –15 volts to +15 volts.

The outer shell of the BNC is connected to the Reference 3000's floating ground.

CAUTION
The shell of the Ext Sig In BNC is connected to the Reference 3000's Floating Ground. Connection of this BNC to earth ground referenced equipment can compromise the Reference 3000's ability to float and invalidate data collected on earth grounded cells.

The Sig Gen Out BNC connector is lightly filtered using an RLC circuit. It has a bandwidth of approximately 3 MHz when connected to a high impedance input. This bandwidth will be further reduced if a coaxial cable is connected to the BNC. Its output impedance is approximately 200 Ohms in parallel with 220 pF.

Aux In BNC

The Aux In BNC connector allows you to measure a voltage from outside the Reference 3000 using the Reference 3000's internal A/D. The scaling is: ±3 volts in equals ±30000 A/D counts. This is a resolution of 100 µV per bit. The results will be reported in volts. The input is differential (see Appendix D).

The allowed input voltage range is ±5 volts. Input voltages outside this range could result in damage the Reference 3000.

Consult Appendix D for additional information concerning this connector.

Expansion Interface

The expansion interface is a D-connector on the Reference 3000 reserved for use with future Gamry Instruments' products.

Chapter 7 -- Auxiliary Electrometer Option

Overview

The AE is a factory-installed option for the Reference 3000. The AE acronym stands for **Auxiliary Electrometer**.

The AE allows eight independent, high voltage differential electrometer channels available to be read by the Reference 3000's A/D converter. Difference voltages (between the two inputs of each channel) of up to ± 5 V can be measured.

All AE inputs are rated to operate at all voltages available at the Reference 3000's Counter Electrode terminal. This allows operation between –18 volts and +18 volts in the 3 amp/15 volt compliance setting and between -36 volts and +36 volts in the 1.5 amp/30 volt compliance setting. These voltages are all versus the Reference 3000's Floating Ground.

The channels are all completely independent. One channel can measure the difference between -1 V and -2 V while a different channel measures the difference between 30V and 31V.

The primary function of the AE is simultaneous measurement of individual cells within a multi-cell battery, fuel cell, or super-capacitor stack. Both AC parameters and DC performance of the cells can be measured. The stack is often polarized using Galvanostatic control. Alternatively, you can use the Reference 3000 in Stack mode to control the voltage of the entire stack or of one cell in the stack.

Regardless of the control mode used, the same cell current flows though all the cells in the stack. As a result, we only need voltage measurements to measure the current and voltage of each cell in the stack. You can also use the AE to use to measure non-electrochemical signals. The voltage input to an AE channel can be the output from a temperature, pressure, or other transducer.

AC Performance and CMRR

Each AE channel has 2 differential inputs. The channel measures the difference voltage between these inputs, labeled as the **+ input** and the **- input**.

The AE inputs can operate with input voltages as high as 36 volts and can still maintain pA level input currents. They are also capable of high-speed measurements. The AE is specified to have less than 2° of phase shift for 100 kHz input signals applied to an input channel.

Another very important, although often disregarded, specification for differential inputs is common mode rejection (CMR). CMR is a measure of how well differential inputs reject a signal applied equally to both inputs (often called a common mode input). The ratio of output voltage to common mode voltage is called the common mode rejection ratio, CMRR. By convention, it has units of dB, a logarithmic scale where 20 dB represents a factor of 10. Assuming one volt of common mode voltage, 20 dB of CMRR corresponds to 100 mV of output voltage, 40 dB corresponds to 10 mV, 60 dB corresponds to 1 mV, etc.

CMR is generally dependent on frequency. As frequency increases, CMRR falls. Each AE channel is specified to have better than 94 dB CMRR at frequencies between DC and 5 kHz and better than 76 dB of CMRR between 5 kHz and 100 kHz.

NOTE

AC CMR is highly dependant on resistance in the measurement leads. The AE's CMR specifications only apply when the there is less than 10 Ω of resistance in the input leads. A typical aqueous reference electrode has 500 Ω of resistance. Gamry does not recommend use of reference electrodes in high frequency AE measurements.

CMR is especially important when the AE is used to measure the voltage of individual cells in a battery or fuel-cell stack. Cells near the Working Electrode have relatively low DC voltages, since the working electrode voltage is near ground. Cells near the Counter electrode have higher DC voltages. When an AC signal is applied to the stack, the counter electrode end of the stack has higher AC voltages.

Let's look at a hypothetical example. A battery stack has 22 cells, with an average DC cell voltage equal to 1.5 volts. The bottom cell in the battery stack in attached to the working electrode and the top cell is attached to the counter electrode. A 100 kHz AC signal is applied, creating an average AC voltage of 10 mV_{rms} per cell.

Assume the working electrode is at zero volts versus floating ground. The DC voltages on the top cell are 31.5 volts and 33 volts. This can also be described as 31 volts of common mode voltage plus a 1.5 volt differential voltage. The AC voltages on the top cell are 210 mV of common mode voltage and 10 mV of differential voltage.

Applying the 94 dB minimum low frequency CMRR spec, we can calculate the DC error in the voltage due to the DC common mode voltage.

Maximum DC Error = V_{cm} / CMRR = 31 V / 94 dB = 31 V/ 50,000 = 620 µV.

This is quite small compared to the 1.5 volt cell voltage, so it can be ignored.

At 100 kHz, the CMRR is specified to be at least 74 dB.

Maximum AC error = V_{cm} / CMRR = 0.21 V / 74 dB = 0.21 V/ 5,000 = 42 µV.

If this AC error is 90° out of phase with the true AC voltage on the cell, it creates a phase error of 0.2° in the measured AC voltage. This is not significant, since the AC accuracy specification at 100 kHz is ± 2°.

Experiments

The AE option is supported only by the Galvanostatic EIS, Galvanostatic Single Frequency EIS, and Hybrid EIS Framework scripts, as well as the experiments performed through Gamry PWR800 Software.

Connections Using Standard Cables

The AE connects to an electrochemical cell using one, two, three or four cables. Other than labeling, all four cables are identical. Each cable supports two AE channels.

NOTE

The cables are interchangeable, but we do not recommend using a numbered cable in a differently numbered connector. The connections get much too confusing.

Table 7-1 shows the pin-out of these cables.

Table 7-1
AE Cable Connections

Pin	Type	Name	Wire Color	Connector Color	Normal Connection
1	Analog Input	Odd Ch -	Black	Yellow	Low side of odd channel reference side
2	Analog Input	Odd Ch +	Black	Purple	High side of odd channel working side
3	Ground	Floating Ground	--	--	
4	Analog Input	Even Ch -	Red	Yellow	Low side of even channel reference side
5	Analog Input	Even Ch +	Red	Purple	High side of even channel working side
6	Ground	Floating Ground	--	--	
7	Digital input	!Cable			Ground if cable present
8	Digital In	!Power On			Ground if AE powered
9	Ground	Floating Ground			

Note that pins 8 and 9 must be grounded on any cable that will be used to take voltage readings.

The analog inputs are both labeled (with labels on the wires) and color coded. The wires are black for odd numbered channels (Channel 1,3, 5, and 7) and red for the even numbered channels (Channels 2, 4 ,6 and 8).

The working side plug (the positive input) is purple, and the reference side (the negative input) is yellow.

Connections Using Custom Cables

The user can build custom cables for AE connections. Follow in pin out in the table above. Pins 7 and 8 must be grounded.

AE Specifications

See Appendix E.

Chapter 8 -- 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 Reference 3000 Potentiostat can be 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 Reference 3000 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 kΩ. With reference electrode impedances greater than 20 kΩ, the Reference 3000 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.

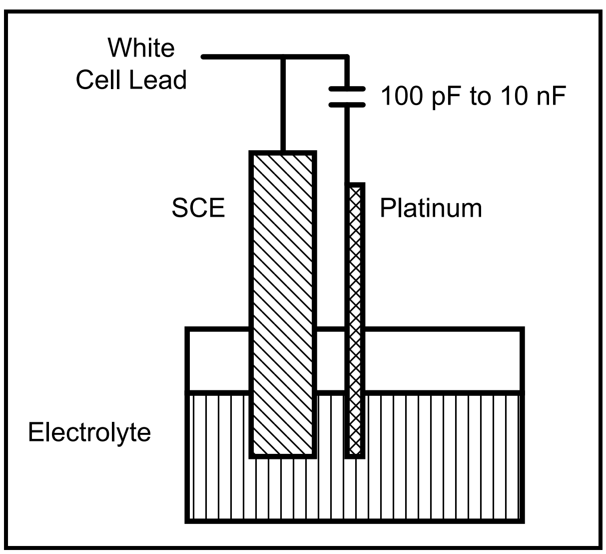
Even when the system is stable (not oscillating), it may exhibit ringing whenever there is a voltage step applied to the cell. The Reference 3000's D/A converters routinely apply steps, even when making a pseudo-linear ramp. While this ringing is not a problem with slow DC measurements, it can interfere 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 Reference 3000 potentiostat/cell system. This list is not in any particular order. Any or all of these steps may help.

- Slow down the potentiostat. The Reference 3000 has five control amplifier speed settings, which can be selected in software. Slower settings are generally more stable.
- Increase the Reference 3000's I/E stability setting. The Reference 3000 includes three 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 Luggin capillaries. If you do have a Luggin capillary, make sure that the capillary’s 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 8-1. 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.

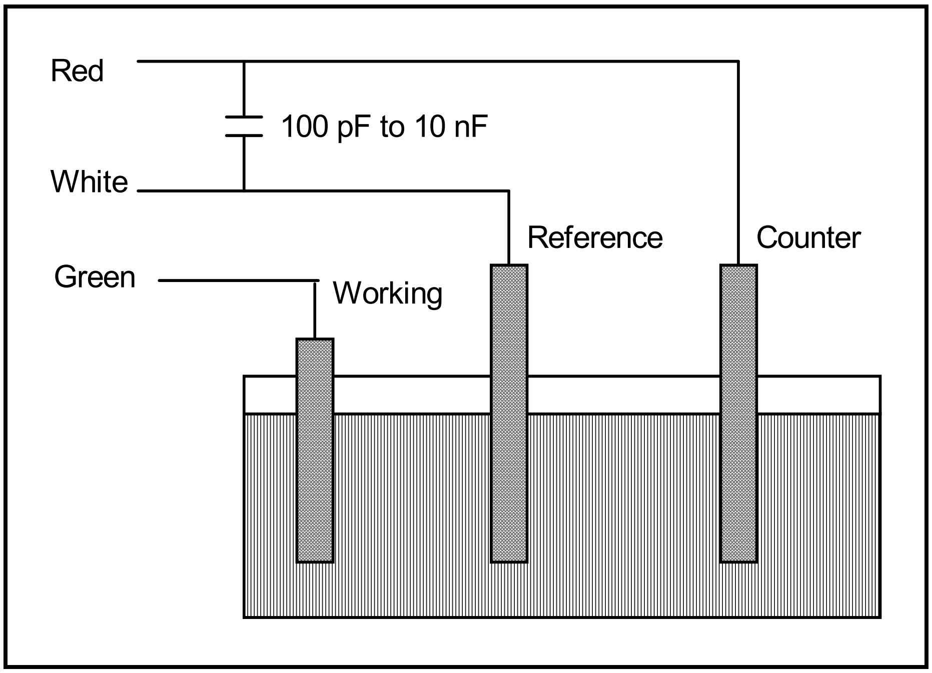
Figure 8-1
Fast Combination Reference Electrode



- 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 8-2. The capacitor value is generally determined by trial and error. Ten nF (10000 pF) 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.

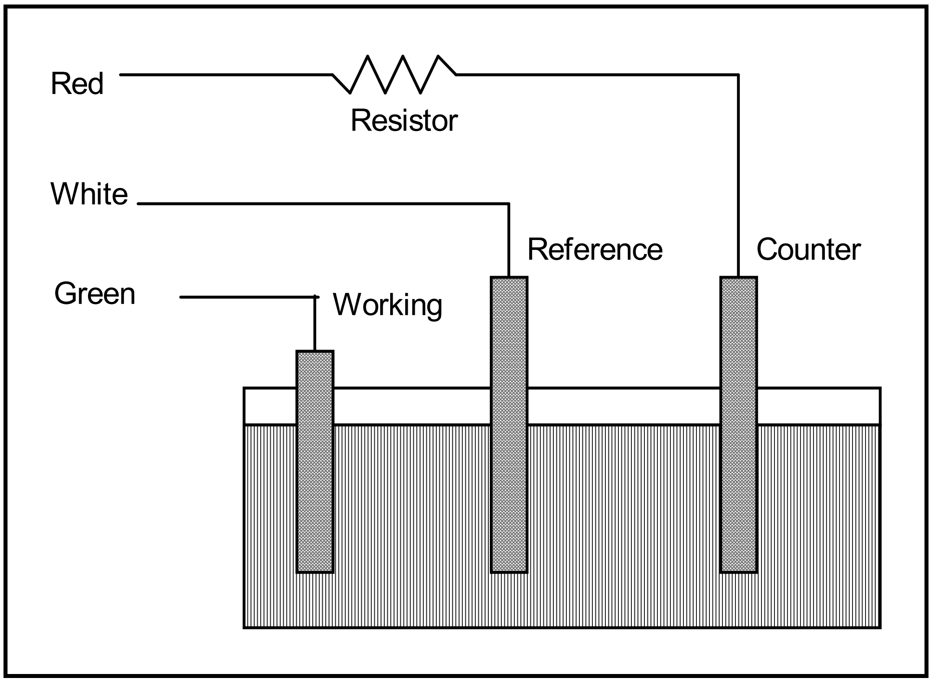
Figure 8-2
High Frequency Shunt



- Add resistance to the counter electrode lead. See Figure 8-3. This change lowers the effective bandwidth 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 kΩ resistor.

  This resistor has little or 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 8-3
Resistor Added for Stability



Chapter 9 -- Measurement of Small Current Signals

Overview

The Gamry Instruments Reference 3000 is a high performance measurement instrument used for all types of electrochemical testing. Unlike many other electrochemical instruments, it offers outstanding performance for both test with small current signals and high impedances and for tests involving large currents and very small impedances.

Chapter 10 is a discussion of the latter problem, when currents are large, voltages and cell impedances are small, and inductance limits measurements. These measurements include those encountered in research on:

- Batteries
- Fuel cells
- Super-capacitors

Problems in the measurement of very small currents are discussed here. Examples of this type of testing include:

- Cells for testing painted metal samples
- Cells for testing corrosion of bare metals
- Microelectrode cells
- Most cells for fast CV (cyclic Voltammetry)
- Super capacitors

Problem Description

The Reference 3000 is a very sensitive scientific instrument. It can theoretically resolve current changes as small as 100 femoamp (1×10^{-13} amps). To place this current in perspective, 100 fA represents the flow of about 600,000 electrons per second!

The small currents measured by the Reference 3000 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 Reference 3000.

Measurement System Model and Physical Limitations

To get a feel for the physical limits implied by very sensitive current measurements, consider the equivalent circuit shown in Figure 9-1. We are attempting to measure the cell impedance given by Z_{cell}.

This model is valid for analysis purposes even though the real Reference 3000 circuit topology differs significantly.

In Figure 9-1:

E_s	Is an ideal signal source
Z_{cell}	Is the unknown cell impedance
I_{cell}	Is the “real” cell current
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

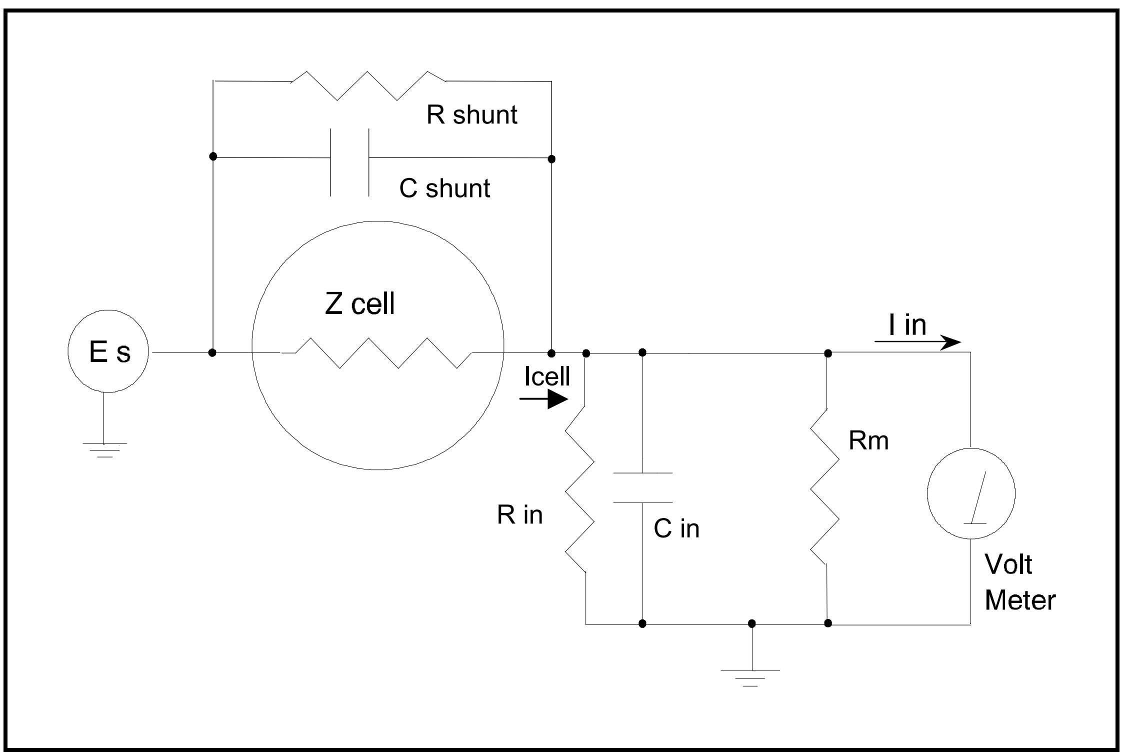
In the ideal current measurement circuit R_{in} is infinite while C_{in} and I_{in} are zero. All of the cell current, I_{cell}, flows through R_m.

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 9-1
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 equations:

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

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

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 ± 0.4%. 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 ± 0.4%. Again, reducing the bandwidth helps. At a noise bandwidth of 1 mHz, the current noise falls to 0.013 fA.

With E_s at 10 mV, an EIS system that measures 10^{11} ohms at 1 Hz is about 2 ½ decades away from the Johnson noise limits. At 10 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 9-1 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:

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

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 6 nA full scale current range, a practical estimate for R_m is 10^7 ohms.

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

In general, one should stay two decades below f_{RC} to keep phase shift below one degree. The uncorrected upper frequency limit on a 6 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 9-1, both R_{in} and I_{in} affect the accuracy of current measurements. The magnitude error due to R_{in} is calculated by:

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

For an R_m of 10^7 ohms, an error < 1% demands that R_{in} must be greater than 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 AC signal by more than a factor of 10.

The Reference 3000 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 Reference 3000. In practice, the input current is approximately constant, so current differences or AC current levels of less than one pA can usually 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 40 µF. This could represent a 1 cm^2 polished noble metal immersed in an electrolyte solution. You can roughly estimate the capacitance of the electrical double layer formed by a metal/electrolyte interface as 20 µF/cm^2. The area is the microscopic area of the surface, which is larger than the geometric area, because even a polished surface is rough. The impedance of this 40 µF electrode, assuming ideal capacitive behavior, is given by:

$$Z = 1/\omega C$$

At sixty Hertz, the impedance magnitude is about 66 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, V_n, of 10 µV (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:

$$I = V_n/Z \approx 10 \times 10^{-6}/ 66 \approx 150 \text{ nA}$$

This rather large noise current will prevent accurate DC current measurement in the low nA or 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 1 to 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, 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 Teflon™, which is one of the best insulators known, has a bulk resistivity of about 10^{12} ohms•m. 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 Reference 3000 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 <u>mandatory</u> 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 paint on 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 a cell cable to enter the shield.

The shield <u>must be electrically connected</u> to the Reference 3000's floating ground terminal.

An additional connection of both the shield and the Reference 3000 floating ground to an earth ground may also prove helpful.

NOTE

Only connect the Reference 3000 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 Reference 3000 is shipped with 60 cm shielded cell cables. We also offer extended length cables and unshielded cables as extra cost options.

Cell cables longer than 1 meter will 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 Reference 3000 with any cables not supplied by Gamry Instruments. The Reference 3000 cable is not a simple cable like a typical computer cable. The Reference 3000 cable includes a number of individually shielded wires contained within an overall shield. The Counter/Working cable contains fuses. 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 Reference 3000 involve cells with small capacitances, the value of which may be important.

In these cases, the capacitance between the Reference 3000's cell leads can result in an error. The Reference 3000 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 physical separation between the working electrode/ working sense leads and the counter/ counter sense/ reference electrode leads.
- 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 measuring 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 Teflon are the preferred cell construction materials. Even glass may be a problem when 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 if you are measuring high impedances.

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 Luggin capillaries.
- Poorly conductive solutions - especially in Luggin 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 Reference 3000 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, should be less than 10^9 ΩHz for good EIS measurements with a Reference 3000.

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

Ancillary Apparatus

Do not use the Reference 3000 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 Reference 3000 cell leads.

Floating Operation

The Reference 3000 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 Reference 3000'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 Reference 3000 is operated in a floating mode. The instrument specifications only apply on isolated cells with the Reference 3000 earth ground referenced (not floating).

Special precautions must be taken with the cell connections when the Reference 3000 must float. Make sure that all the cell connections are isolated from earth ground. In this case, you must disconnect the chassis ground terminal of the Reference 3000 from earth ground.

Finally, ancillary apparatus connected to the Reference 3000 must be isolated. External voltmeters, ammeters, FRA's etc. must be isolated. This includes devices connected to the monitor connectors located on the Reference 3000 rear panel.

Chapter 10 – EIS Measurement of Small Impedances

Overview

The Gamry Instruments Reference 3000 is a high performance measurement instrument used for all types of electrochemical testing. Unlike many other electrochemical instruments, it offers outstanding performance for both test with small current signals and high impedances and for tests involving large currents and very small impedances.

Problems in the measurement of very small currents were discussed in the previous chapter.

This chapter is a discussion of a very different type of problem, when currents are large, voltages and cell impedances are small, and inductance limits measurements. These measurements include those encountered in research on:

- Batteries
- Fuel cells
- Super-capacitors

Results from fast transient techniques (CV, Chronopotentiometry, etc,) or high frequency EIS measurements on low impedance systems are often limited by the cell cable and connections to the cell. An improper cell cable or a proper cell cable badly connected can cause significant errors in the data obtained.

This chapter should answer these questions:

- Why is Galvanostatic operation preferred when measuring Low Impedance?
- What are the sources of error in measuring low impedance cells?
- Why Use Four-terminal Measurement Techniques
- What is mutual inductance?
- How do I connect a cable to my cell to minimize errors?

Why Galvanostatic Mode?

Even though Potentiostatic EIS is the most commonly used EIS technique, it is poorly suited to impedance measurements of low impedance batteries, fuel cells and super-capacitors.

This is why:

Current, voltage, and impedance are related through Ohm's Law. Assume that a high-rate battery has an impedance of 1 mΩ. A voltage of 1 mV across a 1 mΩ impedance leads to 1 A of current. No commercial potentiostat is specified to control a cell's potential (typically 0.5 V to 4.5 V) with less than 1 mV of absolute error. When a potential with a 1 mV (or larger) error is applied to a low impedance battery or fuel cell a very large DC current will flow. This current, given enough time, can alter a battery's state-of-charge.

Conversely, a galvanostat can easily control ampere currents to an accuracy of a few milliamps. The voltage on a battery or fuel cell is usually unaffected when the galvanostat is connected. The DC current is zero or some user defined value.

A modern EIS system with AC coupling or offset and gain in the voltage measurement can measure microvolts of AC voltage superimposed on a large DC voltage, as long as that DC voltage is stable.

DC Errors and Four-terminal Measurements

Four-terminal measurements are a common technique used in precision measurement of small impedances. In a four-terminal measurement, a nominally two-terminal device, such as a resistor or a battery, is connected using four leads. Two of the leads carry the current that must flow through the device to make the measurement. The other leads measure the voltage created by that current.

An illustration of two-terminal measurements versus four-terminal measurements can be seen in Figure 10-1. Both schematic diagrams show a resistance measurement made up passing a known current through an unknown resistance, R_{test}. The wires in the circuit have a resistance R_{wire}. A high input-impedance voltmeter reads a voltage that is dived by the current value to calculate the value of R_{test}.

In the two-terminal case, the voltage measurement is made using the same wires that carry the current. The voltmeter measures:

$$V = I_{test} \text{ x } (2 \text{ H } R_{wire} + R_{test})$$

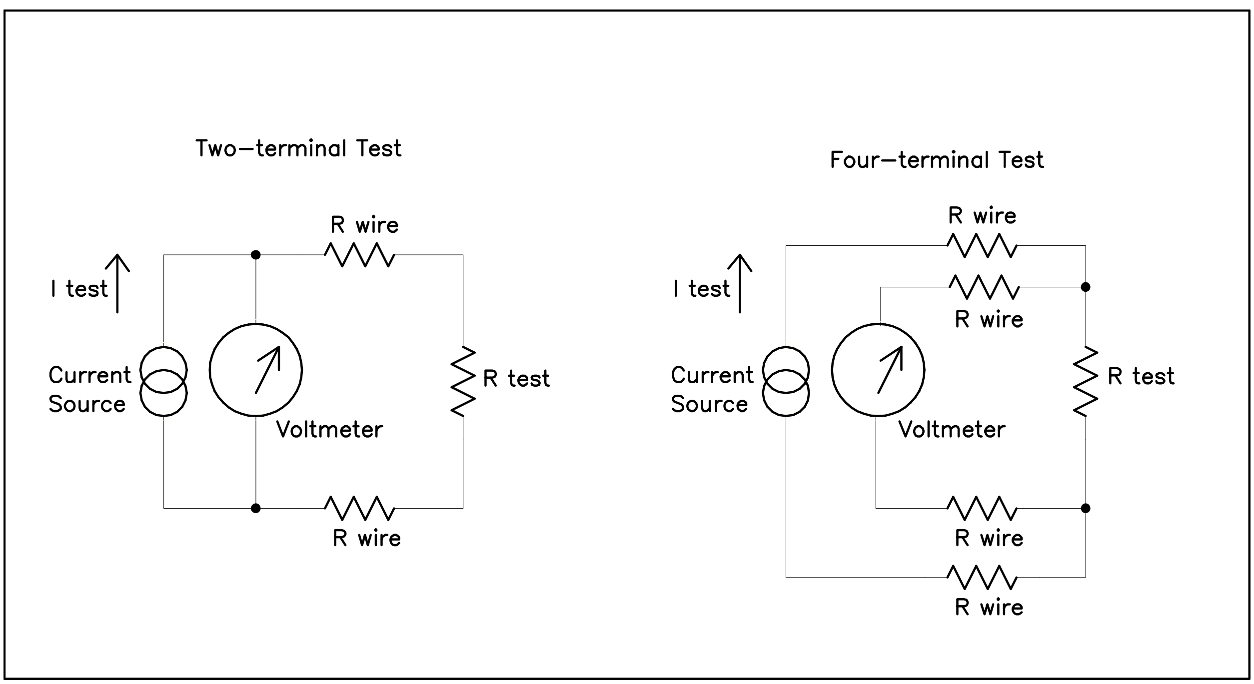
The calculated R_{test} is too high, since the resistance of the wires is added to the unknown resistance.

In the four-terminal case, the voltmeter uses two additional wires to measure the voltage close to R_{test}. The current is carried through the original pair of wires. There is no current through the voltmeter wires, so the wire resistance does not create voltage drop. The voltmeter measures:

$$V = I_{test} \text{ x } R_{test}$$

The addition of two wires to the circuit eliminates the error caused by the resistance of the wires.

Figure 10-1
Two and Four Terminal Measurements



Four-terminal measurements are also useful in AC measurements, although there is a factor called mutual inductance (discussed below) makes the AC case more complicated. Ignoring this complication for a moment, a simple extension of the discussion above will show that four-terminal measurements can also eliminate the effects of wire inductance.

In the real world, true four-terminal measurements are rarely possible. There is almost always some metallic conductor shared by both current carrying leads and the voltage sensing leads. The metal volume shared between the current carrying function and the sensing function can be minimized, but not eliminated.

What is Mutual Inductance?

Before we can define Mutual Inductance, we must define some terms. As discussed above, four leads connect to the cell in an electrochemical system used to test small impedances. We will group them into two pairs.

One pair is the counter and working leads (red and green). They carry the cell current so we will call them the current carrying leads.

The reference and working sense leads (white and blue) form the second pair. They measure the voltage across two points in the cell. These leads will be called the sense leads.

A "mutual inductive" effect limits the ability of any system to measure small impedances at higher frequencies. The term mutual inductance describes the influence of the magnetic field generated by the current carrying leads on the sense leads.

In essence, the current carrying leads are the primary of a transformer and the sense leads are the secondary. The AC current in the primary creates a magnetic field that then couples to the secondary, where it creates an AC voltage.

You can minimize the unwanted effect in a number of ways:

- Avoid higher frequencies
- Minimize the net field generated by the current carrying leads.
- Separate the current carrying leads from the sense leads.
- Minimize pickup of the field in the sense leads.

Each of these ways will be discussed below.

Avoid high frequencies

Mutual inductance is an inductive effect. The voltage error is given by:

$$Vs = M\, di/dt$$

where Vs is the induced voltage on the secondary, M is the coupling constant (with units of Henries), and di/dt is the rate of change in the <u>primary</u> current. M depends on the closeness of the coupling and can range from zero up to the value of the primary inductance (the inductance in the current carrying leads).

Assuming a constant amplitude waveform in the primary, di/dt is proportional to frequency. There is always a frequency below which the effect of mutual inductance errors is unimportant. Unfortunately, many electrochemical systems need information at frequencies above this limit.

Minimize the Net Magnetic Field

A current passing through a wire creates a magnetic field. The field strength is proportional to the current. Fortunately, passing the same current in opposite directions through adjacent wires tends to cancel the external field. This also minimizes the net inductance in the wires. In all Gamry Instruments Reference 3000 Counter/Working cable, the current carrying leads are bound together.

From your basic physics course, you may remember that the E ⊗ B cross-product relationship for current through a wire obeys the Right-Hand-Rule. If you thumb points in the direction of the current flow in a wire, when you curl your fingers around the wire, the magnetic field curves around the wire in the same direction as your fingers.

The current in the primary wires is flowing in opposite directions in the two wires, so your thumb points in opposite directions for each wire, causing some cancellation of the fields. If the wires were in exactly the same place, the cancellation would be perfect.

Since the wires cannot be in identically the same location, the cancellation is imperfect, and some net magnetic field is always present. The more the wires are separated, the larger the net field.

The most common arrangement for inductance and field minimization is the twisted pair. Two insulated wires are simply twisted together. A coaxial wire arrangement with current flowing in opposite directions in the center conductor and the outer conductor is also effective.

Separate the pairs

If you place a magnetic field probe near a wire passing current, you will measure a field inversely proportional to the square of the distance between the probe and the wire.

In an electrochemical system, the probe is our sense wiring. Separating the sense wires from the current carrying wires can dramatically reduce the magnetic coupling, reducing errors in the EIS measurement.

The Reference 3000 has two cell cables, so that we can separate the current carrying wires from the sense wires. The current carrying pair is in the Counter/Working Cable and the sense pair is in the Sense Cable.

Twist the Sense Wires

The concept of a magnetic loop probe is useful in understanding why twisted wire minimizes magnetic pickup. A loop of wire in a changing magnetic field will see a loop voltage proportional to the area of the loop.

Twisting the sense wires together helps in two ways – even though twisting the wire forms loops. First, the twisted wires are forced to lie close to each other, minimizing the loop areas. Secondly, adjacent loops pickup opposite polarity voltages resulting in cancellation.

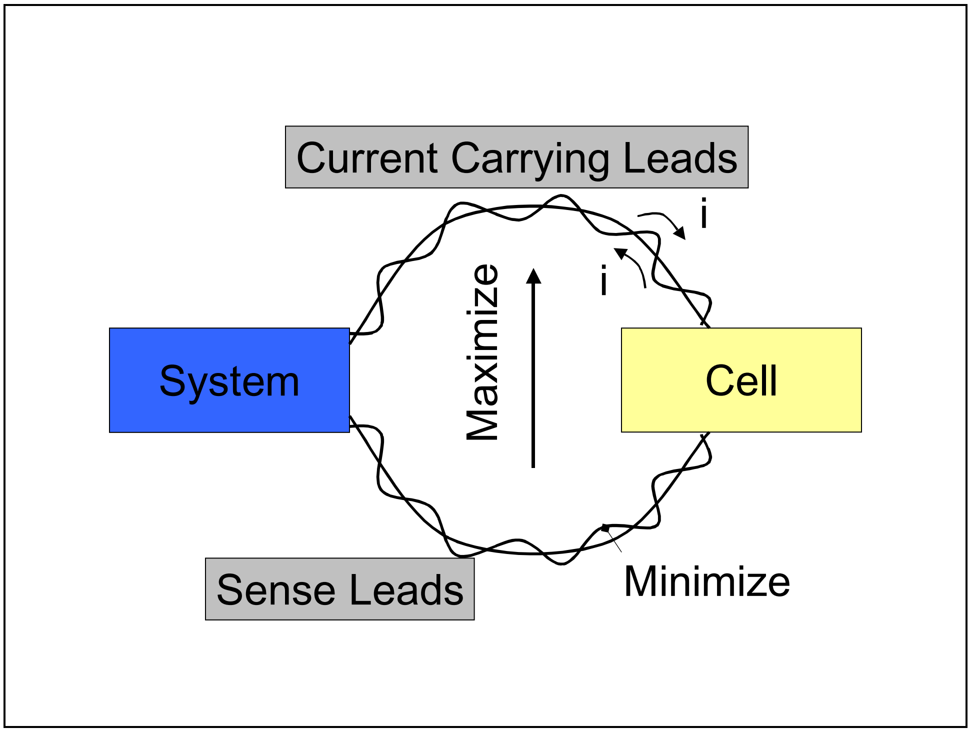
How Should You Hook Up Your Cell?

Always use four-terminal connections to the cell. Try to avoid conductors that are shared by both the current carrying path and the voltage sensing bath.

If your experiments are in the region where mutual inductance may limit performance, keep the voltage sensing leads in a twisted pair and the current carrying leads in a different twisted pair. Keep the pair of sensing wires far away from the pair of current carrying wires. Try to arrange each pair so that they approach the cell from opposite directions.

These recommendations are summarized in the Figure below.

Figure 10-2
Wiring Recommendations



Appendix A -- Reference 3000 Specifications

All specifications are at an ambient temperature of 25 °C, with the Reference 3000 powered using the power adapter shipped with the unit, standard shielded 60 cm cell cables, and the cell enclosed in a Faraday shield. All specifications are after software calibration.

A numbered note qualifies many of the specifications. Many of these notes describe the method used to measure a specification. The notes are found at the end of this appendix.

All specifications are subject to change without notice.

Control Amplifier

High Voltage, Low Current Mode

Compliance Voltage	Min Typ	± 30 ± 31.5	volts	Note 1a
Output Current	Min	± 1500	mA	Note 2

Low Voltage, High Current Mode

Compliance Voltage	Min Typ	± 15 ± 16.2	volts	Note 1b
Output Current	Min	± 3000	mA	Note 2

Both Modes

Unity Gain Bandwidth	Typ	1100, 330, 50, 5.0, 0.5	kHz	Notes 3, 4
Slew Rate	Typ	10, 3, 0.5, 0.06, 0.006	V/µsec	Notes 3,4

Differential Electrometer

Max Input Voltage	Min	± 10	volts	Note 5
Input Current	Max	6	pA	Notes 6
Input Resistance Differential (between inputs) Common Mode (input to ground)	Typ	 100 1	TΩ	Note 7
Input Capacitance Differential (between inputs) Common Mode (input to ground)	Typ	 0.2 12	pf	Note 7
Bandwidth (-3 dB)	Min	15	MHz	Note 8
CMMR DC to 100 kHz 100 kHz to 1 MHz	Min	 80 60		Note 9

Voltage Measurement

A/D Full Scale Ranges	Typ	±12.0, ± 3.0, ± 0.3, ± 0.03	Volts	Note 3
Resolution	Typ	400, 100, 10, 1	µV/bit	
Zero Offset Error	Max	1	mV	Note 11
Gain Error	Max	0.2	%	Note 11

Offset Range	Typ	± 10	Volts	

Current to Voltage Converter

Maximum Full Scale Range		3000	mA	Note 12
Minimum Full Scale Range		300 3 (after x100 gain)	pA pA	Note 12
Voltage across Rm	Typ	150	mV at full scale	Note 13
Output Voltage (at BNC and ADC in)	Typ	3.0	Volts full scale	
Input Offset Current	Max Typ	5 2	pA	Note 14
Range Zero Offset	Max	0.05	% of range	Note 14
Gain Tolerance 3000 mA to 3 nA ranges 300 pA range	Max	 0.2 0.5	% of reading	Note 14
Zero drift	Typ	0.03	% FS /°C	Note 15
Bandwidth 3000 mA to 600 µA ranges 30 µA range 3 µA range	Typ	 > 10 > 1.5 > 0.15	MHz	Note 16

Current Measurement

Resolution	Typ	0.00333…	% FS /bit	
Offset Range	Typ	± 100	% of range	
Post- Offset Gain	Typ	1x, 10x, 100x		
Accuracy	Typ	Dominated by current to voltage error (see above)		

Potentiostatic Mode

Applied Voltage Range	Min	± 11	volts	Note 5
Accuracy DC zero offset Gain	Max	 1 0.2	 mV % setting	Note 17
DC Bias	Typ	± 8	volts	
Scan DAC ranges	Typ	± 6.4, ± 1.6, ± 0.4	volts	
Drift	Max	< 20	μV/°C	Note 18
Noise and Ripple 1 Hz to 1 kHz 1 Hz to 200 kHz	Typ	 < 5 < 20	μV rms	Note 19

Galvanostatic Mode

Maximum Full Scale Current		± 30000	mA	Note 12
Minimum Full Scale Current		300	pA	Note 12
Accuracy		Dominated by current to voltage converter accuracy shown above		
Sig Gen Voltage for Full Scale Current		± 3.0 volts		

Auxiliary A/D Input (see Appendix D)

Range (differential)	Typ	± 3	volts	
Input voltage range (either input)	Max	± 3.6	volts	
Gain Error	Max	0.2	%	
Input Impedance a) as shipped b) re-jumpered for high Z input	Typ	 100 10	 kΩ GΩ	Note 20

Auxiliary D/A Output

Range	Typ	0 to 4.096	volts	
Resolution	Typ	1	mV	

Environmental

Operating Temperature Range		0 to 45	°C	
Relative Humidity	Max	90 (non-condensing)	%	
Storage and Shipping Temperature		-25 to 75	°C	
Maximum Shipping acceleration		30	G	

General

Power Input Voltage	Range	22 to 26	volts	
Power	Max	120	W	
Leakage Current (floating, earthed Working Electrode)		± 1 nA		Note 21
Dimensions (approximate) (whd)		20 x 23 x 30	cm	Note 22
Weight (approximate)		5	kg	Note 22
Dimensions of External Power Adapter (approximate)		7.5 x 5 x 22	cm	Note 23
Weight of External Power Adapter (approximate)		900	grams	Note 23

NOTES:

1. **a)** Measured in potentiostatic mode with a high wattage 20 Ω load connected from counter electrode lead to the reference lead and a 2 Ohm load between the reference lead and the working electrode lead. The compliance voltage is measured using an external voltmeter across the 22 Ω load. Under these conditions, the output current is approximately 1.4 A.
   b) Measured in potentiostatic mode with a high wattage 3 Ω load connected from counter electrode lead to the reference lead and a 2 Ohm load between the reference lead and the working electrode lead. The compliance voltage is measured using an external voltmeter across the 5 Ω load. Under these conditions, the output current is approximately 5 A.
2. Measured with a 4-terminal 0.05 Ω load, in potentiostatic mode.
3. Unity gain bandwidth and slew rate are correlated. Each has five settings, with the highest slew-rate occurring at the highest bandwidth, down to the lowest slew-rate occurring at lowest bandwidth. Both are measured with 20 kΩ between counter and reference and 100 Ω between the reference and the working and working sense leads
4. Measured with an external function generator connected to the Ext Sig In BNC.
5. The Differential Electrometer Amps are Analog Devices AD8065 Op amps specially selected for low Vos drift versus temperature. These amps have a dual input stage, with a JFET input over most of their input range and a bipolar transistor input at input voltages greater than + 9.5 volts. They are only a high impedance buffer from –12 volts to +9.5 volts, though they are a unity gain buffer over their whole input voltage range.
6. The input current of the JFET inputs on the AD8065s is less than 6 pA. When the Bipolar input is operative, the input current can be in the microamps. The specified current is only applicable at voltages of 2 volts or less.
7. The differential impedance is measured between the Reference and Work Sense inputs. This is the impedance you measure when you record the EIS spectrum of an infinite impedance cell.
   There is also a common mode resistance and capacitance associated with the differential electrometer inputs. These values tell you how much the electrometer response is modified by a resistance in series with the source.
8. The bandwidth is for a sine-wave source with a 50 Ω output impedance driving either input. The bandwidth is well in excess of this specification, which is limited by the measurement equipment used in testing the Reference 3000.
9. CMRR is common mode rejection ratio. It specifies the ability of the differential electrometer to reject signals connected to both inputs. The CMRR is measured driving both inputs with a sine-wave source with a 50 Ω output impedance, and measuring the error as a function of frequency. Resistance in either input will cause a loss of CMRR.
10. Voltage measurement is actually performed with a ±3 volt signal input to the ADC signal chain. A ÷4 attenuator divides down higher voltage electrometer outputs so they fit into a ±3 volt input, thus

making a ±12 volt full scale range. Gains of 10 and 100 are available to generate 300 mV and 30 mV ranges.

11. The total error in a voltage measurement is:

Error = Zero Offset Error + Gain Error * Voltage

For a 1 volt signal the error can be as high as 3 mV.

12. There are 11 hardware current ranges, separated in sensitivity by decades. The ranges are: 300 pA, 3 nA, … 300 mA, 3 A full scale. The x10 and x100 gains add two virtual ranges of 30 pA and 6 pA full scale.

13. The voltage across the current measurement resistor, Rm, is as shown. Slightly higher voltages may be seen at the working electrode terminal on the cell cable, since the cable has both resistive and inductive impedance.

14. The total error in a current measurement is:

Error = Input Current Offset + Range Zero Offset * FS Current + Gain Tolerance * Measured Current

For small currents (pA) the first term is usually dominant.
For large currents (uA), the first term can usually be ignored.
The units for the error are amps.

15. Drift can be approximated by simple drift in the Range Zero Error. In reality all three terms in the equation above can have drift.

16. The Current to Voltage converter bandwidth is a function of the current range, the cell cable, and the IEStability setting.. The bandwidth can be very low on very sensitive ranges. Longer cell cables add capacitance and slow the current measurement.

17. The total error in a voltage setting is:

Error = DC Zero Offset + Gain * Voltage Setting

For a 1 volt signal the error can be as high as 3 mV.

18. This specification is guaranteed by design. It is not tested.

19. This specification is measured by applying zero voltage across a 1 Ω resistor and measuring current noise on the 30 µA scale. 1 µV of voltage noise will create a current of 1 µA. The filters in the ADC Chain for the I Signal are used to limit the bandwidths as shown in the spec.
Signal averaging via Gamry's DSP mode will further reduce the measured noise.

20. See Appendix D.

21. Isolation quality has both DC factors and AC factors (predominately at the 300 kHz power supply frequency). Only the DC leakage current is shown here. Consult Gamry's technical support for additional information.

22. Excluding external power adapter and any cables supplied with unit.

23. Excluding removable line cord.

Appendix B -- Reference 3000 Cell Connectors

Chapter 5 describes the connections between a cell cable and an electrochemical cell. This appendix describes the other end of the cell cable.

Multiple pins assigned to the same signal are connected together on the Reference 3000's Potentiostat board. If you need to connect this signal outside the Reference 3000, you need a wire connected to any one of the D connector pins.

Table B-1
Counter/Working Connector

Pin(s)	Signal Name	Use
1,9	Working	Connected to the working electrode (see Chapter 5).
2, 10	Working Shield	The shield for the working electrode. Connected to Floating Ground on D end of the cable Left open at the cell end of the cell cable.
3	No connect	
4, 6,11,13	Ground	The potentiostat's floating ground. Can be used to shield the cell if very low currents need to be measured. Also used as a shield for the counter electrode cable.
5,12	Counter	Connected to the Counter Electrode
7	CBL_ID1	One of 4 cable ID bits. Used to identify the type of cell cable attached to the unit. Pull to a logic High through a resistor. Ground to set the bit low.
8	CBL_ID2	One of 4 cable ID bits. Used to identify the type of cell cable attached to the unit. Pull to a logic High through a resistor. Ground to set the bit low.
14	CBL_ID0	One of 4 cable ID bits. Used to identify the type of cell cable attached to the unit. Pull to a logic High through a resistor. Ground to set the bit low.
15	CBL_ID3	One of 4 cable ID bits. Used to identify the type of cell cable attached to the unit. Pull to a logic High through a resistor. Ground to set the bit low.

Table B-2
Sense Inputs Connector

Pin(s)	Signal Name	Use
1	CBL_ID2	One of 4 cable ID bits. Used to identify the type of cell cable attached to the unit. Pull to a logic High through a resistor. Ground to set the bit low.
2	CBL_ID1	One of 4 cable ID bits. Used to identify the type of cell cable attached to the unit. Pull to a logic High through a resistor. Ground to set the bit low.
3,4	Ground	The potentiostat's floating ground. Can be used to shield the cell if very low currents need to be measured. Also used as a shield for the counter electrode cable.
5,6,12,14	Reference Shield	The shield for the reference electrode input. Driven to the same potential as Pin 16. Left open at the cell end of the cell cable.
7,15	Work Sense Shield	The shield for the work sense electrode input. Driven to the same potential as Pin 8. Left open at the end of the cell cable.
8	Work Sense	Connected to the working electrode in most cases (see Chapter 5). This lead has a 261 Ohm resistor in the cell end of the cable. Custom cell cables are likely to require a similar resistor.
9	CBL_ID3	One of 4 cable ID bits. Used to identify the type of cell cable attached to the unit. Pull to a logic High through a resistor. Ground to set the bit low.
10	CBL_ID0	One of 4 cable ID bits. Used to identify the type of cell cable attached to the unit. Pull to a logic High through a resistor. Ground to set the bit low.
11	Counter Sense	Connected to the counter electrode in ZRA-mode and stack-mode experiments (see Chapter 5). This lead has a 261 Ohm resistor in the cell end of the cable. Custom cell cables are likely to require a similar resistor.
13	Reference Electrode	Connected to the reference electrode in most cases (see Chapter 5). This lead has a 261 Ohm resistor in the cell end of the cable. Custom cell cables are likely to require a similar resistor.

Appendix C -- Misc I/O Connector

This connector contains a number of signals, used to interface the Reference 3000 to external apparatus. It is the miniature 15 pin female D shaped connector on the rear panel of the Reference 3000. Be careful, the ground on this connector is not the Reference 3000 floating ground.

The auxiliary analog output, derived from a D/A converter, is on this connector. The scaling is normally 1 mV per bit, for a 0 to 4.096 volt full-scale range.

The pin out of this connector is shown in Table C-1.

Table C-1
Miscellaneous I/O Connector

Pin	Name	Use
1	Analog Output High	The auxiliary output signal (DAC output).
2	Analog Output Low	The auxiliary output ground connection (ground)
3	Sync In	Used in slave mode – starts data acquisition 2.2 kΩ input impedance
4	Sync Out	A TTL pulse output before the start of a data point 330 Ω output impedance
5	no connection	
6	Ground	Digital ground
7	Digital Out 0	A TTL compatible digital output- 330 Ω output impedance
8	Digital Out 1	A TTL compatible digital output- 330Ω output impedance
9	Digital Out 2	A TTL compatible digital output- 330Ω output impedance
10	Digital Out 3	A TTL compatible digital output- 330Ω output impedance
11	Digital In 0	A TTL compatible digital input- 2.2 kΩ input impedance
12	Digital In 1	A TTL compatible digital input- 2.2 kΩ input impedance
13	Digital In 2	A TTL compatible digital input- 2.2 kΩ input impedance
14	Digital In 3	A TTL compatible digital input- 2.2 kΩ input impedance
15	+5 Volts	Power- 50 mA maximum current

Appendix D -- Auxiliary A/D Input Characteristics

Overview

The Controller board used in the Gamry Instruments Reference 3000 Potentiostat has jumpers or switches that configure the input circuitry used for the Aux A/D function. Early units have jumpers and later units have CMOS switches set using software. The changeover occurred in 2009.

We usually ask that you return your Reference 3000 to Gamry Instruments if you need to change the hardware jumpers. This information is provided so a qualified service technician can change the Aux A/D input jumpers in the field.

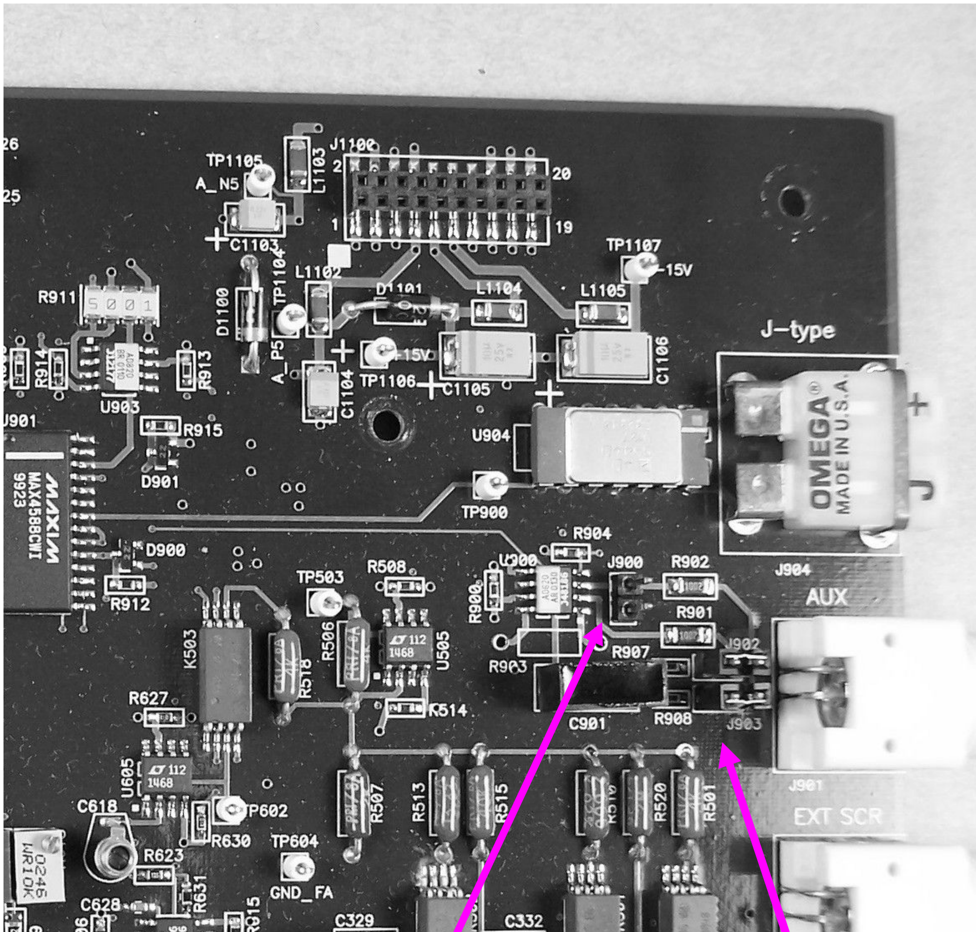
The CMOS switches are set using a function call in an Explain script. Once the CMOS switches are set, they remain in the selected position until another script resets them. Note that the settings will return to their default values on reset or Power Up of the Reference 3000.

Call or Email your local Gamry representative if you need to change your Auxiliary A/D input characteristics and you are uncertain which type of control board you have.

Jumper Identification

The three jumpers that configure the Aux A/D input are in a cluster located at the upper right side of the Controller Card. See the figure below for jumper locations.

Figure D-1
Auxiliary A/D Input Configuration Jumpers
View of Reference600 Controller Board



Input Impedance Selection

Two jumpers are associated with the input impedance – J902 and J903. With J902 and J903 installed, the Aux A/D input has a 100 kΩ input impedance. This is the default setting. With the jumpers installed, the potentiostat can be calibrated without a cable on the input BNC connector.

With both J902 and J903 removed, the Aux A/D input impedance is 10 GΩ (typically). This setting is suitable for use with a high impedance source such as a reference electrode. If you have removed these jumpers, <u>do not</u> calibrate the potentiostat unless you have a cable connecting both Aux A/D inputs to floating ground.

The CMOS switch shorts the circuit nodes connected by these jumpers. As with the jumpers, in the Low Impedance setting, the input impedance is set to 100 kΩ. In the high impedance setting, the CMOS switches are opened increasing the input impedance to about 10 GΩ**.**

Bandwidth Selection

J900 (or on some boards J901) controls the bandwidth of the Aux A/D input. With J900 (or J901) removed, there is no filtering on this input and the –3 dB bandwidth is greater than 300 kHz.

With J900 (or J901) 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 kΩ will appreciably lower this cutoff frequency. When the Aux A/D input is driven by a source with an output impedance of 1 MΩ, the frequency cutoff will be less than 0.25 Hz.

The CMOS switch performs the same function as the jumper.

Aux A/D Specifications

Range	±3.276 volts	
Input Impedance	100 kΩ (approx)	Low Impedance Selected
	or	
	10 GΩ (typical)	High Impedance Selected
Input Bias Current	< 10 nA	High Impedance selected
Filter Cutoff	20 Hz ± 20%	With Low Bandwidth selected

Function Call to Set the Aux A/D BNC Characteristics

The CMOS switch is set using an Explain function call. The syntax of this call is:

```
Pstat.SetAuxBNCSettings (Impedance, Bandwidth)
```

Both variables passed to the function are Booleans (with a value of TRUE or FALSE).

The following definitions can be used to make a script that calls this function more readable.

```
#define SETAUXBNCSETTINGS_IMPEDANCE_HIGH  TRUE
#define SETAUXBNCSETTINGS_IMPEDANCE_LOW   FALSE

#define SETAUXBNCSETTINGS_BANDWIDTH_HIGH  TRUE
#define SETAUXBNCSETTINGS_BANDWIDTH_LOW   FALSE
```

A TRUE in the Impedance variable opens the switches across J902 and J903, selecting high input impedance. A FALSE selects 100 k input impedance.

A TRUE in the Bandwidth variable opens the switch across J901, selecting high bandwidth. A FALSE selects low pass filter at nominally 20 Hz.

Appendix E – Auxiliary Electrometer Specifications

Unless otherwise mentioned, all specifications apply at 22° C, zero common mode voltage versus Ground FA, input voltages with Z_{out} < 10 Ohms, and all channel inputs (other than those of the channel under test) at zero volts versus Ground FA. All measurements are made with the Aux Channel A/D with normal Framework calibration.

DC Voltage Measurement

Offset Voltage	< 500 µV	20° C to 25° C	At all gain ranges
Temp Drift	< 10 µV/°C	from 0 to 45° C	
Ranges	± 50 mV, ±500 mV, ± 5V	Full Scale	Differential Input Voltage
Resolution	1.666 µV, 16.66 µV, 166.6 µV	per bit	Differential Input Voltage
Gain Error	< 0.3%		on all ranges
Offset Range	± 5.12 V		offset of differential signal
Offset Resolution	166.6 µV/bit		
Input Current	< 10 pA	zero volts input	measure by voltage

Input Impedance

Common Mode	> 30 GΩ in parallel with < 100 pF	-36V < Vcm < 36 V	versus floating ground
Differential	> 100 GΩ in parallel with < 40 pF	-5V < Vdiff < 5 V	measured between the two inputs

Common Mode Rejection

CMR Range	-36 V < Vin < 36V		versus Floating Ground
CMRR	> 94 dB > 86 dB	@ 3 Hz @ 100 kHz	

Crosstalk

Low Frequency	< -90 dB	DC to 10 kHz
High Frequency	< -80 dB	10 kHz to 100 kHz

Other AC Specifications

Bandwidth	> 2 MHz	- 3 dB
Phase Shift	< 1°	DC to 20 kHz
	< 3°	20 kHz to 100 kHz
Noise	< 4 μV_{pp}	0.1 Hz to 10 Hz
	< 10 $nV/Hz^{1/2}$	at 1 kHz

Appendix F – CE Certificate

GAMRY INSTRUMENTS

Redefining Electrochemical Measurement

Declaration of Conformity

According to ISO/IEC Guide 22 and CEN/CENELEC EN 45014

Manufacturer's Name and Location:

Gamry Instruments
734 Louis Drive
Warminster, PA 18974
USA

This declaration is for the Gamry Instruments product models: Reference 3000 Potentiostat/Galvanostat/ZRA.

The declaration is based upon compliance with the following directives:

EMC Directive 89/336/EEC as amended by 92/31/EEC and 93/68/EEC
Low Voltage Safety Directive 73/23/EEC as amended by 93/68/EEC

The declaration is based upon product compliance with the following standards as defined in report number R0295-000 from Ergonomics, Inc. for safety analysis and report number RSI-2772L from Radiation Sciences, Inc. for EMC test and analysis.

EMC Standards	Title	Class/ Criteria
EN 61000-4-2	EMC – Electrostatic discharge, Immunity	B
EN 61326:2002-2	EMC – Radiated Emissions	A

Low Voltage Directive Safety Standards	Title
EN 61010-1:2001	Safety requirements for electrical equipment for measurement, control and laboratory use, Part 1: General requirements.
EN 61010-2-081: 6/2003	Safety requirements for electrical equipment for measurement, control and laboratory use, Part 2 Particular requirements for automatic and semiautomatic laboratory equipment for analysis and other purposes

Signature

January 19, 2009
Date

Dr. Gregory A. Martinchek, PhD
Title: President

Formal signed declaration is on file at Gamry, Inc.

Certificate of Conformance

GAMRY INSTRUMENTS

Redefining Electrochemical Measurement

Declaration of Conformity

This declaration is provided according to ISO/IEC 17050-1: 2004 and ISO/IEC 17050-2: 2004

Manufacturer's Name and Location:

Gamry Instruments, Inc
734 Louis Drive
Warminster, PA 18974 USA

This declaration is for the Gamry Instruments product models PC5 3000 Series product family. This includes:

1. Gamry's p/n 990-00224 PC5 3000 Reference Potentiostat/Galvanostat/ZRA and any variations thereof; and
2. Gamry's p/n 990-00227 PC5 3000 Reference Potentiostat/Galvanostat/ZRA with its Auxiliary Electrometer option installed and any variations thereof.

The declaration is based upon compliance with the following directives:

- EMC Directive 89/336/EEC as amended by 92/31/EEC, 93/68/EEC and 2004/108/EC.
- Low Voltage Safety Directive 2006/95/EC as dated 12 December 2006.

The declaration is based upon product compliance with the following standards as defined in report number R0422-000 from Ergonomics, Inc. for safety analysis and report number R-1160P from Retlif Testing Laboratories, Inc. for EMC test and analysis.

EMC Standards	Title	
EMISSION		
EN61326:2003	Electrical Equipment for Measurement, Control and Laboratory Use - EMC Emission Requirements-Second Edition	Pass
IEC61000-3-2	Harmonics	Pass
IEC61000-3-3	Flicker	Pass
CISPR 16-2:1996	Class A Power Line Conducted Emissions	Pass
CISPR 16-2:1996	Class A Electric Field Radiated Emissions	Pass
IMMUNITY		
EN 61000-4-2:1995	Electrostatic Discharge	Pass Criteria B
IEC 61000-4-3:1995	Radiated Field Immunity	Pass Criteria A
IEC 61000-4-4:1995	Electrical Fast Transient Immunity (AC Power)	Pass Criteria B
IEC 61000-4-5:1995	Surge Immunity	Pass Criteria B
IEC 61000-4-6:1996	Power Line Conducted Immunity	Pass Criteria A
IEC 61000-4-11:1994	Voltage Dips and Interrupts	Pass Criteria C

Low Voltage Directive Safety Standards	Title
EN 61010-1:2001	Safety requirements for electrical equipment for measurement, control and laboratory use, Part 1: General requirements.
EN 61010-2-081: 2003	Safety requirements for electrical equipment for measurement, control and laboratory use, Part 2 Particular requirements for automatic and semiautomatic laboratory equipment for analysis and other purposes

Signature

1/19/2009
Date

Dr. Gregory A. Martinchek, PhD
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Comprehensive Index