



Dr. Bob's Cell for Small Scale Electrochemistry Operator's Manual



Copyright © 2016
Gamry Instruments, Inc.
Revision 1.2
September 10, 2012
988-00001

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 one year from the original shipment date of your purchase.

Gamry Instruments, Inc. makes no warranties regarding either the satisfactory performance of this Cell Kit 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 by replacement, as determined by Gamry Instruments, Inc., and shall not include other damages.

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

There are no warranties which extend beyond the description herein. This warranty is in lieu of, and excludes any and all other warranties or representations, expressed, implied or statutory, including merchantability and fitness, as well as any and all other obligations or liabilities of Gamry Instruments, Inc.; including but not limited to, special or consequential damages.

This Limited Warranty gives you specific legal rights and you may have others which vary from state to state. Some states do not allow for the exclusion of incidental or consequential damages.

No person, firm or corporation is authorized to assume for Gamry Instruments, Inc., any additional obligation or liability not expressly provided herein except in writing duly executed by an officer of Gamry Instruments, Inc.

If You Have Problems

Please visit our service and support page at www.gamry.com/service-support/.

This page contains information on installation, software updates, and training. It also contains links to the latest available documentation. If you are unable to locate the information you need from our website, you can contact us via email using the link provided on our website. Alternatively, you can contact us one of the following ways:

Internet	www.gamry.com/service-support/
Telephone	(215) 682-9330 9:00 AM - 5:00 PM US Eastern Standard Time (877) 367-4267 Toll Free US & Canada Only

Replacement parts for this kit are available from Gamry Instruments, Inc. Optional parts may be available from Gamry Instruments, or from 3rd party vendors. Contact your local Gamry sales representative to discuss any special requirements or accessories that you need.

Disclaimer

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.

Copyrights and Trademarks

Dr. Bob's Cell Manual copyright© 2012 Gamry Instruments, Inc.

Teflon® is a register trademark of DuPont, Inc.

Viton®, and Kalrez® are registered trademarks of DuPont Dow Elastomers, LLC.

Vycor® is a registered trademark of Corning, Inc.

No part of this document may be copied or reproduced in any form without the prior written consent of Gamry Instruments, Inc.

Table of Contents

Limited Warranty	i
If You Have Problems	ii
Disclaimer	ii
Copyrights and Trademarks	ii
Introduction	1
Chemical Compatibility of Dr. Bob's Cell	2
Unpacking and Checking a Cell Kit	3
Checking for Shipping Damage	3
Parts List	4
Assembly of and Use of Your Cell Kit	5
Cell Assembly- General Information	5
Gas-Flow Overview and Terminology	8
Pre-Saturation of the Purge Gas	8
Dr. Bob's Cell Gas Bubbler Assembly	8
Attaching Gas Tubing to the Cell	10
Counter Electrode Assembly	12
Counter Electrode Overview and Terminology	12
Dr. Bob's Cell Counter Electrode - Standard Isolated Assembly	12
Direct immersion of the Platinum in the Electrolyte	14
High Density Graphite Counter Electrodes	14
Reference Electrode and Bridge Tube	15
Overview and Terminology	15
Bridge Tube and Reference Electrode Assembly	15
Bridge Tube and Reference Electrode – Maintenance and Care	17
Working Electrode Installation	19
Working Electrode Overview	19
Working Electrode Surface Preparation	20
Working Electrode Installation	20
Spare Port	22
Addition of reactants	22
Temperature Sensing and Control	22
Addition of a pH electrode	22
Getting a Stir Bar into the Cell	22
Moving the Pieces About	22
Electrode Connections	23
Troubleshooting	24
Specifications	26
Index	1

Introduction

Gamry Instruments designed Dr. Bob's Cell kit for electrochemical testing. Enzyme and catalysis studies, development of electrochemical sensors, basic research into battery mechanisms and determination of redox potentials of inorganic complexes represent a few of its many applications.

Dr. Bob's Cell can be used with electrolyte volumes as small as 2 ml and as large as 50 ml. It works well with conventional sized electrodes, such as 1-3 mm diameter disks. It also can be used with micro-electrodes (typically 1 to 10 μm diameter disks). This cell provides simple, flexible, and reliable operation in a wide variety of testing situations.

Gamry Instruments provides platinum, gold and, glassy carbon working electrodes designed for use with this cell. These materials are the most popular for studying heterogeneous and homogeneous chemical reactions. Chemical modification of the surface of these materials is a common technique to gain specificity in a chemical sensor.

Most of the pieces required to run routine experiments are included in Dr. Bob's Cell kit.

NOTE: Neither a reference electrode nor a working electrode is included in the cell kit. Requirements for these electrodes vary too much user-to-user to make their inclusion in the standard kit practical. Gamry Instruments sells both reference electrodes (SCE, Ag/AgCl, and Hg/Hg₂SO₄) and macro- and micro-disk electrodes (in platinum, gold, and carbon) that are suitable for use with Dr. Bob's Cell kit. Contact Gamry Instruments directly or contact your local sales representative if you need working or reference electrodes.

Dr. Bob's Cell uses five standard ports to implement its required functions. You can customize the cell by rearranging some of Gamry's standard fittings and/or making or buying additional fittings, electrodes, sensors or adapters.

Too often, temperature control is neglected in designing electrochemical experiments. Temperature is an important variable in the rate of chemical reactions. Comparing test results recorded at different temperatures can be vital in gaining a full understanding of a chemical system. For these reasons, Gamry offers a special jacketed version of Dr. Bob's Cell. When this cell is connected to a circulating water bath, accurate temperature control of your experiments becomes possible.

Chemical Compatibility of Dr. Bob's Cell

The components in Dr. Bob's Cell were selected to be as chemically inert as possible. In normal use the only materials in contact with the test solution are:

- the working electrode material and the insulator surrounding the working electrode
- borosilicate glass (Pyrex® or equivalent),
- unfired Vycor®,
- PTFE (Teflon®),
- platinum,
- polyethylene,
- ACE Glass's FETFE o-ring material

Chemical resistance tables for most of these materials are available. One exception is FETFE, which is a elastomer proprietary to ACE Glass, which consists of PTFE particles in a fluorinated rubber base similar to Viton®. According to ACE Glass, it offers slightly better chemical resistance than Viton®.

The black ACE-Thred fittings supplied with the cell do not normally come in contact with the cell electrolyte. These are nylon fittings, so you can use nylon's properties (which are generally available) as an indication of these fitting's suitability for use in any specific chemical environment.

CAUTION: The nylon bushings in the ACE Thred fittings and the FETFE o-rings may not be suitable for use in some electrolytes (particularly non-aqueous media). If you need better chemical resistance than that offered using the standard ACE-Thred components, ACE Glass (www.aceglass.com) can provide replacement fittings made from PTFE and Kalrez®, which are extremely resistant to chemical attack. Contact Gamry Instruments, if you need help selecting the proper replacement fittings.

Dr. Bob's cell was not designed for use in electrolytes that dissolve glass (extremely basic solutions or HF containing solutions).

CAUTION: The glass components in the cell and the Vycor™ frits used in the reference bridge tube are not suitable for use with extremely basic solutions or solutions containing hydrofluoric acid. We don't know of any substitute cell components that will completely overcome this limitation. If you need to work with solutions that will damage the Dr. Bob's cell, we recommend that you design and build an all plastic cell.

The simple construction of the polyethylene stoppers used to seal the unused port makes them easily adaptable as a vent for purge gas – you simply poke a hole in the flat surface of the stopper. While they provide chemical resistance to most aqueous electrolytes, they may not be a good choice for use with some aggressive solvents. If polyethylene is not suitable for your application, glass and PTFE stoppers are available from most laboratory supply houses. If you use these "more solid" stoppers, don't forget the need to vent purge gas from the cell.

Unpacking and Checking a Cell Kit

This section is primarily intended for the user who has just received a new Dr. Bob's Cell Kit.

Checking for Shipping Damage

Your new Dr. Bob's Cell kit was shipped disassembled to minimize shipping damage. All of the pieces have been carefully packaged in anticipation of rough handling in shipment. Unfortunately, no matter how carefully glass pieces are packaged, damage will sometimes occur.

When you first receive your Dr. Bob's Cell kit, please check it for any signs of shipping damage. Be especially careful if the shipping container shows signs of rough handling.

Obviously, the glass pieces are the most susceptible to damage. Check the glass pieces for chipping and small cracks as well as for major damage.

WARNING: Do not use any glass parts that are chipped or cracked. Any damage to glass increases the probability of additional damage. Broken glass can have extremely sharp edges that represent a significant safety hazard. Injuries from broken glass can be quite severe.

If any parts have been broken in shipment, please contact our US facility or your local Gamry representative as soon as possible. In most cases, Gamry should have replacement parts in stock. Please retain the shipment's packaging material for a possible claim against the shipping company.

Parts List

Please check the contents of your kit versus the Dr. Bob's Cell kit packing list in Table 1. When shipped, all of the Dr. Bob's Cell kit components should be labeled with their Gamry Instruments, Inc. part number.

If you are checking the completeness of an older kit, most of the components are shown in photographs throughout this manual.

Table 1
Dr. Bob's Cell kit Packing List

Quantity	Part Number	Description
1	900-00055	Manual, Dr. Bob's Cell
1	930-00031*	Dr. Bob's Cell Kit Cell Body
1	930-00037**	Dr Bob's Cell Kit Jacketed Cell Body
1	930-00044	Dr. Bob's Cell Bridge Tube w/ Vycor Frit
1	930-00033	Dr. Bob's Cell Gas Flow Adapter
1	930-00034	Dr. Bob's Cell Bubbler Tube
1	930-00035	Fritted Counter Isolation Tube
3	930-00042	Frit, Unfired Vycor®, 3.5 mm diameter, with tubing
3	935-00052	#7 ACE-Thred Bushing, Nylon, with FETFE o-ring
1	935-00053	#11 ACE-Thred Bushing, Nylon
1	935-00054	Adapter, #7 ACE-Thred to ¼" hose
150 mm	935-00056	Platinum Wire, 0.4 mm diameter
1	935-00057*	Support Stand for Dr. Bob's Cell
5	935-00059	Polyethylene Stoppers for 14/20 Joint
1	935-00065	Stir bar, Micro, 6.35 mm by 2 mm

Contact us as soon as possible if any of the essential parts are missing.

The contact information for our US facility can be found immediately following the title page of this manual. If you're located outside the US, you may want to contact your local Gamry representative.

*Only included in the Standard Dr Bob's Cell configuration, 990-00193.

**Only included in the Jacketed Dr. Bob's Cell configuration, 990-00200.

Assembly of and Use of Your Cell Kit

This section of the manual tells you how to assemble and use a Dr. Bob's Cell kit in its standard configuration.

This "standard" cell configuration has:

- A standard cell body for use at room temperature
- a working electrode in the center port (#7 ACE-Thred) of the cell,
- a 3-way gas purge/blanket/vent adapter in one 14/20 standard taper port
- a frit isolated platinum counter electrode in one #7 ACE-Thred port
- a reference electrode and bridge tube in one #7 ACE-Thred port
- one unused 14/20 standard taper port (may be closed with a stopper)

This is one of many possible cell configurations. Feel free to customize your Dr. Bob's Cell. You are only limited by your imagination and the number and size of the ports available on the top of the cell.

Cell Assembly- General Information

A picture of an assembled cell can be seen in Figure 1.

If you are assembling your Dr. Bob's Cell kit for the first time, you may want to assemble the entire cell dry first. Once you are comfortable with the cell's assembly, you can fill the cell with a test solution and run real tests.

We recommend that you start the assembly of your cell by placing the cell body in the epoxy coated cell stand supplied with your cell kit. The cell body is not stable when laid on a flat surface such as a lab bench and can easily roll off a bench onto the floor with cell-shattering results. Gamry Instruments can always use additional sales, but we'd hate to have them come in the form of replacement cell bodies! Make use of the cell stand to avoid problems.

CAUTION: Always assume that the cell body will roll a substantial distance if laid down on a flat surface. Guard against it rolling off your test bench. Gamry's cell stand can be very useful in preventing this type of accident.

In many cases, you can even run your experiments with the cell placed in the cell stand. If you feel you need a more stable test setup, the cell can be mounted in a ring-stand.

Two of the ports on Dr. Bob's cell are 14/20 standard taper ground glass joints. These joints should not be greased.

CAUTION: In vacuum work in a chemical laboratory, ground glass joints are often greased. This is unnecessary with Dr. Bob's Cell, and may even cause problems if the grease gets into the test solution or an electrode. Do not grease any of the ground glass joints on your Dr. Bob's Cell.

Figure 1
The Standard Configuration of Dr. Bob's Cell



You should pay careful attention to cell cleanliness. In most electrochemical testing situations, contaminants in the cell and test solution can lead to poorly reproducible results.

If you touch the cell components with your fingers, you can inadvertently add salts and organic compounds to your cell solution. We recommend that you carefully clean the cell components using good laboratory practice. Once the components are clean avoid touching their wetted surfaces.

Dr. Bob's Cell includes a number of ACE-Thred connectors used for a wide variety of functions. #7 ACE-Thred connectors are particularly common on Dr. Bob's Cell. ACE-Thred fittings are designed to seal cylindrical objects into the cell. These objects can include glass tubes, glass plugs, thermometers, and plastic electrode bodies. ACE-Threds are designed to be tightened with finger pressure only.

CAUTION: ACE-Thred fittings should always be tightened "finger tight". Do not use tools such as a wrench or pliers to tighten an ACE-Thred fitting. Overtightening a fitting can break the cell. In extreme cases this can cause personal danger because broken glass can have very sharp edges.

Assembly of and Use of Your Cell Kit--Cell Assembly- General Information

A given ACE-Thred size can only accommodate specific diameter objects. A #7 ACE-Thred is specified to work with object with a diameter between 6.5 mm and 7.5 mm. If you need to add non-standard options to your Dr. Bob's Cell kit, make sure you are aware of this restriction.

Figure 2
Picture of Jacketed Dr Bob's Cell Configuration



Gas-Flow Overview and Terminology

The Gas Bubbler Assembly may or may not be required for your experiment. Most of the cases in which you use it involve the removal of atmospheric oxygen from the test solution.

Oxygen is an electrochemically active gas. An aqueous solution in contact with the atmosphere usually contains millimolar concentrations of oxygen. If oxygen can be reduced in the potential region you wish to study, it can interfere with your electrochemical measurements.

You can remove oxygen from the test solution by bubbling nitrogen, or another electrochemically inert gas, through the solution. This process is often (imprecisely) called de-aeration. It is more correctly called de-oxygenation. Other commonly used terms for the process of oxygen removal are gas purging or sparging. At least 15 minutes of vigorous bubbling with nitrogen will be required to remove most of the oxygen from a test solution.

Bubbling gas through your test solution can cause noise while you are running your experiment. To avoid this noise, you can stop gas purging during the data acquisition phase of your experiment. Instead you can flow the inert gas over the top of the test solution, often referred to as "blanketing" the cell. In general, blanketing is used after solution purging, where blanketing prevents dissolution of oxygen from the gas above the solution.

Many modern electrochemical test systems include automatic control of gas flow in their experimental sequencing. This is true of Gamry Instruments' PV220 and PHE200 systems. These systems output a digital signal that is intended to control a solenoid valve, which in turn routes gas flow to the cell. Gamry's VistaShield™ Faraday Cage, when equipped with its Purge and Stir option, provides a complete solution for purge gas control.

Pre-Saturation of the Purge Gas

Bubbling dry purge gas through your cell electrolyte can cause significant evaporation of the electrolyte's solvent during the purge process. This can be a significant source of error in some experiments. This problem can often be avoided by pre-saturation of the purge gas with the electrolyte prior to it entering the cell. This is commonly done using a "gas washing bottle", which can be obtained at most laboratory supply companies.

Dr. Bob's Cell Kit does not include a gas washing bottle, since they are already available in many laboratories.

Dr. Bob's Cell Gas Bubbler Assembly

The standard gas bubbler assembly consists of four pieces, the Gas Flow Adapter, the Gas Bubbler Tube, a #7 ACE-Thred nut, and an ACE-Thred To Hose adapter. A photograph of these pieces can be seen in Figure 2. Note the o-rings, which are required.

Figure 3. Gas Bubbler Assembly



Figure 3 is representative of the Gas Bubbler used for purge only (no blanketing). A plastic hose (not shown) should be connected to the Gas Bubbler Tube using the ACE-Thred To Hose adapter. The other end of this hose should be connected to a source of purge gas.

At Gamry, we often refer to the gas bubbler assembly as a 3-way adapter, because it can be used to implement three functions: purge, blanket and vent.

The vent function is critical. Regardless of whether gas is flowing through or over the test solution, you must provide a way for it leave the cell. If you, do not, the gas may not flow or worse, the cell may burst apart unexpectedly. Not providing a vent for the escape of purge gas is a very common and often dangerous "mistake" made when setting up an electrochemical cell.

CAUTION: If you use purge or blanket gas, you must provide a vent for the gas to escape the cell. Dr.. Bob's Cell was not designed to withstand gas pressure! Failure to vent the cell so can cause damage to the cell, uncontrolled loss of electrolyte from the cell, and risk of personal injury to the cell's operator.

In normal use, the Gas Flow Adapter is installed in one of the 14/20 ground glass ports on your Dr. Bob's Cell. The Gas Bubbler Tube, with an o-ring installed as shown in Figure 3, is slid into a #7 ACE-Thred port on top of the Gas Flow Adapter. When you are satisfied with position of the Gas Bubbler Tube, you tighten the ACE-Thred nut.

Attaching Gas Tubing to the Cell

The position of the Gas Bubbler Tube is normally adjusted so its orifice end sits in the cell's electrolyte. The hose barb on the side of the Gas Flow Adapter can be used as a vent or as an inlet for blanket gas.

Your gas flow system should include a needle valve to control the gas flow rate. All gas tubing connections to the cell should be made with this valve turned all the way off. Making connection with a cell filled with electrolyte or adding electrolyte to a system when the gas flow is on can lead to horrible accidents.

Warning: Excessive gas flow can damage the cell and result in a loss of electrolyte. In extreme cases, this can represent a significant safety hazard.

The gas flow system should be connected and the cell electrolyte added before the needle valve is turned on. The valve should be opened slowly, while you watch the bubbles in the cell. Bubbling should not be vigorous enough to splash large quantities of electrolyte on the cell walls .

In addition to the needle valve, a 3-way valve is very useful in purge and blanket gas control. 3-way valves are available in both electrically switched and manual versions. A 3-way valve switches one gas stream so it flows from a single inlet to one of two outlets.

If your system includes a 3-way valve for switched purge and blanket gas control, we recommend that you:

- Connect the purge gas to the ACE-Thred to Hose adapter on top of the Gas Bubbler Tube
- Connect the blanket gas to the hose barb on the side of the Gas Flow Adapter,
- Use the spare port to provide a vent. A small hole poked into one of the polyethylene stoppers in the cell kit is generally a sufficient vent.

If you do not have a 3-way gas control valve, you can switch from purge mode to blanket mode manually. Connect the gas flow to the ACE-Thred To Hose adapter. When you want to purge, loosen the ACE-Thred nut holding the Gas Bubbler tube in place, slide the Gas Bubbler Tube deeply into the cell so its orifice is in the cell solution, then retighten the ACE-Thred fitting. When you want to blanket, slide the Gas Bubbler Tube far out of the cell, so its orifice is above the solution. When you use the cell in this way, the hose barb port on the Gas Flow Adapter provides a convenient vent.

Counter Electrode Assembly

Counter Electrode Overview and Terminology

The counter electrode in a 3-electrode electrochemical experiment is generally an inert metal or carbon electrode that provides a source or sink of electrons to the cell. Another term used for this electrode in the auxiliary electrode.

The electrochemist is generally not interested in the reactions that occur at the counter electrode. One exception is when the reactions at the counter electrode produce a soluble product that can diffuse to the working electrode and interfere with its operation. In this case, the electrochemist may want a diffusion barrier to isolate the counter electrode compartment from the rest of the cell. A glass frit is commonly used as an isolation barrier.

Dr. Bob's Cell Counter Electrode - Standard Isolated Assembly

In the standard configuration of Dr. Bob's Cell, the counter electrode is a length of platinum wire, isolated from the bulk solution by a glass frit. There are three pieces in the counter electrode assembly:

- a fritted isolation tube
- a #7 ACE-Thred nut,
- 150 mm of platinum wire.

A complete counter electrode assembly is shown in Figure 4. Note the placement of the required o-ring between the ACE Thred nut and the fritted end of the tube.

Figure 4. Counter Electrode Assembly



Assembly of and Use of Your Cell Kit--Counter Electrode Assembly

The fritted tube is slid into a #7 ACE-Thred port on the cell. The top end of the frit must be below the electrolyte level. If you are working with very small electrolyte volumes, you may need to abandon the isolation tube – see the section below.

Slide the platinum wire into the isolation tube. The lower end of the platinum wire must be in contact with electrolyte. A sharp bend in the platinum wire at the upper rim of the isolation tube can help prevent loss of contact between the electrolyte and the platinum. When the counter electrode wire is clipped to the platinum wire below this bend, gravity helps keep the counter electrode in place.

Direct immersion of the Platinum in the Electrolyte

When you are working with electrolyte volumes of less than 5 ml, the fritted isolation tube can get in the way of the other cell components, or can fail to fill with solution. In this case, you must place the platinum counter wire directly in the electrolyte.

Excessive resistance in the frit can also cause problems, especially when the cell electrolyte is poorly conductive and the cell currents are high. Typically, this will cause the cell current to limit at a value smaller than the compliance current of the potentiostat you are using. It can also cause slower than expected potentiostat response in fast experiments. As in the case above, when this happens, you can place the platinum wire directly in the electrolyte.

There are several approaches to counter electrode placement when you don't have an isolation tube. You can simply insert the platinum wire through the #7 ACE-Thred port normally used for the isolation tube. You can do this with or without an ACE Thred nut in the port.

You have more control of the wire placement if you put a piece of 7 mm glass tube into the port and put the wire into this tube. You can even melt the end of a 7 mm tube until it almost collapses, leaving a ½ to 2 mm hole. You can slide this tube into the #7 ACE-Thred port, with the small end down, and then slide the wire into the tube.

Regardless of how the platinum wire is placed in the cell, make sure that the exposed platinum wire does not touch the conductive portion of the working electrode or any other metal components present in the cell.

High Density Graphite Counter Electrodes

You can also use high density graphite as a counter electrode material. Graphite is less expensive than platinum, offers a larger surface area, and can often provide cell current via surface reactions that don't involve soluble products.

Gamry sells a 150 mm long high density graphite rod that can be used in a #7 ACE-Thred port. The rod diameter is approximately 6.5 mm. The Gamry Instruments part number for this rod is 935-00014.

To use this graphite rod as the counter electrode in Dr. Bob's Cell, simply slide the o-ring from the ACE-Thred port directly onto the graphite rod and place the rod into the port, until the desired length of the rod is immersed in the electrolyte.

Reference Electrode and Bridge Tube

Overview and Terminology

Most modern electrochemical measurements are performed using a 3-electrode potentiostat. The cell includes a reference electrode that has a constant electrochemical potential. All working electrode potentials are measured with respect to this reference electrode.

In many cases, placing the reference electrode directly in the test electrolyte can be a problem. Examples include:

- when the reference electrode is large, making it inconvenient to use in a small volume,
- when the reference electrode's filling solution will contaminate the electrolyte,
- when the cell is heated and you don't want the reference potential to change with cell temperature.

To avoid these problems, Dr. Bob's Cell always uses a bridge tube to locate the reference electrode above the cell. The bridge tube is a glass tube filled with electrolyte that provides a conductive path from the cell electrolyte to the tip of the reference electrode. The electrolyte in the bridge tube is usually identical to the cell electrolyte, but in some cases a different electrolyte may be called for.

A bridge tube is similar, but not identical, to a Luggin capillary. A Luggin capillary attempts to move the "sensing point" of the reference electrode close to the working electrode surface. The tip of the bridge tube in Dr. Bob's Cell is too large to qualify as a true Luggin capillary.

The bridge tube in Dr. Bob's Cell is particularly convenient, because it terminates in an unfired Vycor® frit, which makes filling the bridge tube easy yet doesn't add a lot of resistance to the reference electrode circuit. Most other bridge tube or Luggin capillary designs either have excessive resistance causing noisy data or potentiostat oscillation or are difficult to fill with electrolyte.

Bridge Tube and Reference Electrode Assembly

Figure 5 shows the Dr. Bob's Cell Bridge Tube and Reference Electrode. Note the placement of the o-rings. These o-rings are critical in sealing the ACE-Thred fittings holding this assembly together.

Dr. Bob's Cell does not include a reference electrode, because different tests may call for different reference electrode types. The reference electrode shown in Figure 5 is Gamry's standard saturated calomel reference electrode (SCE) P/N 930-00003. Gamry also offers an Ag/AgCl Reference (P/N 930-00015) and a Hg/Hg₂SO₄ reference (P/N 930-00029). Contact your local Gamry sales representative if you need a new or a replacement electrode.

Figure 5. Bridge Tube and Reference Electrode Assembly



Dr. Bob's Cell can be used with 3rd party reference electrodes, as long as the reference electrode diameter is between 9 and 10.5 mm.

These are the steps required to fill, assemble, and install the bridge tube and reference electrode:

- 1) Place an o-ring and #7 ACE-Thred fitting on the middle section of the bridge tube (see Figure 5).
- 2) Place an o-ring and #11 ACE-Thred fitting on the reference electrode (see Figure 5).
- 3) Pour electrolyte into the larger diameter end of the bridge tube, leaving about 1.5 cm between the bottom of the ACE-Thred and the top of the electrolyte. Make sure there are no air bubbles in the electrolyte between the frit and the top of the electrolyte.
- 4) Place the reference electrode, tip first, into the larger end of the bridge tube and tighten the #11 ACE-Thred fitting until it is finger tight and the reference electrode is held in place.
- 5) Place the smaller end of the bridge tube into one of ACE-Thred ports on your Dr. Bob's Cell
- 6) Adjust the height of the bridge tube so that it's tip will be in the electrolyte and close to the working electrode

- 7) Tighten the bridge tube's #7 ACE-Thred fitting until it is finger tight and the bridge tube is held firmly in place.

Bridge Tube and Reference Electrode – Maintenance and Care

The unfired Vycor® tips used on both the reference electrode and the bridge tube are subject to cracking when allowed to go from a wetted to a dry state.

CAUTION: Do not allow the Vycor® frits on the reference electrode or the bridge tube to dry out. They are likely to crack, greatly increasing the flow of bridge tube or reference filling solution into your cell. If the frit does dry out, we recommend that you replace it. Your Dr. Bob's Cell kit contains three replacement frits with Teflon heat-shrinkable TFE sleeves. Use a this kit whenever you need to replace a damaged frit.

Whenever possible the bridge tube tip should be stored in the electrolyte used in your system. The bridge tube can simply be placed tip down in a flask containing the electrolyte you use in your tests.

If you cannot keep the frit wetted with electrolyte, you can store the bridge tube tip in the solvent that it will be exposed to during testing. In aqueous testing, always use high quality de-ionized or distilled water. The Vycor® frits have a very large surface area which will absorb contaminants from impure solvents.

Periodically, it may be necessary to replace the Vycor® frits on the reference electrode and bridge tube. Dr. Bob's Cell comes with 2 spare Vycor® frits with Teflon heat shrink tubing. To replace the frit of the bridge tube, make sure the bridge tube is clean and dry. Cut the old frit off with a sharp blade, taking care not to cut yourself. Turn the tube upside down and place the Teflon sleeve over the end of the tube. Insert the piece of Vycor® frit in the sleeve and then heat the sleeve with a heat gun to shrink the Teflon sleeve around the Vycor® frit. Lastly, trim the sleeve to be flush with the exposed end of the Vycor® frit. A similar procedure can be accomplished with the reference electrode, however it may be difficult to empty. Instead just turn it upside down and keep the solution away from the tip.

Caution: Be careful when using a sharp knife because of the danger of cutting oneself. Never cut towards your body. Also take care when using a heat gun to avoid burning oneself.

The reference electrode is also supplied with a clear plastic sleeve covering a fill hole in its glass body. This fill hole serves two purposes. It allows you to refill the electrode with saturated KCl if the liquid level in the electrode drops. It also provides a vent, so the filling solution flows slowly out of the electrode. In normal use, we recommend that the fill hole be kept slightly open. When storing the electrode, the fill hole should be closed.

Note: If the electrode or the bridge tube has been stored in a pure, poorly conductive solvent, the Vycor® tip must refill with ions prior to use. In the case of the reference electrode, ½ hour with the vent hole open should suffice. In the case of the Bridge Tube, ½ hour with a vented reference in place should also be sufficient.

Assembly of and Use of Your Cell Kit--Reference Electrode and Bridge Tube

Gamry's Reference electrodes are shipped with a plastic sleeve covering the electrode tip. This tip is effective in keeping the reference electrode's Vycor® tip wet. A plastic sleeve on one side of Bridge Tube's Vycor® tip will not keep the bridge tube tip wet, unless the tube is filled with solvent or electrolyte.

Caution: Do not use a plastic sleeve to cover the Bridge Tube's Vycor® tip, unless the other side of the tip is covered with solvent or electrolyte. If the tip dries out, it is likely to crack, causing irreproducible results in your electrochemical tests.

Working Electrode Installation

Working Electrode Overview

An electrochemist is interested in the reactions that occur at, or near to, the working electrode. In some cases, the working electrode is treated as an "inert metal" that functions as a simple source or sink of electrons. In other cases, the properties of the electrode are critical to the tests being performed.

Dr. Bob's Cell can be used with standard electrodes supplied by Gamry Instruments, or custom electrodes made by the cell's user or a third party vendor. In the latter case, the working electrode must be compatible with either a #7 ACE-Thred or a 14/20 ground glass joint. The discussion that follows assumes a 7 mm diameter working electrode mounted in the center port of the cell.

Working electrodes sold by Gamry Instruments include:

<u>Part Number</u>	<u>Description</u>
932-01	Disk electrode, 3 mm dia glassy carbon
932-02	Disk electrode, 3 mm dia gold
932-03	Disk electrode, 3 mm dia platinum
932-04	Microdisk electrode, 11 μm dia, glassy carbon
932-05	Microdisk electrode, 10 μm dia, gold
932-06	Microdisk electrode, 10 μm dia, platinum

All of these electrodes include a 7 mm section, suitable for mounting in a #7 ACE-Thred fitting. Figure 6 shows Gamry's macro-electrodes.

Figure 6. Macro Working Electrode Assembly



Working Electrode Surface Preparation

Solid electrodes are notorious for problems with surface reproducibility. With use, the electrode surface gets covered with contaminants that can include reaction products, trace impurities in the electrolyte, trace impurities from lab air and purges gas, organics from a chemist's handling of the cell.

A lot of care can be required to prepare of a clean electrode surface. One of the most common techniques to clean an electrode is polishing the electrode surface with a very fine abrasive. This removes a thin layer of electrode material and insulator from the electrode face. Usually you don't polish your electrode to remove scratches from the surface – you polish to remove accumulated surface contamination.

Gamry provides a electrode polishing kit that you can use to resurface your electrodes. The part number is 990-00195. It contains a flat glass plate, polishing cloths, and a bottle of alumina suspension.

Polishing can leaving polishing abrasive on the electrode surface. Many electrochemists recommend ultrasonic cleaning to remove this residue. Ultrasonic cleaning is generally done in pure solvent (for example ultra high purity water).

Electrodes can also be cleaned chemically and electrochemically. The specific cleaning regimen required prior to a given test is dependant on many factors, so this manual cannot give specific information.

Working Electrode Installation

The Working Electrode is generally the last part inserted into the cell. If you are deoxygenating your test solution, you might want to purge the cell before you place the Working Electrode into the solution.

Assembly of and Use of Your Cell Kit--Working Electrode Installation

Gamry's standard electrodes all mount in the central #7 ACE-Thred port on top of the cell. Custom electrodes with an electrode diameter between 6.5 and 7.5 mm can mount in the same port. If your electrode is smaller than 6.5 mm, we recommend that you add plastic heat shrink tubing or a machined plastic bushing to increase the diameter in the area where the ACE-Thred fitting will grip the electrode body.

You must slide a FETFE o-ring and an ACE-Thred fitting onto the electrode body before the electrode can be installed into the cell. The electrode in Figure 6 has this piece properly installed.

Slide the electrode into the cell until the tip is immersed in the electrolyte, then tighten the ACE-Thred nut. If your working electrode has both a lower glass and an upper plastic region, we recommend that only the glass end contact the solution.

Spare Port

The normal cell configuration includes a spare 14/20 port. If this port is truly not used, you can cap it with one of the 14/20 plastic stoppers included in your cell kit. Remember to poke a vent hole in this stopper if you will have gas flowing into your cell and there is no other gas vent available.

You can also use this spare port for customizing your system. A few examples are listed below.

Addition of reactants

In many experiments, you record a baseline curve before you add a vital reactant to the cell. You then add that reactant, stir the cell, then record another curve. Many of Gamry's analysis packages allow you to subtract the baseline curve from the data curve. The resulting curve shows only electrochemistry related to this reactant.

Another common use for added reactant is current versus concentration studies.

To add reactant, simply remove the stopper, add the reactant, then replace the stopper.

Temperature Sensing and Control

The rate of almost all chemical reactions is strongly temperature dependant. For this reason, you might want to either measure or control the temperature of your cell.

ACE Glass has thermometer adapters that are designed to mount a standard lab thermometer to a 14/20 ground glass joint. One example is ACE Glass part number 5028-26. This is an convenient way to add temperature measurement to your system.

In many cases, temperature must be controlled, not measured. One way to do this is:

- Purchase the jacketed option for Dr. Bob's Cell. This is a special cell body (Gamry part number 930-00037) that allows a flowing temperature transfer fluid to encase the cell.
- You plumb the jacket on the cell to a re-circulating constant temperature bath
- If the bath offers remote temperature sensing, you place a sensor in the spare port of the cell. This may require purchase of another option (for example an RTD to 14/20 port adapter).

In some cases, Gamry's software supports automatic temperature setting. The controlled temperature is simply added to the experiment's Setup window and the software controls the temperature bath via an RS232 port.

Addition of a pH electrode

Another possible use for the space port is addition of a pH electrode. Again, an adapter will be required.

Getting a Stir Bar into the Cell

If you want to magnetically stir, and you forget to add a stir bar to your cell, you can add it using the spare port.

Moving the Pieces About

There are several circumstance in which the standard cell configuration may not work. One is a larger than normal working or reference electrode.

There is no requirement that any electrode or adapter mount in any specific port. If your working electrode diameter is larger than 7.5 mm, you may be able to insert it into the cell through the spare port.

Electrode Connections

If you are using your Dr. Bob's Cell with a Gamry Instruments Potentiostat, the following connections are made to the electrodes.

The Reference Electrode lead plugs into the White pin jack on the cell cable.

The Green and Blue leads from the cell cable are attached to the Working Electrode. Cell current in a Dr. Bob's Cell experiment are normally small enough that the Blue and Green leads can be clipped together, then clipped to the working electrode.

NOTE: Some potentiostats may not include a Blue clip lead. In this case, you only connect the Green lead to the Working Electrode.

The Red lead on the cell cable clips to the Counter Electrode. A sharp bend in the platinum wire right at the rim of the counter electrode tube will help keep the platinum wire in place.

Make sure that the long Black lead on the cell cable cannot touch any other cell connection. You may find that connection of this lead to a source of earth ground, such as a water pipe, will reduce noise in your experimental results.

If you are measuring very small currents, you may find that a metal enclosure completely surrounding your cell will further reduce noise. In this case, the shield, known as a Faraday Cage, should be connected to an earth ground. The Black lead from the cell cable is then connected to the Faraday Cage.

Gamry's VistaShield is a versatile, easy to use Faraday Cage that was designed to work well with Dr. Bob's Cell. When equipped with a Purge and Stir option, it provides a complete electrochemistry test stand, well integrated with Gamry's cells, potentiostats, and software systems.

Always double check your cell connections. Even an experienced experimenter will occasionally leave one of the cell cable leads lying on the desktop.

Troubleshooting

By far, the most common source of problems is lack of a connection between a cell lead and the cell electrolyte. The lack of connection can be between the potentiostat and the electrode or between the electrode and the electrolyte.

One very common and often embarrassing error is to forget to connect one of the cell leads! Always double check your cell connections. Even an experienced experimenter can leave one of the cell cable leads lying on the desktop.

A more subtle problem is a gas bubble or air gap blocking an electrode's access to the electrolyte. Places where this can happen include:

- Purge gas or gaseous reaction products that collect on the face of the working electrode
- The counter electrode wire is too high and has pulled out of the solution
- The counter isolation tube doesn't fill with electrolyte
- The Reference Bridge tube contains a bubble between the reference electrode and the electrolyte
- A bubble collects on the Vycor® fit at the end of the reference electrode

Another common problem is two electrodes shorting together (coming into mutual electrical contact). This can occur within the cell (especially with a bare wire counter electrode). It can also occur between the cell cable connections.

The following section of the manual is organized as a list of problems that you may encounter. Following each problem is a list of some possible causes for that problem. Neither the list of problems nor the list of their causes is comprehensive.

NOTE: This troubleshooting guide only applies if you are running a potentiostatic experiment on the cell. Galvanostatic experiments will show different symptoms.

Very small current or no current when you run an experiment but no overload indication

- The working electrode (green) lead in the cell cable is not connected to the cell properly.
- There is a gas bubble on the face of the working electrode

Stop the experiment, fix the error and restart. The working electrode is not damaged.

Very small current or no current when you run an experiment, with a control amp overload

- The counter electrode (red) lead in the cell cable is not connected to the cell properly.
- The counter electrode is partially pulled out of the cell
- The counter electrode isolation tube has not filled with electrolyte

Stop the experiment, fix the error and restart. The working electrode is not damaged.

Full scale current and voltage when you run an experiment, overload indications seen

- The reference electrode (white) lead in the cell cable is not connected to the cell properly.
- The working sense (blue) lead in the cell cable is not connected to the cell properly.
- You have incorrect experimental settings (e.g., wrong potential).
- You have a high impedance frit (dirty or filled with water)
- There is a gas bubble in the Luggin Capillary or blocking the face of the Vycor® frit.

Large currents have passed through the working electrode. It may need to be resurfaced.

Noisy Cell Current – overloads may be present

- Your de-oxygenation gas is still bubbling through the solution.
- You have a high impedance in the reference electrode path
- There is a gas bubble in the Luggin Capillary.
- You are picking up noise – try a Faraday Cage.

Excess back pressure required to bubble deoxygenation gas

- No vent is available for the gas to escape.

Specifications

Cell

Volume	50 ml maximum 2 ml minimum
Port Types	Two 14/20 standard taper ground glass Three #7 ACE-Thred

Reference Electrode

Size	9 to 11 mm diameter	(using the standard bridge tube)
------	---------------------	----------------------------------

Working Electrode

Diameter	6.5 to 7.5 mm	(using central #7 ACE-Thred port)
Length	50 mm minimum 120 mm preferred	(using large cell volumes) (to use electrolyte volumes below 5 ml)

Index

ACE-Thred, 7
Assembly, 5

basic solutions, 2
bridge tube, 14

Cell connections, 21
cell stand, 5
Chemical resistance, 2
circulating water bath, 1
counter electrode, 11

damage, 3
deaeration, 8

Electrode Connections, 21, 23
electrolyte, 1

Faraday Cage, 21

Gas Bubbler Tube, 8
Green and Blue cell leads, 21
ground glass joints, 5

jacketed version, 1

nitrogen, 8
noise, 21

Parts List, 4
platinum wire, 11
polyethylene stoppers, 2
Problems, iii
purging, 8

Red cell lead, 21
Reference electrode lead, 21
Replacement of Vycor® Frit, 16

shield, 21
Shipping Damage, 3

temperature control, 1

vacuum grease, 5

vent, 10
VistaShield, 8, 21

Warranty, ii
working electrode, 17