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HIGH PURITY ELECTROCHEMICAL EXPERIMENTAL SYSTEM

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ABSTRACT

A closed system is described here in which freshly purified water and gases may be directed into a sealed test cell for electrochemical studies which require conditions of ultra high purity. The apparatus consists of purification trains for He, H₂, and O₂ gases, an in-situ still for repeated distillation of large quantities of water, and a well-sealed test cell which maintains the high-purity conditions during extended electrochemical experiments. The apparatus features quartz and teflon construction throughout and the connecting gas lines are pyrex glass with glass and teflon valves. The cell is quite versatile in that up to five samples may be loaded at one time with only 120 ml solution in the test compartment. A variety of experiments may be performed with the cell, including fast voltage scans, capacitance measurements, photoelectrochemical studies and steady state current-voltage, or Tafel measurements.

INTRODUCTION

Research in some areas of electrochemistry requires ultra-clean experimental conditions before reliable information can be obtained.¹ Both the gases and the solutions used in the experiments must be extensively purified after they are received as stock items such as tap-distilled water, cylinders of gas, and the appropriate acid, base, or salt. If only dilute solutions are used, the last item (acid, base, or salt) may be obtained in pure enough form that it may be injected directly into the solution mixing flask.

All of the necessary features of an ultra-clean system are seldom found in one reference. A newcomer to this field of research will find only scattered literature references, some quite old and inappropriate to today's research needs. This report describes in detail the features of a gas purification train, a water distillation system, and an electrochemical test cell. Even the experienced worker is faced with both new contaminants in water supplies that were not there a little more than a decade ago,¹ and new experiments which demand increasingly higher conditions of purity. The most notable problem area in this regard is the electrochemistry of oxygen. The correct rest potential of 1.23 V (versus the hydrogen electrode) for oxygen reduction in acid solutions can be obtained only under incredibly stringent conditions of purity and on carefully prepared electrodes.²⁻⁴ Fortunately, a good Tafel plot, with the correct slope and exchange current can be obtained under somewhat less stringent conditions, but the problem is still serious.

A common practice that has come into being is that of "pre-electrolyzing" the solution, usually with large platinum electrodes.⁵ However, it is now known that trace amounts of platinum are dissolved from these electrodes⁶ and can even plate out onto the test electrodes.⁷⁻⁸ If the electrode being studied is also platinum, then no problem should result, but such a situation limits the use of pre-electrolysis to a minority of experiments. Therefore, a cell of sufficiently high purity had to be constructed which would permit studies of oxygen reduction to be performed without the use of pre-electrolysis. To eliminate airborne contaminants, the test cell was connected to a high purity water distillation unit that permitted the in-situ distillation of water and solution preparation. Conway et al.¹ describe a distillation apparatus that features a catalytic column of platinum-iridium gauze heated to 800°C. At that elevated temperature, in an oxygen rich environment, all organic contaminants are hopefully reduced to H₂O and CO₂. However, such a column was not implemented in the system described here because of possible Pt contamination of the water.

TECHNICAL DETAILS OF THE STILL

The still described here features repeated distillations in quartz of large quantities (4-6 liters) of water, after the water has received the normal distillation over permanganate.

A summary of the literature will help indicate the components and materials requirements of a high purity still. The recommended construction materials are quartz and teflon.^{9,10} Borosilicate glass leaches impurities into the water until it is "well aged" and this criterion is never very well-defined. Oxygen can be bubbled through the system to oxidize organic impurities and to carry off any gases dissolved in the water.^{1,10} The oxygen bubbles also provide steam nucleation sites and so prevent bumping of the distillate. An efficient spray trap¹¹ and a throat heater¹⁰ are important components of a high purity still, especially the spray trap. The patented spray traps are an important component of commercially available high purity water stills such as the Barnstead brand stills. Supply water for the still should be the best obtainable by ordinary distillation methods. The best available is usually water distilled from a potassium permanganate-potassium hydroxide solution. The permanganate is a very strong oxidizer and attacks the organic impurities present in both "tap distilled" and deionized water. Distillation from the permanganate solution may not eliminate all organic impurities from the water.¹ The water may be further distilled by the method of Conway et al.,¹ or it may be distilled several times more in a quartz still. The latter method is described here.

The distillation unit is shown in Fig. 1. This apparatus consists mainly of quartz with Fischer and Porter quartz and teflon joints and stopcocks. The Fischer and Porter "solv-seal" joints make excellent high purity connectors for quartz or pyrex tubing, and provide some degree of mechanical flexibility. The various valves and waste drains are of pyrex construction as is the acid flask and automatic burette. All components that contact the water are quartz. The boiling and receiving flasks are each seven liters in volume, large enough to allow for two or even three distillations of the first charge of water without opening the system to the atmosphere. Two separate charges can first be distilled to fill the receiving flask the first time. Repeated distillations are possible because the boiling flask can be drained without opening it to the atmosphere, rinsed, and refilled through a drain from the receiving flask. The entire system is always kept under a positive pressure (3-4 cm of water) of high purity oxygen. Water used to fill the boiling flask should already be of the best "conductivity water" quality in order to prevent contamination of all parts of the still. (The term "conductivity water" arose from the work of earlier researchers who determined the conductivity of dilute electrolytic solutions.) The advantages of a quartz and teflon still are lost completely in redistilling ordinary tap distilled water. Supply water used in this still is taken from a Barnstead tin block "conductivity still" and has a specific conductivity of $5 \times 10^{-7} (\Omega\text{-cm})^{-1}$.

The first charge of water, 5 to 6 liters, is held at low boil for 15-20 hours, while oxygen is bubbled through the still. After the slow

Figure 1. Quartz and teflon still for in situ distillation of high purity water. All stopcocks and water lines are also of quartz and teflon construction

boil, the water is brought to a vigorous boil to remove as many impurities as possible from both the water and the surfaces of system components further along the line. After 20 to 30 minutes of the hard boil, the secondary (horizontal) condenser is turned on and the stopcock on the stillhead is opened to the receiving flask. Condenser start up must be very slow to avoid the rapid condensation of steam and subsequent formation of a partial vacuum in the system. A partial vacuum will draw outside air and impurities into the system. The first condenser is a vertical refluxing condenser which is used only if a vigorous boil is desired for long periods of time without collecting any water. Normally the refluxing condenser is not used because some volatile impurities may be continually refluxed also.

An efficient spray trap must be used in any distillation process to prevent the carryover of tiny mist particles formed by bursting bubbles of steam in the boiling flask. On this still a quartz tube filled with crushed quartz chips effectively eliminates any mist carryover. The spray trap is between the two condensers. The top of the spray trap is fitted with a throat heater to eliminate the creep of soluble impurities along the otherwise moist surface into the final condenser and receiving flask. Eleven liters of water are first distilled in two separate distillations to fill the receiving flask with six liters of water. The boiling flask is then drained without being opened to the atmosphere, rinsed three times with a little water from the receiving flask and filled with the remaining water. The entire distillation procedure is then repeated, resulting in two or three liters of high purity water.

After distillation, the distilled water from the receiving flask is mixed with acid from the automatic burette in a separate one liter quartz flask. The mixing flask drains directly into the main compartment of the electrochemical test cell.

THE ELECTROCHEMICAL TEST CELL

The complete cell is shown in Fig. 2. Except for the reference electrode compartment, the test cell is composed entirely of quartz and teflon. Three-compartment cells are standard equipment for much of the electrochemical work done today. This cell is based on a standard design¹² with several improvements and modifications for greater experimental flexibility and convenience. An important feature of this cell design is the teflon cell cap with teflon to glass tubing seals, shown in Figs. 3, 4, and 5. These tubing seals provide an excellent airtight seal with only fingertip tightening. The size 71/60 tapered cell cap and the seals were turned from solid teflon rods. Teflon (TFE fluor-carbon) machines beautifully with the correct tools, and is flexible, giving an airtight seal. The teflon cell cap could be made more compact than a 71/60 glass joint, resulting in a cell with less dead air space. Six 6 mm tubing seals were fitted on the top of the cap for solution inlet and electrode supports. Gas inlet and exit is made through the two side ports. For sample loading, the cell is opened at the 71/60 joint by slightly heating the teflon cap with a heat gun. Samples are loaded from beneath, the cell cap being clamped permanently in position. Gas lines are disconnected quickly at two "tapertite" Chemplast brand teflon tubing connectors.

The reference electrode compartment is separated from the main cell by a closed high vacuum stopcock and Luggin capillary. Maintaining ultra-clean conditions requires the use of a palladium hydride reference electrode,¹³ shown in Fig. 6. The counter electrode compartment,

Figure 2. Electrochemical test cell showing Pd-H reference electrode on the left and the double jacketed hydrogen counter electrode compartment on the right. The test compartment in the middle is a 71/60 quartz joint with a lathed teflon cap, and six (not all shown) teflon tubing seals

Figure 3. Teflon to glass tubing seal. The cap and body were turned from KEL-F and teflon rods

Figure 4. Teflon cell cap with one tubing seal shown. The cap was turned from a solid 3 inch dia. Teflon rod

Figure 5. Top view of the cell cap. The six holes are for the six tubing seals. Gas inlet and exit ports are on the side

Figure 6. Palladium-Hydride reference electrode of the design by McHardy (13)

shown in Fig. 7, is separated from the main cell by a quartz fritted disc. The disc is contained in a machined teflon plug which replaces the F&P teflon seal. A gold foil of 20 cm^2 area, immersed in an H_2 saturated compartment, provides an inert auxillary or "counter" electrode. The hydrogen prevents gold dissolution when the counter electrode is subjected to anodic potentials. Contamination of the main cell with hydrogen is prevented by isolating the counter electrode in an inner compartment, shown in Fig. 8.

With Fischer and Porter 9 mm and 15 mm quartz-teflon joints, the reference and counter electrode compartments may be detached from the test compartment. This feature allows for easier cleaning of the cell, independent alterations of any one of the three compartments, and easy replacement of the luggin capillary and quartz fritted disc.

The main or test compartment of the cell was constructed from an inner 71/60 ground quartz joint, Fig. 9, and is filled with approximately 120 ml solution for most experiments. Total volume of the cell is 400 cm^3 . The test compartment is of sufficient size that a large platinum or gold electrode may be held by one of the five sample holders to serve as a counterelectrode during capacitance or photolysis studies. One hundred ml is a small enough volume of solution that pre-electrolysis can be performed in 36 hours using the large Pt foil as an anode and the gold counter electrode as the cathode, if pre-electrolysis is desired. The solution in the test compartment may be vigorously stirred with a 1.5 inch magnetic stirring bar. Two millimeter teflon-quartz stopcocks provide drainage for the test and counter electrode compartments.

Figure 7. Outer counter electrode compartment

Figure 8. Inner counter electrode compartment. A gold foil can be inserted from the top and suspended by a gold wire (not shown). The wire seal is made by two viton O-rings and then hydrogen is bubbled from the bottom up onto the gold foil

Figure 9. Test compartment of the cell, made from a 71/60 quartz joint

All parts of the still and cell were cleaned by soaking at least 24 hours in a 50-50 mixture of sulfuric and nitric acids before the final assembly. Each part was then rinsed at least six times with conductivity water from a Barnstead tin block still.

GAS PURIFICATION

Elaborate purification trains were constructed in order to clean the gases before they enter the electrochemical cell and still. The gas purification trains and gas valving system are shown in Fig. 10. Any one of three different gases (O_2 , H_2 , He) may be independently passed through the test and counter electrode compartments of the cell. The gas bubbled into the outer counter electrode compartment is always the same as the gas passed through the test compartment. Stock gases (used thus far) have been of the low hydrocarbon type, with the trade names "zero hydrogen", "zero oxygen", and "zero helium". Absolute purities of the stock gases are greater than 99.99%.

The "zero oxygen" with < 0.2 ppm total hydrocarbons (THC) is forced at low pressure through a quartz tube containing 25 grams of 5% platinized asbestos (BDH Chemicals LTD. Poole, Eng.) at $450^\circ C$ to reduce the remaining hydrocarbons and CO to CO_2 and H_2O . The oxygen then passes over wet KOH pellets in a long tube to remove the CO_2 . As a final cleaning step, the oxygen passes through two tubes containing Linde 13X molecular sieve.

The "zero helium" contains < 0.5 ppm THC and is further purified by a tube containing hot ($400^\circ C$) copper turnings in a quartz tube to remove traces of oxygen. Remaining hydrocarbons and CO_2 are removed by two liquid nitrogen cold traps containing Linde 13X molecular sieve. The copper turnings become oxidized after extensive use (one cylinder of gas) and are periodically reduced by running a mixture of H_2 and He over the heated turnings. The copper was reduced in the same manner

Figure 10. Gas purification and valving system for the helium, hydrogen, and oxygen gases used in the experiments

immediately after the system was assembled. Copper turnings often contain considerable amounts of oil from the lathe and must be cleaned with a good solvent beforehand.

The "zero hydrogen" contains < 0.5 ppm THC and is purified only by two traps containing Linde 13X molecular sieve. All molecular sieve are periodically outgassed (several times per gas cylinder) at 300°C using woven glass heating tapes and aluminum foil for insulation.

All gas lines for the system were cleaned with acid, the stainless steel by etching with nitric acid, and the borosilicate glass tubing by the method just described. Stainless steel tubing was used as the connections to the gas cylinders. The remaining tubing is of borosilicate glass. No glass blowing was performed after cleaning the parts. All glass tubes were connected with swagelock brand stainless steel tubing connectors with teflon ferrules. All parts of the still are connected by Fischer and Porter teflon-quartz "solv-seal" joints.

SOME EXPERIMENTAL RESULTS

Two indicators of the cleanliness of the system are the rest potential of a platinum electrode in O_2 saturated solutions and the features of a potentiodynamic scan on a platinum electrode. Rest potentials on Pt in fresh solutions are normally 1.050 V RHE or higher. Acceptable potentiodynamic scans¹ on platinum are routinely obtained and an example is shown in Fig. 11. The system was used to study the effects of traces of platinum on the catalytic activity of sodium tungsten bronze crystals for oxygen reduction. Tafel plots were obtained for these crystals with current densities down to 10^{-8} A/cm².^{7,8}

Figure 11. CV curve for Pt, taken in the high purity test cell. The large negative background current between 0.2 and 0.6 volts is due to traces of O_2 remaining in the cell. The well-defined H_2 adsorption and desorption peaks near 0.0 V, and the PtO formation and reduction peaks near 0.7 V indicate very pure experimental conditions in the cell

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