

## CHAPTER THREE

### EXPERIMENTAL

#### 3.1. Introduction

Cyclic voltammetry was used to investigate the metal deposition and the electrochemical enantioselectivity response of different chiral organic molecules at platinum single crystal electrodes.

In order to collect reproducible and quantitative electrochemical data, the glassware used had to be kept clean during the whole experiment. Because of the great affinity of platinum surfaces for organic materials and ions, the water used for any electrochemical measurement had to be cleansed of all contaminants. The cleanliness of the glassware was very important during the research work and, in order to obtain accurate and precise results, the electrolyte solutions were always prepared from high purity reagents.

#### 3.2. Apparatus

The following apparatus was utilised in the present study:

- an electrochemical cell together with cell accessories (platinum counter electrode, palladium reference electrode, Teflon crystal holder, capillary glass holder incorporating platinum wire connection, Teflon screw and gas caps).
- a variety of Pyrex glassware (beakers, measuring cylinders, volumetric flasks, pipettes and gases bubblers, all of which had to be scrupulously cleaned prior to any electrochemical procedure (see below).
- Electronics for cyclic voltammetry, including a computer and electrochemical analyser incorporating a three-electrode potentiostat.
- a series of platinum single crystal electrodes cut to expose the following crystallographic planes:
  - flat single crystals: Pt(111), Pt(100) and Pt(110).
  - stepped single crystals: Pt(755), Pt(533), Pt(211), Pt(311), Pt(511), Pt(711), Pt(911), Pt(11,1,1), Pt(13,1,1) and Pt(332).

- chiral kinked single crystals: Pt(531)<sup>R</sup>, Pt(531)<sup>S</sup>, Pt(321)<sup>R</sup>, Pt(321)<sup>S</sup>, Pt(643)<sup>R</sup>, Pt(643)<sup>S</sup>, Pt(976)<sup>R</sup>, Pt(976)<sup>S</sup>, Pt(841)<sup>R</sup>, Pt(841)<sup>S</sup>, Pt(11,7,1)<sup>R</sup> and Pt(11,7,1)<sup>S</sup>. All of these platinum single crystals were manufactured in Cardiff (see later).
- a travelling microscope to measure the surface area of the Pt single crystals.
- high purity chemical reagents and gases. The grade of purity and source of all of these chemicals are listed in Table 3.1.
- an electronic balance (Sartorius) with a top pan to measure accurately the mass of solid compounds to a precision of  $\pm 0.0001\text{g}$ .
- a Milli-Q plus system to provide ultra-pure water.

In the following, a more detailed account of each of these pieces of apparatus will be given.

### 3.3. The Milli-Q-Water System

The Milli-Q plus system (Millipore, Watford, Hertfordshire) was used to produce ultra-pure water which contained very low levels of organic material. The system was capable of producing up to 1.5 litres per minute of ultra-pure 18.2 M $\Omega$  cm resistivity water with a total organic content of less than 10 parts per billion. Ultra-pure water was used for cleaning glassware and for the preparation of all electrolyte solutions. The system consisted of two individual parts:

- a “ Milli-RO 10 Plus” system which provided initial purification of the laboratory mains water supply. It consisted of a semipermeable, reverse osmosis membrane to remove contaminants, such as inorganic matter, colloids and bacteria, from the feed water. A pre-treatment pack was utilised which incorporated active carbon for the removal of chloride, organic compounds, particulate matter greater than 5  $\mu\text{m}$  in diameter. It also contained an anti-scaling compound. The purified water was then stored in a sixty litre tank where it was connected to the Milli-Q system for further purification. The system was provided with some monitoring facilities, such as feed water conductivity, temperature, permeate conductivity and membrane performance as a percentage of ionic rejection. An indicator was also provided showing when the pre-treatment pack was to be changed. The membrane was cleaned regularly (monthly) by the addition of a “chlorine” tablet into the membrane housing and a separate cleaning cycle carried out.
- a “ Milli-Q plus system” consisting of a purification pack of mixed bed resin designed to remove inorganic, organic, particulate and microbiological material. The Milli-Q plus system

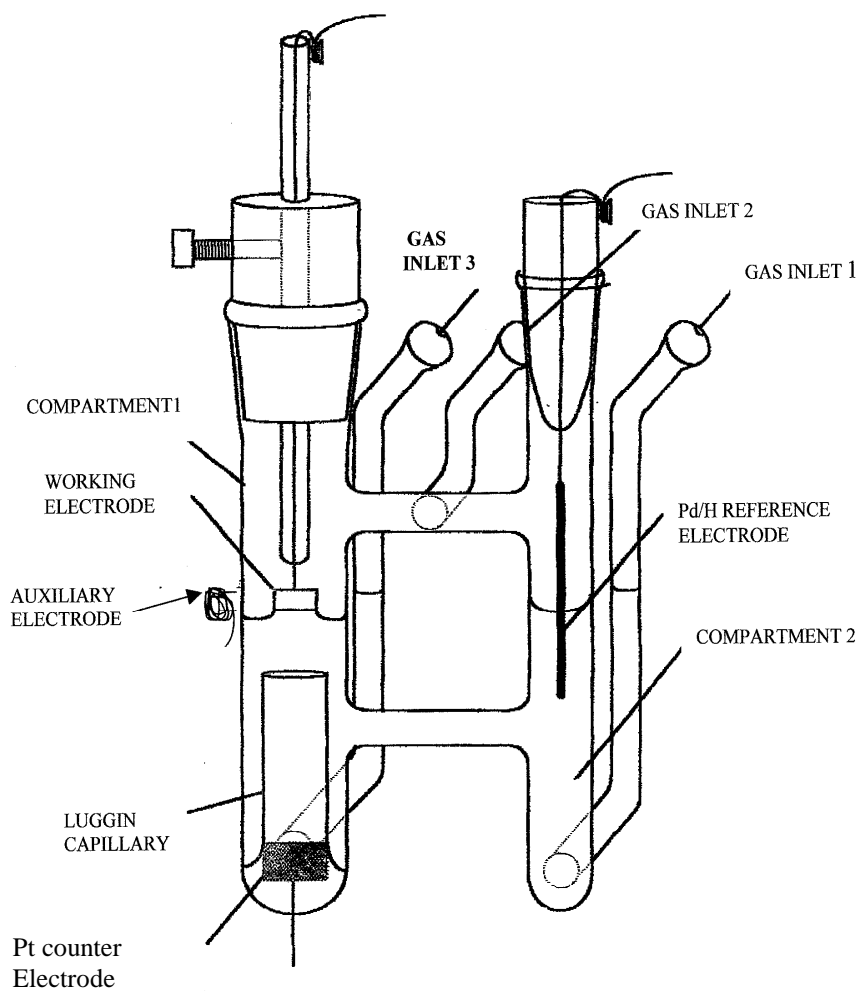
could produce 18.2 M $\Omega$  cm resistivity ultra-pure water at 25 °C. The final filter unit was a pre-sterilised, vented microporous membrane filter. This was used to remove micro-organisms and particulate matter larger than 0.22  $\mu$ m. The resistivity of the water was continuously measured by a sensor located at the outlet of the purification pack. This was electrically connected to a PC board where its reading was displayed on an alpha-numeric display. An automatic test on the accuracy of the resistivity measuring system was carried out before the unit went into operation mode. The system was provided with a unit to display the current temperature of the water in the system in °C [1].

### **3.4. Electrochemical Apparatus**

#### **3.4.1. The electrochemical cell**

A two compartment Pyrex glass electrochemical cell was used for all electrochemical experiments. A diagram of the cell is shown in Fig. 3.1. The cell contained four electrodes:

- the working electrode (W.E) which was a platinum single crystal electrode.
- the removable palladium/hydrogen (Pd/H) reference electrode (R.E), which was housed in a small adjoining compartment to the working electrode, maintaining a stable and fixed reference potential for the W.E.
- the platinum mesh counter electrode (C.E) placed down stream from the working electrode in a Luggin capillary to reduce the effect of Ohmic drop in the solution. The function of the counter electrode was to complete the electrical circuit by measuring the current passing between it and the working electrode. This electrode was introduced in order to make the current only flow between it and between the working electrode. This function was very important because if the current passes through the R.E, its potential will change and it will not be constant and thus can no longer be considered as a reference electrode. A potentiostat was used to control these three electrodes to ensure that current only flows between the working electrode and the counter electrode whilst maintaining an appropriate potential between the W.E. and the R.E.
- the auxiliary electrode was used when the working electrode had to be immersed at a fixed potential.



**Fig. 3.1.** The electrochemical cell used for conventional cyclic voltammetry.

### 3.4.2. The reference electrode

A palladium-hydrogen (Pd/H) reference electrode was used during the course of this study. This electrode was used since it could be kept clean and free of contamination that may originate from more conventional reference electrodes (such as chloride contamination from silver/silver chloride). It consisted of a palladium wire (Goodfellows Ltd, Cambridge) spot-welded to a platinum wire and sealed in a glass holder. After initial cleaning of the electrode in an acidic solution of  $\text{KMnO}_4$ , the palladium wire was heated in a Bunsen flame [2] in order to oxidise and remove surface contaminants. This was followed by a charging procedure involving the passage of hydrogen over the wire via the gas inlet of the reference compartment of the electrochemical cell for a period of 30 - 40 minutes. This allowed for the formation of a stable  $\beta$ -hydride phase, which exhibits a constant potential of 50 mV versus SHE for several hours.

As mentioned earlier, the palladium/hydrogen reference electrode had a distinct advantage over other reference electrodes in that the risk of any foreign chemical components being passed into solution was negligible.

### 3.5. The Cleaning Procedure

All glassware to be used for electrochemistry had to be thoroughly cleaned before use, otherwise the results gained would be affected by contaminants. This was achieved by carrying out the following procedure rigorously:

All glassware was soaked overnight in "green acid" (a dilute solution of potassium permanganate ( $\text{KMnO}_4$ ) in concentrated sulphuric acid (98.8%). The light green colour of the solution is associated with  $\text{MnO}^{3+}$  ions. The solution may detonate, however, if too concentrated because of the presence of  $\text{Mn}_2\text{O}_7$  [3]. Hence, this cleaning solution was eventually superseded by a so-called "pink solution". The pink solution was prepared by adding a small amount of  $\text{KMnO}_4$  to a dilute aqueous solution of sulphuric acid. The pink solution was less dangerous to use than the "green acid" and a fume cupboard was not required. However, the green acid was preferred for use on very dirty glassware or for glassware being used for the first time. In some cases, especially with solutions used for metal deposition, a pre-cleaning step of soaking the glassware in concentrated nitric acid was undertaken prior to treatment with the "pink" or "green" acid in order to remove metal ions.

The glassware was then washed well with ultra-pure water in order to remove all traces of the acid solution. When difficulties in removing the last traces of the acid were encountered, hydrogen peroxide was added to the glassware for 30 minutes to remove the last traces of acid present on the inside walls of the glassware. The glassware was then washed and steamed two or three times, for at least three hours, using ultra-pure Milli-Q water. Conical flasks, volumetric flasks and bubblers were steamed by placing a small amount of ultra-pure water inside, and heated on a hotplate, with a small length of flamed-annealed platinum wire placed between the cap and the top of the vessel in order to allow for steam-jet cleaning. Smaller items were placed in a beaker, covered with ultra-pure water and boiled. Finally, before electrochemical use, the glassware was washed again using Milli-Q water and was then ready for use. When not in use, all glassware was covered with ultra-pure water and never allowed to become dry.

### **3.6. Preparation of Electrolyte and Metal Deposition Solutions**

#### **3.6.1. Electrolyte solutions**

All electrolytes were prepared using high quality reagents (Aristar). The quality of the acid was the most important factor in determining the level of contamination. In this study several different electrolyte solutions were used.

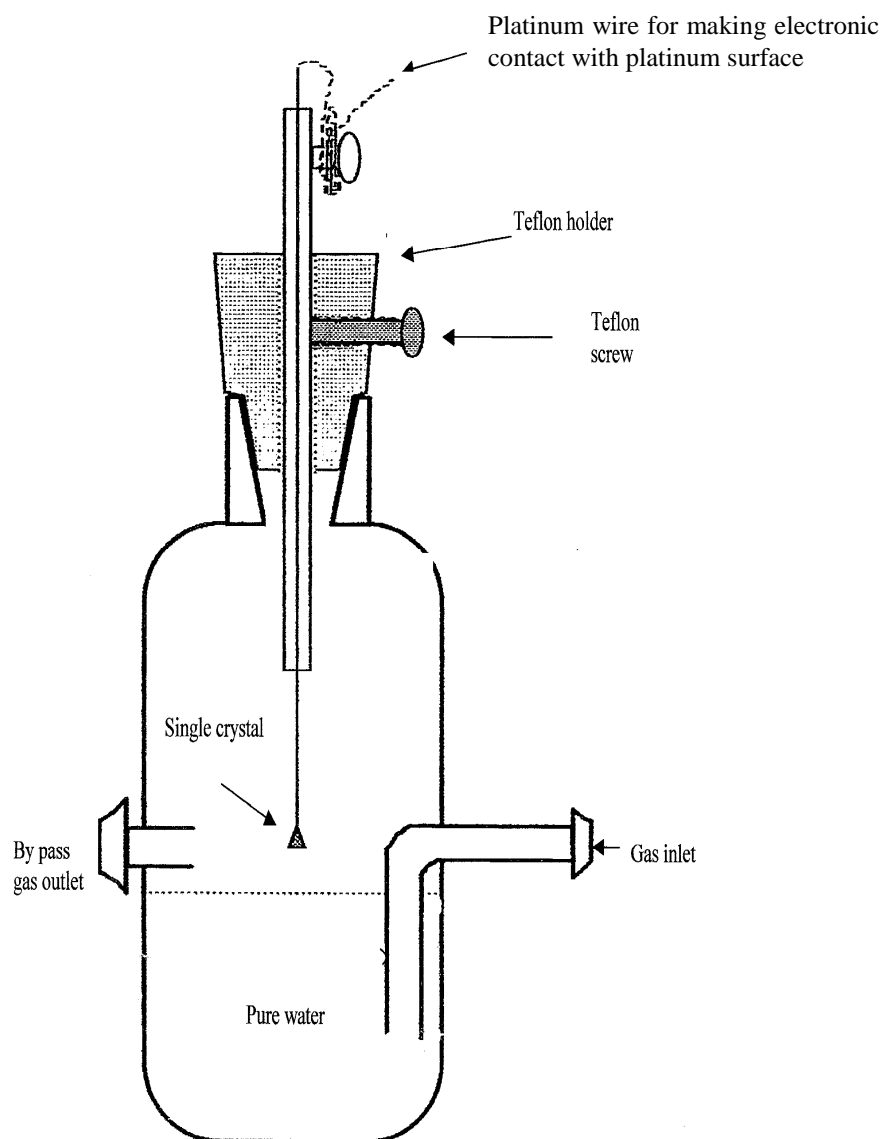
Sulphuric acid electrolyte was prepared from ARISTAR grade concentrated acid (BDH) using ultra-pure water from the Milli-Q purification system. The concentration of sulphuric acid was usually 0.1 M. D-glucose and L-glucose diluted in 0.1 M H<sub>2</sub>SO<sub>4</sub> at a concentration of  $5 \times 10^{-3}$  M and allowed to equilibrate overnight in order to avoid problems associated with mutarotation [4]. All other organic electrolyte solutions used were made up in 0.1 M H<sub>2</sub>SO<sub>4</sub> in the concentration range  $10^{-3}$  and  $10^{-6}$  M in order to study their chemisorption from solution onto flat, stepped and chiral platinum surfaces. All electrolyte solutions were purged of dissolved oxygen by bubbling white spot nitrogen through the electrochemical cell for 15-20 minutes. Similarly, exclusion of oxygen from the electrochemical cell was maintained via a small positive pressure of N<sub>2</sub>.

### 3.6.2. Metal deposition electrolytes

Solutions of  $\text{Au}^{3+}_{(\text{aq})}$  and  $\text{Ag}^{+}_{(\text{aq})}$  were prepared from chloroauric acid  $\text{HAuClO}_4$  (Johnson Matthey 99.99% pure) and silver perchlorate  $\text{AgClO}_4$  (Johnson Matthey 99.99% pure) in the concentration range  $10^{-6}$  to  $10^{-5}$  M. The  $\text{Bi}^{3+}_{(\text{aq})}$  solution was prepared from bismuth nitrate  $\text{Bi}(\text{NO}_3)_3$  (BDH, 99.9% pure). Since the bismuth nitrate was rather insoluble, a saturated solution, formed by adding a few solid crystals to a 50 ml beaker containing ultra-pure water followed by stirring in order to dissolve most of the solid, was used.

### 3.7. Procedures Used in Typical Electrochemical Experiments

Before each cyclic voltammogram was recorded, the appropriate Pt single crystal working electrode was selected and connected to a long Pt wire, about 20 cm in length. The wire was then placed inside the glass capillary holder. The capillary was devised to be held in the Teflon holder and could be moved up and down by loosening the screw connected to the Teflon holder, hence the height of the sample above the electrolyte could be adjusted. The sample was manoeuvred by tweezers until its face was centred and parallel relative to the electrolyte solution in the cell. The crystal was etched initially in nitric acid for ten seconds to ensure any previous adsorbates were removed, and then rinsed in Milli-Q water. The crystal was then flame annealed in a Bunsen burner flame (in the hottest part of the flame) for about one minute, such that a “yellow-hot” state was achieved before use. This ensured that all contaminants from the surface were oxidatively removed and that the surface was well ordered [2]. The crystal was then removed from the flame and as soon as the red colour of the hot crystal had diminished it was quickly placed into the hydrogen bubbler (Fig. 3.2). It should be noted that the very hot crystal was never placed into the bubbler directly, otherwise an explosion could have occurred. The crystal was then allowed to cool down in a flow of hydrogen for approximately thirty seconds followed by quenching. Sufficient time had to be allowed for the crystal to cool since quenching at too high a temperature could, over a period of time, induce crystal stresses which eventually would give rise to a polycrystalline sample. Thus, fast quenching could quickly reduce the lifetime of the crystal [2,5,6]. The crystal was then immersed for 1 second into the hydrogen saturated pure water and the surface isolated by a water droplet to protect its surface from being contaminated by

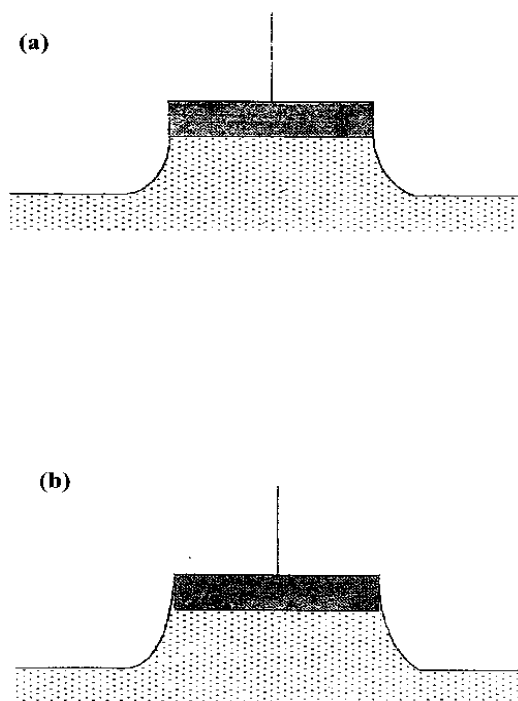


**Fig. 3.2.** A schematic diagram of the bubbler used for cooling the well-defined flame-annealed platinum electrode in a stream of hydrogen for electrochemistry

air during its transfer to the electrochemical cell. After placing the crystal in the cell, the nitrogen gas line was transferred to the gas inlet (2)(Fig. 3.2) to ensure that a constant stream of nitrogen was kept flowing over the solution for the duration of the experiment. By raising the height of the hemispherical electrode, a good meniscus contact was achieved between the electrode and the electrolyte (Fig. 3.3 (a)). At this point the Teflon screw was re-tightened and the position of the sample fixed. The meniscus was given time to drain off prior to a voltammogram being recorded. Electrical contact was then made between the three electrode potentiostat and the cell by three leads starting in the order:

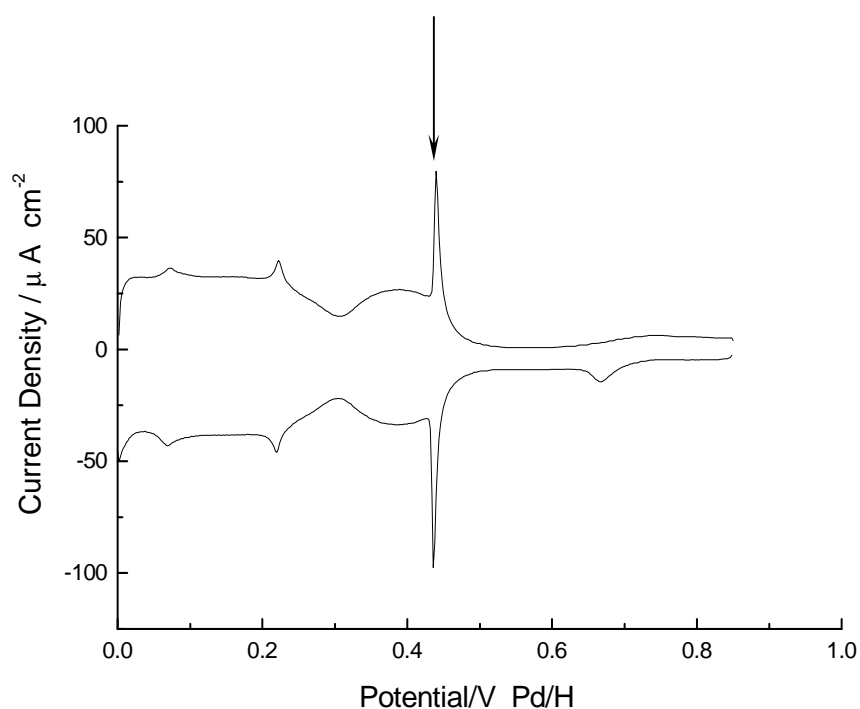
C.E  $\longrightarrow$  R.E  $\longrightarrow$  W.E (and the opposite process when the cell was being disconnected). All cell connections were then checked and a cyclic voltammogram measurement was performed. The initial state of the electrode was assessed in order to obtain information on the surface structure and cleanliness of the solution. The characteristic Pt(111) “spike” at 0.42 V(Pd/H) can be used to monitor contamination levels in the electrolyte [7] (Fig. 3.4). A diminishing spike intensity was a sign of serious experimental contamination levels.

Unless stated otherwise, all voltammetric data was collected at a sweep-rate of 50 mV s<sup>-1</sup>.



**Fig. 3.3.** (a) Formation of a good meniscus contact between crystal and electrolyte; (b) Poor meniscus formation due to wetting of crystal edges by electrolyte.

The peak magnitude is an indicator of the contamination levels of the electrolyte and the degree of surface long-range order.



**Fig. 3.4.** Cyclic voltammogram for Pt(111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> at sweep rate 50 mV s<sup>-1</sup>.

### 3.8. Procedure Used for Metal Deposition

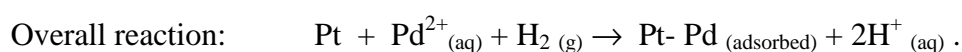
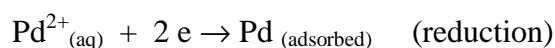
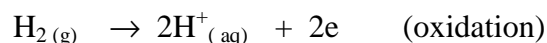
In order to obtain a full range of metal coverages, two methods of irreversible adsorption were employed, the “forced deposition method” [8] and the “immersion technique” [9]. Very dilute metal ion solutions are preferred in both methods since the growth of the adlayer is relatively slow and hence three dimensional crystallisation, due to a high adsorbate flux to the substrate, is avoided

#### 3.8.1. The forced deposition method

The forced deposition method [8] was used to produce high coverages of metals (multilayer formation and submonolayer coverages > 0.3 monolayers). Chemical reduction was used to deposit metals onto platinum single crystals. In this case, hydrogen was used as a reducing agent since the hydrogen can be adsorbed on the surface of platinum by breakage of the dihydrogen bond and the only bi-products are protons. Hydrogen as a reducing agent is

limited to those metal substrates which can adsorb hydrogen such as platinum and palladium. Substrates such as Au and Ag are not amenable to deposition by chemical reduction using hydrogen. This method has already been used, for example, to deposit palladium on platinum [8]. The method involved placing a flame-annealed Pt single crystal, protected by a droplet of ultra-pure water, into an aqueous solution of the cation to be deposited. The sample was then transferred with a droplet of metal solution attached to the crystal surface to the hydrogen bubbler, where the hydrogen gas was passed over a droplet of aqueous solution containing metal ions. The electrons generated by the dissociation of hydrogen gas at the platinum surface cause the “forced deposition” of metal cation in solution onto the platinum surface via a local cell mechanism ( $\text{Pd}^{2+}$  reduced,  $\text{H}_2$  oxidised). The ultimate coverage obtained using this method of deposition was a function of both metal cation concentration and hydrogen overpressure. Any excess metal solution was then rinsed off and the electrode was transferred to the electrochemical cell and electrical contact made under potential control. The potential of the substrate when hydrogen gas is flowing is between  $-0.06$  V and  $0.1$  V [8] versus a reversible hydrogen electrode (RHE) and as such, all redox couples positive of this value should be reduced.

The deposition of Pd at Pt single crystals therefore occurs as follows:



### 3.8.2. The immersion technique

Simple immersion of an electrode surface into a metal ion solution at open circuit can sometimes result in spontaneous irreversible deposition [10]. Usually, the extent of adsorption in this case may be limited to a fraction of a monolayer. In this method, the flame-annealed Pt electrode protected by a droplet of water was immersed in the aqueous metal solution for a fixed length of time to produce an overlayer of the desired metal coverage. Any excess of metal solution was then rinsed off and the electrode was transferred

to the electrochemical cell as usual. The immersion in the same metal cation solution could be repeated many times in order to increase the number of adatoms. One could also simply increase the time of exposure of the single crystal to the metal cation solution. However, it was found that a much more controlled method of deposition using immersion was to use different concentrations of metal ion. Finally, after completion of all metal deposition experiments, the platinum crystal was removed from the solution and etched in nitric acid to dissolve away any residual surface adatoms prior to flame-annealing in order to avoid the possibility of forming an alloy.

### **3.9. Procedure for Carrying out the Electro-Oxidation of D-Glucose and L- Glucose at a Platinum Single Crystal Electrode Covered with Adatoms**

D-glucose is inexpensive and can be obtained in a very pure form that gives rise to a strongly surface-sensitive electrochemical oxidation current at platinum single crystal electrodes [9,11-13]. In this experiment, the steps outlined in section 3.6 and section 3.7 were repeated. The electrolyte in the second cell consisted of an acidified aqueous solution of D-glucose or L-glucose. However, some important differences in procedure should be noted. Since glucose undergoes mutarotation in aqueous solutions, all solutions were left for at least 12 hours prior to any electrochemical measurement to enable time for equilibration between the  $\alpha$ - and  $\beta$ -glucose moieties present in the aqueous solution [14,15]. The start potential for this experiment was always 0V (Pd/H) because adsorbed CO and other molecular fragments are formed at the open circuit potential [16]. Since CO gives rise to strong adsorption on platinum, it blocks surface sites and hence precludes subsequent glucose surface reaction in the potential range in which glucose is normally electro-oxidised [15]. In surface electrochemistry the main experimental difficulty is always surface contamination. Therefore the clean surface voltammetry of the chiral platinum crystals used in the experiments was checked in both solutions (D- and L-glucose) prior to any deposition of adatoms. This ensured that any new behaviour (after deposition of metals on the surface) could be associated purely with compositional changes in the electrode surface.

### 3.10. Procedure for Studying the Adsorption and Reaction of Chiral Organic Molecules at Platinum Single Crystal Electrodes

Several different chiral organic molecules and their adsorption were examined using platinum single crystals, in order to investigate the experimental features of the reaction:

- i) the rate of adsorption as a function of surface structure.
- ii) the surface enantioselective response of chiral crystals towards chiral organic molecules when they reacted on the surface.

The experiments were performed as follows:

Two cells were used in this experiment, the first one was filled with 0.1 M H<sub>2</sub>SO<sub>4</sub> to check the surface structure and composition of the clean electrode surface. The second cell was filled with the electrolyte containing an acidified aqueous solution of the organic molecule under investigation. The nitrogen gas line was connected to both cells via inlet (1) and both solution electrolytes degassed with nitrogen for twenty minutes. After degassing to remove any oxygen in or around the solution, the gas lines were then transferred in both cells to the gas inlet (2) and the overpressure of nitrogen was increased to avoid the electrolyte solution being contaminated by back-diffusion of oxygen from the air. The crystal was then prepared via flame-annealing as described earlier.

Upon collection of a stable CV in cell 1, the crystal was then transferred immediately to the second cell. Cyclic voltammetry data was then collected, starting at 0 V and sweeping to 0.85 V for several cycles (between 10 to 25 cycles) at 50 mV s<sup>-1</sup>.

### 3.11. Single Crystal Manufacture

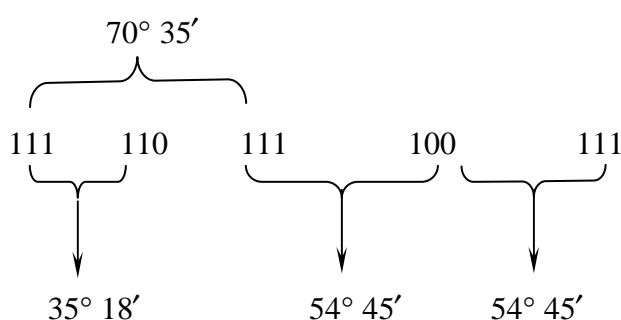
All single crystals used in the present study were manufactured at the University of Wales, Cardiff, according to the method originally developed by Clavilier [7]. The following provides a detailed description of this novel method:

The end of a length of pure platinum wire (99.999% purity, Goodfellow Metals Ltd) 0.5-1mm in diameter was first melted using a methane gas-oxygen flame. When a spherical molten bead of approximately 2 - 3 mm in diameter had been formed, it was allowed to cool slowly at a constant rate, without vibration. This gave rise to a platinum single crystal sphere. The method of single crystal formation is based on a melting zone technique, which concentrates impurities in the final part of the crystal to solidify. Hence it may also be used to eliminate impurities contained in the base metal. This may be achieved by both etching the

single crystal bead in aqua regia followed by re-melting of the bead, or removal of the “contaminated” region by grinding and polishing (see later). The melting/etching procedure may be repeated several times. The presence of impurities may be suspected when difficulties appear in the crystallisation of the metal (irregular shape of the final region of crystallisation from the melt) [17]. Single crystal facets are visible on the bead possessing a (111) or (100) orientation. The facets could be used to align the crystal precisely by using optical methods (He-Ne laser, 4 mW), by comparing reflected and diffracted laser light. The type of facet present was identified by the reflected beam, with (111) facets giving bright, sharp spots, and (100) facets giving duller, more diffuse spots.

### 3.11.1. Calculation of cutting angles for crystal planes

The angles between the (111), (100) and (110) facets of an f.c.c. crystals were as follows:



By simple geometry the angles for cutting the crystal plane relative to a given plane starting at either a (111) or (100) facet for the manufacture of the required crystal could be calculated as follows:

(100) facet was chosen as a starting point, the angle of cut from that facet was calculated as follows:

$$\tan \alpha = \sqrt{k^2 + l^2} / h$$

$$\tan(\beta + 45^\circ) = l/k$$

where  $h$ ,  $k$  and  $l$  represent Miller indices of the required crystal plane and  $\alpha$  and  $\beta$  represent the angles of rotation to obtain the required plane (Fig. 3.5). The degree of rotation of  $\beta$  is equal to zero when flat or stepped surfaces are prepared, but non-zero when chiral crystals are prepared such as (321)<sup>R</sup> and Pt(321)<sup>S</sup>.

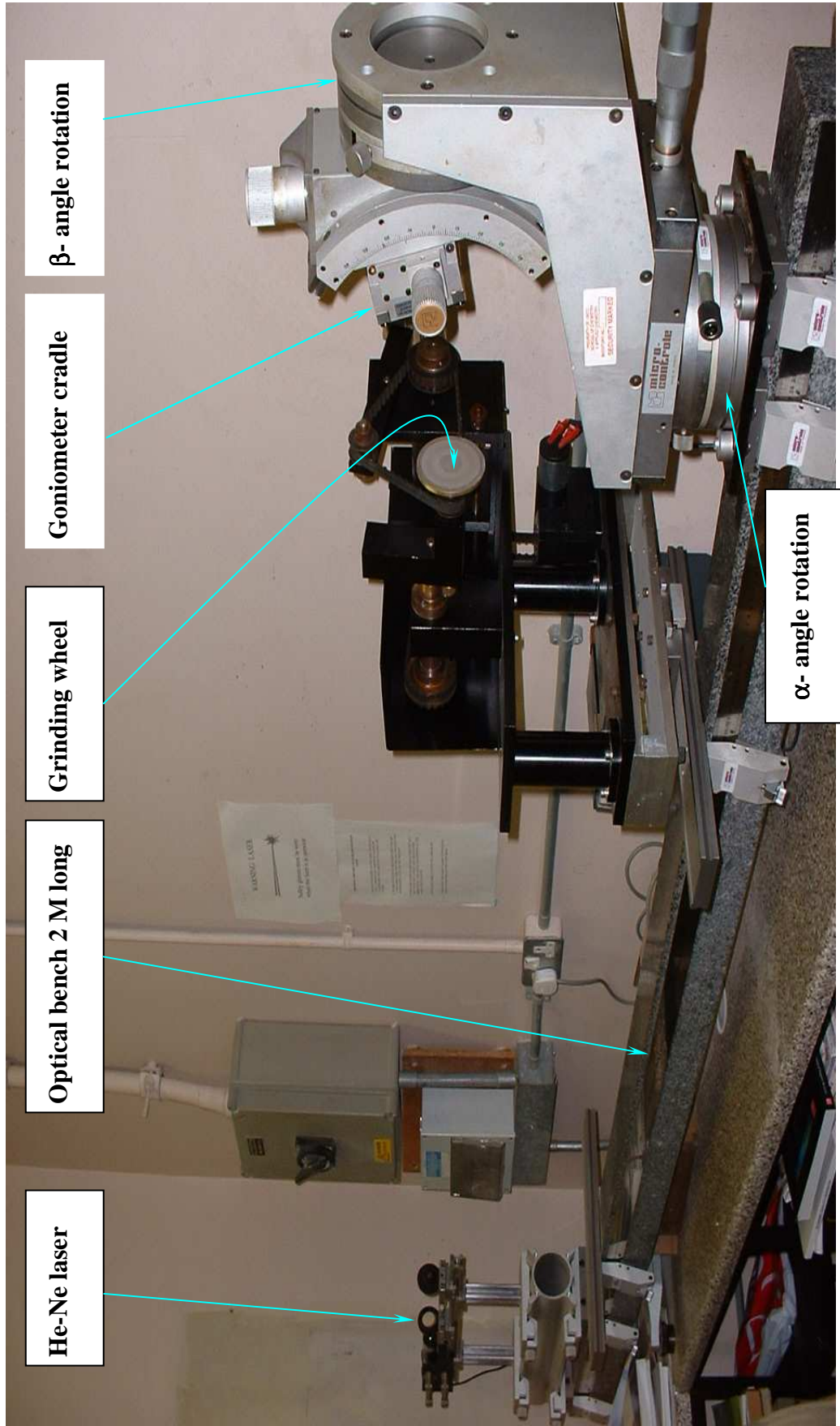


Fig. 3.5. Cutting and polishing machine for making platinum single crystals.

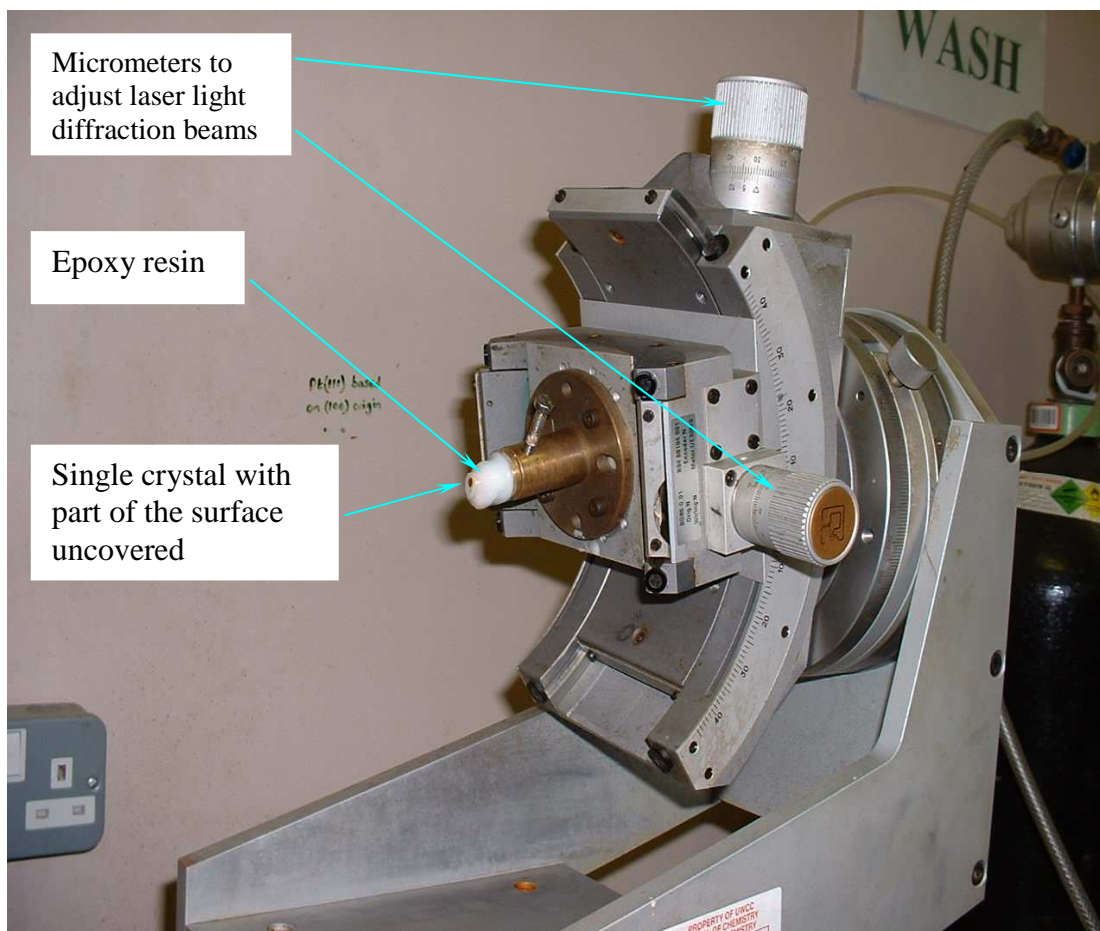
### 3.11.2. Crystal cutting

After formation of the spherical bead, the crystal was etched in aqua-regia solution ( $1\text{HCl}:3\text{HNO}_3$ ) and then mounted at the centre of rotation of a goniometer cradle situated at one end of a 2 m long optical bench (Fig. 3.5). Light from a He - Ne laser (placed at the opposite end of the optical bench) incident on the spherical crystal was diffracted by the edges of the (111) and (100) facets arranged symmetrically around the crystal. Utilising these (111) and (100) diffracted beams, the crystal was readily oriented. The crystal was then embedded in epoxy resin (for stability) but with part of the surface still uncovered (Fig. 3.6). The epoxy resin was allowed to set overnight, and the reflection from the facets checked to ensure that the crystal was still correctly oriented. The crystal was then moved to the calculated cutting angle, and the grinding wheel brought in close to the crystal. The diameter of the crystal was measured and recorded in order to expose the maximum possible surface area of the surface being prepared. A second coating of epoxy glue was applied, this time covering the entire crystal to ensure that the position of the crystal remained constant during grinding and polishing. This was also allowed to set overnight.

Grinding was begun using “600 grit” carborundum (Buehler U.K. Ltd., Coventry) discs to remove the epoxy around the head of the single crystal. This usually took about 20-30 minutes. “1200 grit” paper discs were then used until the crystal diameter was attained for the flat surface. This point could take one hour or less depending on the size of crystal. Thus, it was very important to check the diameter of the crystal every 15 minutes, otherwise cutting could reach a point beyond the maximum diameter which could result in a small crystal face or, at worse, just the stem of the crystal being polished! For both the 600 and 1200 grits, distilled water was used as the lubricant.

### 3.11.3. Polishing of crystals

After grinding to produce the hemispherical crystal (the flat face of which would become the active, oriented surface), polishing of the crystal was begun in order to give a ‘mirror-like’ finish by using finer and finer grades of diamond paste. Initially, small and large scratches, together with holes could appear on the surface during cutting. This problem was solved by using “2400” then “4000” grit’ papers for at least one hour each. These gross blemishes were then polished away using water as the lubricant. The surface was checked every half an hour to make sure that an improvement was seen with polishing and no more larger scratches



**Fig. 3.6.** Single crystal electrode with epoxy resin around for stability.

or holes appeared. The reflection at the He-Ne laser light from the polished surface was then employed to judge the quality of the finish and the precision of the cut. Once all defects were removed, a nylon polishing cloth (No 40-7052, Buehler U.K. Ltd., Coventry) sprayed with 3  $\mu\text{m}$  diamond spray (Struers Ltd., Glasgow) was used, with 60% blue (Struers Ltd., Glasgow) and 40% red (Struers Ltd., Glasgow) lubricating fluid for at least two hours. This procedure was stopped when there was no change in the reflection of the He-Ne spot. The polishing cloth was then changed to a Texmet polishing cloth (No 40-76-02. Buehler U.K. Ltd., Coventry) sprayed with 1  $\mu\text{m}$  diamond grit, using 60% red and 40% blue lubricant and polishing continued for approximately two hours. A final polish was accomplished with the finest grade of diamond paste spray ( $\frac{1}{4}$   $\mu\text{m}$ ) lubricated solely with 100% red lubricant on Textmet polishing pads, for about one hour. After this was completed, a sharp laser reflection spot was observed and a mirror finish to the flat surface.

At this point, the crystal was removed from the goniometric head, and the holder heated gently, until the epoxy glue had softened sufficiently to remove the crystal. After removal of the crystal from the glue, it was annealed in a Bunsen flame for at least one hour at  $\sim 1000$   $^{\circ}\text{C}$  to remove surface impurities and restore any surface damage produced by the grinding and polishing [5], so that a well ordered surface was obtained. After this procedure, electrochemical measurements of the surface were performed to ascertain that the surface structure was correct. The surface area of each crystal was a critical parameter to be determined. Therefore, a travelling microscope was employed which was accurate to  $\pm 0.002$  mm. Hence, uncertainty in all charges quoted would depend on the absolute surface area of the electrode. In the experiments reported in this thesis, it was estimated that a typically uncertainty of  $\pm 5$   $\mu\text{C cm}^{-2}$  in charge measurements arises from uncertainties in measuring the electrode sample area.

### **3.12. Electronic Equipment Used for the Collection of Cyclic Voltammograms**

One computer was used to obtain and analyse cyclic voltammograms. This was a 500 MHz Celeron-processor. This computer was attached to a three electrode potentiostat, and the latter was connected by electrical leads to the electrochemical cell and the potential was applied to the working electrode via the potentiostat. All of these components were incorporated into a single module called a Model 600 Electrochemical Analyser (CH instruments, UK) [18]. The software used with this module allowed for rapid data acquisition

and easy data analysis. This software contains a fast digital function generator, high speed data acquisition circuitry and a potentiostat. The potential control range in this analyser is  $\pm 10$  V and the current range is  $\pm 250$  mA. The instrument is capable of measuring current down to picoamperes ( $1 \times 10^{-12}$  A). The instrument was controlled by an external PC using Windows 98<sup>®</sup>. The instrument provided many powerful functions, such as file handling, experimental control, graphics, data analysis and digital simulation. The Faradic current and potential from the working electrode in the electrochemical cell was transferred to the computer whereby the data of each voltammogram could then be stored for subsequent analysis on the hard disk or on a zip drive disk. A monitor gave one the opportunity to observe the cyclic voltammogram in real time as it was being collected. Certain details of the cyclic voltammogram were analysed using the computer software. These included peak position (potential and current) and peak areas. A photograph of the system is shown in Fig. 3.7. The convention adopted for the plotting of cyclic voltammetric data was that anodic (oxidation) currents were plotted as positive on the Y-axis and cathodic (reduction) currents were plotted as negative on the Y-axis. Positive potential was plotted as positive on the X-axis and negative potential was plotted as negative on the X-axis.

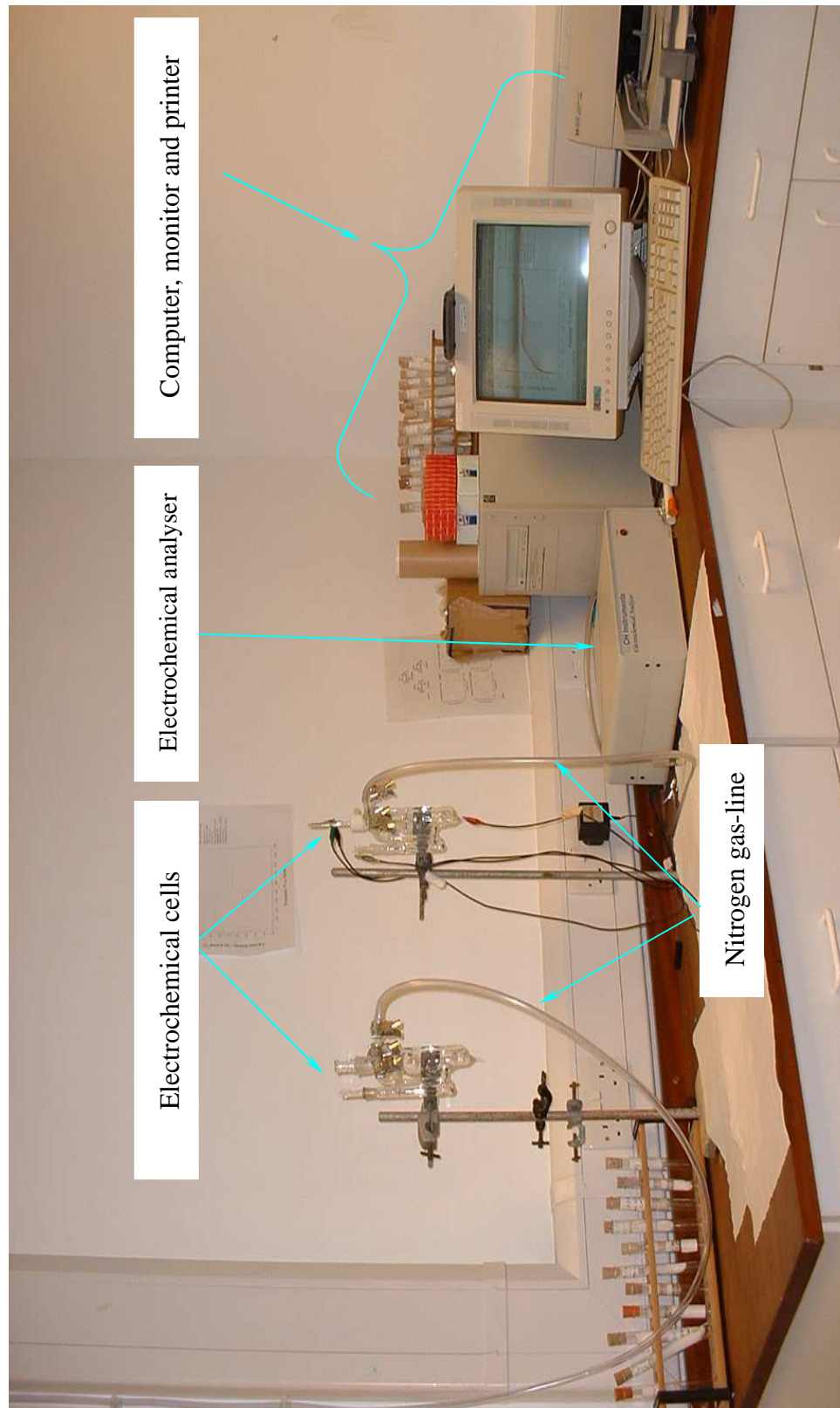
### 3.13. Calculation of Charge in Cyclic Voltammetry

Charge associated with a cyclic voltammetry could be determined by two methods:

- Manual technique of cutting and weighing the peaks and then taking the ratio of the peak weight to a rectangle of a known area and weight.
- the second method, which was employed in the present study, by using a computer program to calculate the charge.

In the second method, after displaying the cyclic voltammogram on a monitor, the area between two potential limits could be calculated automatically by computer which then converts this number to charge density.

Fig. 3.8 shows a calibration plot of current obtained by applying a linear potential sweep  $E$  between the potential limits  $E_i$  and  $E_f$  across a resistor of known resistance. By applying Ohm's law, the value of the current at Y-axis could be determined.



**Fig. 3.7.** A photograph of the equipment used for the collection of cyclic voltammograms.

The time taken to sweep from potential  $E_i$  to  $E_f$  could be estimated by dividing  $E_f - E_i$  by the sweep rate  $v$ . Therefore the charge could be calculated using the equation:  $Q = I \times t$  where  $I$  is the current and  $t$  is the time.

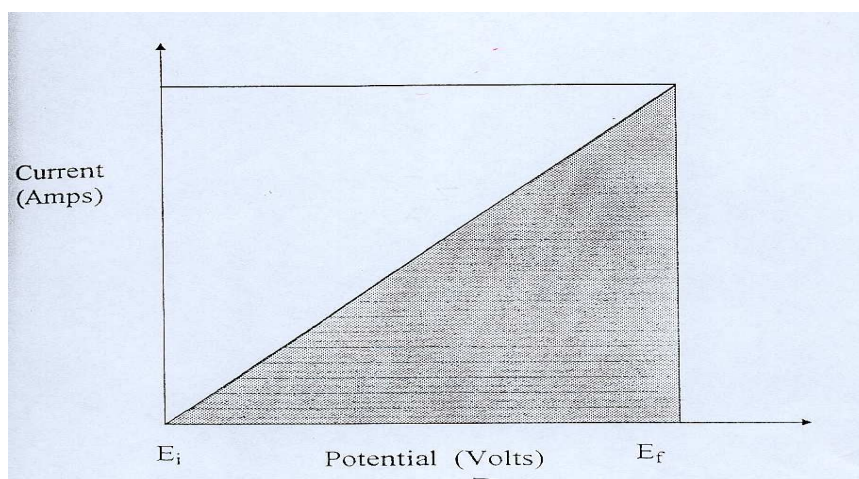
The charge,  $Q$  corresponding to the shaded region in Fig. 3.8 was calculated since the current as a function of time  $t$ , was known:

From Fig. 3.8:

$$Q = \frac{\left(\frac{E_f - E_i}{R}\right)\left(\frac{E_f - E_i}{v}\right)}{2}$$

where  $R$  is the known resistance and  $v$  is the sweep rate.

The manual “cut and weigh” technique of calculating the charge is still necessary in order to check the accuracy of the computer calibration.



**Fig. 3.8.** The calibration plot

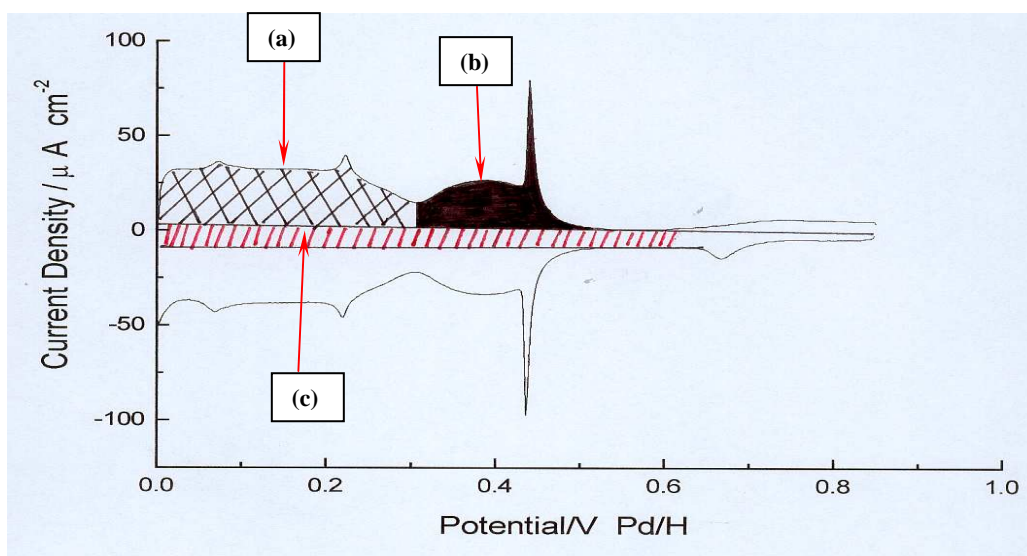
Fig. 3.9 shows the anodic response for Pt(111) electrode in  $H_2SO_4$ . The hatched region (c) was assigned to the charging of the electrochemical double layer, and this was subtracted from the total charge in order to obtain the charge corresponding to hydrogen adsorption (region (a)).

By relating the weight of a “simple” shape such as a rectangle to the weight of the voltammogram, accurate values for the charge could be calculated.

From the calibration of charge and assigning the number of electrons transferred in the adsorption process to one per hydrogen adatom, a charge density value of  $240 \mu C cm^{-2}$  was expected for a monolayer of hydrogen on the Pt(111).

In general, the following equation holds for the calculation of adatom coverage,  $\theta$ , a single monolayer being defined as  $1.5 \times 10^{15}$  platinum atoms  $cm^{-2}$  ( $\theta = 1$ ) on Pt(111) surface.

$$\text{adsorbate coverage } \theta = \frac{\text{charge associated with adatom adsorption}}{\text{charge associated with one monolayer of adsorbed hydrogen}} \times \frac{1}{\text{No. of electrons transferred in the redox process}}$$



**Fig. 3.9.** Pt(111) surface indicating:  
 (a) The hydrogen region,  
 (b) The “anomalous” region associated with anion (bi-sulphate) adsorption,  
 (c) The double layer region.

### 3.14. Experimental Problems

The main problem encountered during the course of the work was obtaining cyclic voltammograms free of artifacts. There were several reasons for anomalous or spurious experimental data. For instance, contaminants in the solution or glassware which resulted in a gradual diminution in the magnitude of electroadsorption peaks; poor meniscus contact [19]; crystal imperfections and impurities; oxygen in the electrolyte solutions due to insufficient time for degassing or low pressures of nitrogen. The following points may be helpful to others in obtaining the best CVs and avoid wasted time or chemicals consumption without reproducible results:

- Check the purity of the electrolyte solutions used.
- Check the cleanliness of the glassware used: (beakers, measuring cylinders, cell, bubbler, volumetric flasks, caps, Teflon holder) by repeated steaming or soaking in “green acid” overnight.

- Discard any electrolyte solution and replace it with fresh solution. If after de-gassing the cell there is no change in the rate of contamination, the glassware should be re-cleaned using “green acid” and steamed in pure water.
- Bubble the electrolyte solution for a few seconds before forming a meniscus to remove any contaminants on the surface of the solution.
- Ensure the cleanliness of all gas tubing used.
- Use an oxygen scrubber for oxygen-free nitrogen.
- Always use clean gloves, and never touch the glassware without them.
- Make sure that there is no water in the crystal holder or in the glass holder of the R.E since this may give rise to pseudocapacitances.
- Anneal the crystal well for at least one minute, and immediately transfer it to the bubbler when the red hot state diminishes.
- Never quench the crystal in water when it is too hot. This will change the electrode after a period of time to a polycrystalline sample.
- Never expose any steamed glassware to the air. Always fill it with ultra pure water when not in use.
- Check the membrane of the Milli-Q water system regularly to make sure that the membrane still works properly and that the water is pure.
- In the case of adsorption by organic molecules on the surface of the electrode, stable partial pressures of nitrogen should flow over the electrolyte solutions. High pressures of nitrogen induce molecules to adsorb quickly on the surface and this makes the comparison between the rates of adsorption between two molecules inaccurate (see Chapter Six, Section 6.3). Therefore, stable and constant conditions should be applied when organic adsorption is studied.
- Never expose the glass holder to the flame during annealing the crystal to avoid forming contaminants that could be transferred to the electrolyte solution while making the meniscus contact.

### 3.15. Chemical Reagents

**Table 3.1.** lists the grades and sources of all reagents used in this study.

Chemical	Formula	Grade	Source
Silver Perchlorate monohydrate	$\text{AgNO}_3 \cdot \text{H}_2\text{O}$	99.999%	Aldrich
Chloroauric Acid in solution	$\text{AuCl}_3$	99.99%	Johnson Matthey
Potassium Permanganate	$\text{KMNO}_4$	GPR	BDH, Poole
Sulphuric Acid	$\text{H}_2\text{SO}_4$	GPR	Fisher
Sulphuric Acid	$\text{H}_2\text{SO}_4$	Aristar	BDH
Nitric Acid	$\text{HNO}_3$	GPR	Fisher
Hydrochloric Acid	$\text{HCl}$	Analar	BDH
Hydrogen	$\text{H}_2$	High Purity	BOC, Guilford Surrey
Nitrogen	$\text{N}_2$	Oxygen Free	BOC, Guilford, Surrey
Palladium Wire	Pd	99.999%	Goodfellows
Platinum Wire	Pt	99.999%	Good fellows
Bismuth Nitrate	$\text{Bi}(\text{NO}_3)_3$	98%	BDH
Cinchonidine	$\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$	98%	Sigma
Dihydrocinchonidine	$\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}$	99%	Hull University
Cinchonine	$\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$	98%	Hull University
N-acetyle-L-tyrosine	$4-(\text{OH})\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{NHCOCH}_3)\text{CO}_2\text{H}$	98%	Aldrich
N-acetyl-L-phenylalanine	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NHCOCH}_3)\text{CO}_2\text{H}$	99%	Aldrich
Codein	$\text{C}_{18}\text{H}_{21}\text{NO}_3$	99%	Sigma
D- proline	$\text{C}_5\text{H}_9\text{NO}_2$	99%	Aldrich
L-proline	$\text{C}_5\text{H}_9\text{NO}_2$	99%	Avocado
D-(-)-tartaric Acid	$\text{C}_4\text{H}_6\text{O}_6$	99%	Acros

D-(+)-glucose	$C_6H_{12}O_6$	99.5%	Sigma
D-(+)-glucose monohydrate	$C_6H_{12}O_6$	99.5%	Sigma
L-glucose	$C_6H_{12}O_6$	99%	Sigma
L-dopa	$C_9H_{11}NO_4$	99%	Acros
R-(-)-2-butanol	$CH_3CH(OH)CH_2CH_3$	99%	Aldrich
S-(+)-2-butanol	$CH_3CH(OH)CH_2CH_3$	99%	Aldrich
R-(-)-1,3- butandiol	$C_4H_{10}O_2$	98%	Acros
S-(+)-1,3-butanediol	$C_4H_{10}O_2$	98%	Acros
(2R,3R)-(-)-2,3- butandiol	$CH_3CH(OH)CH(OH)CH_3$	99%	Acros
(2S,3S)-(+)- 2,3-butandiol	$CH_3CH(OH)CH(OH)CH_3$	99%	Acros
R-(-)-2-chloropropanol	$CH_3CH(Cl)CH_2OH$	96%	Acros
S-(+)-2-chloropropanol	$CH_3CH(Cl)CH_2OH$	96%	Acros
(1R,2S)-(-)-ephedrine	$C_6H_5CH[CH(NHCH_3)CH_3]OH$	99%	Aldrich

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