2 EXPERIMENTAL

2.1 Apparatus

2.1.1. *Glassware and Cleaning*

All glassware were soaked in concentrated chromic acid overnight and then washed thoroughly with tap-water before rinsing and soaking in distilled water.

2.1.2. *Sample bottles (polyethylene)*

Polyethylene sample bottles were used for storage of aqueous solutions. They were cleaned by prewashing with detergent and soaking in 10% nitric acid overnight. They were then washed thoroughly with large quantities of tap-water, rinsed with distilled water followed by soaking in distilled water overnight. They were then rinsed with doubly distilled water and allowed to dry in an air-conditioned room.

2.2. **Chemicals used**

Chemical	Source
Analytical Grade Aniline	*Reinst-Merck
Analytical Grade Pyrrole	*Acros
AR Grade Sodium polystyrene sulphonate salt, *m.w.* 70,000 and 1,000,000	Aldrich.
AR Grade Sulphuric acid, (95-97)%	Riedel-de Haen
AR Grade Orthanilic acid	**Fluka
AR Grade Chloroplatinic acid	BDH Chemicals
Analytical Grade Methanol and ethanol	R&M Marketing , Essex
Analytical Grade Acetone	BDH Chemicals.
AR Grade Sodium hydroxide pellets	Merck
AR Grade Copper sulphate	Fluka.
AR Grade Sodium perchlorate	Fluka
Titanium foil	BDH laboratory reagents.
SnO_2 plate [94]	Prepared by Dr. C. Y. Chan
Platinum foil, 0.127mm thick, 99.99 % pure	Aldrich

* Solutions were freshly distilled under vacuum before used.
** Recrystallized before used.

2.3. **Instruments and equipment**

A *BAS100B/W* Electrochemical Workstation was used to carry out the Cyclic Voltammetry study.

A scanning *Potentiostat / Galvanostat model 363*, manufactured by EG&G Princeton Applied Research was used in the constant potential and constant current applications.

A *Keithley Digital Multimeter Model 197* was used in the measurement of resistance, current and potential.

Denver Instrument Company AA-250 microbalance (for weighing accuracy up to ±0.0001g) and *top-loading balance Fx-3000 manufactured by AND* (for up to ±0.01g) were used for weighing purposes.

A *Volac digital micropipetter model R880/G* was used for transferring solutions of volumes between 1 - 10 mL. For smaller volumes (10 - 100 μL) an *Eppendorf varipette micropipetter model R 4710* was used.

A *30 TON HYDRAULIC PRESS model H30-1* (Research & Industrial instrument company, England) was used for applying high pressure.

A "home-made" A*ir Bath* was used in order to achieve constant temperature to ± 0.5 C°. A temperature probe is placed inside the bath and connected to a temperature controller together with a bulb. A fan is used for air circulation to make sure the constant temperature in the whole bath. A diagram of the bath is given below:

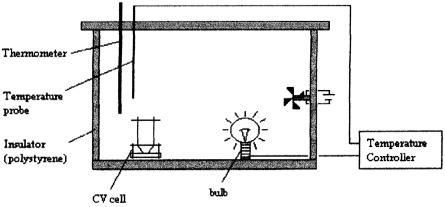

Figure. 2.1 A diagram of the air bath.

A home-made *Four-point probe* instrument was used for measuring the surface conductivity of conducting polymer films. A diagram of four-point probe is showed at figure 2.5. The probes were the tapered gold-plated legs of an I.C. holder.

The “two-pellet” cell for measuring body or bulk conductivity of conducting polymer films is constructed from two hard chrome stainless steel pellets with smooth surface and identical dimensions as shown at figure 2.8.

2.4. **Cleaning process for working electrodes**

The working electrodes including Platinum, Titanium, Tin dioxide (on Ti) and Platinised Titanium were polished and cleaned using the same steps. They were polished using Alumina and 15, 5, 1 μm diamond paste from BAS Bioanalytical System Polishing Kit, followed by soaking in acetone and ethanol. They were then washed and soaked in doubly distilled water. They were left to dry in a covered beaker in an air-conditioned room just before each experiment.

2.5. **Solutions preparations**

Stock 1011.4 ppm $CuSO_4$ solution

0.5057g of $CuSO_4$ was weighed accurately and dissolved in a 500 mL standard flask and made up to the mark with doubly distilled water. Standard Cu^{2+} solutions were prepared by dilution of stock solution.

0.2M Sodium perchlorate ($NaClO_4$)

Approximately 7.0228g anhydrous $NaClO_4$ were weighed accurately and dissolved with 250.00g doubly distilled water in a 500mL stoppered conical flask.

0.5M pyrrole + 0.5M Polystyrene sulphonic acid (PSS)

10.3099g of PSS were weighed accurately into 100.00g doubly distilled water and stirred until all the PSS dissolved (PSS has poor solubility in water). Then 3.3545g of pyrrole were weighed into the solution mentioned above. The solution must be freshly prepared due to its instability, even when stored in the dark and under an inert atmosphere (N_2).

2.6. Cyclic Voltammetry

Cyclic Voltammetry studies were carried out using a single compartment cell containing three electrodes connected to the BAS 100B/W Electrochemical Workstation. A diagram of the cell is given by figure 2.2. A volume of about 40mL test solution is needed. The exposed flat surface of the working electrode was circular with a geometrical surface area 0.97 cm^2. The counter electrode was a platinum ring (circumference 76.4 ± 0.3mm), made from 1.03 ± 0.01 mm diameter platinum wire.

The cell containing 1.0M H_2SO_4 and 0.1M aniline was placed in a thermostatted air bath for about 10 minutes to achieve temperature equilibrium. The solution was equilibrated prior to transfer to the cell. The Cyclic Voltammetry studies of polyaniline were carried out by cycling the potential from +1400 to -300 mV with sweep rate 50 mVs^{-1}. At least 60 sweeps were taken for each test sample.

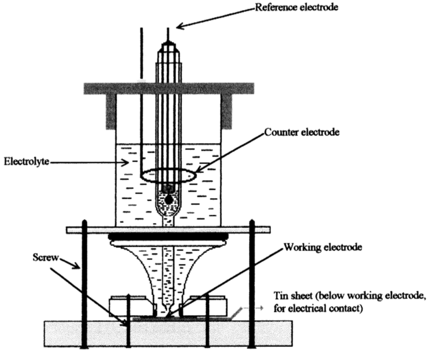

Figure 2.2 A diagram for the cell used in Cyclic Voltammetry studies.

2.7. Preparation of conducting polymer film

A solution of 0.5 mol L^{-1} pyrrole and 0.5 mol L^{-1} Na-PSS (Polystyrene sulphonic acid sodium salt) was freshly prepared and the desired volume placed in a 150mL beaker. The solution must be fresh due to ease of oxidation of the pyrrole monomers to form undesirable compounds. The solution changed from yellowish to black when left to stand for two days. The electrodes were placed into the solution as shown in the figure 2.3. Counter electrode used was platinised Titanium gauze from Morgett Electrochemicals Ltd., U.K.

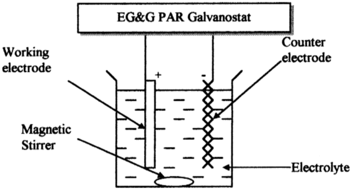

Figure 2.3 Ordinary arrangement for electropolymerization.

The polymerisation occurred rapidly over the whole surface of the working electrode while H_2 evolved at the counter electrode. A problem with this electrode arrangement was poor throwing power and difference in smoothness of polymers formed on different sides of the electrode. The polymer surface, which faced the counter electrode, was found to be smoother. To improve throwing power another piece of counter electrode, as shown in figure 2.3, was added.

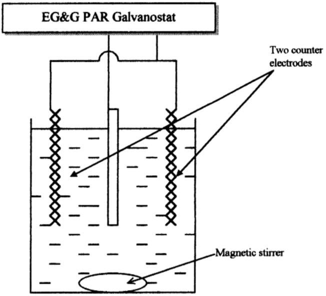

Figure 2.4 Diagram for film preparation using two counter electrodes.

After the electropolymerisation was stopped, the black polymer formed on the working electrode was rinsed with doubly distilled water and peeled off as a free-standing film. The polymer film was then dipped in doubly distilled water to remove any unreacted monomers on the back surface of polymer. The smooth and flexible film was then dried in an oven at 50°C overnight and kept dried in a vacuum desicator.

A mixture of 0.5M pyrrole in 0.2M $NaClO_4$ was also used in the preparation of Ppy-ClO_4 films. The method used was similar to that for preparation of Ppy-PSS film.

2.8. **Conductivity measurement**

2.8.1. *Method of four-point probe*

The four-point probe method is commonly used to measure surface conductivity[72, 73]. A four-point probe was constructed as shown in figure. 2.5. The probes were gold-coated copper, and were contact legs of an I.C. socket, and were of equal length.

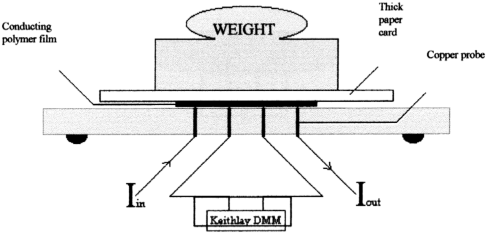

Figure 2.5 Diagram of four-point probe method

All four probes were fixed in position so that the force to polymer films was equivalent for every measurement. Conducting films were cut into circular shapes with a diameter of about 13-14mm. It was placed on the probes followed by a piece of card, and then a 250g brass weight was placed as shown in figure 2.5 to ensure a good electrical contact between probe points and polymer film. A small constant current was passed through the outer probes and the potential was measured between inner probes. At first 20, 50, 100, and 200g of weights were tested, but no stable reading obtained until the added weights were greater or equal to 250g.

The four probes should be positioned at the centre of the film. Six different located directions were considered in the surface conductivity measurements. These directions differing by 30° variations (Figures 2.6 and 2.7). After that, the film was turned over to measure the conductivity of the other surface. Conductivities of both electrode and solution sides were compared. An EG&G PAR galvanostat was used for current supply.

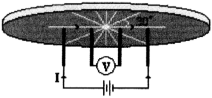

Figure 2.6 Four probes on centre of the film

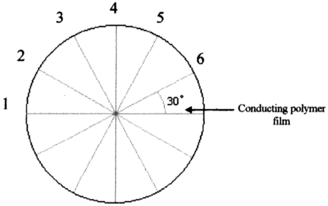

Figure 2.7 Six directions of consideration in surface conductivity measurement

2.8.2 *Method of double pellets for Bulk Conductivity Measurements*

Two hard stainless steel pellets of diameter 12.94 ± 0.01mm were used to measure the conductivity across the polymer films. A Ppy-PSS film was placed in between the two pellets (Figure 2.9) and a cyclic voltammogram was taken. Scan rate used was 10 mVs^{-1}, and scan limits were from +50 to -50mV.

Two ranges of pressure were applied to the conducting polymers, 'High pressure range' and 'Low pressure range'. 'Low pressure' referred to pressures around a few hundred kPa while 'high pressure' means in the range of a few thousand kPa. High pressure was achieved by incorporating a hydraulic press.

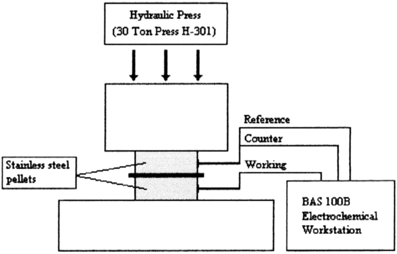

Figure 2.8 A diagram of Double Pellet method for bulk conductivity measurements.

2.9. **Ion-exchange**

$CuSO_4$ sample solutions were prepared by diluting the 1000ppm stock solution. The concentration of the solution was measured by using a pre-calibrated copper electrode(See Appendix 1 for details). A Ppy-PSS coated Ti plate as working electrode was dipped into 70 mL sample solution in a 150 mL beaker. The counter electrode was a pair of Platinised Titanium gauze. A potential of -400mV with reference to Ag/AgCl was applied to the working electrode. Copper deposition occurred on the polymer surface by exchanging Cu^{2+} with H^+. A colour change on polymer surface from black to blue and then brown occurred during the ion-exchanging process.

After a certain period of time the Ppy-PSS film was taken out from the sample solution and the concentration of copper in the solution was determined again. The copper plated film was then soaked into dilute sulphuric acid to remove the copper layer. The whole procedure was repeated until the copper concentration dropped below 1 ppm.

2.10 **Platinised Titanium**

2% platinic chloride in 2N HCl solution was prepared in a 100 mL beaker. The titanium foil used was polished with emery paper (Phoenix Brand, grid 600 CW) followed by a finer one (John Oakey & sons limited, Wellington, 4 / O) with circular motion. Current density applied was about 10-20 $mA^{-} cm^{-2}$ and electroplating time within 10-20 minutes. The platinum plated appeared as a golden shinny layer or black in colour. The weight differences before and after plating was measured, to estimate the efficiency of electroplating of platinum (For details see Appendix 2).

Poor adhesion of platinum on the titanium electrode surface caused platinum to strip out from the titanium surface during cyclic voltammetry. This problem was overcome by sintering the freshly platinised titanium plate over a reducing Bunsen flame.

2.11. **Surface morphology**

The surface morphology of samples (electrode and polymer surfaces) was investigated using a Leica Microscope System. The image analyser consisted of a Leica Image Processor and analysis system microscope interfaced to a 486-microcomputer system via a Sony video camera.

2.12. **Microanalysis**

Several samples were sent to the Microanalysis Laboratory, Chemistry Dept., University of Otago, New Zealand for microanalysis:

(a) Polyaniline incorporated with orthanilic acid

(b) Polypyrrole-Polystyrene sulphonic acid (*mw.*70,000)

(c) Polypyrrole-Polystyrene sulphonic acid (*mw.*100,000)

The elements analysed including C, N, S and H (Results see Appendix 3).

2.13. **Insertion of cation and anion in Ppy-PSS film**

Investigation of insertion processes was carried out using the Ppy-PSS or Ppy-ClO_4 coated on the chosen metal subtracts and prepared as mentioned in section 2.7. The film was mounted under the electrolysis cell (Figure 2.2) as working electrode.