3. METHODOLOGY

3.1 Electrochemical Method

Voltammetry is an electrochemical method in which current is measured as a function of the applied potential. It is a branch of electrochemistry in which the electrode potential, or the faradaic current or both are changed with time. Normally, there is an interrelationship between all these three variables. The principle of this technique is a measurement of the diffusion controlled current flowing in an electrolysis cell in which one electrode is polarisable. In this technique a time dependent potential is applied to an electrochemical cell, and the current flowing through the cell is measured as a function of that potential. A plot of current which is directly proportional to the concentration of an electroactive species as a function of applied potential is called a voltammogram. The voltammogram provides quantitative and qualitative information about the species involved in the oxidation or reduction reaction or both at the working electrode [23, 24].

3.1.1 Cyclic Voltammetry

Cyclic voltammetry is a type of potentiodynamic electrochemical measurement. Cyclic voltammetry consists of cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The method uses a reference electrode (RE), working electrode (WE), and counter electrode (CE) which in combination are sometimes referred to as a three-electrode setup. Electrolyte is usually added to the test solution to ensure sufficient conductivity. Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. Analysis of the current response can give considerable information about the

thermodynamics of redox processes, the kinetics of heterogeneous electron-transfer reaction and the coupled chemical reactions or adsorption processes. It is often the first electrochemical experiment performed in an electrochemical study especially for any new analyte since it offers a rapid location of redox potentials of the electro active species and convenient evaluation of the effect of media upon the redox process. In cyclic voltammetry, the electrode potential ramps linearly versus time as shown. This ramping is known as the experiment's scan rate (V/s). The potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. The controlling potential which is applied across working electrode and reference electrode such as saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl) can be considered an excitation signal. The excitation signal for CV is a linear potential scan with a triangular waveform as shown in **Figure 3.1**. This triangular potential excitation signal sweeps the potential of the electrode between 2 values, sometimes called the switching potentials. The excitation signal in **Figure 3.1** causes the potential first to scan negatively from +0.80 V to -0.20 V versus SCE at which point the scan direction is reversed, causing a positive scan back to original potential of +0.80 V. The scan rate, as reflected by the slope is 50 mV/s. A second cycle is indicated by the dashed line. Single or multiple cycles can be used. Modern instrumentation enables switching potentials and scan rate to be easily varied. A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the response signal to the potential excitation signal. The voltamogram is a display of current (vertical axis) versus potential (horizontal axis). Because the potential varies linearly with time, the horizontal axis can also be thought of as time axis. This is helpful in understanding the fundamentals of the technique.

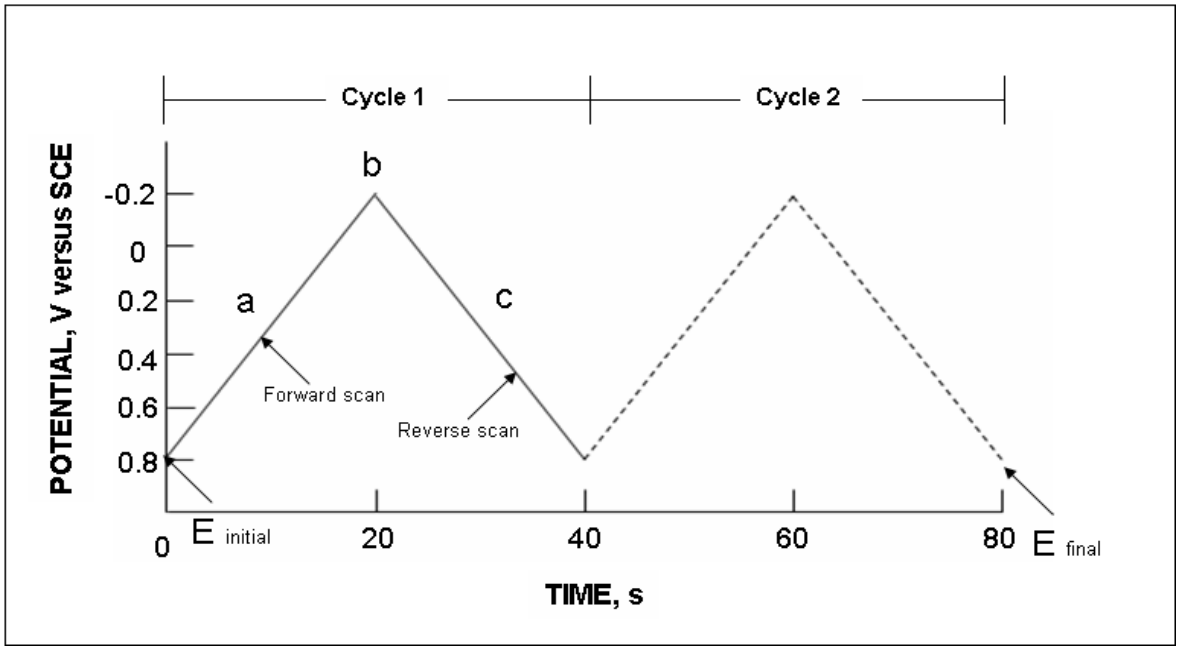

Figure 3.1: Typical excitation signal for cyclic voltammetry – a triangular potential waveform with switching potential at 0.8 and -0.2 V versus SCE

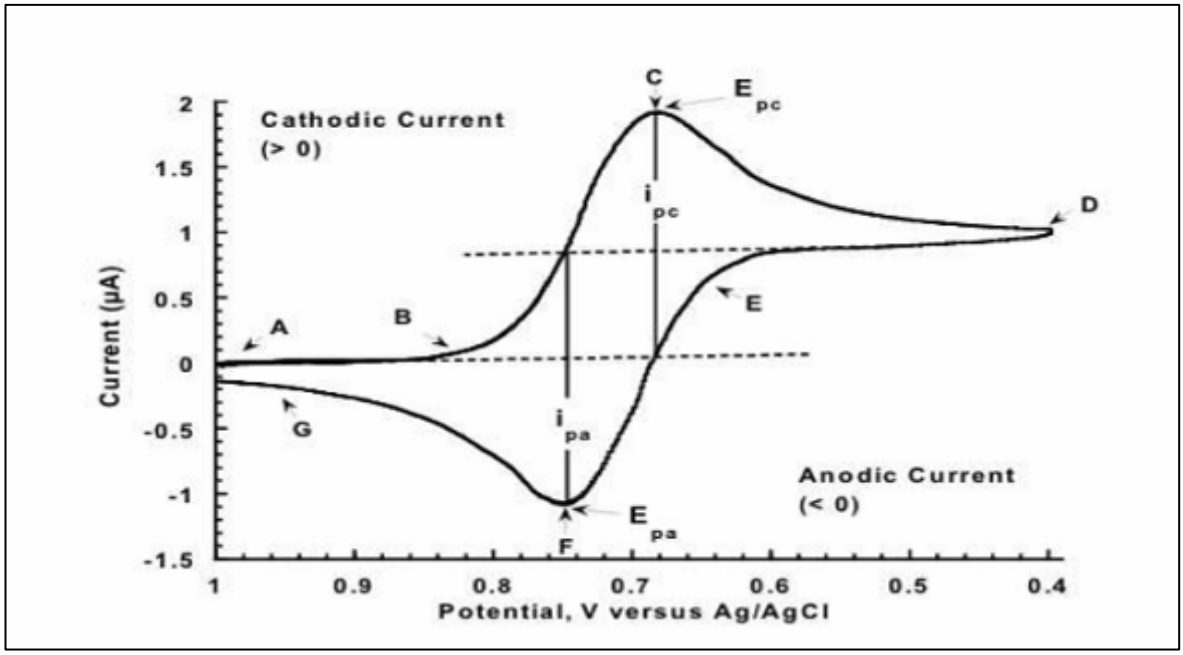

Figure 3.2: A typical cyclic voltammogram

Figure 3.2 illustrates a typical cyclic voltammogram. In the parts “A”, “B” and “C”, the potential is applied and an increasing amount of current is observed. This is the cathodic part of the wave, where reduction of the electrolyte molecules is occurring. Maximum flow of electrons is observed at point “C”. After point “C”, potential is still applied, but the current associated with the reduction decreases due to depletion of electrolyte molecules at the electrode. Ion diffusion toward the electrode must occur before reduction. Here diffusion is slower than reduction and therefore there is a reduction in the current flow between the parts “C” and “D”. Parts “E”, “F” and “G” describe the reverse process. When the voltage is decreased, the reverse oxidation process occurs, and the electrolyte molecules are returned to their initial state. The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (i_{pa}) and cathodic peak current (i_{pc}), and the anodic peak potential (E_{pa}) and cathodic peak potential (E_{pc}). These parameters are labeled in **Figure 3.2**. A redox couple in which both species rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. The formal reduction potential ($E^{\circ\prime}$) for a reversible couple is centered between E_{pa} and E_{pc} [13, 25-27].

$$E^{\circ\prime} = \frac{E_{pa} + E_{pc}}{2} \qquad \textbf{(3.1)}$$

The number of electrons transferred in the electrode reaction (*n*) for a reversible couple can be determined from the separation between the peak potentials

$$\Delta E_p = E_{pa} - E_{pc} \cong \frac{0.059}{n} \qquad \textbf{(3.2)}$$

The peak current for a reversible system is described by the Randles-Sevcik equation.

$$I_p = (2.69 \times 10^5)\, n^{3/2} A D^{1/2} C \upsilon^{1/2} \qquad \textbf{(3.3)}$$

where;

n = number of electron

A = electrode area (cm^2)

C = concentration (mol cm^{-3})

D = diffusion coefficient (cm^2 s^{-1})

υ = scan rate (V s^{-1})

Accordingly, I_p increases with $\upsilon^{1/2}$ and is directly proportional to concentration. The relationship to concentration is particularly important in analytical application and in studies of electrode mechanisms. The value of i_{pa} and i_{pc} should be identical for a simple reversible (fast) couple. That is

$$\frac{i_{pa}}{i_{pc}} = 1 \qquad \textbf{(3.4)}$$

However, the ratio of peak currents can be significantly influenced by chemical reactions coupled to the electrode process.

3.1.2 Chronoamperometry

Chronoamperometry (CA) is an electrochemical method in which a step potential is applied and the current, i, is measured as a function of time, t. This i-t response is comprised of two components: the current due to charging of the double-layer and the other due to the electron transfer reaction with the electro active species. The results are most easily interpreted when a planar (flat) electrode is used in a quiet, unstirred solution, and the applied potential is sufficient to reduce or oxidize the electro active species as fast as it gets to the electrode surface, i.e., at a diffusion-controlled rate. When Current, i, vs. time t, response in the presence of an electro active species that

undergoes an electron transfer reaction at a diffusion-controlled rate, under these conditions, the current is given by the Cottrell relationship [13,15,28].

In electrochemistry, the Cottrell equation describes the change in electric current with respect to time in a controlled potential experiment, such as chronoamperometry. the current measured depends on the rate at which the analyte diffuses to the electrode. That is, the current is said to be "diffusion controlled." The Cottrell equation describes the case for an electrode that is planar [24, 29-34].

$$i(t) = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} \qquad \textbf{(3.5)}$$

Where

i = current, in unit A

n = number of electrons (to reduce/oxidize one molecule of analyte j, for example)

F = Faraday constant, 96,485 C/mol

A = area of the (planar) electrode in cm^2

C = initial concentration of the reducible analyte j in mol/cm^3;

D = diffusion coefficient in cm^2/s

t = time in s

Application of Chronoamperometry are as follows:

- Analyze the shape of the current-time curve in order to study coupled chemical reactions.
- Determination of: n (moles of electrons); A (surface area of electrode); D (diffusion coefficient of analyte)

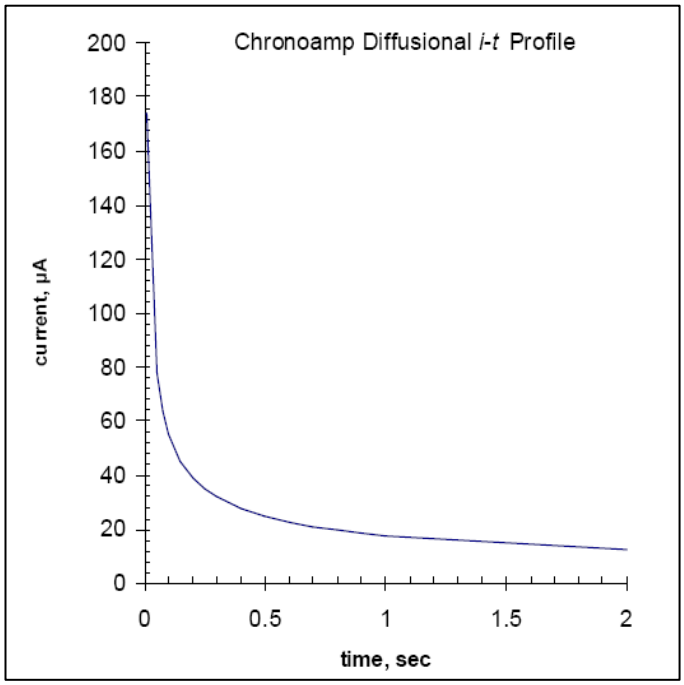

Figure 3.3: Chronoamperometry Diffusional *i-t* profile

3.2 Spectroscopy and Microscopy Analysis

3.2.1 Scanning Electron Microscopy (SEM)

Figure 3.4: SEM and EDX: Philips XL and EDAX Analyzer Genesis

The scanning electron microscope (SEM), **Figure 3.4**, is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface morphology, composition and other properties such as electrical conductivity. The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to

the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes [35,36].

Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample. Electron Gun- The source of electrons in located at the top of the column where electrons are emitted from a hot tungsten filament and accelerated down an evacuated column (**Figure 3.5)**. The three gun components are the filament, the Wehnelt, which controls the number of electrons leaving the gun, and the anode, which accelerates the electrons to a selectable voltage between 1 – 30 kV. A vacuum is necessary because electrons can travel only short distances in air [37-39].

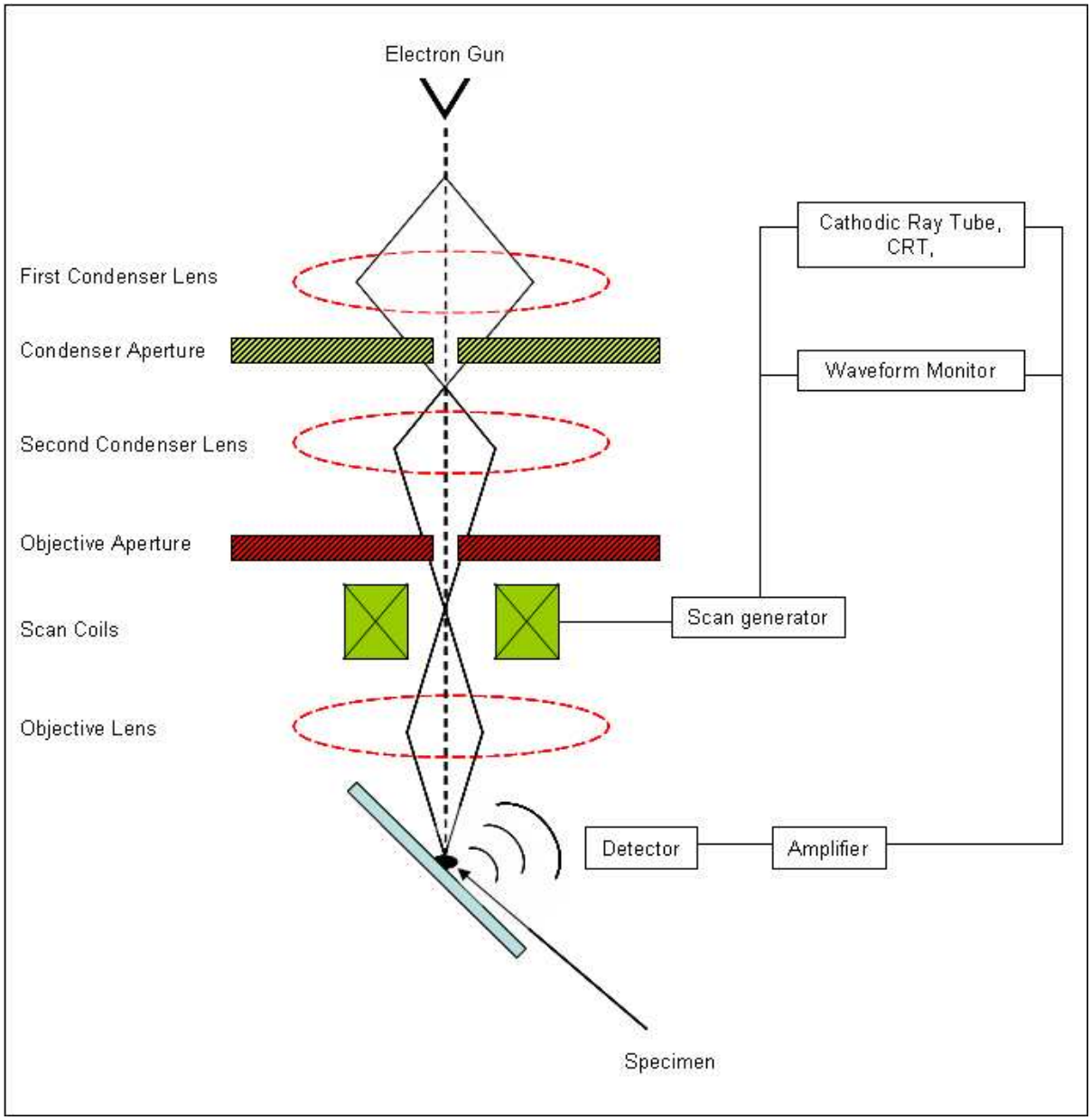

Figure 3.5: Schematic for an SEM

The main components of SEM (**Figure 3.5)** are as follows [35]:

Electron Lenses- Electron lenses are used to de-magnify the electron beam to a small spot about 1μm in diameter. The condenser lens is located closest to the electron gun and the final or objective lens is located closest to the specimen. The objective lens moves the smallest spot formed by the beam up and down in space (working distance, WD) to meet the specimen surface, which is a focused condition.

Scanning System- The image is formed by pushing the beam across the specimen surface in a regular manner in synchronism with a beam scanning within the computer

monitor on the console. Scan coils, used to push or deflect the beam, are located within the objective lens.

Objective Aperture- A foil with a small hole (~100 μm), located above the objective (final) lens. Its function is to limit the angular width of the electron beam to reduce aberrations and to improve depth-of-field in the image.

Electron detector- Backscattered electrons are energetic enough to directly excite the detector, which is mounted on the bottom of the objective lens. Secondary electrons are drawn to the secondary electron detector by a positive charge placed in front of the detector. They are accelerated towards a scintillator screen where they produce light which is amplified to produce an electronic signal later sent to the computer to be displayed on the monitor.

Vacuum system- Vacuum is produced by an oil diffusion pump backed by a mechanical pump. In the diffusion pump a stream of hot oil vapor strikes and pushes air molecules toward a mechanical pump that expels them from the system. A mechanical pump and valve system are used to pre-evacuate the system because a diffusion pump only operates after a vacuum is created.

3.2.2 Energy-dispersive X-ray spectroscopy (EDX)

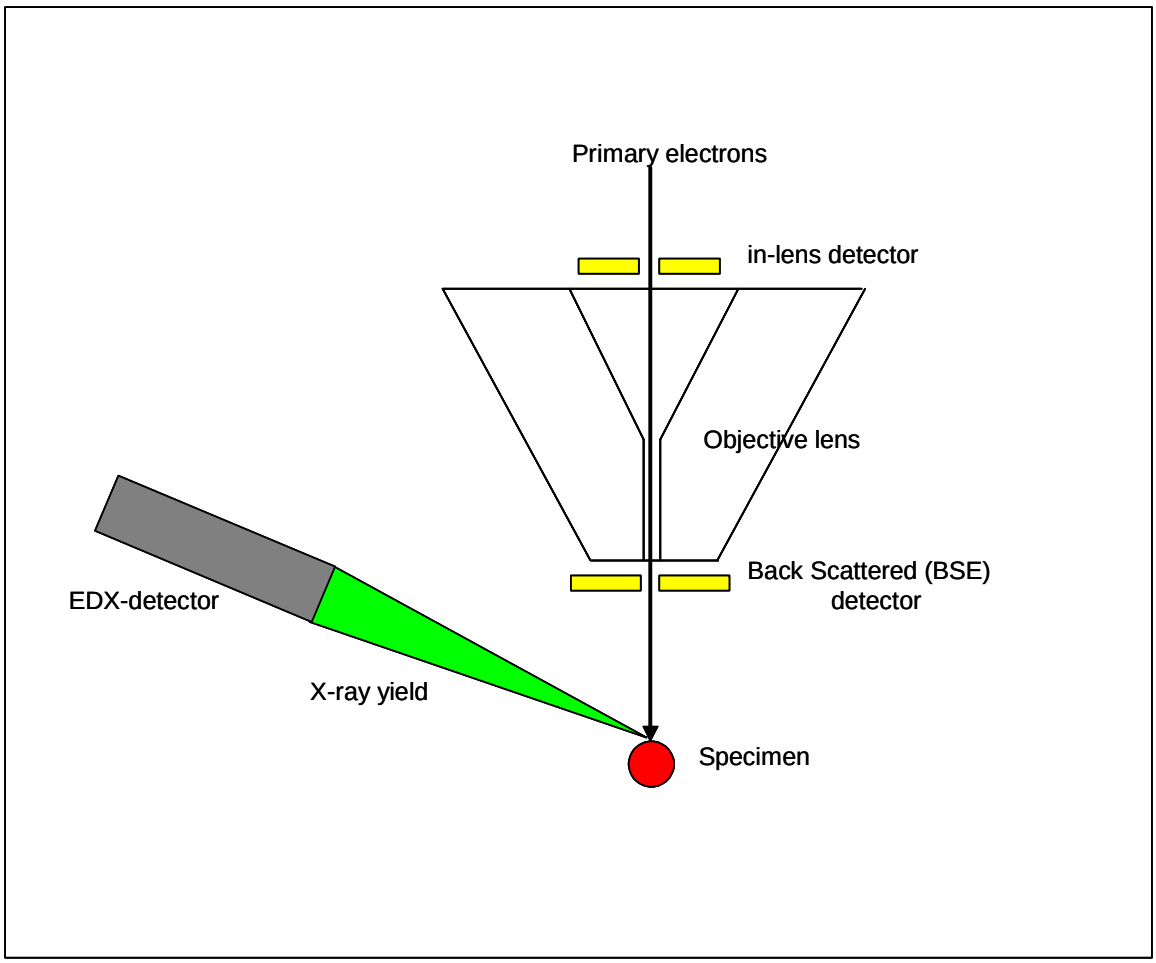

Figure 3.6: Schematic for an EDX

Energy dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample as shown in **Figure 3.6**. It is one of the variants of XRF. EDX is a chemical microanalysis technique performed in conjunction with a scanning electron microscope (SEM). The technique utilizes x-rays that are emitted from the sample during bombardment by the electron beam to characterize the elemental composition of the analysed volume. Features or phases as small as about 1µm can be analysed. When the sample is bombarded by the electron beam of the SEM, electrons are ejected from the atoms comprising the sample's surface. A resulting electron vacancy is filled by an electron from a higher shell, and an x-ray is emitted to balance the energy difference between the two electrons. The EDS x-ray detector measures the number of emitted x-rays versus their energy. The energy of the

x-ray is characteristic of the element from which the x-ray was emitted. A spectrum of the energy versus relative counts of the detected x-rays is obtained and evaluated for qualitative and quantitative determinations of the elements present in the sampled volume [35].

There are four primary components of the EDS setup: the beam source; the X-ray detector; the pulse processor; and the analyzer. A number of free-standing EDS systems exist. However, EDS systems are most commonly found integrated with scanning electron microscopes (SEM-EDS) and electron microprobes. Scanning electron microscopes are equipped with a cathode and magnetic lenses to create and focus a beam of electrons, and since the 1960s they have been equipped with elemental analysis capabilities. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis [40].

3.2.3 Atomic Force Microscope (AFM)

Figure 3.7: AFM: Digital Instruments Nano Scope 3a

The atomic force microscope (AFM) or scanning force microscope (SFM) as shown in **Figure 3.7** is a very high-resolution type of scanning probe microscopy, with resolution of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The precursor to the AFM, the scanning tunneling microscope, was developed by Gerd Binnig and Heinrich Rohrer in the early 1980s, a development that earned them the Nobel Prize for Physics in 1986. Binnig, Quate and Gerber invented the first AFM in 1986. The AFM is one of the foremost tools for imaging, measuring and manipulating matter at the nanoscale. The information is gathered by "feeling" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the

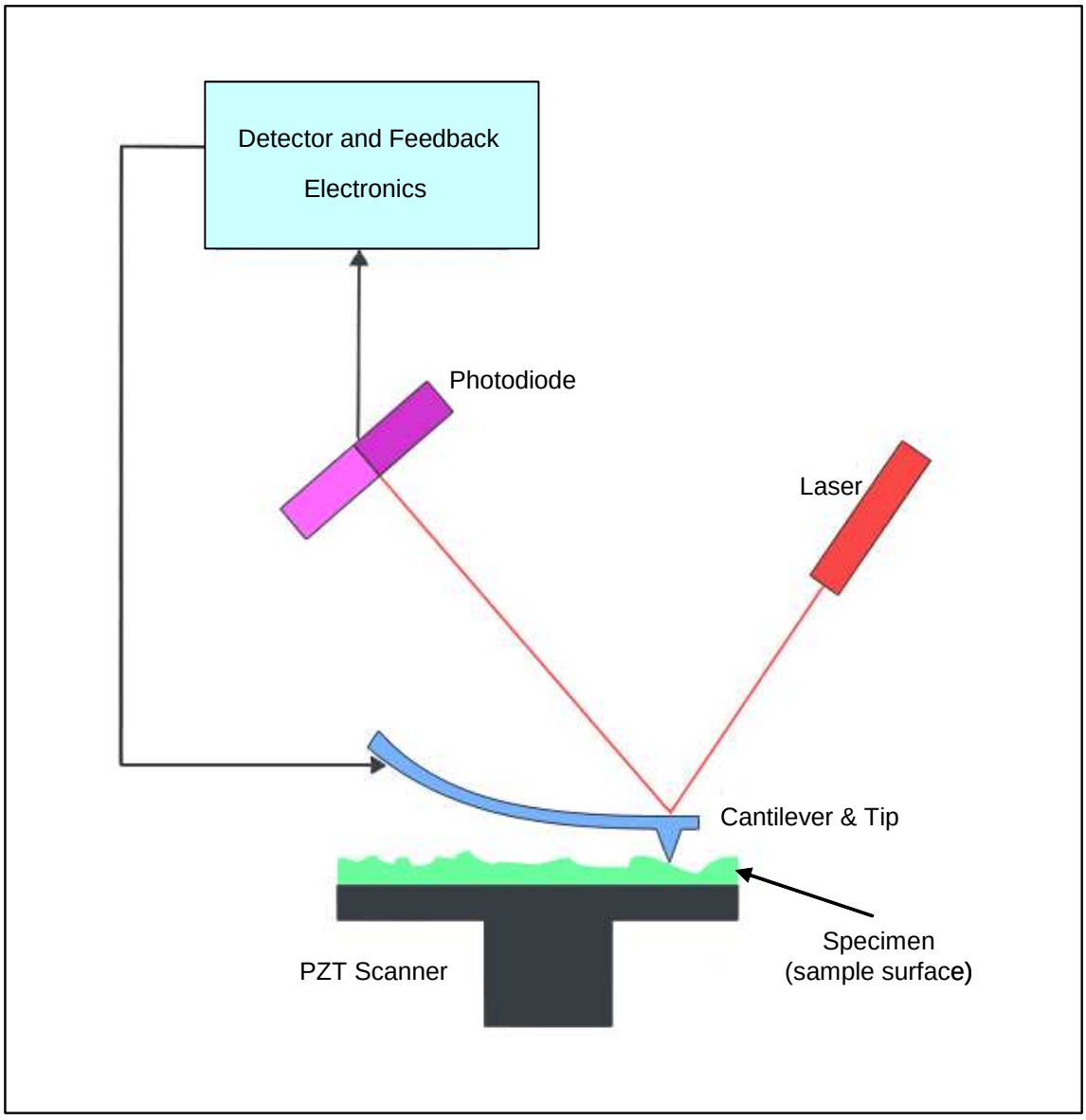

Figure 3.8: Schematic for an AFM

specimen surface as shown in **Figure 3.8**. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, Van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces (see magnetic force microscope, MFM), Casimir forces, solvation forces, etc. As well as force, additional quantities may simultaneously be measured through the use of specialized

types of probe (see scanning thermal microscopy, photothermal microspectroscopy, etc.). Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry. If the tip was scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube, that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Alternatively a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x,y and z directions. This eliminates some of the distortion effects seen with a tube scanner. In newer designs, the tip is mounted on a vertical piezo scanner while the sample is being scanned in X and Y using another piezo block. The resulting map of the area s = f(x,y) represents the topography of the sample. The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or non-contact) modes where the cantilever is vibrated [35,41].

3.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3.9: FTIR: Perkin Elmer Spectrum RX1

FTIR (Fourier Transform Infrared) Spectroscopy **(Figure 3.9)**, or simply FTIR Analysis is a failure analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. It is used in failure analysis to identify unknown materials present in a specimen, and is usually conducted to complement EDX analysis. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials in the FTIR library. Unlike SEM inspection or EDX analysis, FTIR

spectroscopy does not require a vacuum, since neither oxygen nor nitrogen absorbs infrared rays. FTIR analysis can be applied to minute quantities of materials, whether solid, liquid, or gaseous. When the library of FTIR spectral patterns does not provide an acceptable match, individual peaks in the FTIR plot may be used to yield partial information about the specimen. Radiation of all frequencies from the IR source is reflected into the interferometer where it is modulated by the moving mirror on the left as shown in **Figure 3.10**. The modulated radiation is then reflected from the two mirrors on the right through the sample in the compartment at the bottom. After passing through the sample, the radiation falls on the detector. A data acquisition system attached to the detector records the signal and stores it in the memory of a computer as an interferogram [35,42].

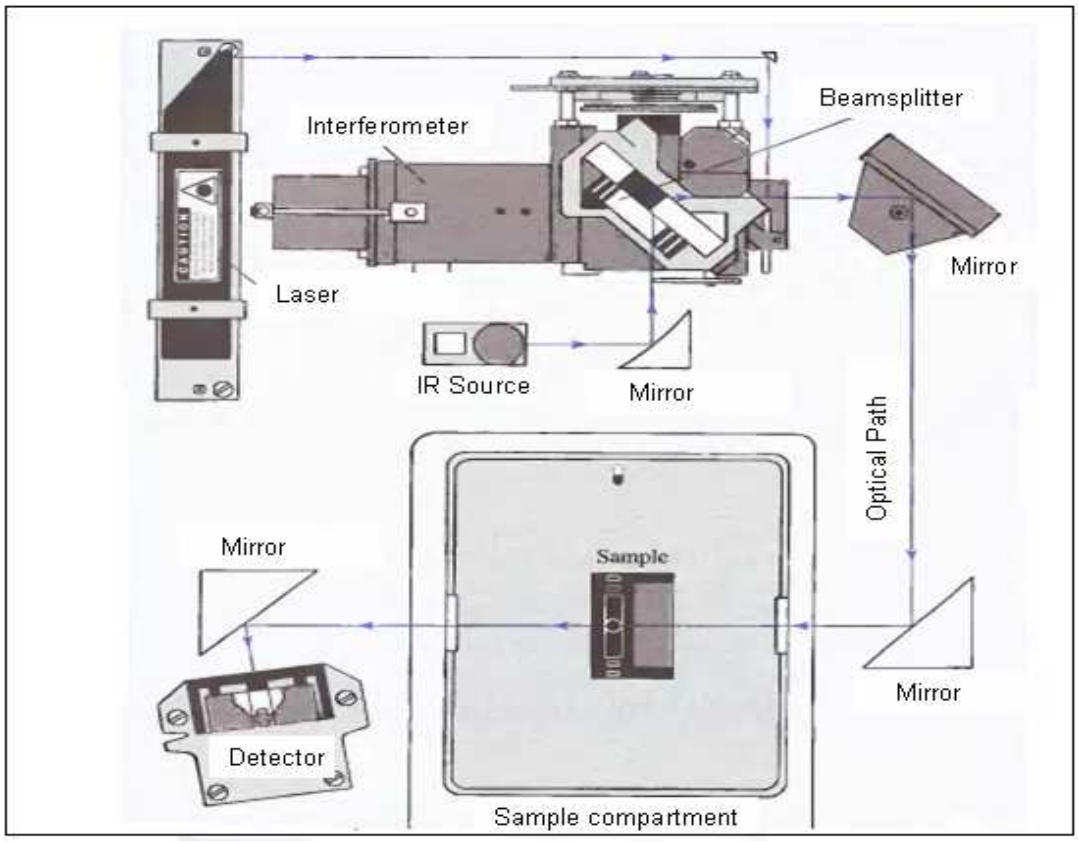

Figure 3.10: Instrument diagram for a basic FTIR spectrometer.

3.3 Wetting Balance Test

Tin electrodeposition has been gaining a significant role in Semiconductor assembly process since the past few decades. Tin electrodeposition in semiconductor industry **(Figure 3.11)** is the process of applying a coat of metal over the leads of an IC to:

1) Protect the leads against corrosion;

2) Improve the solderability of the leads;

3) Improve the appearance of the leads.

Figure 3.11: Semiconductor component that electroplated with tin

The wetting balance test, sometimes called a meniscograph **(Figure 3.12 and 3.13)** is one of the methods used to test the solderability of IC leads. The wetting balance test is classified in ANSI/ J-STD-002 as a "Test without establishes Accept/Reject Criterion". This test method is recommended for engineering evaluations only and not as a production pass/fail monitor. The wetting balance test is a device which measures the forces exerted on a surface by the metallurgical wetting of solder and then plots these forces with respect to time. The method of measuring the forces is an LVDT (linear variable differential transformer) attached to the sample which is suspended in molten solder. **Figure 3.13** shows a schematic of the apparatus. To begin the test, the part to be tested is loaded into the weighing system. The solder pot containing the molten solder, which is part of the test equipment, is then raised at the controlled rate to the surface to be tested. The depth to which the part is immersed in the solder and dwell time of the

surface in the solder bath are set by gauge user. Initially, forces on the weighing machine are upward due to buoyancy of the sample and friction with the solder. As wetting proceeds the forces change direction, pulling downward due to the surface tension of the meniscus which forms between the solder and the part being tested. **Figure 3.14 and 3.15** show a typical curve generated by the instrument [43-48].

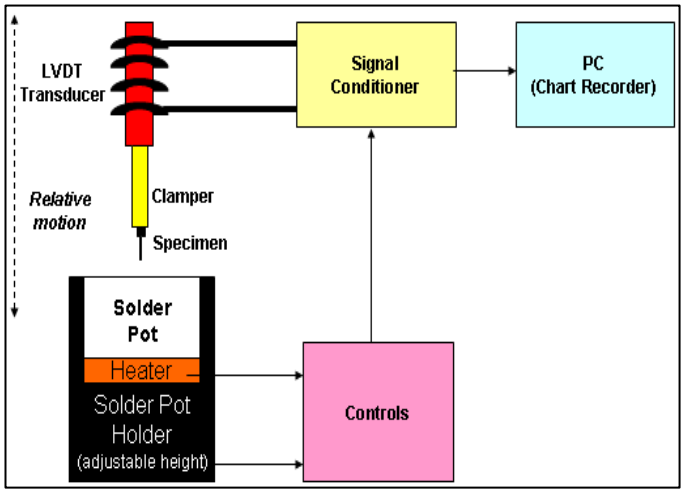

Figure 3.12: Schematic of wetting balance gauge

Figure 3.13: RHESCA SAT-5100 wetting balance gauge

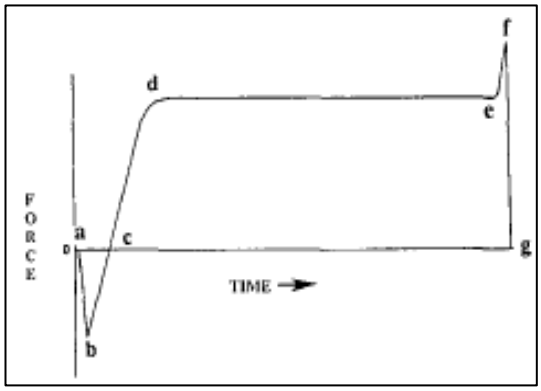

Figure 3.14: Typical wetting balance curve

The lettered points represent the following actions or occurrences.

a. Immersion into the solder begins.

b. Maximum buoyant/frictional force prior to wetting.

c. Solder surface is normal to the surface being tested.

d. Maximum wetting force achieved due to meniscus rise and equilibrium is established.

e. Solder pot withdrawal begins.

f. Maximum withdrawal force is achieved and the molten solder fractures.

g. Solder contact is fully broken and force returns to near zero (actual zero is not achieved due to weight of solder deposited on part)

One commonly used performance measure is the time to cross the zero axis of wetting force. This point indicates the transition from non-wetting (F<0) to wetting (F>0).

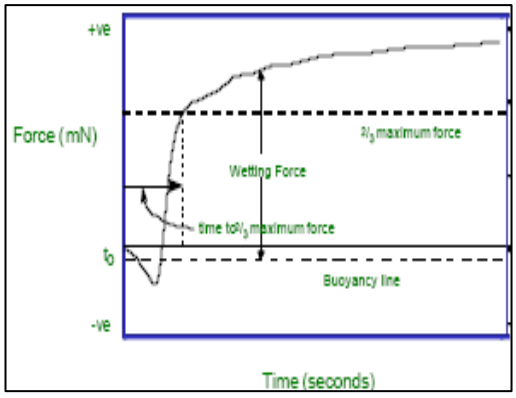

Figure 3.15: Typical wetting balance curve

3.4 Electrochemical Experiments

The electrochemical experiments were carried out using an Autolab PGSTAT 10 potentiostat as shown in **Figure 3.16**. The electrochemical behavior of tin reduction and oxidation was studied in the water and air stable ionic liquid 1-butyl-1-methyl-pyrrolidinium trifluoro-methanesulfonate, (BMPOTF) which was purchased from Merck KGaA and Tin Methane Sulfonate, $(CH_3SO_3)_2Sn$ that was supplied by OM Group, Inc. The working electrode was a copper rod; the counter electrode was a platinum wire. The potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. The reference electrode was silver chloride (Ag-AgCl) electrode due to its non-toxic character.

3.4.1 Reagent and Chemicals

The reagents and chemicals used throughout the experiments:

Component	Percent (%)
Stannous Methane Sulfonate, $(CH_3SO_3)Sn$	≤55
Water, H_2O	≤30
Methane Sulfonic Acid, CH_3SO_3H	≥15

Table 3.1: Component of Tin Methane Sulfonate

Component	Percent (%)
Assay (electrophoresis)	≥ 98
Water, H_2O	≤1
Halides	≤0.1

Table 3.2: Component of Ionic Liquid: 1-butyl-1-methyl-pyrrolidinium trifluoro-methanesulfonate, (BMPOTF)

3.5 Cyclic Voltammetry and Chronoamperometry Experiments

The 3-electrode cell with a volume of 50 cm^3 was used in this experiment (**Figure 3.17)**. 15 cm^3 of electrolyte was placed in the cell which contained counter electrode, working electrode and reference electrode. The working electrode was a copper rod with diameter of 4 mm and exposed area of 0.1257 cm^2 **(Figure 3.18)**. Before each experiment, the copper rod was prepared as follows: wet grinding with SiC type abrasive paper grade 100, 1000 and 1200 to a mirror finish. Cleaning 10 minutes in ethanol and then de-scaled with 10% Methane Sulfonic Acid (10%) and final rinsing in de-ionized water. The counter electrode was a platinum wire with 4 cm length and 0.1 mm diameter **(Figure 3.19)**. The working electrode potentials reported herein were measured against Ag|AgCl reference electrode and correspond to this scale **(Figure 3.20)**. The electrochemical experiments were carried out using an Autolab PGSTAT 10 potentiostat. All experiments were conducted at room temperature, 29 ± 1 ºC in a mixture of BMPOTF ionic liquid and MSA based tin methane sulfonate salts. Tin Methane Sulfonate, $(CH_3SO_3)_2Sn$, was added in the desired amounts. No organic additives were included in the solutions in this study. The electrolyte volume for the mixture was fixed at 15 mL in these experiments as shown in **Table 3.3**. Molarity of stannous (Sn^{2+}) was calculated based on **Equation 3.6**.

$$Y\ \mathrm{M}\ \mathrm{Sn}^{2+} = Y\ \frac{\mathrm{mol}}{\mathrm{L}} \times \frac{118.710\ \mathrm{g}}{\mathrm{mol}}$$

$$= \frac{118.710\ Y\ \mathrm{g}}{\mathrm{L}} \times V\ \mathrm{L} \qquad \textbf{(3.6)}$$

$$= 118.710\ Y.V\ \mathrm{g} \times \frac{1\ \mathrm{L}}{300\ \mathrm{g}}$$

$$= 0.3957\ Y.V\ \mathrm{L}$$

Where,

Y = Desired Molarity of Sn^{2+};

Tin, Sn atomic weight = 118.710 g/mol;

V = Volume of electrolyte make-up in L;

Concentration of tin metal in Tin Methane Sulfonate Salt = 300 g/L

Stannous, Sn^{2+} Concentration (Molarity)	Tin Methane Sulfonate Salt Volume (mL)	Ionic Liquid, BMPOTF volume (mL)
0.1	0.59	14.41
0.2	1.19	13.81
0.3	1.78	13.22
0.4	2.37	12.63
0.5	2.97	12.03

Table 3.3: Quantity of tin methane sulfonate and ionic liquid-BMPOTF in 15 mL electrolyte

3.5.1 Oxygen Removal:

The electrochemical reduction of oxygen usually proceeds via two well separated two-electron steps. The first step corresponds to the formation of hydrogen peroxide:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad \textbf{(3.7)}$$

and the second step corresponds to the reduction of the peroxide:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad \textbf{(3.8)}$$

The exact stoichiometry of these steps is dependent on the medium of electrode. The large background current accruing from this stepwise oxygen reduction interferes with the measurement of many reducible analytes. In addition, the products of the oxygen reduction may affect the electrochemical process under in verification [15]. As a result, Precaution measure was taken to eliminate oxygen from the system by purging high purity nitrogen through the solution prior to the experiments for 3 minutes.

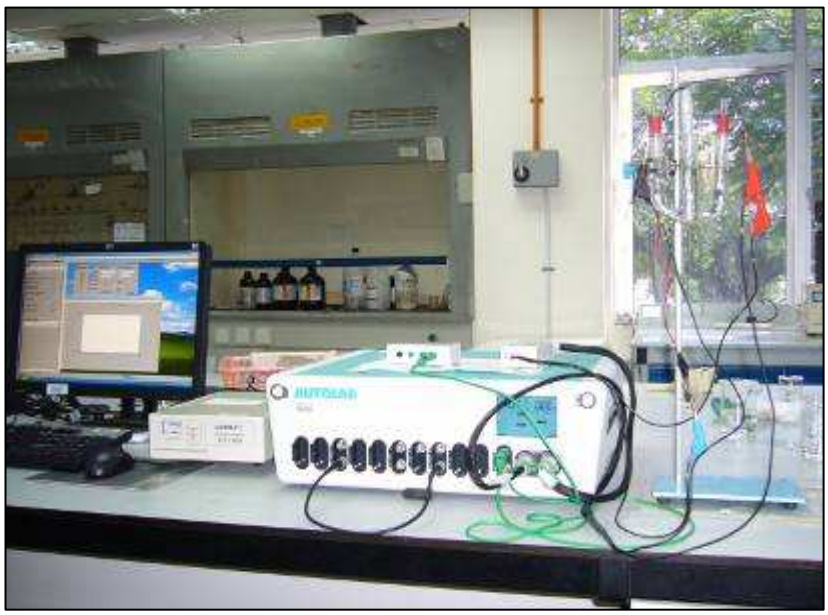

Figure 3.16: Cyclic voltammetry and Chronoamperometry experiments set up

Figure 3.17: 3-electrode cell, A:Counter electrode, B:Reference electrode, C:Working electrode

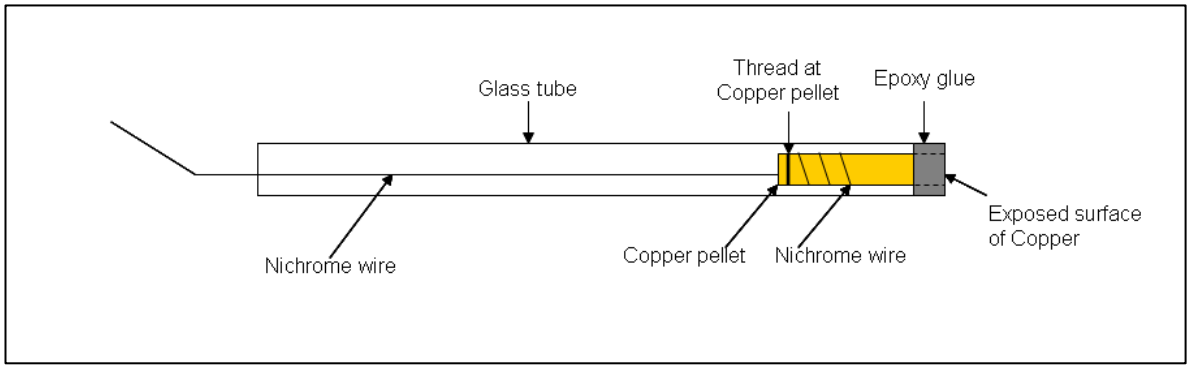

Figure 3.18: Structure of working electrode- Copper

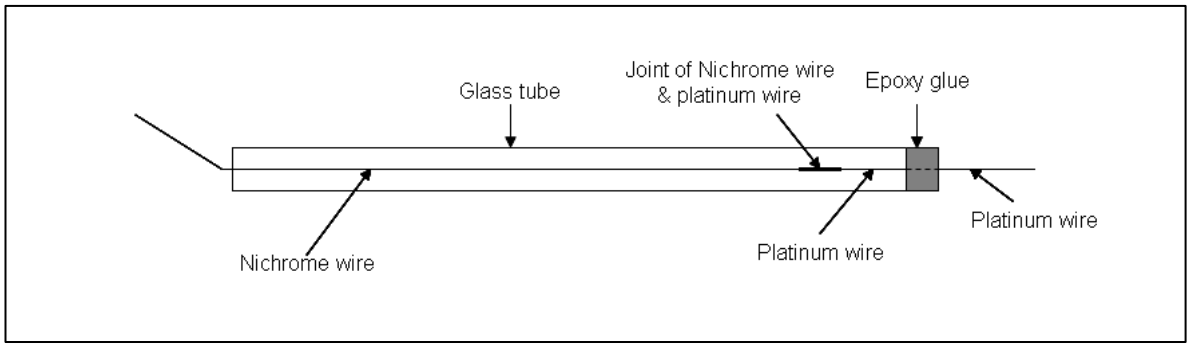

Figure 3.19: Structure of counter electrode- Platinum wire

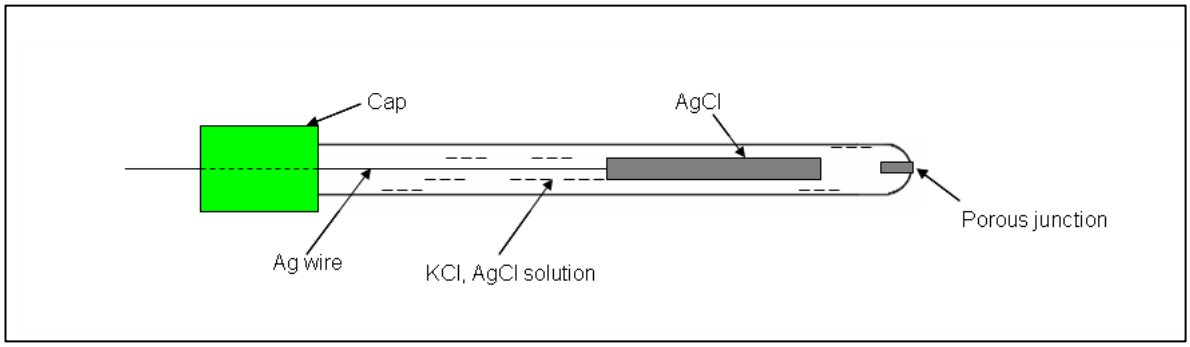

Figure 3.20: Structure of Silver-silver chloride reference electrode

3.5.2 NiChrome wire

Nichrome is a brand name for a nickel-chromium resistance wire, a non-magnetic alloy of nickel and chromium. A common alloy is 80% nickel and 20% chromium, by weight, but there are many others to accommodate various applications. It is silvery-grey in colour, is corrosion resistant, and has a high melting point of about 1400 °C (2552 °F). Due to its relatively high resistivity and resistance to oxidation at high temperatures, it is widely used in heating elements, such as in hair dryers, electric ovens and toasters. Typically, Nichrome is wound in wire coils to a certain electrical resistance, and current passed through to produce heat. The properties of Nichrome wire as follows [49-51]:

Material property	Value	Units
Modulus of elasticity	2.2×10^{11}	Pa
Specific gravity	8.4	None
Density	8400	kg/ m^3
Melting point	1400	°C
Electrical resistivity at room temperature	1.0×10^{-6} to 1.5×10^{-6}	Ωm
Specific heat	450	$Jkg^{-1}°C^{-1}$
Thermal conductivity	11.3	$Wm^{-1}°C^{-1}$
Thermal expansion	14×10^{-6}	$°C^{-1}$
Standard ambient temperature and pressure		

Table 3.4: Physical properties for Nichrome

3.6 Electroplating experiments

Copper panels were used as the substrate for tin electroplating experiments (**Figure 3.6 and 3.7**). Their dimension was 20 mm × 20 mm. Precautionary measures were taken to eliminate oxygen from the system by bubbling high purity nitrogen through the solution prior to the experiments for 3 minutes. Before each experiment, the copper panel was prepared as follows: Cleaning 10 minutes in ethanol and then de-scaled with 10% Methane Sulfonic Acid (10%) and final rinsing in de-ionized water and dried by using an air dryer.

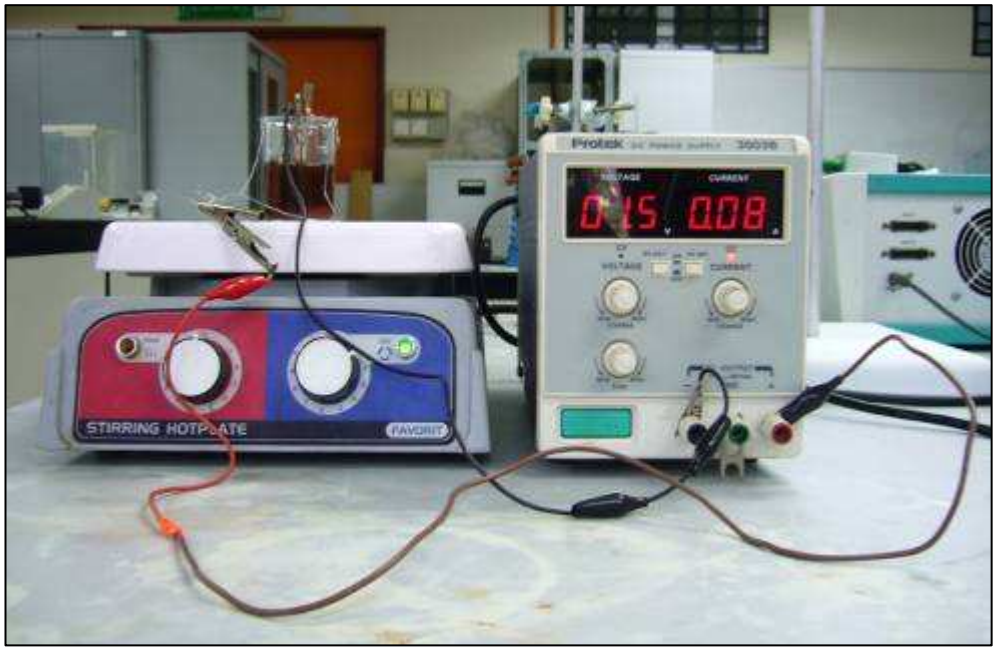

Figure 3.21: Electroplating experiments set up

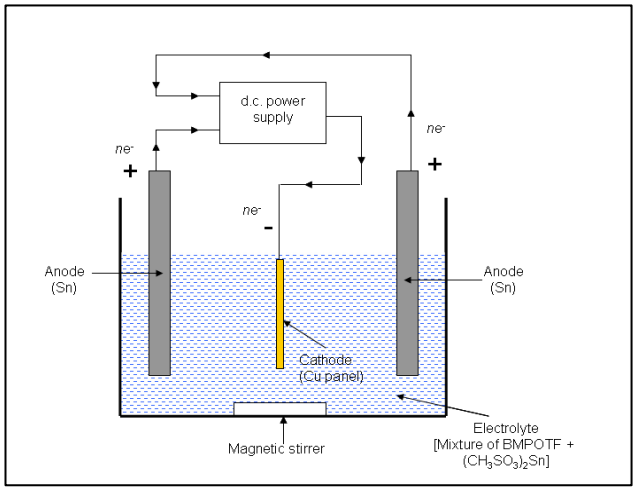

Figure 3.22: Schematic for an electroplating experiments

The panels were weighted and attached to the circuit with a wire electrical contact. It was placed in the cell with a tin anode on both of its adjacent side. After electrodeposition, the panel was removed, rinsed in hot de-ionized water, dried and weighted. By using Faraday's law of electrolysis, the increase in mass of the copper panels after electrodeposition and the charge passed, the current efficiency can be estimated. Stannous ions, Sn(II) was introduced into the BMPOTF ionic liquid along with $(CH_3SO_3)_2Sn$. The tin concentration was varied from 0.1 M to 0.5 M with 0.1 M interval. The cell has a volume of 80 cm^3 and 40 cm^3 of solutions were used. Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX) and Atomic force microscopy (AFM) were used to examine the surface morphology and analyze the elemental compositions of the electrodeposits.