

CHAPTER 2: EXPERIMENTAL METHODS

The reagent and chemical, substrate preparation, aqueous electrolyte, experimental setup and methodology of characterization are described in this chapter.

2.1 Chemical and Reagents

The reagents and chemical used throughout the experiment:

- a. Copper (II) Acetate Monohydrate, $C_4H_6CuO_4 \cdot H_2O$ *R&M Chemicals*
- b. Lead (II) Acetate Trihydrate, $C_4H_6O_4Pb \cdot 3H_2O$ *Sigma-Aldrich*
- c. Galvanized Steel
- d. Distilled water
- e. Methane Sulfonic Acid, $\geq 99.5\%$ CH_3SO_3H *Sigma-Aldrich*
- f. Hydrochloric Acid, HCl 36.5 – 38% *Sigma-Aldrich*
- g. Acetone Dimethyl Ketone Ar Grade, C_3H_6O *Friendemann Schmidt*

2.2 Preparation of Cathodes and Anodes

2.2.1 Preparation of Steel Cathode Substrate

Steel plates 1.0 cm x 2.5 cm with a thickness of 1.0 mm was used as the substrate (Figure 2.1). Surface preparation prior to deposition is an important factor and can be achieved by mechanical and electrochemical methods. The procedures used in this preparation were removal of surface scales using acid dipping, mechanical polishing to obtain a smooth surface and degreasing with acetone. The specimen will be referred to as the cathode.

2.2.2 Cleaning and Bright Dipping of Cathode

The specimen was cut out from a large galvanized steel panel to sizes of 5.0 cm x 5.0 cm which was cleaned by dipping into 20% diluted hydrochloric acid solution for about 4-5 minutes and followed by a washing with tap and distilled water. The cathode specimens were free from oxide layer.

2.2.3 Polishing and Degreasing of Cathode

The steel panels were then mechanically polished to a mirror finish by 600, 1200 and 2000 mesh Silicon Carbide (SiC) abrasive paper electro coated and thoroughly cleaned with distilled water. The specimens were then placed in a degreaser after they were cleaned free from the Silicon Carbides particles. Acetone was used as a degreasing agent. The specimens were degreased for about 30 minutes or more. The degreaser provides for both vapour and liquid degreasing. All grease would have been removed by now and resulting steel panel substrates were smooth and very bright.

2.2.4 Final Preparation, Rinsing and Drying of Cathode

The steel panel was then cut into dimensions of 1.0 cm x 2.5 cm which were fully covered at the back side of the panel and partial in front with cellophane tape to ensure the exposed area are 1 cm x 1 cm squared (Figure 2.1). Before plating special care must be taken to remove all traces of chemical substances which have been used in the several previous operations from the surface of the cathode. Repeated rinsing with distilled water was to remove any traces of acid which might still cling onto the cathode. The steel plates cathode specimen was then rinsed with Analar acetone and dried in an oven at 60°C for almost 1 hour before placed in a dessicator. Each of the cathode specimens was labelled for identification purpose. After the weighing, each cathode specimen was stored in dessicator before electroplating.

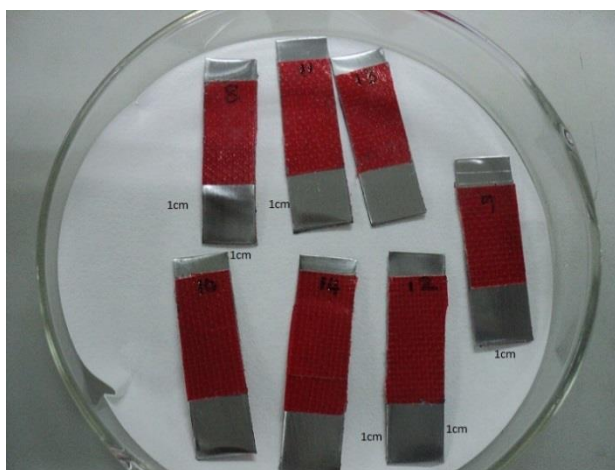


Figure 2.1: Steel plate Cathode

2.2.5 Graphite Anodes

High purity of graphite rod as anode was used. The anode washes with soap water and repeatedly rinsed with distilled water. Then it was dried before used for electrolysis.

2.3 Preparation of electrolyte bath for plating

To prepare the electrolyte solution, different amount of Pb^{2+} and Cu^{2+} were added to 1 mol dm^{-3} $\text{CH}_3\text{SO}_3\text{H}$. The 1 mol dm^{-3} $\text{CH}_3\text{SO}_3\text{H}$ solution prepared from $\geq 99.5 \text{ wt\%}$ $\text{CH}_3\text{SO}_3\text{H}$ (Sigma-Aldrich). All solutions used through these experiments were freshly prepared from analytical grade reagent and mono-distilled water. The electrodeposition of Cu-Pb alloys on steel plates was carried out by using the generic bath composition as shown in Table 2.1.

Table 2.1: Typical composition of the electrodeposition Cu-Pb alloys generic bath

Ingredients	Concentration / mol dm^{-3}
Copper (II) Acetate Monohydrate $\text{C}_4\text{H}_6\text{CuO}_4 \cdot \text{H}_2\text{O}$	0.1
Lead (II) Acetate Trihydrate $\text{C}_4\text{H}_6\text{O}_4\text{Pb} \cdot 3\text{H}_2\text{O}$	0.3
Methane Sulfonic Acid $\text{CH}_3\text{SO}_3\text{H}$	1.0

A mixture of copper acetate and lead acetate was used with addition of methane sulphononic acid. The composition of concentration ratio was 3:1 for the lead acetate and copper acetate.

2.4 Electroplating Experiment

Steel plate cathodes were used as the substrate for Cu-Pb alloy electroplating experiment. The working electrode had dimensions $1.0 \times 2.5 \times 0.1 \text{ cm}$ with only one side exposed to the electrolyte (Figure 2.1). The effective area of WE was around 1 cm^2 . The steel plate cathodes were pre-treated as mentioned in previous ‘preparation of steel cathode substrate’ and weighed before electroplating experiment.

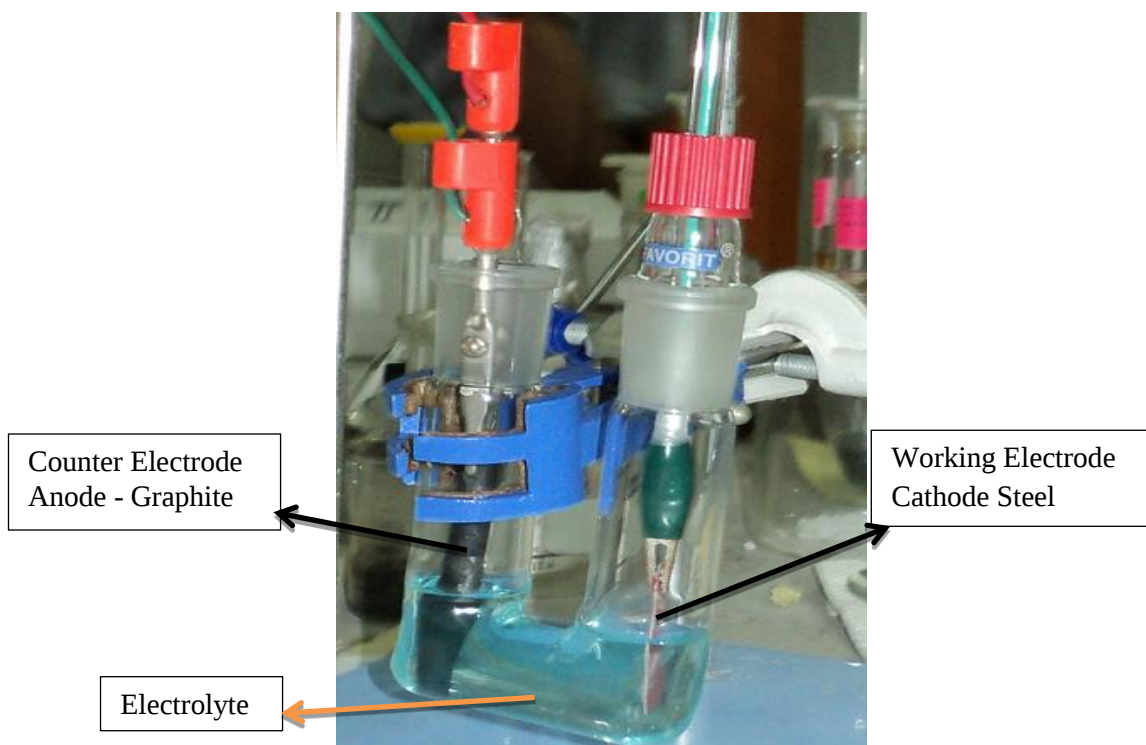


Figure 2.2: Electroplating experiment set-up

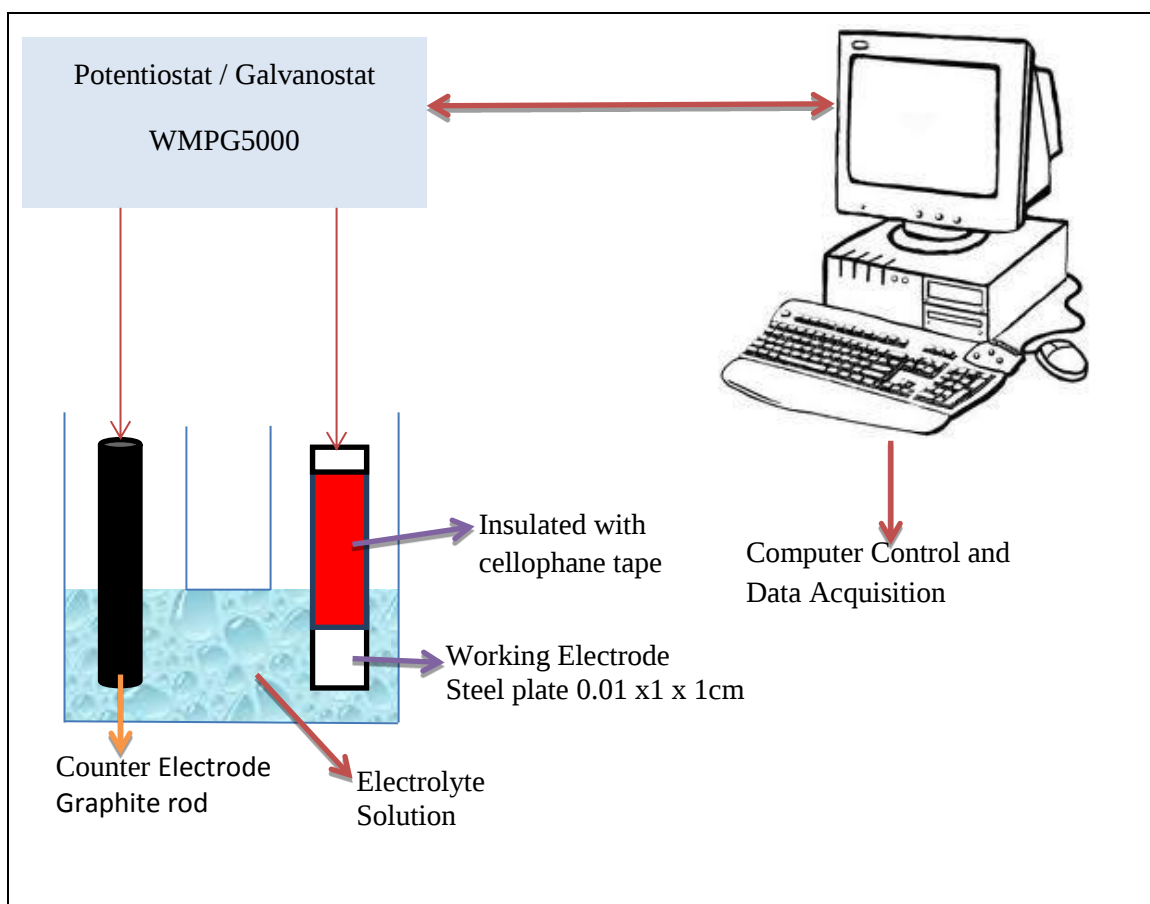


Figure 2.3: Schematic for an Electrodeposition Experiment

The experiments of electrodeposition Cu-Pb alloy were done in an undivided glass cell. The electrolyte volume was approximately 25 cm³. The deposition bath solution consisted of C₄H₆O₄Pb.3H₂O, C₄H₆CuO₄.H₂O and CH₃SO₃H. The electrolyte was free from additives such as levelers and brighteners. All solutions used through were freshly prepared from analytical grade reagent chemicals and mono-distilled water. The experimental setup shown in (Figure 2.2 & 2.3) which consisted of an undivided glass cell provided with a plane parallel steel plate cathode and a graphite rod as anode with an inter-electrode gap of 4.0 cm. Those were placed face to face (parallel) and vertical position. The electrodeposition was done by two-electrode system. All electrochemical measurements were done using a Multichannel Potentiostat / Galvanostat WMPG5000 computer controlled potentiostat using WMPG software. Constant current deposition was carried out in an undivided parallel plate ‘beaker’ cell at the different current densities (4, 6, 8, 10, 12 and 18 mA cm⁻²). The electrodeposition time was 45 min and operated in quiescence solution. All experiments were carried out at room temperature (r.t). After electrodeposition, the steel plate cathode was removed, washed and rinsed with distilled water and dried in an oven at 60°C before placed in a dessicator. Then the steel samples were weighed to determine the mass electrodeposited. From the Faraday’s law of electrolysis, the increase in mass of the steel plate after electrodeposition and the charge passed the current efficiency can be estimated.

Range of operating condition for Cu-Pb alloy electrodeposition

- a. Controlled WMPG5000 and quiescent bath
- b. Room temperature
- c. Time electrodeposition is 45 minutes
- d. Current density 4mAcm⁻² to 18mAcm⁻² (mill amperes/centimeters²)

2.5 Effect of Current Density on Cu-Pb Alloys Deposition Weight

The amounts of deposited Cu-Pb alloys on steel plate were studied by varying the current density of the electrodeposition process. The mass of Cu-Pb alloy electrodeposited layers were calculated from the difference of mass before and after electrodeposition on the steel plate. The steel plates were placed in an oven at 60°C for 1 hour, before being allowed to cool at room temperature in a desiccator and weighed. The mass was recorded as A. The process was repeated for other steel panels used for electroplating in various current densities (4, 6, 8, 10, 12 and 18 mA cm⁻²) for duration of forty five minutes. The plates were washed with distilled water and allowed to dry in an oven at 60°C for 1 hour. The plates were transferred into a desiccator and allowed to cool for 30 minutes to room temperature before weighed with using an analytical balance of 0.0001g sensitivity. The mass increase was recorded as B. The mass of Cu-Pb alloys electrodeposited in the electrochemical process are expressed as a (B-A). From the difference in weight of the plates the current efficiency of the bath was calculated using the following formula.

$$\text{Current Efficiency} = (\text{Actual weight gain} / \text{Theoretical weight as per Faradays law}) \times 100$$

Then, from the mass deposition of the Cu-Pb alloys, the graph of the mass deposition to the current density was plotted.

2.6 X-Ray diffraction

The X-ray diffraction is widely used to determine the structure and composition of the deposit materials. Diffraction patterns contain information showing various phases of a material and also residual stresses present within the coating material. The X-ray diffraction pattern for the all six (6) samples of electrodeposited copper – lead alloys specimens obtained from MSA bath were recorded using XRD instrument (EMPYREAN PANalytical , Netherland) instruments. A X-ray diffractometer

EMPYREAN PANalytical using Cu-K α , $\lambda=0.15406$ nm as the radiation source and a position sensitive detector (PSD) were used for identification of the different phases. Measurement were made at 0.026° intervals of 2θ over the range 5° to 80° . After X-ray identification, the samples were transferred to the scanning electron microscope for further examination.

2.7 Scanning electron microscopy (SEM)

The SEM was used to record the image of the deposited surface and the microstructures. X-ray elemental mapping was used to furnish the information of elemental composition. The six (6) samples of electrodeposited copper-lead alloys obtained from MSA bath specimens were mounted suitably and examined under the microscope. The morphology of the electrodeposits was characterized by SEM Quanta FEI FEG250 XT Microscope Control model with an acceleration voltage range of 20,000 V and with the magnification ranges of 500, 1000, 2500 and 5000. The morphology of the electrodeposits was examined under high magnification to assess the deposit nature, heterogeneities and pores present in the deposits using a scanning electron microscope. The scanning electron microscope which makes use of reflected primary electrons and secondary electrons enable one to obtain information from regions that cannot be examined by others.

2.8 Energy Dispersive X-Ray (EDX) Analysis

The elemental composition present in the copper-lead alloys deposits obtained from MSA bath were analysed using Energy Dispersive System Oxford Instrument INCA 4.14. An energy-dispersive x-ray detector is used in the elemental mapping. To visualize the spatial distribution of each element, a series of micrographs from the same field is taken but in different modes such as back-scattered electrons, x-ray mapping and secondary electrons. WDS were used to analyze the composition of the alloy with the INCA 4.14 microprobe which quantitatively determines the elemental composition.

2.9 Cyclic Voltammetry

For the electrochemical characterisation of Cu-Pb, steady state cyclic voltammetry was carried out by using a purpose-built three electrode undivided glass cell with a volume 50 cm^3 (Figure 2.5). Approximately 15 cm^3 of electrolytes were placed in the cell which contained a counter electrode, a working electrode and a reference electrode. The working electrode were steel plates with thickness of 1 mm and the exposed area was approximately 1 cm^2 (Figure 2.1). Before each experiment, the steel plates were prepared as follows: mechanically polishing with SiC type abrasive paper electro coated grade 600, 1200 and 2000 mesh to a mirror finish and thoroughly cleaned with distilled water, degreasing by acetone and covering the back side of the steel plates with cellophane tape for insulation. The counter electrode was a platinum wire with 1.5 cm length and 1 mm diameter (Figure 2.6). The working electrode potentials reported herein were measured against a saturated calomel electrode (SCE) reference electrode (Figure 2.7). All electrochemical experiment were carried out using an Autolab PGSTAT 302N potentiostat/galvanostat from Autolab with the General Purpose Electrochemical Software (GPES) Version 4.9, installed in a computer as shown (Figure 2.4) and conducted at room temperature $29 \pm 1^\circ\text{C}$. The electrolytes contained 0.1 mol dm^{-3} Copper acetate in 1.0 mol dm^{-3} methanesulfonic acid, 0.3 mol dm^{-3} lead acetate in 1.0 mol dm^{-3} methanesulfonic acid and mixture of 0.1 mol dm^{-3} copper acetate and 0.3 mol dm^{-3} lead acetate in 1.0 mol dm^{-3} methanesulfonic acid. Nitrogen bubbling was used to remove the dissolved oxygen from the medium electrolytes for at least 2 to 3 minutes. For comparison, CV behaviour of Cu-Pb was also investigated by changing of working electrode from steel plate to a glassy carbon (GC) with 2 mm diameter. The CV analysis were perform in the standard electrochemical cell using platinum wire (Pt) as the counter electrode, and a saturated calomel electrode as reference electrode. In addition solutions for CV experiment prepared are 0.01 mol dm^{-3}

lead acetate in 2.0 mol dm^{-3} methanesulfonic acid and 0.02 mol dm^{-3} copper acetate in 2.0 mol dm^{-3} methanesulfonic acid. No organics additives were used in the solutions in this study. The cyclic voltammogram of a given solution was obtained by initiating the potential scan at 0 V and scanning to the negative direction. The potential scan was reversed at -0.1 V. However for comparison to the Cu^{2+} solution, the potential window range for the CV was set from 0.5 V to -0.7 V. The analyses were done at a scan rate of 25 mV sec^{-1} using the single scan method.

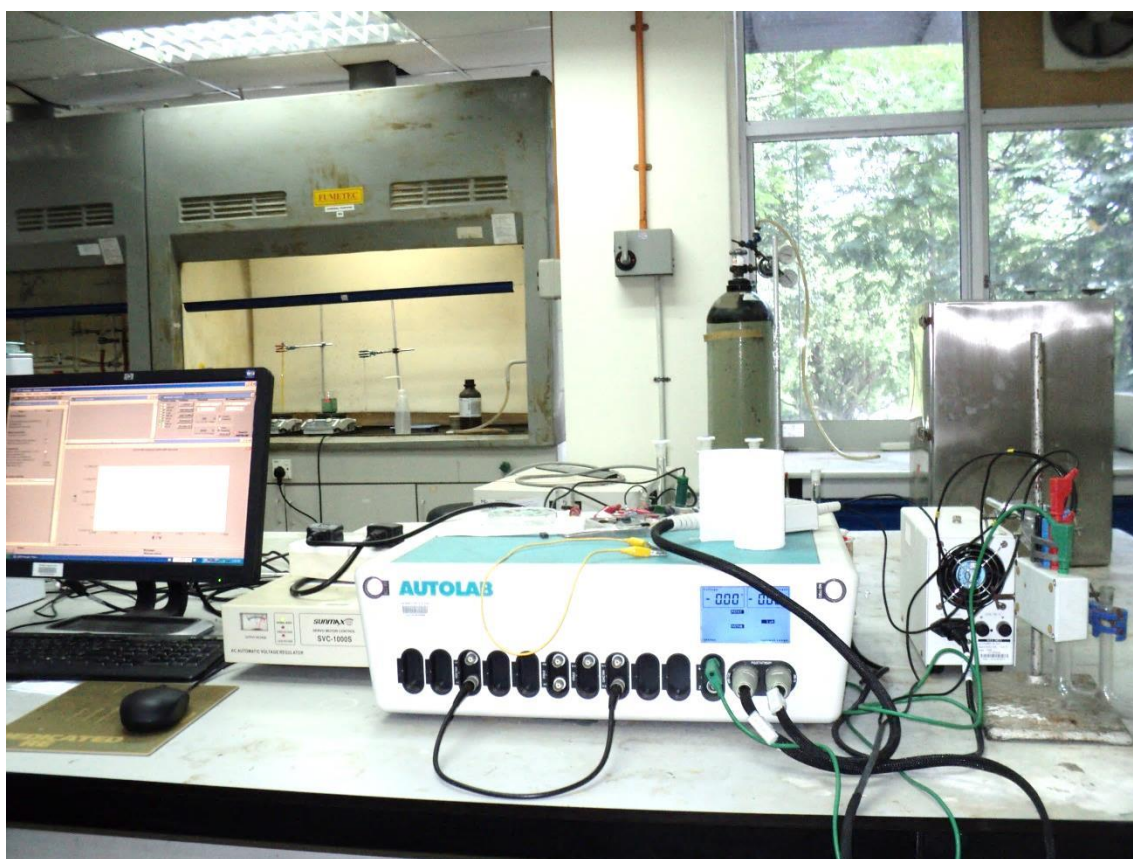


Figure 2.4: Cyclic voltammetry experiment set up

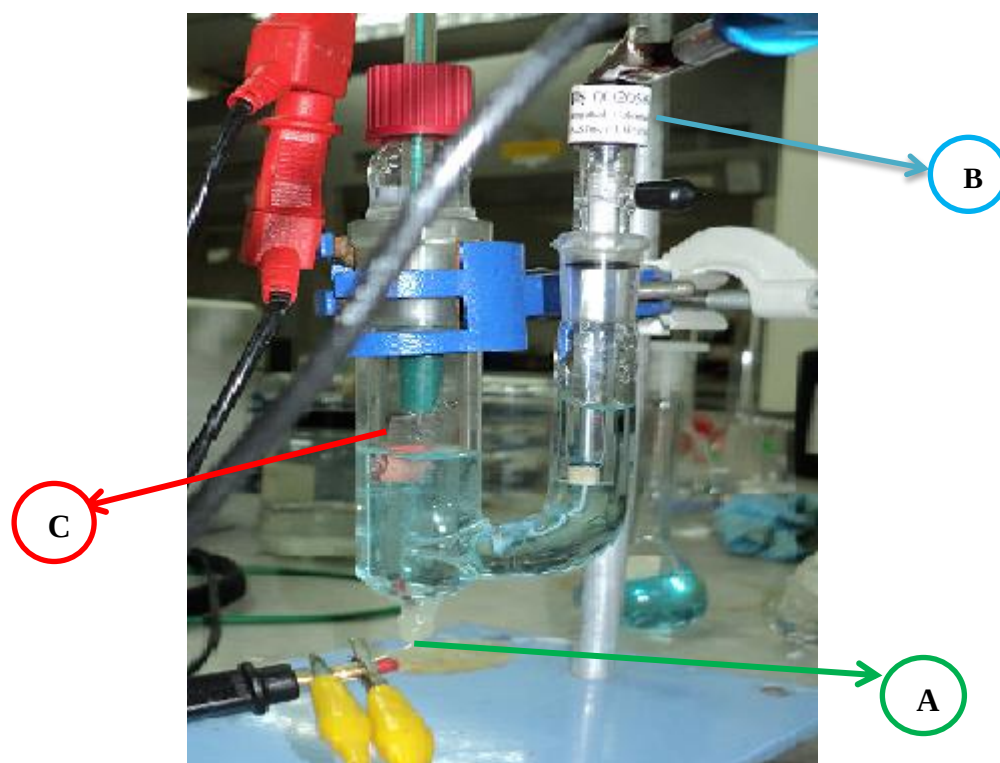


Figure 2.5: 3 electrode cell, A: Counter Electrode, B: Reference Electrode, C: Working Electrode

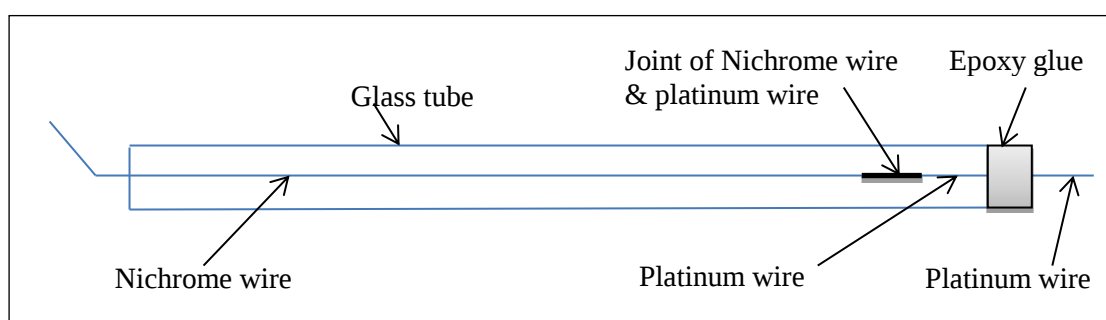


Figure 2.6: Structure of counter electrode – Platinum wire

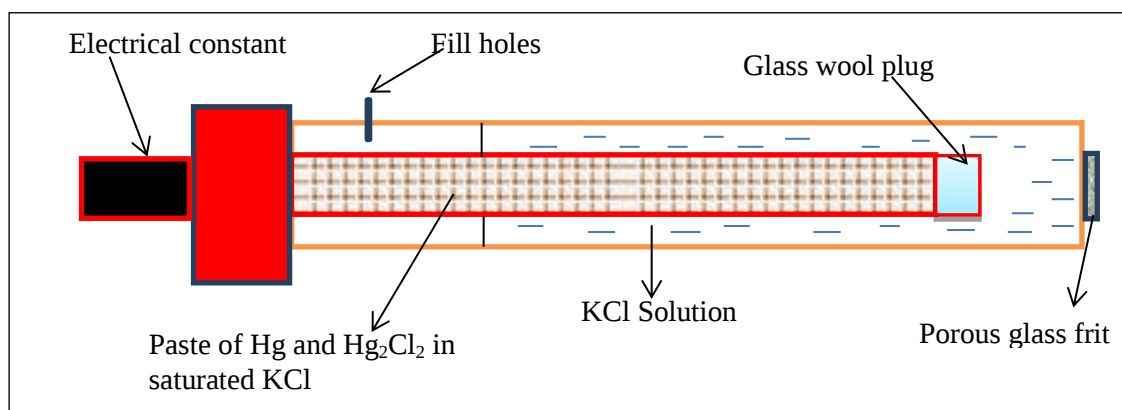


Figure 2.7: Structure of saturated calomel electrode SCE

2.10 Instrumentations

The *in-situ* electrodeposition process was investigated by WonATech Instrument to produce the electrodeposition film. In other hand the electrodeposited layer were tested by following instrument:

2.10.1 Electrodeposition of Cu-Pb Alloys by WonATech

A WonATech WMPG 5000 Potentiostat / Galvanostat have been successfully used for investigation of the Cu-Pb alloys electrodeposition. System hardware was designed for stable and accurate instrument furthermore for easy expansion and maintenance. The WMPG5000 series plug-in type module with independent power suppliers per 8 channels substation. Each substation can be used as independent system with optional "Stand Alone Kit" or can be built up integrated system as add-on. These give flexibility to the users' application. Software WMPG English V1.11 can run useful techniques such as cyclic voltammetry, linear sweep voltammetry, tafel plot, potentiodynamic, zero resistance ammeter (ZRA), chronoamperometry, square wave voltammetry and charge/discharge battery test. The software consists of 32 bit multi-tasking tool bar for quick access, easy operation and user friendly. The experiments could be done at various current densities in wide range of general graph current/voltage versus time window through the WonATech WMPG 5000 (Figure 2.8)

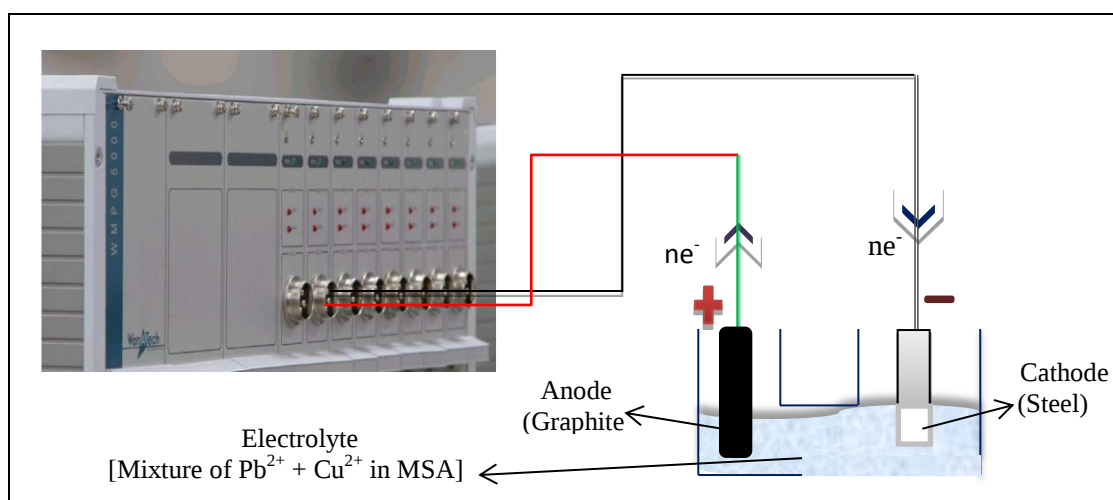


Figure 2.8: Schematic of WonATech WMPG5000

2.10.2 X-Ray Diffraction (XRD)

One of the most important non-destructive tools for the analysis of all kinds of crystalline materials is X-Ray diffraction. Two important characteristics can be obtained using X-ray diffraction (XRD). These include a fingerprint characterization material and a determination of their structure. The method to identify the arrangement of atoms within a crystal is X-ray crystallography (XRD). Wilhelm Conrad has discovered the X-rays in 1895. The studies of crystal symmetry and XRD technique is based on the radiated beam of X-ray strikes on a crystal and diffracts it to many specific directions. Three-dimensional picture of the density of electrons is illustrated from the angles and intensities of those diffracted beams. Crystals are made from regular arrays of atoms and the electromagnetic radiation can be considered as X-rays. William Lawrence Bragg and William Henry Bragg have suggested the Bragg diffraction as first proposed in 1913. They found specific wavelength and incident angles, intense peaks are reflected from the crystals. When the electromagnetic radiation and subatomic particles waves are of comparable wavelength, the Bragg diffraction will take place (Figure 2.9). With regards to the structure of the sample, the path difference between two waves is given by $2d\sin\theta$ (Eq.2.1)

$$2d\sin\theta = n\lambda \quad \dots\dots\dots (2.1)$$

Where θ is the scattering angle, n is an integer determined by the order given, d is the distance between two lattice planes and λ is the wavelength.

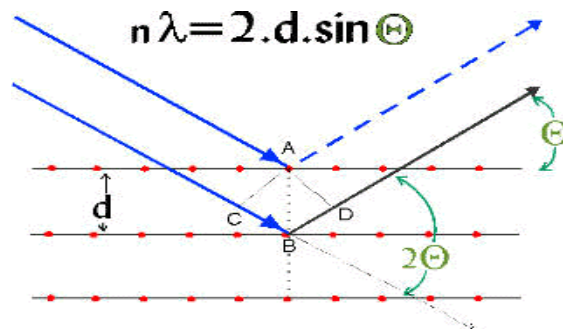


Figure 2.9: Schematic representation of a crystalline lattice. The arrow indicates directions of the incident and reflected X-Ray beams

The angular velocity is θ/second . The data are reported with 2θ , because the detector is rotating $2\theta/\text{second}$ depending on the sample movement (θ/second). All orientation of the samples, position of detectors and the direction of reflected beams are controlled by a computer. This leads to Bragg's law, which can be described based on the symmetry and crystallographic planes (h,k,l) of the crystalline lattice. Moreover, Bragg's law, as described above, can be used to determine the lattice spacing i.e., for a particular cubic system d factor. The energy of reflected x-ray beam is converted to voltage pulse by using a specific detector (scintillator, silicon or germanium diodes) (Lawes, 1987; Lifshin, 1999). The sample and detector are moved during the characterization operation, which can be control by goniometer depending on the X-ray direction while the source is fixed.

The X-ray diffraction pattern for the all six (6) samples electrodeposited copper – lead alloys specimens obtained from MSA bath were recorded using XRD instrument (EMPYREAN PANalytical Netherland) instruments(Figure 2.10). The XRD analysis was performed by Mr. Zaharudin Bin Md. Salles (Geology Faculty University of Malaya).



Figure 2.10: Schematic of XRD instrument

2.10.3 Scanning Electron Microscopy (SEM) study

A type of the electron imaging technique to identify the images of the sample surface is the scanning electron microscopy (SEM). Max Knoll has reported the first SEM image of silicon steel at 1935 (Knoll and Max). With regards to this technique the surface of samples could be scanned with a high-energy beam of electrons in a faster scan pattern where the information about the sample topography from the producing signals due to the electrons interacts with the atoms on surface. The various types of signal in SEM comes from the secondary electrons, back-scattered electrons (BSE), characteristics X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Commonly, the SEM is included by secondary electron detectors. Rarely, the SEM can be found with detectors for all possible signals. The secondary electrons with low energy ($<50\text{eV}$) which are ejected from the k-orbitals of the specimen atoms by inelastic scattering interactions with the beam electrons is detected by common detectors. The SEM is able to produce very high-resolution images of a sample surface with less than 1 to 5 nm in size. In other words, the SEM images can be magnified over 10 to 500,000 times. To understand the surface structure of a sample, the SEM instruments are able to reveal with large depths of field when a very narrow electron beam irradiated to the surface. As aforementioned, the SEM-FEI Quanta 250 FEG was used to capture images of surface morphology of electrodeposited samples, which included the EDX analyzer (Oxford Instrument INCA 4.14).

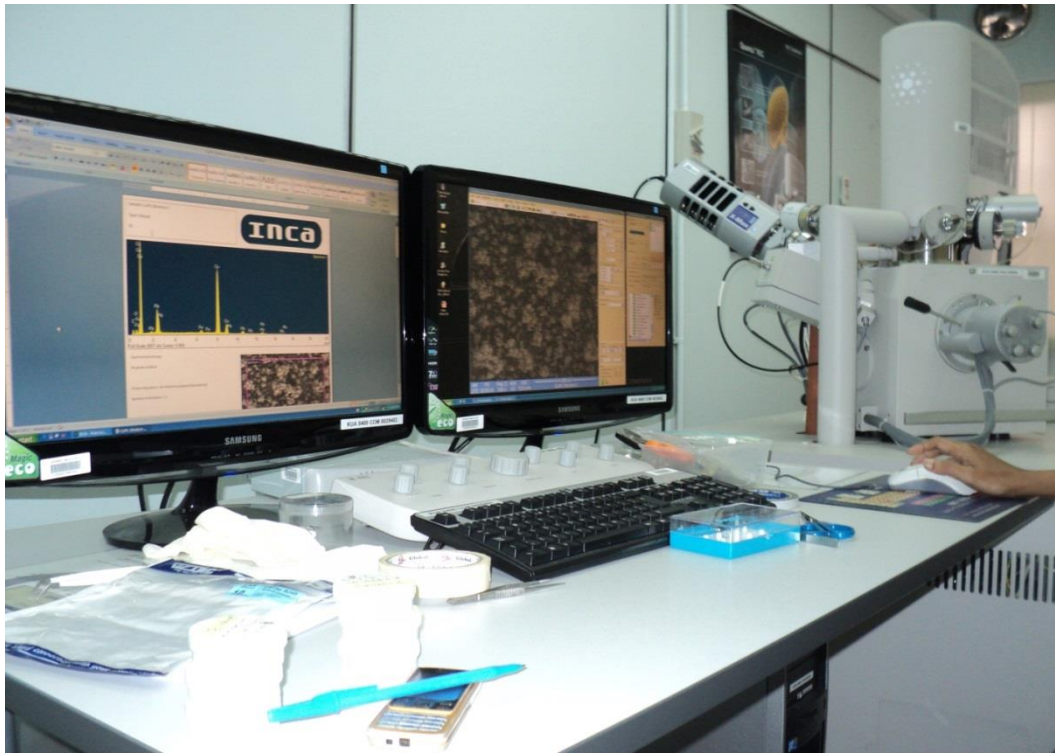


Figure 2.11: Schematic of SEM-FEI Quanta 250 FEG

2.10.4 EDX analysis

One of the techniques used to identify the presence elements is Energy Dispersive X Ray Analysis (EDX), by analyzing the energies of X-ray photons emitted from the bombardment of the sample using an electron beam. This technique is based on different energies which are emitted from different elements. However, the same energy could not be emitted from two elements because the binding energy of the electron is different for each element. They may excite an electron in an inner shell, ejecting an electron and creating a hole from the shell layer of the atom. An electron from an outer, higher-energy shell then fills the hole and the difference in energy between the higher energy shell and the lower energy shell may be released in the form due to the X-ray radiation. The difference in energy between the two shells from the energy spectrum of the X-rays could be determined and the elemental composition of the specimen can be measured and recognized. This technique is non-destructive and the elements and their concentration in the sample can be determined accurately. The EDX systems are mostly

available as an attachment to a scanning electron microscope since SEM has an in built source of electrons. Notably, the detection of an element and accuracy varies from sample to sample.

All of electrodeposited layer was tested with the EDX analyzer which is attached with the SEM-FEI Quanta 250 FEG, was used to capture images of surface morphology of electrodeposited samples which was included the EDX analyzer (Oxford Instrument INCA 4.14). The SEM and EDX analysis were performed by Mr. Hassan (Dental Faculty University of Malaya).

2.10.5 Cyclic Voltammetry of Cu-Pb Alloys by means of Autolab

Autolab PGSTAT-302N Potentiostat / Galvanostat have been successfully used for the electrochemical characterisations of Cu-Pb. The GPES software is installed in a computer and interfaced with the Autolab PGSTAT-302N. This software can run some useful DC techniques such as cyclic voltammetry, chronoamperometric, chronopotentiometry and so on. The cyclic voltammetry technique was used for the determination of electrokinetic properties of charge species. Furthermore, the chronoamperometry and chronopotentiometry were used for electrodeposition of the alloys. The experiments could be done at various scan rates in wide ranges of potential window with the Autolab PGSTAT-302N. Figure 2.12 shows schematic of Autolab PGSTAT-302N which includes connection to: the working electrode, reference electrode and counter electrode.

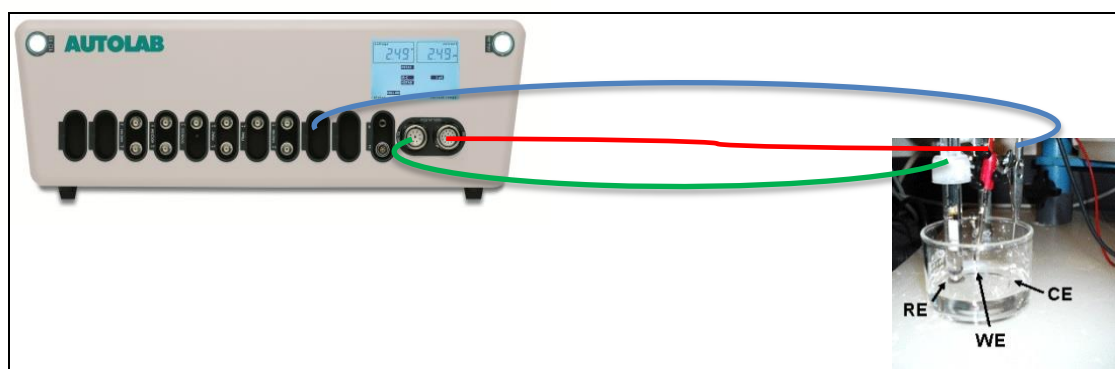


Figure 2.12: Schematic of Autolab PGSTAT-302N