CHAPTER 3

EXPERIMENTAL METHODS

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3.1 Materials

The materials used for preparing lead sulphide are thiourea (AR, assay 99 %) and $PbNO_3$ (AR, assay 99 %) obtained from FLUKA. As for the preparation of tin(II) sulphide, tin(II) sulphate, ($SnSO_4$) was obtained from Ajax Laboratory Chemicals (Assay 95%). The anode materials prepared in the present work are compounds of the inoganic sulphide salts. These materials are lead sulphide (PbS) and tin sulphide (SnS) and they were prepared by the chemical bath deposition and double decomposition techniques respectively.

3.1.1 Preparation of lead sulphide

Lead sulphide was prepared by chemical bath deposition technique. Equal volume of 1 M thiourea ($(NH_2)_2CS$) and 1 M lead nitrate, ($Pb(NO_3)_2$) in aqueous solution were mixed in a cleaned reaction vessel. The cleaning of the reaction vessel include ultrasonic cleaning for 10 minutes, acetone rinsing and finally distilled water rinsing. The reaction mixture was stirred continuously using a magnetic stirrer for ~ 6 hours. The water bath was maintained at 50 – 60°C. 30 mL of 28 % NH_4OH was later added to the reaction vessel and lead sulphide was deposited at the walls of the reaction vessel. The black precipitate was filtered, washed several times with distilled water and dried. Figure 3.1 shows a schematic diagram of the chemical deposition technique.

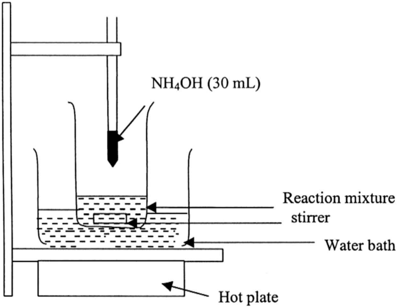

Figure 3.1. Chemical bath deposition technique

3.1.2 Preparation of tin(II) sulphide

12.88 g of tin (II) sulphate salt was dissolved in 50 mL of 2 M H_2SO_4 and make up to 500 cm^3 with distilled water. The cloudy solution was filtered to obtain a clear solution. The clear solution is acidic and the measured pH is ~4.

Sn^{2+} ion is a reducing agent (Holderness, 1975). The presence of Sn^{2+} ion was confirmed by the following observations.

(i) with iodine – the clear solution turned the dark brown I_2 solution to colourless

$$\underset{\text{dark brown}}{Sn^{2+} + I_2} \longrightarrow \underset{\text{colourless}}{Sn^{4+} + 2I^-}$$

(ii) with potassium dichromate ($K_2Cr_2O_7$) – the clear solution turned the orange ($K_2Cr_2O_7$) solution to green.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 3Sn^{2+} + 14H^+ \longrightarrow \underset{\text{green}}{2Cr^{+3}} + 3Sn^{4+} + 7H_2O$$

H_2S gas was then bubbled through the clear tested solution for 3 hours. The hydrogen sulphide gas was prepared by the action of dilute hydrochloric acid (2 M) and iron (II) sulphide sticks.

$$FeS(s) + 2HCl\,(aq) \longrightarrow FeCl_2\,(aq) + H_2S(g)$$

The hydrogen sulphide produced was bubbled through distilled water to remove hydrogen chloride. The apparatus used is as shown in Figure 3.2. The H_2S gas was recognized by its strong smell of rotten eggs. The presence of the H_2S gas was confirmed when a moist lead (II) ethanoate paper turned black when exposed to the gas owing to the formation of lead (II) sulphide.

$$\underset{\text{lead (II) ethanoate}}{(CH_3\,COO)_2\,Pb\,(aq)} + H_2S(g) \longrightarrow \underset{\text{lead sulphide (black)}}{PbS(s)} + 2CH_3COOH\,(aq)$$

Dark brown precipitate of SnS was precipitated in the flask. The precipitate was filtered, washed several times with distilled water and dried. It turned black on drying.

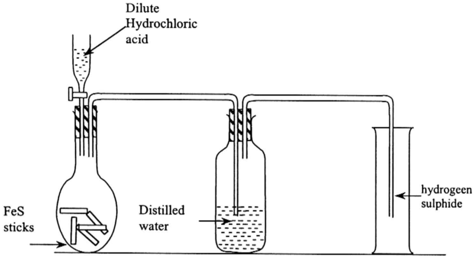

Figure 3.2. Apparatus for the preparation of hydrogen sulphide gas

3.2 Materials characterization

The prepared samples were characterized using various techniques.
Among which are X-ray diffraction (XRD), Energy Dispersive Analysis of X-Rays (EDAX), impedance spectroscopy and cyclic voltammetry.

3.2.1 X-ray diffraction

X-ray diffraction is one of the techniques employed for qualitative analysis.

The XRD diffractogram is unique for every crystalline substance. The line position in the diffractogram depends on the unit cell size and the line intensity depends on the type of atoms present and on the arrangement in the crystal (Whiston, 1987). Thus a sample can be confirmed from its unique powder pattern which can be obtained from the JCPDS powder diffraction file

X-ray diffraction has also been used by researchers to study whether a material is amorphous or cystalline (Arof et al., 1993; Arof et al., 1994).

In this work, X-ray diffraction spectroscopy was carried out using the Shimadzu X-Ray Diffractometer Model XD-5 at the Geology Department, University of Malaya. The samples were scanned with a beam of monochromatic CuK_α radiation of wavelength $\lambda = 1.5418$ Å. The X-ray tube was operated at 40 kV and 20 mA. X-ray profiles were recorded for 2θ ranging from 3° to 70° where θ is the angle of diffraction.

The diffractometer composed of (i) X-ray generator, (ii) X-ray detector and (iii) Counting / recording system. The specimen to be inserted in the diffractometer is prepared by grinding a small amount of the sample in a mortar and smeared with acetone onto a glass slide.

When a monochromatic X-ray beam strikes a sample at some angle θ, a portion is scattered by the layer of atoms at the surface. The unscattered portion of the beam penetrates to the second layer of atoms where again a fraction is scattered and the remainder passes on to the third layer. The cummulative effect of this scattering from regularly spaced centers of the crystal is a diffraction of the beam (Whiston, 1987).

Diffraction would only occur if the Bragg equation (equation 1) was obeyed and a reflection would 'shoot out'. Thus the condition for X-ray diffraction is,

$$2d \sin \theta = n\lambda \qquad (1)$$

where n is an integer (1, 2, 3 etc.) indicating the order of diffraction called the order of reflection, λ is the wavelength of the reflected X-ray, d is the interplanar spacing, θ is the angle of reflection. Figure 3.3 shows the Bragg condition (Whiston, 1987).

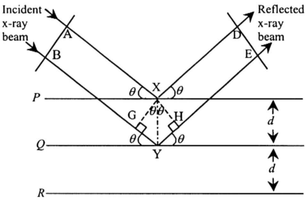

Figure 3.3. Bragg condition

3.2.2 Energy Dispersive Analysis of X-rays (EDAX)

The Energy Dispersive Analysis of X-rays (EDAX) gives useful analysis of elemental composition. It is a nondestructive analytical technique. The analysis of the samples were carried out on a Philips Dx-4*I* instrument. Observations were made at various selected areas of the samples and a fine beam of electrons was scanned across the surface of the selected area.

An electron bombarding the target may have sufficient energy to completely displace an electron from the innermost orbit of the target atom and produces an unstable ion. An electron from an outer shell could fill the vacant position. This transition is accompanied by the emission of a characteristic X-ray, a photon of definite wavelength.

The characteristic X-rays from the sample irradiated with a primary X-ray beam enter a cooled detector. It is necessary to cool the detector to liquid nitrogen temperature in order to reduce electronic noise and to ensure optimum resolution (Whiston 1987). To reduce electrical charge build up, the sample was coated with carbon or gold .

3.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscope is used primarily for the study of surface topography of solid materials. It gives useful analysis of structure and morphology of heterogeneous organic and inorganic materials [Braun, 1987]. Any solid material can be studied and sample size is limited to specimens less than 10 cm in diameter. However, samples must not be electron-beam-reactive and contain no volatile or corrosive components.

An electron beam passing through an evacuated column is focused by electromagnetic lenses onto the specimen surface. The beam is then rasted over the specimen in synchronism with the beam of a cathode ray tube

(CRT) display screen. Inelastically scattered secondary electrons are emitted from the sample surface and collected by a scintillator, the signal from which is used to modulate the brightness of the cathode ray tube. In this way the secondary electron emission from the sample is used to form an image on the CRT display screen. Differences in secondary emission result from changes in surface topography. If (elastically) back scattered electrons are collected to form the image, contrast results according to compositional differences will be obtained. Cameras are provided to record the images on the display screen (Reimscussel et al., 1988).

Observations were made at various spots of the sample which is coated with carbon or gold to reduce electrical charge build up.

3.2.4 Cyclic voltammetry

Cyclic voltammetry (CV) is an electrochemical technique which enable scientist to test and discover the ability of a material to intercalate ion and hence suggest new materials as electrodes in batteries (Basirun, 2000).

Cyclic voltammetry is the most popular electrochemical method in use today. The tests of the samples prepared were done using the BAS

Electrochemical Workstation at the Chemistry Analytical Laboratory, University of Malaya. The working electrode, Figure 3.4, was prepared by mixing the samples with PVDF as binder and compressed in an empty glass rod with a copper wire in it. In this work test, Li foil was used as the counter electrode as well as the reference electrode. The electrolyte used was 1M solution of $LiCF_3\ SO_3$, EC-DMC (1:1)

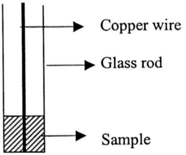

Figure 3.4. Working electrode

The electrochemical cell used in this experiment is as shown in figure 3.4. The system was purged by nitrogen gas before the start of the experiment to eliminate any dissolved gas that can interfere with the reaction (Arof et al., 1999). The cyclic voltammograms were recorded at three different scan rates, i.e. 50, 100 and 400 mV s^{-1}, in the potential range from –3 V to +3 V at room temperature. The experimental set up is shown in Figure 3.5.

To obtain a cyclic voltammogram, the current at the working electrode in an unstirred solution was measured during the potential scan. The potential was ramped linearly to a more negative potential and then ramped in reverse, back to the starting voltage.

Consider a reversible reaction, $O + e^- \longrightarrow R$. For this reaction, during the negative scan where oxidized species are reduced to R, the depletion of O in the vicinity of the electrode is accompanied by an accumulation of R. The reduction continues until the applied potential becomes sufficiently positive to cause oxidation of the accumulated R. Oxidation of R is signaled by the appearance of anodic current. The current increases as the potential moves increasingly positive until the oxidation of R depletes the region near the electrode of R to cause the current to peak and then to decrease. Thus the physical phenomena that caused a current peak during the oxidation cycle also caused a current peak during the reduction cycle. The oxidation peak will usually have a similar shape to the reduction shape. This can be seen Figure 3.6 (Basirun, 2000).

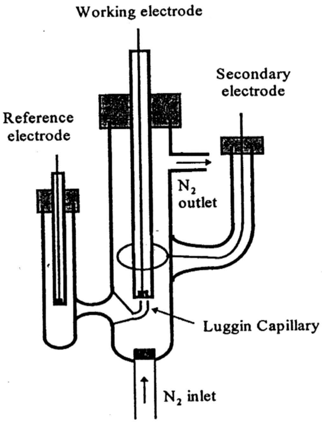

Figure 3.5. Experimental set up for cyclic voltammetry

The important parameters of a cyclic voltammograms are the magnitudes of the peak currents, I_p^A and i_p^C and the potentials at which the peaks occur E_p^A and E_p^C (Kissinger and Heineman, 1996). For a reversible reaction as shown in Figure 3.7 the peak current I_p is proportional to the square root of the scan rate as described by the Randles–Servik equation (Basirun, 2000).

$$I_p = 0.4463nF(nF/RT)^{1/2} (D\nu)^{1/2} C_0^{\infty} \qquad (2)$$

where

n = number of electrons which is transferred in the electron transfer step

F = Faraday's constant 96500 C mol^{-1}

R = gas constant 8.3142 J mol^{-1} K^{-1}

D = diffusion constant ($m^2 s^{-1}$)

ν = scan rate ($V s^{-1}$)

C_0^{∞} = electroactive species concentration in solution.

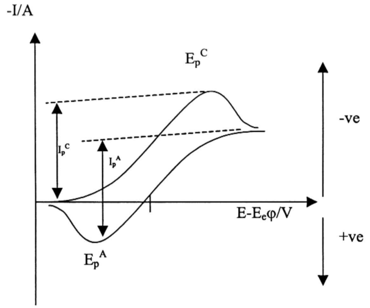

Figure 3.6. Cylic voltammogram for a reversible process. Only species O present in solution ($O + e^- \rightarrow R$)

(Basirun, 2000)

3.2.5 Impedance spectroscopy

The technique of impedance spectroscopy was employed to determine the electrical conductivity of the sample. Impedance spectroscopy also refers to measurements of real and imaginary part of impedance at different frequencies.

Impedance is a more general concept than resistance because it takes phase differences into account. In this work, the impedance was measured with a HIOKI 3531-01 LCR Hi-Tester that has been interfaced to a computer for data collection. The experimental set up used is as shown in Figure 3.7. The impedance measurements were made in the frequency range from 42 Hz to 5 MHz using an a.c. bridge at room temperature and at 90 °C. The software controlling the measurement also calculates the real and imaginary components of the impedance for every frequency. The data is computed and graphs of negative imaginary impedance versus real impedance having the same scale were then plotted. From the complex impedance plot, the value of R_b (bulk resistance) can be determined. Knowing the bulk resistance, the electrical conductivity of the sample can be calculated using the equation;

$$\sigma = \frac{l}{R_b A} \qquad (3)$$

where

σ = electrical conductivity

l = thickness of sample

R_b = bulk resistance

A = effective area of contact

The samples tested were grounded, formed into pellets and placed in a conductivity mount (between two stainless steel pellets) connected to the HIOKI bridge as shown in Figure 3.8. The thickness of the samples was measured by a micrometer screw gauge and the diameter of the samples was measured with a vernier caliper.

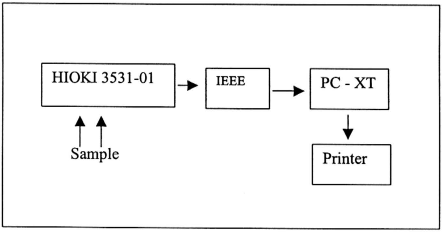

Figure 3.7. Connection for conductivity measurement

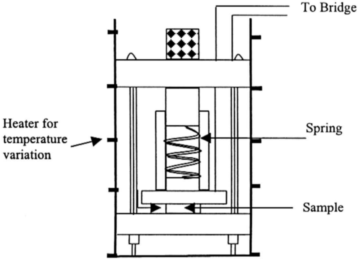

Figure 3.8. Connections for conductivity measurement.

3.3 Battery fabrication

In the present work, the fabrication and analysis of a lithium secondary battery which makes use of lithium transition metal as the cathode and inorganic sulphides salts (MS) as the anode was carried out. The battery system considered for study in this work is of the type Li transition metal/polymer electrolyte/MS. Chitosan based solid polymer electrolyte was used in this fabrication.

3.3.1 Anode preparation

Polyvinylidene fluoride (PVDF), dibutyl phthalate and anode material were mixed in the weight ratio of 16%:10%:84%. The mixture was dissolved in acetone, stirred and heated for one hour at 50 °C. The mixture was then cast to form a film. The film was cut into 2.7 cm x 4.5 cm square. The cut square was then pressed on to copper current collector to make sure a good contact is obtained. Figure 3.9 shows the preparation process of the anode.

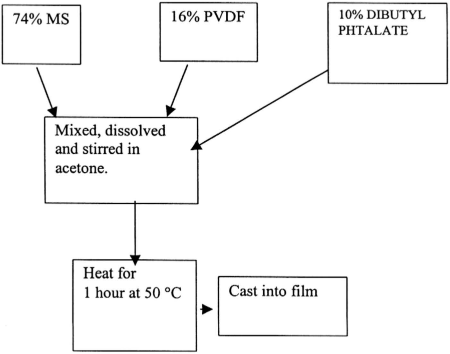

Figure 3.9. Anode preparation process

3.3.2 Cathode preparation

The lithium transition metal was cut into 2.7 x 2.5 cm squares and pressed onto an aluminium current collector.

3.3.3 Cell assemble

The cathode material used for the fabrication of cell is lithium transition metal compound. Both anode and cathode materials were heated at 180 °C for two hours. The electrolyte (chitosan film) was cut into pieces which are bigger than the sizes of the anode and cathode. The electrolyte was then sandwiched between the electrodes. The three layered materials (Lithium transition metal oxide /polymer electrolyte/MS) were then placed in a cell holder. The assembling of the cell took place under argon atmosphere in a glove box, under dry and inert condition.

3.3.4 Charge/discharge characteristics

The charge/discharge characteristics of the cells were studied using the BAS LG50 computer-controlled galvonostatic instrument. By estimating the plateau time from the charge/discharge characteristic, knowing the mass of the cell and the voltage of the cell, parameters like discharge capacity, energy density and power density can be calculated using the following equations;

$$\text{Discharge capacity} = \frac{\text{current, } I \times \text{plateau time, } t_p}{\text{Weight of cell}} \qquad (4)$$

$$\text{Energy density} = \frac{\text{plateau voltage, } V_p \times \text{discharge current, } I}{\text{Weight of cell}} \qquad (5)$$

$$\text{Power density} = \frac{\text{current, } I}{\text{Area of electrode, } A} \qquad (6)$$

Several charging and discharging currents were tried until the appropriate currents were selected. The cell using SnS as the anode was charged at a constant current of 50.0 mA for 2 hours and discharged at 1.0 mA for 7 hours. The cell employing PbS anode material was charged at 50.0 mA for 1 hour and discharged at 1.0 mA for 15 hours. The voltage readings were recorded at a suitable time intervals and a plot of potential against time was obtained.