CHAPTER 3

MATERIALS AND METHODS

In this chapter presented the details of Al-Zn alloy cathode and Cu anode. Characteristic were studied on microstructure, density, hardness, resistance, relative of current-voltage and then electrochemical cells fabrication. The Al-Zn alloy cathode and Cu anode was investigated electrochemical properties and fabricated electrochemical batteries application, the materials and method are as detail below.

MATERIALS

Table 5 The chemical source for preparation

Material name	Chemical formula	Company	Purity
Aluminum	Al	QReC	99.8%
Copper	Cu	QReC	98%
Zinc	Zn	QReC	98%
Sodium Chloride	NaCl	QReC	99.8%

METHODS

1. Al-Zn alloy cathode

1.1 Balance atomic weight of Al and Zn metal powder by Zn (0, 1, 2, 3, 4 and 5 wt %) - doped Al.

1.2 Al and Zn metal powder was mixed by solid state reaction technique.

1.3 The mixed metal powder was pressed to bulks diameter of 2 cm by hotpress (model OTF-1200X-VHP-4) at 670 ^{o}C at 1.0 MPa. Ar gas was flowed at a pressure of 0.08 MPa, as shown in figure 33.

Figure 33 Vacuum heated pressing furnace

1.4 The bulks were cut by Isomet Low Speed Saw (model 11-1280-250) to samples of diameter 2 cm, thickness 0.2 cm and scrub by Grinder-Polisher (model Metaseve 3000), as shown in figure 34

Figure 34 Isomet Low Speed Saw

1.5 The samples were polished (Metaseve 3000) using sandpaper No.100 (30 min) and then No.2000 (30 min), as shown in figure 35.

Figure 35 Grinder-Polisher

2. Cu anode

2.1 Balance of Cu metal powder

2.2 The metal powder was pressed to bulks diameter of 2 cm by hotpress (model OTF-1200X-VHP-4) at 900 ^{o}C at 1.0 MPa. Ar gas was flowed at a pressure of 0.08 MPa..

2.3 The bulks were cut by Isomet Low Speed Saw (model 11-1280-250) to samples of diameter 2 cm, thickness 0.2 cm and scrub by Grinder-Polisher (model Metaseve 3000).

3. X-ray diffraction

The XRD is performed by using an X-ray diffractrometer equipped with CuKα radiation, λ = 0.15406 nm (X-Ray Diffractometer, model XRD-6100) at 40 kV and 30 mA. The scanning mode was θ-2θ with scanning range and rate of $20^{\circ} \leq 2\theta \leq 80^{\circ}$ and 0.02° /sec, respectively.

The X-ray diffraction (XRD) method is a method used to determine the crystal structure, lattice constant and grain size of the thin film. In the XRD method, the X-rays from the generator are sent towards the films and scattered to the detector, with each atom in the crystal lattice acting as a source of scattering. By considering how the crystal lattice reflects from parallel reflecting planes, as shown in Figure 36, the maximum intensity of the reflected beam of X-ray can be obtained when the path difference between two reflected waves of two different planes is an integral multiple of wavelengths.

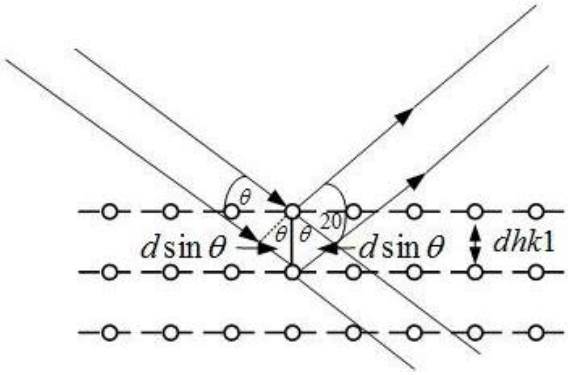

Figure 36 The parallel reflecting planes of crystal lattice, path difference of two reflected wave (red lines)

The condition can be explained using Bragg's law and is given by the relation,

$$2d_{hkl}\sin\theta = n\lambda \tag{3.1}$$

where d_{hkl} is inter planar spacing of the reflection planes, λ is the wavelength of the CuK$_\alpha$ radiation, θ is the Bragg's angle and n is an order of diffraction. The lattice constant of the cubic zinc blend structure can be calculated from the following relation.

$$\frac{1}{d_{hkl}} = \sqrt{\frac{h^2+k^2+l^2}{a^2}} \tag{3.2}$$

where d_{hkl} is the inter planar spacing of the reflection planes, h, k and l are Miller's indices and a is the lattice constant.

The crystallite size (D) can be estimated from the full width at half maximum (FWHM) of the XRD peak using the Debye-Scherer relation,

$$D = \frac{k\lambda}{B_s\cos\theta} \tag{3.3}$$

where k = 0.9 is a constant, λ is the wavelength of the CuK$_\alpha$ radiation, B_s is the full width at half maximum contribution from the grain size effect and

θ is the angular position of the peak. The corrected peak width (B_s) of FWHM of the structure can be calculated from the formula $B_s^2 = B_o^2 - B_i^2$ where B_o is the observed data and B_i is the FWHM of the instrument.

Measure crystal structure of Al-Zn alloy cathode and Cu anode by X-Ray Diffractometer (X-Ray Diffractometer, model XRD-6100)

3.1 Crystal structure of Cu

3.2 Crystal structure of Al

3.3 Crystal structure of alloy Al-Zn (1-5 by wt%)

Figure 37 X-Ray Diffractometer

4. Measure resistance of Al-Zn alloy cathode and Cu anode by Picotest (Picotest, model M3500A, 6 ½ digit multimeter)

Figure 38 Picotest multimeter

4. Measure hardness of Al-Zn alloy cathode and Cu anode by Micro Hardness Tester (model HMV-2T)

The hardness micro Vickers testing method using pyramid indents with a square base and an angle of 136 degrees between opposite faces. The indentation subjected to a test force of 1 N. The full load is normally applied about 10 seconds. The indentation in the surface of the material after removal of the load are measured using for calculation. The Vickers hardness values obtained by dividing the load by the square mm area of indentation, as shown in Figure 39.

$$HV = 0.1891\frac{F}{d^2} \tag{3.4}$$

where F = Load in N

d = Arithmetic mean of the two diagonals, $d1$ and $d2$ in mm

HV = Vickers hardness

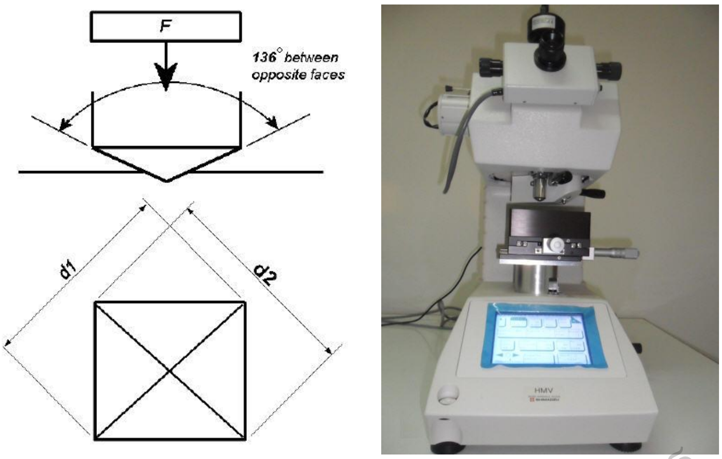

Figure 39 Hardness Tester

5. Measure density of Al-Zn alloy cathode and Cu anode by Density Kit (model MS204)

The density application is based on the formulae below.

Formulae for determining the density of solids with compensation for air density

$$\rho = \frac{A}{A-B}(\rho_0 - \rho_L + \rho_L \qquad (3.5)$$

$$V = \alpha \frac{A-B}{\rho_0 - \rho_L} \qquad (3.6)$$

where ρ = Density of the sample

A = Weight of the sample in air

B = Weight of the sample in the auxiliary liquid

V = Volume of the sample

ρ_0 = Density of the auxiliary liquid

ρ_L = Density of air (0.0012 g/cm^3

α = Weight correction facter (0.99985), to take the atmospheric buoyancy of the adjustment weight into account

Formulae for determining the density of liquids with compensation for air density

$$\rho = \alpha \frac{P}{V} + \rho_L \tag{3.7}$$

where ρ = Density of the liquid

P = Weight of the displaced liquid

V = Volume of the sinker

ρ_L = Density of air (0.0012 g/cm^3

α = Weight correction facter (0.99985), to take the atmospheric buoyancy of the adjustment weight into account

Figure 40 Density Kit

6. Microstructure of Al-Zn alloy cathode and Cu anode by Scanning Electron Microscopy (model SU8230).

Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) was used to observe microstructures of the samples. The SEM observations were performed on a Hitachi High Technologies, S-2600H. The schematic diagram of the SEM equipment is shown in Figure 41.

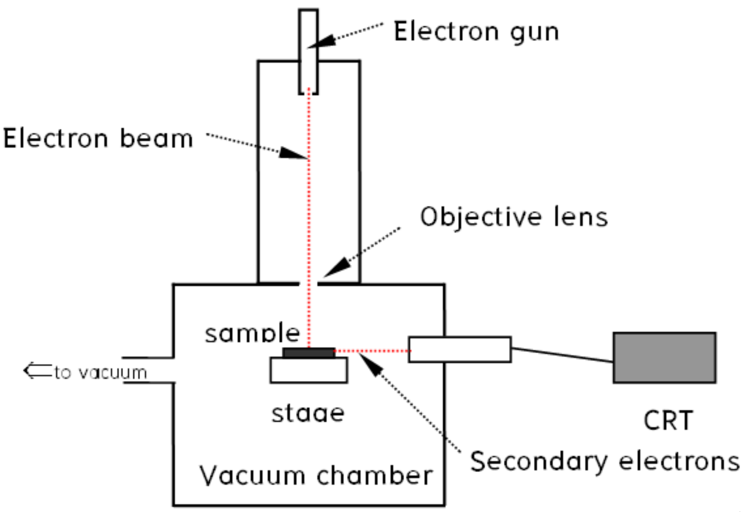

Figure 41 Diagram of the scanning electron microscope technique

Figure 42 Scanning Electron Microscopy

The microstructure of before and after dip in NaCl (2 mol dm^{-3}) + DI water (100 ml) for 40 min and then annealing at 60 °C for 16 h were observed by scanning electron microscope (SEM; SU8230, 5000X-10000X).

Elemental Composition

Energy Dispersive X-ray spectroscopy (EDX) is used to analyze the elemental compounds and distribution of thin film. In this method, the specimen is excited by high-energy electrons and the emitted X-ray energies correspond to the characteristics of the elements within the specimen. The emitted X-rays can be used to identify elements and the relative composition can be estimated. The elemental composition of thin films can be obtained using an EDX detector which is attached to a TEM system (Tecnai G^2).

7. **Electrochemical cells fabrication**

Cathode Al-Zn alloy and anode Cu was balanced weight before dipping into NaCl+DI .The NaCl solution intensities of 2 mol dm^{-3} input bigger size 250 cm^3 (changing solution everytime when changed cathode and anode), and then dipping anode Cu and cathode Al in NaCl solution. The distance was between anode Cu and cathode Al-Zn (1-5 wt%) for 2 cm.

7.1 Measurement electrical chemistry properties

The electrical chemistry properties of samples were measured by cyclic voltammetry technique were connected Potentiostat-446 by anode Cu connected working electrode (Cu) and Al, Al-Zn (1-5 wt%) connected reference electrode and counter electrode (Al, Al-Zn) (1-5 wt%) to show computer monitor. The program in Echem v2.2.2 was run by cyclic voltammetry technique using initial of –300 mV, final of –300 mV, upper of 300 mV, lower –300 mV, rate of 50 mV s^{-1}, Number of Cycle 100 for 24 s and get data for plot graph voltage with the applied with current.

Figure 43 Potentiostat 466

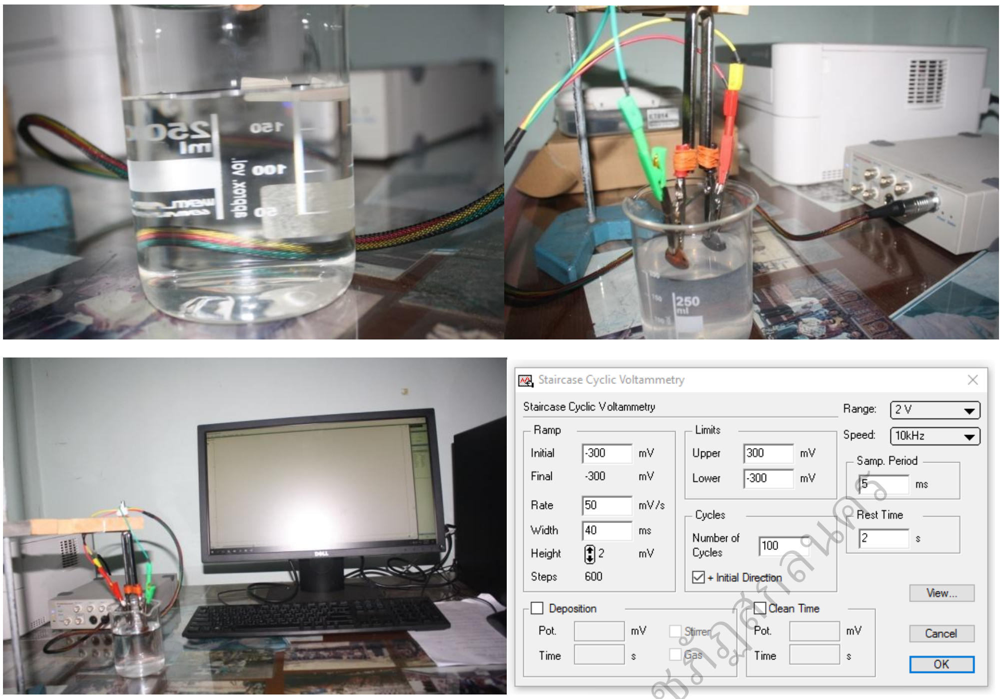

Figure 44 Cyclic voltammetry technique

7.2 Balance weight of pure Cu, Al and alloy of Al-Zn (1-5 wt%) after dipping in NaCl+ DI water solution (cyclic voltammetry technique).

8. Discharge of Cu, Al and alloy of Al-Zn (1-5 wt%)

The discharge of electrochemical cell were measured voltage and current by Picotest, model M3500A, 6 ½ digit multimeter, using load 10 Ω for 40 min, and interface two computer monitors with program setup/run logging worksheet by M35XX Excel Add-In program to evaluate the electrical power for testing current and voltage respectively.

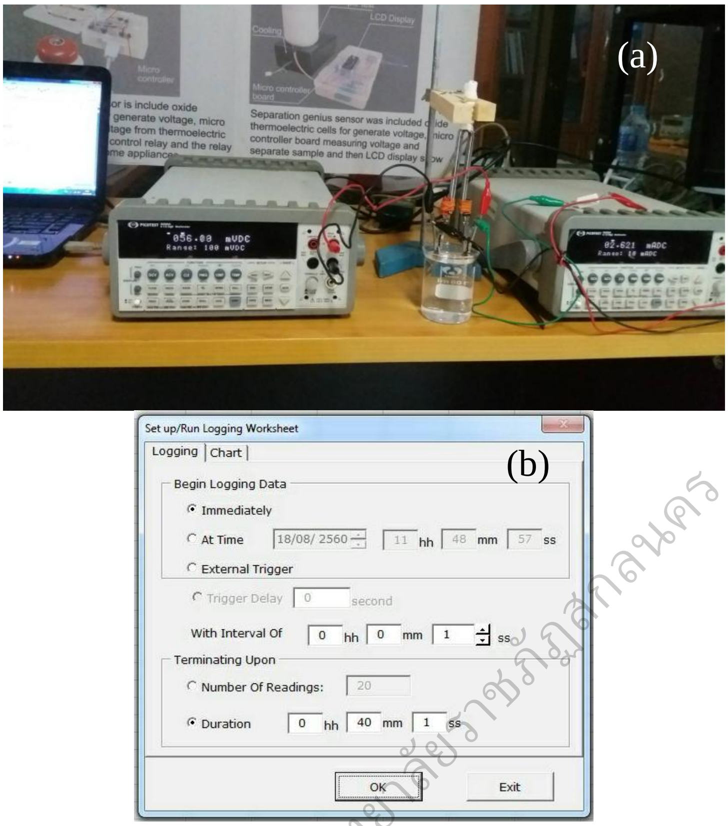

Figure 45 Discharging measurement (a) measured voltage and current of Cu anode/Al cathode dip in NaCl+DI water for 40 min by Picotest digital multimeter (b) program setup/run logging worksheet by M35XX Excel Add-In program to evaluate the electrical power

9. Electrochemical Batteries Application

9.1 Electrochemical batteries fabrication module composed of 4 cells for Al-Zn alloy cathode best condition and Cu anode.

9.2 NaCl 2 mol dm^{-3} was prepared for electrolyte by balance NaCl 11.68 g and deionized water 100 cm^3.

9.3 The electrochemical battery was fabricated by 4 cells in series and applied to load using LED lamp.