# CHAPTER 3 METHODOLOGY

There are three main steps that were to executed to accomplish this work which are catalyst preparation, catalyst characterization and electrooxidation activity test of the prepared catalysts in two types of alcohol (glycerol and ethylene glycol). The steps of each catalyst preparation were started with carbon heat treatment and metal loading on carbon by PVA protected and citrate protected gold sol preparation. After that the catalysts were characterized to determine the metal particle size. Then the catalysts were tested for activity by performing electrooxidation of the alcohol. This chapter presents the detail of each step.

## 3.1 Catalyst Preparation

First, the effect of heat treatment on carbon support was studied by comparing the 20 wt% of Au on untreated carbon with that on heat treated one. Secondly, a series of Au/C catalysts were prepared by varying Au loading at 20%, 30% and 40% wt for both protected gold sol preparation methods. The steps of each catalyst preparation were described below.

### 3.1.1 Pretreatment of Carbon support

Approximately 1 g of Vulcan XC-72R carbon black was transferred into ½″ stainless steel tube which had been packed with a small amount of quartz wool at the bottom. Then $N_2$ gas was flowed through the tube at a flow rate of 30 ml/min. The reactor temperature was set at 600°C and hold at this temperature for 30 min. After the reactor was cooled down to room temperature, the heat treated Vulcan XC-72R carbon black was collected.

### 3.1.2 PVA Protection Method

The solution of 110 µg/ml of $HAuCl_4$ and 2% wt PVA with respect to gold weight were prepared [9]. The 0.1 M of $NaBH_4$ solution was dropped dropwise very slowly under vigorous stirring. After 15 minutes, an ethanol dispersion of the heat treated or untreated Vulcan XC-72R carbon black was added with the required proportion (60%, 70% and 80% wt) and kept stirring for 3 hours. Then the mixture was filtered. The catalyst was washed thoroughly with deionized water for several times and then washed with ethanol. Lastly it was dried in vacuum oven at 70 °C for 30 minutes to give Au/C catalyst by PVA protection method.

### 3.1.3 Citrate Protection Method

An aqueous $HAuCl_4$ solution of 55 µg/ml cooled to 0 °C was added with an aqueous tripotassium citrate of 11 mg/ml. After 5 minutes, a mixture of triprotassium citrate (44 mg) and $NaBH_4$ (0.0189 mg) in $H_2O$ (4 ml) was slowly dropped to the solution under vigorous stirring[1]. Then the mixture was kept stirring for 15 minutes. The heat treated or untreated Vulcan XC-72R carbon black in ethanol was added into the mixture and stirred for 3 hours. Next the mixture was filtered, washed with deionized water for several times and then washed with ethanol. Finally, it was dried in vacuum oven at 70 °C for 30 minutes to give Au/C catalyst by citrated protection method.

## 3.2 Catalyst Characterization

After Au/C catalysts were obtained, they were checked by Atomic Absorption Spectroscopy (AAS) and Transmission Electron Microscopy (TEM).

### 3.2.1 Atomic Absorption Spectroscopy (AAS)

AAS was used to measure the amount of Au that was left in the filtrate (mg/l) after immobilization step. This information was then utilized to determine the amount of Au deposited on carbon support. AAS was performed at the Department of Science Service (DSS), Ministry of Science and Technology.

After the concentration of Au in the filtrate from AAS analysis ($AAS_{results}$ ;mg/l) was obtain, the amount of Au remained in the filtrate ($Au_{filtrate}$ ;mg) was determined by using equation of 3.1.

$$Au_{filtrate} = AAS_{result} \times (\text{Total filtrate volume ; ml}) \quad (3.1)$$

After $Au_{filtrate}$ was known, the amount of Au deposited on carbon support ($Au_{support}$ ;mg) was estimated by using equation 3.2. In equation 3.2, $Au_{total}$ is the total amount of Au used in the catalyst preparation (mg).

$$Au_{total} = Au_{support} + Au_{filtrate} \quad (3.2)$$

$Au_{support}$ was then used to calculate the percentage of Au deposited on carbon support by using equation 3.3. In equation 3.3, S is the weight of carbon support (mg).

$$\%Au_{deposited} = \frac{Au_{support}}{(Au_{support} + S)} \times 100 \quad (3.3)$$

### 3.2.2 Transmission electron microscopy (TEM)

TEM is a technique to determine particle size and size distribution of Au on carbon support. Images of TEM technique were captured at the National Metal and Materials Technology Center (MTEC). The average size and particle size distribution were obtained by counting onto the micrographs at least 500 particles. The source of electron beam was used at 200KeV and the size of Au was measured from TEM image at magnification of 100,000x.

## 3.3 Electrooxidation experiments

The catalyst activity was measured by performing electrooxidation of two types of alcohols, glycerol and ethylene glycol in basic solution. Cyclic Voltammetry (CV) and Chronoamperometry (CA) techniques have been used in this investigation. Since we aimed to investigate the suitable catalyst for electrooxidation of high molecular wight alcohols, glycerol and ethylene glycol were used to test the catalytic activity.

### 3.3.1 Cyclic Voltammetry (CV*)*

This technique was used to determine the electrochemical surface area (ESA) and catalyst activity of Au/C catalyst in alcohol oxidation. The procedure of alcohol oxidation was divided into two main sections, glycerol and ethylene glycol oxidation. However, for both alcohols oxidation, the first step was the ESA determination as described below.

#### 3.3.1.1 Electrochemical Surface Area (ESA)

Electrolyte was prepared by 40 ml of 0.1 M KOH which was saturated with nitrogen gas for 30 minutes to remove dissolved oxygen. Then working electrodes were prepared by ultrasonically dispersing the synthesized catalyst in a solution of 5 wt% Nafion ionomer and isopropanol for 1 hour. Then a 2.85 µL of the suspension was dropped on a 6 mm glassy carbon for 4 times. A gold gauze and a mercury/mercury oxide were used as counter and reference electrodes, respectively. All three electrodes were immerged into the electrolyte solution. The potential was scanned between -0.8 V and 0.8 V at a scan rate of 20 mV/sec. The temperature of solution was controlled at 25 °C. The reduction peak of cyclic votammogram was used to determine the electrochemical surface area. Prior to the electrochemical measurement, the pretreatment of the Au/C electrodes was performed by repeating the potential scan in the range of -0.8 to 0.8 V VS Hg/HgO electrode until a reproducible constant CV characteristic was obtained.

#### 3.3.1.2 Glycerol oxidation

The experimental work was performed with Au/C catalysts as working electrodes by loading the catalyst as mentioned above. The 40 ml of 0.1 M glycerol and 0.1M KOH solution was used as the electrolyte. This solution was purged with nitrogen gas for 30 minutes. The mercury/mercury oxide was used as the reference electrode while gold gauze was used as the counter electrode. The potential was scanned between -0.8 V and 0.8 V with a scan rate of 20 mV/sec. The working electrode was then electrochemically pretreated with the same manner as mentioned above.

#### 3.3.1.2 Ethylene glycol oxidation

This step was the same as the step of glycerol oxidation but the electrolyte was replaced with the mixture of 0.1 M ethylene glycol and 0.1M KOH.

### 3.3.2 Chronoamperometry (CA)

Chronoamperometry technique was used to investigate the stability of the catalysts in different type of alcohol that was indicated by a decaying rate.

#### 3.3.2.1 Chronoamperometry in glycerol

The working, reference and counter electrodes used in this experiment were the same as those in the CV technique. Chronoamperometric experiment was performed by holding the potential at either 0.2 V or 0.4 V for 45 minutes in the mixed solution of 0.1 M glycerol and 0.1M KOH.

#### 3.3.2.2 Chronoamperometry in ethylene glycol

The procedure of chronoamperometry in ethylene glycol was the same as that in glycerol but the electrolyte was used was 0.1 M ethylene glycol and 0.1M KOH solutions instead.