CHAPTER 1

INTRODUCTION

Nowadays, environmental pollutionbecomes amain problem in the world. The pollutantsuch as CO_2, CO, NO_x and SO_2aremain sources ofgreenhouse effect and Global warming[1-3]. The key factorispopulation growth because of human usesfossil resources (such as natural gas,oil and coal) for development.These resources generate more carbon dioxide to creategreenhouse effect[4].Therefore, the new environmental friendly energy sourcessuch as solar cell, wind energy, geothermal energy, and hydrogenenergy[5] are alternatively research. In this research hydrogen technology was studied, called fuel cell.Fuel cells are electrochemical devices that convert chemical energy of fuel into electrical energy. It can run continuously as long as fuel is loaded to the cell.

1.1 History and type of fuel cell

The first fuel cell was invented by William R. Groove in 1839. It was called a “gaseous voltaic battery” which shown in Figure 1.1. This cellused zinc and platinum as electrodes and sulfuric acid as electrolyte. Oxygen and hydrogen gas were filled in the tubethat submerge in dilute sulfuric acid[6,7]. In 1959,Francis Thomas Bacon,British engineer, had developed fuel cellsusing potassium hydroxide as electrolytes. Heand his coworkers demonstrated a practical five-kilowatt system capable of powering a welding machine(shown in Figure 1.2)[8].At the same year,Harry Ihrig hadbuilt a 15 kW fuel cell tractor for Allis-Chalmers(shown in Figure 1.3)[9]. This system used potassium hydroxide as the electrolyte and hydrogen and oxygen as the reactants. In the 1962, Gemini space mission used ion-exchange membranefuel cell to generate electrical power for longer mission.In 1965 for Apollo space mission, an alkaline fuel cell was used to supply electricity and water for crew.Nowadays, the fuel cells areused in more applicationsuch as power plant, car, motorcycle, notebooks, cell phones, and PDAs[10].

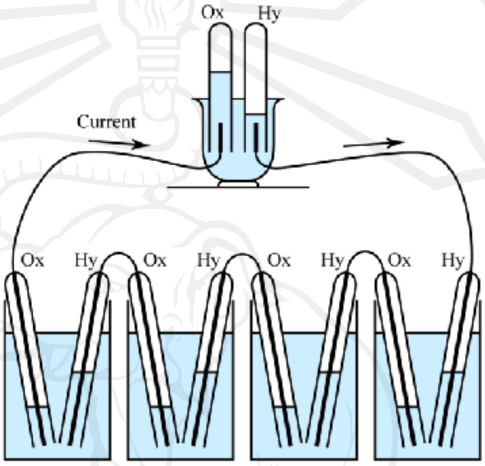


Figure 1.1Gaseous voltaic battery [11]

Figure 1.2 Fuel cell was made by Francis Thomas Bacon[12]

Figure 1.3 Fuel cell tractors for Allis-Chalmers[9]

The types of fuel cell are classified by types of electrolyte into 5 typeswhich arealkaline fuel cell (AFC), phosphoric-acid fuel cell (PAFC), solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), and proton exchange membrane fuel cell (PEMFC). For each fuel cell type, different reaction occurs in anode, cathode,and electrolyte as well as the difference of operating temperature (Table 1.1)[13-15].This research focuses on PEMFC because of its interesting applications which the operating temperature in cell is quite low.

Table 1.1.Type of electrochemical reaction and cell electrolyte in fuel cell

Fuel cell	Anode Reaction	Cathode Reaction	Electrolyte	Operating temperature
AFC	$H_2+2OH^- \rightarrow 2H_2O+2e^-$	$1/2O_2+H_2O+2e^- \rightarrow 2OH^-$	KOH	90-100 ˚C
PAFC	$H_2 \rightarrow 2H^++2e^-$	$1/2O_2+2H^++2e^- \rightarrow H_2O$	H_3PO_4	150-200 ˚C
SOFC	$H_2+O^{2-} \rightarrow H_2O+2e^-$	$1/2O_2+2e^- \rightarrow O^{2-}$	Yttria stabilized Zirconia	700-1000 ˚C
MCFC	$H_2+CO_3^{2-} \rightarrow H_2O+CO_2+2e^-$	$1/2O_2+CO_2+2e^- \rightarrow CO_3^{2-}$	K_2CO_3	600-700 ˚C
PEMFC	$H_2 \rightarrow 2H^++2e^-$	$1/2O_2+2H^++2e^- \rightarrow H_2O$	Nafion polymer	50-100 ˚C

1.2 Proton exchange membrane fuel cell (PEMFC)

As mentioned in the name of PEMFC, membrane is used in this fuel cell type as the electrolyte to transfer hydrogen ion from anode side to cathode side.Hydrogen and oxygen gases are used as fuel and oxidant from this fuel cell.The schematic showing how PEMFC works is shown in Figure 1.4. Among 5 types of fuel cell, PEMFC is very interesting system because of its low temperature operation (below 100°C),produces more than 600 mA/cm^2 at 0.7 V[16], and generates power for several applications such as for personal computer, motorcycles and cars. In PEMFC system, 20% weight platinum supported on carbon catalyst is used as anode and cathode materials. At anode, platinum will catalyze the hydrogen gas dissociation into protons and electrons. After that, protons travel through the polymer electrolyte membrane from anode to cathode which electrons travel along an external load circuit to the cathode side. The basic fuel cell reactions in a PEMFC at 25 °C are shown in Eq 1.1-1.3[17].

Anode Reaction	$H_2 \rightarrow 2H^+ + 2e^-$	$E^o = 0.00$ V	(1.1)
CathodeReaction	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$E^o = 1.27$ V	(1.2)
Overall Reaction	$2H_2 + O_2 \rightarrow 2H_2O$ + heat	$E^o = 1.27$ V	(1.3)

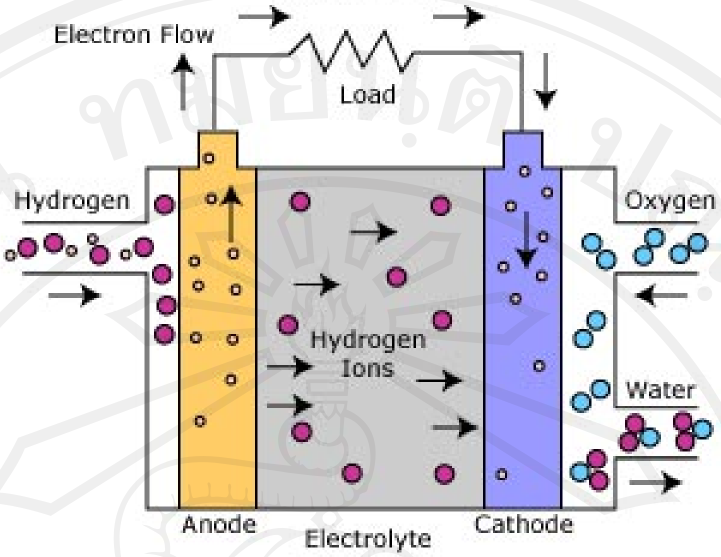


Figure 1.4Schematic function of PEMFC[18]

1.3 Componentsof PEMFC

The PEMFCsingle cell iscomposed of bipolar plates, gaskets, gas diffusion layer, membrane and catalyst(shown in Figure 1.5). Hydrogen and oxygen gases pass through bipolar plates from both sides and diffuse through a porous gas diffusion layer (GDL) toreactwith the catalyst.The protons which are separated from hydrogen gas with catalysts diffuse through membrane from anode to cathode side. The membrane is sandwiched by catalyst and GDL which calledmembrane and electrode assembly (MEA).

1.3.1 Bipolar plate

Bipolar plates from PEMFC areconnectedwith two side (cathode side and anode side) of MEA.They carry hydrogen gas from anode side and oxygen gas from cathode side as well as drain water out of cell.Moreover, the plate is used to protect acid from hydrogen gasat the anode side. At the cathode side , the highly oxidizing plate is used to protect air or oxygen exposure. The bipolar platesporperties are protect the gas leakage, non deformability, resistance less than 20 mΩcm^2 and high thermal conductivity.In general, the materials used for fuel cell bipolar plate are for example metallic(aluminum, steel, titanium or nickel) or graphite(shown in Figure 1.6). The metallic bipolar plate has advantages such as very thin thickness producibility <1mm, high strength and capability for mass manufacturing. However these meterials have disadvantages as high contact resistance and low chemical stabiliy. In this study,graphite was used as bipolar plate because of high conductivity, chemical stability, high temperatures endurance, and low contact resistance [19,20].

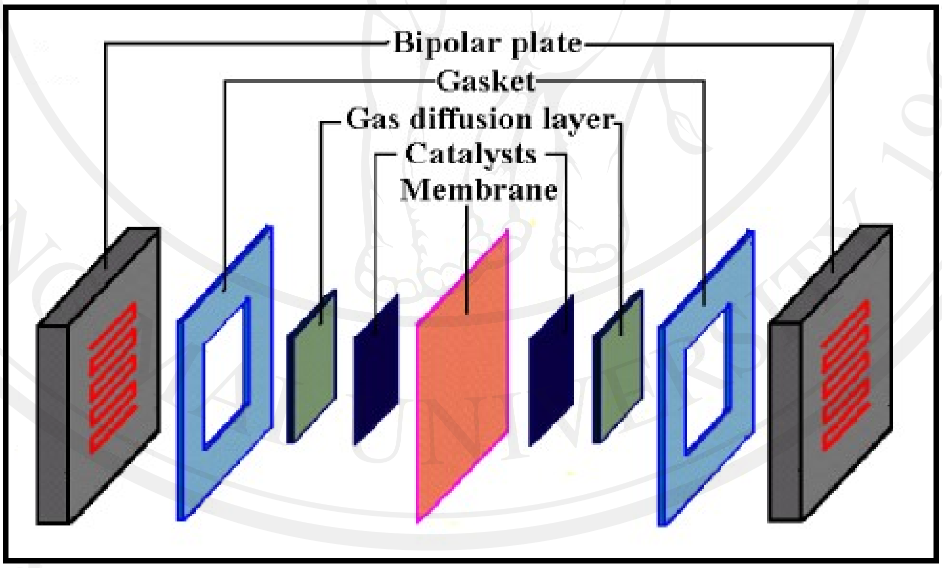


Figure 1.5Components of PEMFC[21]

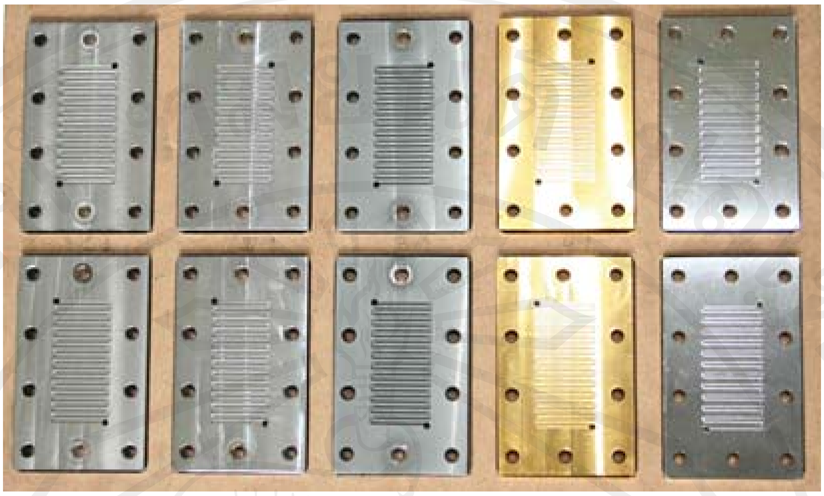


Figure 1.6Bipolar platesfor each material[22]

1.3.2 Membrane

The membrane in PEMFC which consists of solid polymer electrolyte is placed between two electrodes of fuel cell.The hydronium ions from reactioncan move from anode to cathode side by diffusing though membrane. The membrane has high ionic, low electronic conductivity and low permeability of reactant gases[23].The membrane consists of a polymer backbone and ionic group. For new membrane material,Nafion whichcontains a polymerized tetrafluorethylene as backbone and sulfonic acid groups as side-chains is used. The sulfonic acid groups can move the hydronium ion from two electrolyte side because electric change between hydronium ion in sulfonic groups. The structureof nafion and nafion membrane are shown in Figure 1.7. In this study a Nafion NRE 212 membrane by Ion Power was used.

1.3.3 Gas Diffusion Layer

The gas diffusion layer (GDL) is a distributor of reactant gas to the catalyst from both side and a liquid water evacuator on the cathode side. The thermally conductive GDL collects the produced current and provide mechanical support to catalyst. Generally, GDL is made from thin porous layers of carbon fibers.The thickness for this materialis about 0.17 to 0.4 mm, density is between 0.21-0.73 g/cm^3, and porosity is between 70%-80%[20,24]. However,this GDL hasa problem as accumulate water whichblock gas flow.L. R. Jodan et. al[25] and E. Passalacquaet. al[26] hadfixed this problem by makingmicro-porous layer. It was made by applying carbon black powder and Nafion solution on top of the GDL to prevent an accumulationwater[23]. In this study GDL 34 AAby Ion Power was used (shown in Figure 1.8).

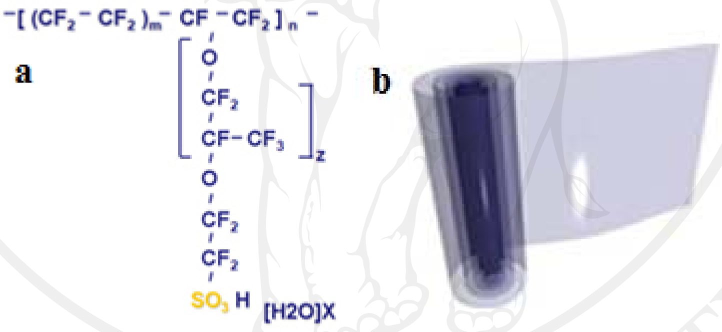


Figure 1.7 Structure of Nafion (a) [27]and nafion membrane (b) [28]

Figure 1.8The GDL 34 AA [28]

1.3.4 Catalysts

The catalyst is importantfor PEMFC because it helpsdissociate hydrogen gas into protons and electrons and helpsprotons and electrons to react with oxygengas to from water.Good catalystsfor high performance PEMFC should provide electrical conductivity, good interplay with the ionomer, accessibility for gas reactant,andreaction on both anode and cathode sides have to occur as close as possible to the thermodynamic potential[23]. The most common catalyst for the PEMFC is platinum metal because the platinum shows all the required characteristics as highly active and stable. The high active catalyst has high surfacearea to react with precusor.In order to increase the active surface area of catalyst, particle size needs to be reduced. In another way, the particles need to well disperse on an inert material such as carbon (shown in Figure 1.9). Vulcan XC-72, is the most commoncarbon used as supporter. It shows good electrical and thermal conductivity[24,29]. The ratio of platinum on carbon is about 10%-60% wt. Whereas, the E-TEK showsthat paricle size will increase and specific surface area will decrease when increase %wt of platinum. For catalyst activity, Ticianelli et. al.[30] compared activity between 10%, 20% and 40% wt Pt/C. The current densities at 900 mV for 10%, 20% and 40% wt Pt/C were 0.01, 0.03 and 0.03 A/mg$_{Pt}$, respectively. As long as the percent wight of platinum was increase, cell activity was maximized as using 20 %wt platinum. Thus, this research will focus on 20 %wt platinum usage.

1.4 Cathode Catalysts

The cathode catalyst for PEMFC is20% weight platinum catalyst.The cathode reactionknown as oxygen reduction reaction (ORR) has two possible pathways as shown in equation (1.4)[31]. The first pathway called 4e$^-$ reduction, the oxygen gas can be directly reduced to water (rate constant = k_1 and E^0 = +1.23V). The second pathway (2e$^-$ reduction), the oxygen gas is reduced with two electrons to form hydrogen peroxide (rate constant = k_2 and E^0 = +0.70 V) which is reduced again with two electrons and then form water molecule (rate constant = k_3 and E^0 = +1.77 V). Hydrogen peroxide which is formed in this pathway will destroy electrode surface which then affect the all activity.Therefore, the oxygen reduction at cathode requires 4e$^-$ for reduction to prevent the formation of hydrogen peroxide. However, pure platinum catalysts has been reported that it activatestwo-electronsreaction because rate constant $k_1<k_2$ and E^0 of hydrogen peroxide to form water reaction is higher than E^0 of oxygen gas to form water reaction. By this reason, pure platinum is not suitable catalyst for oxygen reduction reaction in cathode. Moreover, there are disadvantages for using pure platinum as expensive cost, over potential occurs at cathode (need 10 times more amounts of catalysts to activate the oxygen reduction reaction than anode)and platinum agglomeration after long time PEMFC operation[32].

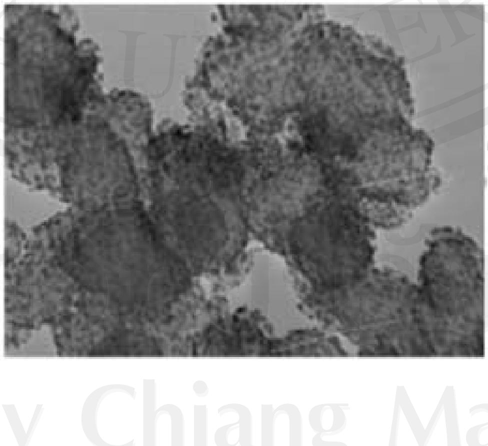
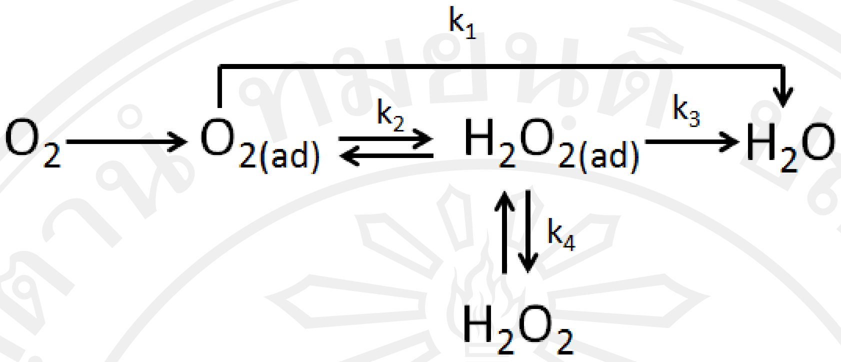


Figure 1.9 Catalyst 20 wt.% platinum on carbon Vulcan XC-72 [33]



(1.4)[31]

Presently, thenewcathode catalysts such as platinum alloy and non-platinum has replaced thepure platinum catalyst. This research focuses on platinum alloy because the reaction does not undergo by $2e^-$ pathway. The catalysts do not agglomerate after long timeoperation and use low platinum [34,35].The platinumalloy is composed of two or more elementsand platinum [36]. The elements which generally form platinum alloy arefirst row transition metals becausethey provide good electrostatic force and low cost.The reaction of platinum alloy at cathode was shown in equation 1.5 and 1.6[35]. The first step, platinum alloy, oxygen gases and hydrogen ions are reduced with two electrons to form platinum-metal-oxygen-hydroxide. The next step, platinum-metal-oxygen-hydroxide and hydrogen ion are reduced again with electrons to form platinum-metal-oxygen and water as the products. This reaction prevent cathode surface from hydrogen-peroxide destruction.

$$PtM + O_2 + e^- \rightarrow PtM\text{-}O\text{-}O^- + H^+ + e^- \rightarrow PtM\text{-}O\text{-}OH^- \qquad (1.5)$$

$$PtM\text{-}O\text{-}OH^- + H^+ + e^- \rightarrow PtM\text{-}O^- + H_2O \qquad (1.6)$$

The platinum alloy catalysts are used in PEMFC cathode in the form ofplatinum binary and platinum ternary catalysts. The platinum binary catalysts such as PtCo[37], PtNi[38], and PtCu[39], were prepared by various methods such as impregnation [40], polyol[21], microemulsion[42] and electrodeposition[43]. Weo et al. [37] preparedPtCoon GDL by pulse electrodeposition. This research used 40mM K_2PtCl_4 and various concentrationsof $CoCl_2$ (20, 40, 60, and 120mM)dissolved in 0.5M NaCl. The parameters ofelectrodepositionwerecurrent density of 300 mA/cm^2, an on/off time of 10/100 milliseconds, andcharge density of 1 C cm^{-2}. Aftercatalyst was heated at 250 °C in H_2 atmosphere for 30 minutes,the thickness ofPtCo catalysts on carbon surface electrode was 5.8 μm. The PtCo catalyst with 76:24 (3:1) wasobservedas the highest performance among the studied compositions. Hsieh et al.[44] preparedPtCo on carbon nanotube by microwave method. They used $PtCl_4$ and $Co(NO_3)_2.6H_2O$ as precursors, ethylene glycol as solvent and carbon nanotube as carbon supported material.The weight ratio of platinum to cobaltwas 36:64.The solvent was adjusted pH to 11.7.The solution was heat for 6 minutes. under microwave power of 720 W.The results showed that particle size ofPtCo catalyst was 3.1-3.2 nm and PtCowell dispersed on carbon nanotube. The activity was stable for several cycles (1000 cycles).FromTseng et al.,[39] the PtCu catalysts were prepared by polyol method. This research used H_2PtCl_6 andtwo different copper precursors ($CuSO_4$ and $CuCl_2.2H_2O$).Metal precursor were mixed to obtain3:1 Pt:Cu as for atomic ratio. The metal precursors and carbon were added to pH 11 adjusted ethylene glycol. Temperaturewas increased to 130 ˚C for 3 hours. Finally catalysts were heat treated at 300, 600 and 900 ˚C for 1 h in a flowing gas mixture of 90% Ar–10% $H_2$and cooled to room temperature under gas flowing condition. The result showed that the catalyst using $CuCl_2 \cdot 2H_2O$ as the precursor had largerparticles size thanusing $CuSO_4$. Additionally using high reduction temperatures causedthe catalytic particles to agglomerate and therefore decreased catalytic activity.Xiong et al. [45] prepared Pt–M (M = Fe, Co, Ni and Cu)alloy supported carbon catalysts by reducinga mixture of chloroplatinic acid and the respective metal saltsolution with sodium formate. Thereaction was carried out at 70 °C. For this condition, particle size of 3.6- 4.5 nmwas obtained. Mild heat treatment at 200 °C in a flowing gas mixture of 10% H_2 and 90% Arwas denoted to improve the catalytic activity according to a cleaning of the surface oxides. While annealing at elevated temperature(900 °C) reduced the activity of the catalysts by an increase in particle size.

For platinum-based ternary catalysts preparation, ultrasonic process followed by heatingin hydrogen and nitrogen atmospheres is widely used [31,35,46,47].This method is widely used to synthesize ternary catalyst.Neergat et al.[31]prepared platinum-based binary and ternary alloy by ultrasonic Pt/C in distilled water and adjusted pH to 8.0 by ammonium hydroxide. The required amount of salt solutions (cobalt(II) nitrate or nickel(II) nitrate or chromium (II) nitrate) were added and adjusted pH to 5.5 by hydrochloric acid. Catalysts were dried and reduced by nitrogen gas at 900 °C. Seoet al.[46] synthesized platinum-based ternary alloy by ultrasonic platinum on carbon (Pt/C). The atomic ratio of Pt-M_1-M_2alloy (M_1, M_2= cobalt, cupper, chromium and nickel) were varied as 2:1:1, 4:1:1, 6:1:1 and 8:1:1.Then,hydrogen gas and nitrogen gas atmospheres at 900 °C were performed as reduction process. Neergatand Seo researchers confirmed to the ternary alloy catalysts show higher electro-catalytic activity towards oxygen reduction compared to Pt/C catalyst. Among the prepared Pt-M_1-M_2catalysts,platinum-cobalt-chromium supported carbon (PtCoCr/C) catalyst shows highest performance. The platinum-vanadium-iron supported carbon (PtVFe/C) catalyst from Luo et al.[47] was prepared by dissolvingmetal precursors (platinum(II) acetylacetonate, vanadyl(acetylacetonate),and Iron pentacarbonyl) in water and adding carbon black to the solution. Dried catalysts were reduced by hydrogen gas and nitrogen gas atmospheres at 350-650 °C. The relative electro-catalytic activity displayed in the order of PtVFe/C>PtFe>Pt/C.Roh et al.[48] reported platinum-copper-iron catalyst on carbon support (PtCuFe/C) that was prepared by ultrasonic 10wt% Pt/C in deionized water. The appropriate amount of iron(II) chloride and copper(II) chloride were added. This solution was adjusted pH to 8.0 by ammonium hydroxide. The sample was filtered and dried, after that, reduced with hydrogen gas and nitrogen gas atmospheres at 900 °C. For oxygen reduction in fuel cell operation, alloy had shown higher catalytic activity than pure platinum catalyst.

From the literatures, platinum-base ternary catalysts are higher cathode electrochemical activity than other catalysts and also provide long life time. The platinum-base ternary has higher electro-activity than platinum-binary because it has high kinetic parameters such as Tafel slope and exchange current density values[46]. Moreover, platinum-ternary catalysts can be used for long time because no particles size changes after long time operation[47].

1.5 Methods

A good catalyst for cathode fuel cell should have nano-size particleswith a good dispersion on carbon supporter. In order to obtain nano-sized product, many processes such as heat treatment in hydrogen gas and nitrogen gas atmosphere[47,48], microwave[49,50], reflux [51],and $NaBH_4$reduction methods[52,53]have been reported fornano-catalystssynthesis. Previously,platinum-ternary catalyst can beprepared only by heat treatment in hydrogen gas and nitrogen gas atmosphere. However, this method requires high energy and complicated procedure. To avoid these drawbacks, this research use simple methods such as microwave, reflux, and $NaBH_4$reduction method to synthesize the catalysts.

For microwavesynthesis, microwave irradiation is used to initiate the reaction. The electromagnetic energy from microwave irradiationwith low frequency about 300-300,000 MHz.[54] only makes molecular rotation without any effect on molecular structure.This research used the benefit from microwave technique to heat the solvent. The solvent heating from microwavetechnique is difference from convention method(shown in Figure 1.10).The conventional heating (Figure 1.10a), chemical synthesis,is aconductive heating with an external heat source. Heat passes through the wall of vessel to the solvent and reactants. This method slowly transfers energy into the system because it depends on the thermal conductivity ofvesselmaterials. Therefore, this process can retard the reaction[55].Differently, microwave technique was couple directly with the solvent moleculesleading to a rapid rise of temperature(Figure 1.10b). Therefore, microwave technique is used in orderto fasten the reaction. This process does not dependon the thermal conductivity of the vessel materials. It causes either dipole rotation or ionic conduction, the two fundamental mechanisms for transferring energy from microwaves to the substance being heated[56].

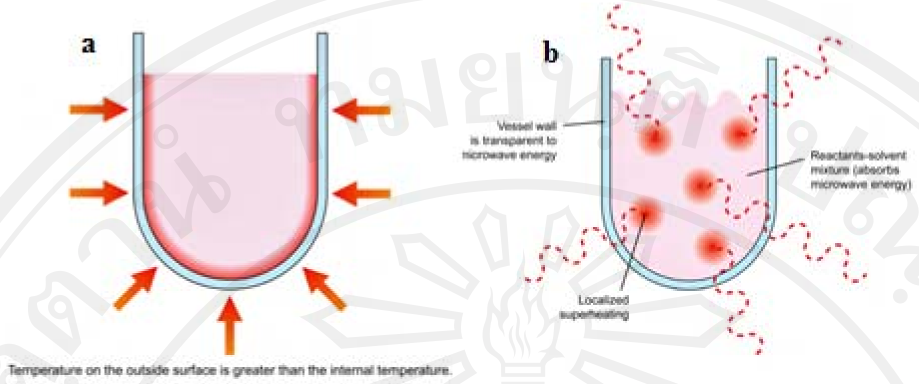


Figure 1.10Schematic diagram of convention heating(a) and microwave heating method(b)[55]

Reflux technique isa distillation technique which is involved with the condensation of vapors and the return of this condensate to the system. In this technique,an hours or a dayof conventional heating is required for the reaction. However, the solvent in this techniqueisrecycled. When the temperature increases to boiling point, solvent becomes vapor which subsequently condenses back to liquid at the condenser[57].

For microwave and reflux methods, solvent (such as water, ethylene glycol, and polypropylene[58-60]) is heated to reduce metal ion into metal. Ethylene glycol was selected in this research because it acts as a reducing agent near the boiling point (198°C). At 170 °C, acetaldehydeand water generate from the dissociation of ethylene glycol as shown in equation (1.7). Acetaldehyde can reduce metal ions to metal alloy and change to diacetylas shown in equation (1.8)[61]. The review for both methods was reported byWang et al.[49], Bayrakçeken et al.[50], and Zhou et al.[51].Wang et al.[49] prepared Pt/C by dissolvingchloroplatinic acid hexahydrate(H_2PtCl_6) in ethylene glycol and adjusting pH with potassium hydroxide.Microwave irradiation at

700 W for 30-120 seconds was used. The best condition to preparePt/C catalysts by microwave was 700 W for 90 secondswhich the particle size of 3.00-5.00 nm. was obtained.Bayrakçeken et al [46] prepared Pt/C by microwave technique. They used hexachloroplatinic acid (H_2PtCl_6) in aqueous solutions mixed with ethylene glycol and adjusted pH by using KOH. Then Carbon Vulcan XC-72 was added to the solution. After ultrasonic for half an hour, solution was put in microwave oven (800W) and heated for 30-120 seconds. The particle size of product obtained from this method was between 2.00- 4.00 nm. The reflux method was used to prepare by Zhou et al.[51] They prepare the PtPd/C by use H_2PtCl_6 and $PdCl_2$ as the substrate. The metal precursors and carbon black was added in ethylene glycolwhich adjusted pH byNaOH.The mixture was heated at 130 °C for 3 hours under nitrogen atmospheres. The particle size for this catalyst was 3.18±0.71 nm.

$$CH_2OH\text{-}CH_2OH \rightarrow CH_3CHO + H_2O \qquad (1.7)$$

$$2M^{+} + 2CH_3CHO \rightarrow 2M^{0} + CH_3COCOCH_3 + 2H^{+} \qquad (1.8)$$

$NaBH_4$reduction method use reducing agent to reduce metal ion in solvent to form metal or metal alloy[62]. First, dissolve the metal salt to the metal ionin solvent. Thenreducing agent(such as Zn, Mn, $NaBH_4$ and H_2) was added to the solution. The metal ion turnsto metal by accepting the electrons from reducing agent. This method was also used in this researchby usingsodium borohydride ($NaBH_4$)as a reducing agentdue to its strong reductive ability. Thereduction reactionof sodium borohydride shows in equation (1.9).The review for this method such as PtCo/C reduce with $Na(BH_4)$ was reported by Antoliniet al.[52]PtCo/C with atomic ratio of 3:1 was dissolved from H_2PtCl_6 and cobalt(II) hydroxide in water and methanol ratio of 1:1.

After that, pH was adjusted by ammonium hydroxide and reduced by $NaBH_4$. The sample was ultrasonicatedat 0, 40 and 80 °C. Particle size of product was in the range of 2.00-6.00 nm and particle sizes increased when the temperature was increased. Tang et al.[53] prepared Pd/C by reducing with $NaBH_4$. First, dissolve $PdCl_2$ in hydrochloricacid to obtain H_2PdCl_4. Then this solution was added tothe mixed solvent between ethylene glycol:deionized water (1:1). Ammonia, carbon Vulcan XC-72 and excessive$NaBH_4$were added and the reaction was stirred for 5 hours. the average particle size for this catalyst was 4.2 nm.

$$BH_4^- + 4OH^- \rightarrow BO_2^- + 2H_2O + 4e^- \qquad E = -1.65V \qquad (1.9)[63]$$

Although these three methods can be used toprepare the nano-sized particle, the prepare metalsalloy catalyst did not show a good dispersion on carbon supporter. To good dispersionability, surface modified carbon is one of alternative way to improve. In order to modify carbon surface, chemical treatment by various kinds of chemicals such as nitric acid, sulfuric acid, potassium hydroxide, and hydrogen-peroxide[58,64-66], have been used.Thechemical treatments introduced oxygenated groups such as carboxylic, hydroxyl, and lactone on carbon surface. The hydrogen peroxide is evidently promising due to its environmental friendly.Carbon surface modification has been pointed out in many studies. Some of interesting researches are discussed here. The study from Moreno-Castilla et al.[58]have confirmed that the prepared PtRu catalyst on treated and untreated carbon. For treated carbon, the surface was modified with hydrogen peroxide for 24 hours. Prepared PtRu catalyst on treated carbon showed a smaller size catalyst and higher electro-catalyst reaction than the one prepared on untreated carbon.

1.6Electrochemical characterization

Apart from the physical characterization by XRD, SEM and TEM to observethe formative phase, particle size and also the distribution of particle,the prepared samples will be also investigated the electrochemical performance by observing polarization curve from single cell testing technique. Polarization curve shows cell voltage versus current density of cell. Typical polarization curve depicts in Figure 1.11. In this curve, voltage loss generally occur by severed which are Open circuit voltage decrease, Hydrogen crossover, Activation loss, Ohmic resistance loss and Mass tranfer resistance loss.

1) Open circuit voltage decrease:The theoretical open circuit voltage (OCV) is E= 1.27 V. However, the OCV for cell testing is practically lower than theortical voltage because of non-standard operating conditions. The atmospheric pressure and operating temperature for cell testing is not at 1 atm and 25 ˚C. The actual OCV is lower than the theoretical value.

2) Hydrogen crossover:since hydrogen molecules are smaller than 3Å, they can diffuse through the membrane to cathode side. These diffused hydrogen will cause mixed potential due to the competition between ORR and hydrogen oxidation.

3) Activation loss: At low current densities, voltage loss is mostly attributed to the activation. Most of this loss is attributed to slow kinetics ORR on cathode side than hydrogen oxidation on anode side.

4) Ohmic resistance loss: the voltage loss is due to electrical resistance of the electron passing through catalyst, GDL, gas distributors, current collectors and

membrane. From the Ohm's Law, the voltage is proportional to actual current density with the combined resistance of materials.

5) Mass tranfer resistance loss: At high current densities the diffusion rate of the reactant can't keep up with reaction rate. At cathode side the diffusivity of oxygen through GDL is 5 times less than diffusivity of hydrogen and the concentration of oxygen on cathode is also lower.[67,20]

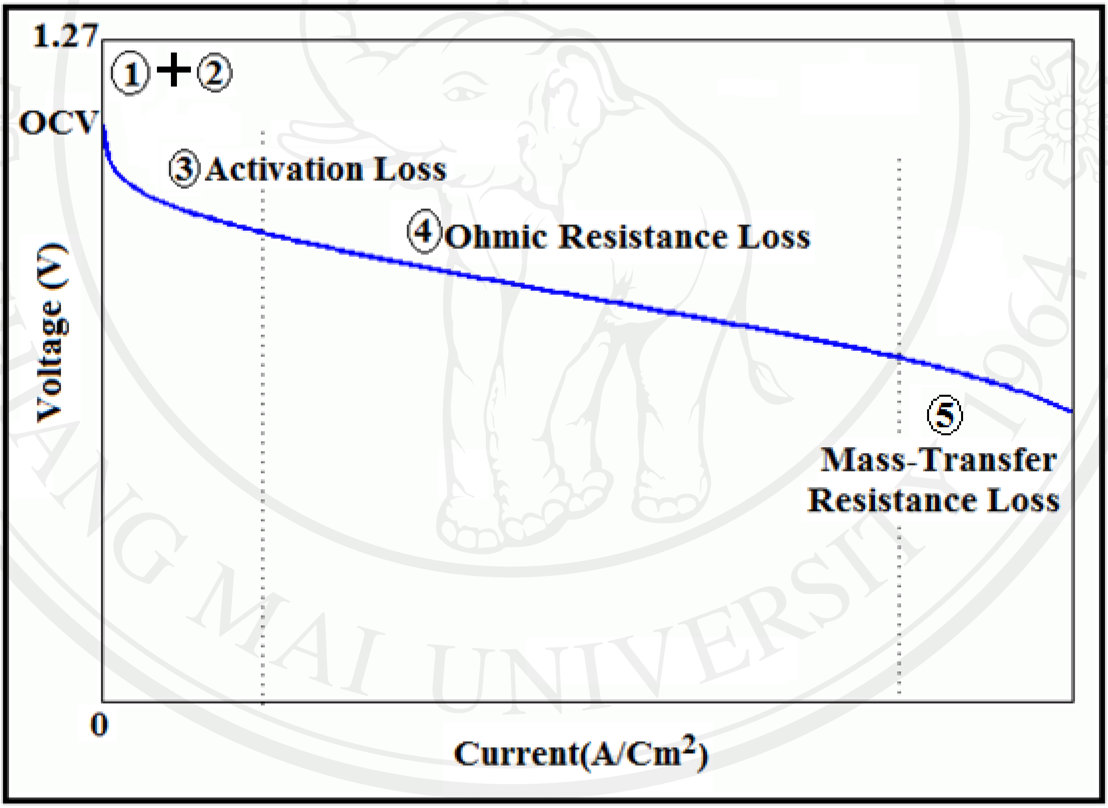


Figure 1.11 Shown polarization curve of PEMFC[68]

1.7 Objectives

The aim of this research was to prepare platinum-based ternary cathode catalyst (Pt-M_1-M_2; M_1, M_2 = Co, Cu, Cr, Fe and Ni) supported on carbon for PEMFC by microwave, reflux, and $NaBH_4$ reduction methods. The platinum-based ternary catalystssuch as PtCoCr, PtCoCuand PtCuFewere confirmed by literature reviewto have higher performance than standard commercialplatinum catalyst because the reaction does not undergo by $2e^-$ pathway.In this study, PtCoCr, PtCoCu, PtCoFe, PtCoNi, and PtCuNi were prepared as cathode catalysts. This research used microwave method to synthesize metal alloy catalyst because this method can be used to reduce metal ions into metals alloy, need short time to synthesis and the nano-particle size metals will be obtained. For reflux method, this method can be used to reduce metal ions into metals alloy and prepare the nano-particle size metals, however it need long time to synthesis. $NaBH_4$ reductionmethod, this method can be used to reduce metal ions into metals alloy and prepare the nano-particle size metals. The nano-particle size catalyst has high active area to activate reaction and deliver higher electro-activity than large particle size catalyst.