CHAPTER 1

INTRODUCTION

Ever increasing energy consumption, rising public awareness for environmental protection and limited existing nature of fossil fuels (such as natural gas, oil and coal), results in much of the research work to focus on alternative energy conversion and storage devices such as solar cell, supercapacitor, battery and fuel cells [1,2]. The alternative energy sources is fuel cells that they have the potential capability of providing power. The fuel cells are devices that continuously produce electrical energy whereas a fuel and an oxidant are being fed to the electrodes. This chemical energy is directly converted into electricity without involving combustion cycles [3,4]. The advantages of fuel cells, when compared to combustion power generators, are higher efficiency, no noise, and less pollution [5]. Fuel cells are one of the key enabling technologies for future hydrogen economy. For the many years ago, applications of the fuel cells are mostly replacing internal combustions engines, and providing power in stationary and portable power applications [6].

1.1 History of fuel cells

Sir William Robert Grove developed simplest form of hydrogen fuel cell in 1839, using two test tubes, platinum coated wires, and a dilute acid [6]. By connecting the wires in Figure 1.1 to a power source, water is electrolyzed. The oxygen and hydrogen gases generated are captured in the test tubes that are physically separated. After the power source is disconnected, the cell, as it was first known, runs in reverse: In the presence of platinum electrodes, which are necessary as catalysts, the

electrolysis essentially run backward, and current can be made to flow through a circuit between the two electrodes since hydrogen and oxygen have a natural tendency to react and form water.

$$\text{Anode:} \quad H_2 \rightarrow 2H^+ + 2e^- \tag{1.1}$$

$$\text{Cathode:} \quad 1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{1.2}$$

$$\text{Overall:} \quad H_2 + 1/2O_2 \rightarrow H_2O \tag{1.3}$$

In the combustion reaction (reaction 1.3), oxygen is reduced and fuel is oxidized. The fuel cell separates hydrogen and oxygen with an electrolyte through which only ions (e.g., H^+, O^{2-}) can migrate. Two half reactions, occur at the electrodes. Since ions are readily transported through the electrolyte, oxygen can react only in its reduced form with hydrogen in its oxidized form. The excess electrons from the cathode (reduction side) are transported to the anode (oxidation side).

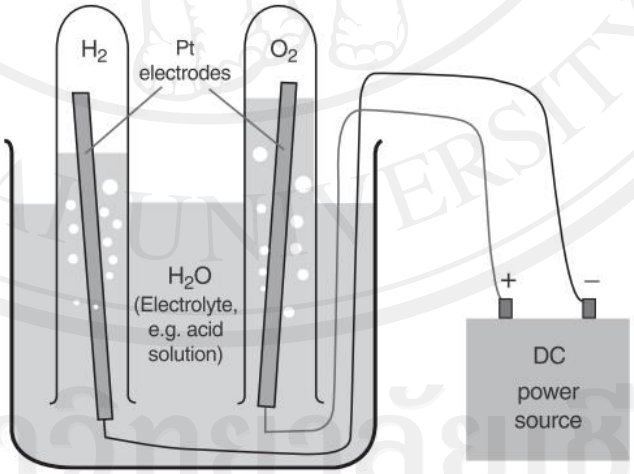

Figure 1.1 Electrolysis setup [7].

Francis Bacon developed the first successful fuel cell made of hydrogen and oxygen in 1932, with practical use. The fuel cell converted air and hydrogen directly

into electricity through electrochemical processes. He began his work by investigating alkaline fuel cells. It was not until 1959, with the support of the company Marshall Aerospace, he presented a fuel cell of 40 cells of 5 kW and 60% efficiency. After that, Harry Karl Ihrig demonstrated a 15 kW for fuel cell tractor from Allis Chalmers in the same year (Figure 1.2) [6]. The most successful applications of fuel cell technology has been in the US space program; 1 kW polymer electrolyte fuel cell (PEFC) systems, also known as polymer electrolyte membrane fuel cells (PEMFCs), were used in the Gemini program; 1 kW alkaline fuel cell (AFC) systems were used in the Apollo program; and 12 kW AFCs are used in the spacecraft to generate electricity [5–7]. On the spacecraft, the water produced by the reaction was available for the astronauts to drink. Recent developments have come thick and fast as the technology begins to come to fruition. Automotive applications are promising due to the huge consumer market and the need for an environmentally friendly, renewable alternative to the internal combustion engine and fossil fuels [7].

Figure 1.2 Fuel cell tractor Allis Chalmers [8].

There are now many manufacturers working on fuel cell applications of very different nature [6]. The applications of fuel cells cover a wide range of possibilities, from mobile systems such as cars and electronic devices to stationary power generation for households and public buildings [7]. On the other hand, there is a growing market for fuel cells for mobile phones, laptops and portable electric devices. Water treatment plants and waste dumps are beginning to use fuel cells to carry out the process of converting the methane gas produced for electricity generation [6]. The suitability of a fuel cell for specific application is determined by the electrolyte, since electrolyte properties also specify most of the crucial system characteristics [7].

A variety of fuel cells are in different stages of development. They can be classified by use of diverse categories, depending on the combination of type of fuel and oxidant, the electrolyte type, the operation temperature, whether the reactants are fed to the cell by internal or external manifolds, etc. Table 1.1 shows different types of fuel cells, classified according to the electrolyte employed, together with their main characteristics [5].

Table 1.1 Types of fuel cells according to the electrolyte employed and their main characteristics.

	AFC	**PEMFC**	**DMFC**	**PAFC**	**MCFC**	**SOFC**
Temperature (ºC)	60 - 90	80 - 110	80 - 110	160 - 200	600 - 800	800 -1000
Electrode material	Metal or carbon	Pt-on-carbon	Pt-on-carbon	Pt-on-carbon	Ni+Cr	Ni/Y_2O_3-ZrO_2
Electrolyte	NaOH/ KOH	Polymer membrane	Polymer membrane	H_3PO_4	$LiCO_3$-K_2CO_3	ZrO_2 with Y_2O_3
Primary	H_2	H_2 reformate	fuel CH_3OH	H_2 reformate	H_2/CO reformate	H_2/CO/CH_4 reformate
Oxidant	O_2/air	O_2/air	O_2	O_2/air	CO_2/O_2/air	O_2/air
Practical efficiency (%)	60	60	60	55[a]	55 - 65[a]	60 - 65[a]

[a] The production of additional electric energy by means of thermal energy cogeneration is not considered, alkaline fuel cells (AFCs), polymer electrolyte membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs).

1.2 Polymer electrolyte membrane fuel cells (PEMFCs)

Among fuel cell systems listed in Table 1.1, PEMFCs are the most widely applied fuel cell systems for portable power generation due to compactness, relatively long operational lifespan, quick start-up, high output power density, clean by-products, and quiet operation. A proton exchange membrane (PEM) connecting the anode and cathode is a fundamental part of PEMFC systems [9]. A PEM functions as a conductor for protons from anode to cathode, a separator to prevent mixing of reactants, an electrical insulator to drive electrons through an external path to the cathode and a structural framework to support the electrocatalysts (in the case of catalyst-coated membrane (CCM)) [10]. Figure 1.3 shows a hydrogen-fueled PEMFC with a proton-conducting membrane.

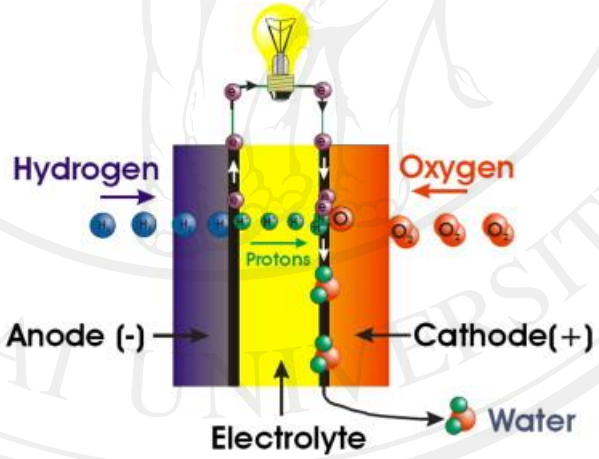

Figure 1.3 Schematic diagram of a hydrogen-fueled PEMFC [4].

When such a H_2/O_2 PEMFC is operating, the anode side is supplied with hydrogen and the cathode side is fed with oxygen or air. Under the electrocatalysis, hydrogen is split into protons and electrons through an oxidation reaction at the anode. The protons travel across the PEM, and the electrons transfer in an external circuit to the cathode. At the cathode, oxygen combines with protons and electrons to

form water through a reduction reaction. Thus, a closed circuit that generates electrical energy is formed [10].

The current PEMFC system usually works at a temperature lower than 80 ^{o}C, as the Nafion membrane would suffer from mechanical stability deterioration and water content reduction at higher temperatures, which can adversely affect the proton-conducting performance of Nafion [9].

Nafion is a perfluorosulfonate ionomer (PFSI), a DuPont product that developed in the early 1970s [9]. The Nafion membrane, has a structure of copolymer from flouoro 3,6-dioxo 4,6-octane sulfonic acid with polytetra-fluorethylene (PTFE) that Teflon backbone of this structure gives the hydrophobic nature for membrane and hydrophilic sulfonic acid groups (HSO_3^-) have been chemically grafted into backbone [4]. The reported chemical structure of Nafion for PEM membranes is shown in Figure 1.4.

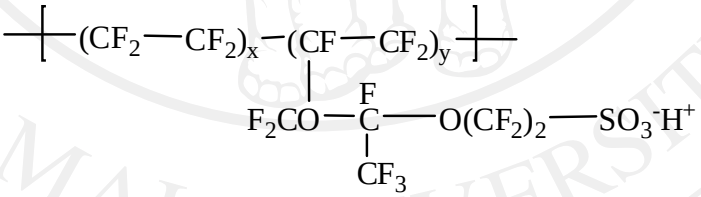

Figure 1.4 Chemical structure of Nafion.

Proton conduction is fundamental for proton exchange membrane fuel cells. At a molecular level, the proton transport in hydrated polymeric matrices is in general described on the basis of either of the two principal mechanisms. The first mechanism is proton hopping or diffusion mechanism which water is as vehicle or vehicular mechanism. In proton hopping mechanism protons hop from one hydrolyzed ionic site (SO_3^- H_3O^+) to another across the membrane. The produced proton by oxidation of hydrogen in anode adheres to water molecule than the provisional hydronium ion is

formed and one different proton from same hydronium ion hops on the other water molecule. The simple scheme of the hopping mechanism has been shown in Figure 1.5. The second mechanism is a vehicular mechanism. In this mechanism hydrated proton (H_3O^+) diffuses through the aqueous medium in response to the electrochemical difference. In vehicular mechanism, the water connected protons ($H^+(H_2O)_x$) in the result of the electroosmotic drag carry the one or more molecules of water through the membrane and itself are transferred with them. The schematic design of the vehicular mechanism as proton conduction in PEM has been shown in the Figure 1.6. The prevalence of one or the other mechanism depends on the hydration level of the membrane. On the other hand, the mechanism of proton transport within nano-composite and hybrid systems based on the aforementioned membranes is a much more complex process as it involves both the surface and chemical properties of the inorganic and organic phases [4].

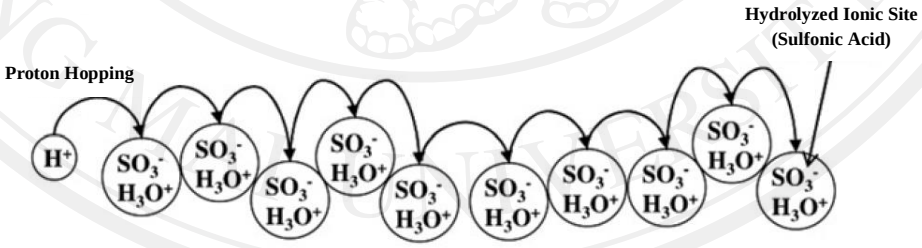

Figure 1.5 The simple scheme of the hopping mechanism [4].

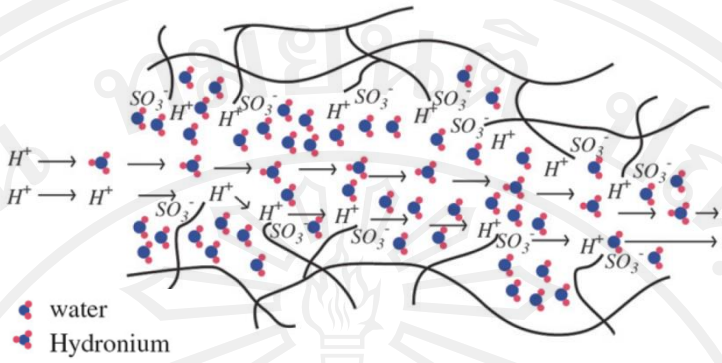

Figure 1.6 The schematic design of the vehicular mechanism as proton conduction in PEM [4].

Low temperature PEMFCs can work with small organic molecules, such as hydrogen, methanol, ethanol, and formic acid [11]. The hydrogen-fueled PEMFC is limited by the high cost of miniaturized hydrogen containers, the potential dangers in the transport and use of hydrogen, and its low gas-phase energy density [12]. Methanol, ethanol and formic acid have all been considered as fuels in a direct liquid fuel cells. Methanol is considered the most appropriate fuel. On the other hand, ethanol electrooxidation was considered to be an important research topic as ethanol has much less toxicity and a higher specific energy. Methanol and ethanol 'crossover' from anode to cathode through the membrane lead to low system efficiency. Methanol and ethanol crossover limit utilization of high concentrations, generally less than 2 M [13]. Feasibility of the PEM-based direct formic acid fuel cell (DFAFC) have been demonstrated. DFAFC is a suitable candidate due to the nature of formic acid which is fast electrooxidation, low fuel crossover through Nafion membrane, non-flammable, non-toxic and ease of fuel availability [11].

1.3 Direct methanol fuel cells (DMFCs)

Direct methanol fuel cell (DMFC) has been a focus for scientist interests because of various advantages, such as light weight, rich resource and environmental friendliness. However, the anode catalyst is easily poisoned by carbon monoxide adsorption (CO_{ads}) [14,15] resulting in reduction of cell efficiency and the barriers limit the development of the DMFC. Platinum (Pt) is generally known as electrocatalyst for the electrooxidation of organic molecules and corrosion resistance in strong acid solution [16,17]. Methanol oxidation giving CO species poisons the Pt active sites resulted in reduction of the Pt catalytic activity. Former studies reported that metal M (M is a precious or transition metal) in bimetal catalyst PtM could achieve oxygen with lower potential to accelerate the Pt–CO oxidation and resist CO–Pt adsorption [15,18,19]. The related mechanism for methanol oxidation on Pt-based catalysts can be expressed as reaction 1.4 to 1.9 [19].

$$Pt\text{-}CH_3OH \rightarrow Pt\text{-}(CH_3OH)_{ads} \quad (1.4)$$

$$Pt\text{-}(CH_3OH)_{ads} \rightarrow Pt\text{-}CO_{ads} + 4H^+ + 4e^- \quad (1.5)$$

$$M + H_2O \rightarrow M\text{-}(H_2O)_{ads} \quad (1.6)$$

$$M\text{-}(H_2O)_{ads} \rightarrow M\text{-}OH_{ads} + H^+ + e^- \quad (1.7)$$

$$Pt\text{-}CO_{ads} + M\text{-}(H_2O)_{ads} \rightarrow Pt + M + CO_2 + 2H^+ + 2e^- \quad (1.8)$$

$$Pt\text{-}CO_{ads} + M\text{-}OH_{ads} \rightarrow Pt + M + CO_2 + H^+ + e^- \quad (1.9)$$

Reaction 1.4 involves C-H bond cleavage (or C-H activation), and reaction 1.6 and 1.7 relate to water activation. Here Pt and element M play complementary roles in

the bifunctional mechanism. The rate-determining step has long been thought to be within steps (reaction 1.6 and 1.7) and (reaction 1.8 and 1.9). PtRu is one of the outstanding bimetal catalysts for the methanol electrooxidation with fine resistance for CO adsorption [14]. However, there are other metals have recently been used to prepare binary electrocatalysts.

1.4 Direct ethanol fuel cells (DEFCs)

As a limit of power supply, there are many alternative resources to solve the problem and fuel cell can be one of the promising choices. Direct methanol fuel cell (DMFC) has also been a focus for scientist interests because of various advantages, such as light weight, rich resource and friendly environment [19-21]. Nowadays, new sources of energy are being searched and small organic molecules such as methanol, ethanol and formic acid can be used as fuel. However, the anode catalyst is easily poisoned by carbon monoxide adsorption (CO_{ads}) resulting in cell efficiency reduction. Platinum (Pt) is commonly known as electrocatalyst and stable in acid solution [15,22,23]. The direct ethanol fuel cell (DEFC) is based on the oxidation of ethanol, involving 12 electrons (cell electromotive force of 1.15 V) [26]:

Anode: $CH_3CH_2OH + 3H_2O \rightarrow 2\ CO_2 + 12H^+ + 12\ e^-$ (1.10)

Cathode: $3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$ (1.11)

Overall: $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ (1.12)

The overall reaction looks like a combustion reaction. The principle by-products are acetaldehyde and acetic acid [26]. Ethanol oxidation giving CO species poisons the Pt active sites resulted in reduction of the Pt activity. Former studies reported that the provided metals generate oxygen containing species leading to CO_2 at low potentials

compared to pure Pt [15]. PtRu is one of the exceptional bimetal catalysts for the methanol electrooxidation with well resistance for CO adsorption [23]. However, there are other precious metals have recently been studied to prepare binary electrocatalysts such as PtAu [24]. Moreover, CNT is a good catalyst support which has high surface area, good electrical conductivity and high stability [25].

1.5 Direct formic acid fuel cells (DFAFCs)

DFAFCs are expected to be the first commercial application as a portable power supply among various fuel cells. The advances in DFAFCs have been reviewed: DFAFCs have higher power density, energy efficiency, and electromotive force than methanol fuel cell. The crossover flux of formic acid through Nafion membrane is several times smaller than that of methanol. The equilibrium and the onset potential of the oxidation of formic acid is less positive compared to methanol, and formic acid is less toxic and has no risk of producing hazardous byproducts during oxidation, while methanol can produce formaldehyde [11,19].

The major disadvantage of formic acid as fuel because it has low volumetric energy density (2104 Wh L^{-1}) that seems to be greatly lower compared to neat methanol which is 4900 Wh L^{-1}.The theoretical energy density of formic acid is determined as: $2F \times OCV \times (MW)^{-1}$. From the molecular weight MW (kg mol^{-1}), molecular weight MW (V), the Faraday constant (F = 96,485 C mol^{-1}) and the density (1.22 kg L^{-1}) [12]. The lower energy density of formic acid is exemplified by the anode reaction, in that only two electrons are produced per molecule of formic acid, fewer than are produced by other organic molecules such as methane (4 electrons), methanol (6 electrons), ethanol (12 electrons) or hydrazine (4 electrons) [19]. Although fewer electrons are produced, there are also fewer steps in the

electrooxidation of formic acid, which increase the likelihood for reaction, and hence, results in better fuel use. One significant advantage of formic acid is the presence of two oxygen atoms in its structure that means no water is requires at the anode for complete oxidation of formic acid to CO_2. Despite advantages in thermodynamic efficiency, the volumetric energy density of formic acid is less than methanol. This requires formic acid to be used at much higher concentrations in fuel cell [19]. Thus, for many systems, especially smaller power systems, the advantages of DFAFC can outweigh those of its primary direct-liquid fuel cell contender, the DMFC [12].

As with all polymer electrolyte membrane-based fuel cells, the DFAFCs also used an air cathode. Oxygen reduction, through a 4 electron reaction at the cathode, is usually facilitated by a platinum (Pt) based catalyst. At the anode, direct oxidation of formic acid releases 2 electrons per molecule. The cathode, anode and overall reactions of DFAFCs are described as:

Anode: $HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$ $E^o = -0.25$ V (1.13)

Cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ $E^o = 1.23$ V (1.14)

Overall: $HCOOH + 1/2O_2 \rightarrow CO_2 + H_2O$ OCV ~ 1.48 V (1.15)

The mechanism of the formic acid oxidation on Pt follows the so-called parallel or dual pathways that are dehydrogenation (reaction 1.13) and dehydration (reaction 1.16) [12]. According to the dehydrogenation path or direct path, formic acid is directly dehydrogenated into carbon dioxide (CO_2) via one or more active intermediates. According to the dehydration path or carbon monoxide (CO) path, formic acid is dehydrated into CO, which poisons the electrode or is further oxidized to produce CO_2 [27,28].

Dehydration $HCOOH \rightarrow CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$ (1.16)

Although platinum (Pt) has been used as a main catalyst for DFAFCs, to date the cell performances of DFAFCs incorporating Pt do not satisfy market needs due to Pt poisoning by carbon monoxide (CO). The subsequent retardation of electrochemical reactions caused by the Pt poisoning of formic acid results in low efficiency and power density. Reaction (1.17) shows the main electrochemical reaction of formic acid under Pt [29].

$$Pt + HCOOH \rightarrow Pt\text{-}CO_{ads} + H_2O \rightarrow Pt + CO_2 + 2H^+ + 2e^- \quad (1.17)$$

The dual pathway mechanism allows for two routes of platinum-based anode catalyst development for formic acid fuel cells and numerous admetals on Pt have been investigated for formic acid oxidation. In the first route, admetals that allow for the dissociation of water to occur at lower potentials can be employed though a bifunctional mechanism thus facilitating the indirect path. In the second, and preferred route, admetals that allow the direct path to proceed uninhibited such as electronic or third body modifications can be employed

1.6 Catalysts and literature reviews

In all of the noble metal nanomaterials (NMNs) such as gold (Au), palladium (Pd), platinum (Pt), ruthenium (Ru), etc. [30], Pt and Pt-based nanomaterials are still indispensable and the most effective catalysts for fuel cells. However, one of the major obstacles for fuel cell commercialization is the cost and reliability issues of Pt nanocatalysts used. Thus, design and synthesis of advanced catalysts to meet the requirements of reducing Pt loading amounts and meantime increasing the activity and stability of the Pt-based catalyst is highly desired [1]. Moreover, Pt catalyst is easily poisoned by carbon monoxide adsorbed (CO_{ads}), a reaction intermediate, one

strategy to improve catalytic activity is to form binary Pt-based catalysts [31]. Due to Pd are high electrocatalytic activity and good stability for formic acid electrooxidation [32]. Pt-Pd is a promising electrocatalyst. Pd and Pt do not segregate and the surface of Pt-Pd is likely occupied by these two metals in the proportions of the alloy [26].

The requisites of carbon supporting materials include large specific surface area for achieving high metal dispersions, good electrical conductivity, suitable pore size for optimum diffusion of reactants and byproduct to and from the catalyst, good corrosion resistance and low cost. Carbon black is the most commonly used material for these applications, in particular carbon vulcan XC-72R, which combines good electrical conductivity and high surface area [33]. However, the corrosion of carbon vulcan XC-72 under fuel cell condition and the poison of Pt nanoparticles originated form organosulfur impurities in carbon vulcan XC-72 were reported [34]. Recently, carbon nanotubes (CNTs) are the most investigated as catalyst support for low temperature fuel cells. The high crystallinity of CNTs makes these materials highly conductive, the high surface area, good corrosion resistance and high amount of mesopores resulting in a high metal dispersion and a good reactant flux in tubular structure. Moreover, CNTs have a positive effect on Pt structure, resulting in a higher catalytic activity and a higher stability than carbon blacks [25].

Godínez-Salomón and co-workers [35] studied the Pt nanoparticles size effect in the formic acid oxidation. The Pt nanoparticles (NPs) were evaluated between 1.5 and 3.7 nm. A well-marked NPs size effect was observed on the electrooxidation of formic acid, and that under certain conditions smaller particles may have a better catalytic activity than larger particles. Rhodes and Steigelmann [36] studied catalytic decomposition of aqueous formic acid on Pt electrodes. Formic acid reacts with the Pt

electrode in aqueous solution to form an adsorbed species which behaves in a way similar to CO_{ads}. This adsorbed species blocks the surface of the electrode and prevents the adsorption of other species. Although pure Pt catalyst is easily poisoned by adsorbed CO_{ads}, a reaction intermediate, one tactic to improve catalytic activity is to form binary platinum-based catalysts [30].

Alternatively, Ru alloy catalysts, mostly with Pt, have been reported as one of the best electrocatalysts for small organic molecules due to their bifunctional mechanism, involving the adsorption of OH species on Ru, which then promote the complete oxidation of CO to CO_2 [18,37]. Santos and co-workers [38] developed preparation and characterization of supported Pt–Ru catalysts with a high Ru content. The oxidation of CO shows that the onset potential of the reaction clearly decreases when the amount of Ru increases. Furthermore, bimetallic Pt-Ru catalysts with high alloying degree and different Pt/Ru atomic ratio have been prepared by a chemical reduction method in the H_2O/ethanol/tetrahydrofuran (THF) mixture solvent was studied by Chen and co-workers [39]. The results of electrochemical measurements illustrate that the alloying degree and Pt/Ru atomic ratio of Pt-Ru catalyst play an important role in the electrocatalytic activity of the Pt-Ru/C catalyst for formic acid electrooxidation due to the bifunctional mechanism and the electronic effect.

Au has long been known to be catalytically far less active than other transition metals. However, it can be dispersed as ultrafine particles and supported on some metal oxides, Au exhibits an extraordinarily high activity for some redox reactions. Au NPs or Au-based alloys have been used as electrocatalysts [40]. Lee and co-workers [41] investigated the influence of Au contents on the performance of direct formic acid fuel cell with AuPt anode catalyst, showing that the maximum power

density of $Au_{0.6}Pt_{0.4}$-based membrane-electrode-assembly was 30% higher than that of commercial $Pt_{0.5}Ru_{0.5}$-based membrane-electrode-assembly at 60 ^{o}C in 9.0 M formic acid. Afterward, Bai and co-workers [42] studied carbon nanotubes-supported PtAu-alloy nanoparticles for electrooxidation of formic acid with remarkable activity. The results show that the PtAu alloy nanoparticles with an average diameter of about 3.5 nm and narrow size distribution are supported on MWCNTs, and the PtAu/MWCNTs catalyst exhibits higher activity and stability for electrooxidation of formic acid than the commercial Pt/C catalyst.

Pd has been also demonstrated to be a good catalyst for low temperature electrooxidation of formic acid. However, the activity and stability of Pd catalyst still need improvements. Pd catalytic activity may be increased by the addition of metal or metal oxide promoters. Another effective method of enhancing catalytic activity is forming bimetallic nanoparticles [11].

Ma and co-workers [32] reported Synthesis of carbon supported palladium nanoparticles catalyst using a facile homogeneous precipitation-reduction reaction method for formic acid electrooxidation. A novel homogeneous precipitation reduction reaction method to synthesize well-dispersed Pd/C catalyst using only gentle heating, in stand of organic molecule surfactants or precipitating agent. The Pd NPs obtained from this methodology are small and highly dispersed on the carbon support surface. The resultant Pd/C-homo showed high electrocatalytic activity and good stability for formic acid electrooxidation.

Matin and co-workers [43] investigated sonochemical synthesis of Pt-doped Pd nanoparticles with enhanced electrocatalytic activity for formic acid oxidation reaction. Pt-doped Pd nanoparticle catalysts (Pd_nPt, n is 12, 15 and 19) supported on

carbon were synthesized by an ultrasound assisted polyol method. $Pd_{19}Pt/C$ catalyst showed the highest catalytic activity in formic acid oxidation reaction (FAOR) than Pd/C, $Pd_{12}Pt/C$ and $Pd_{15}Pt/C$, different from the literature which located the optimal composition at Pd_9Pt. The difference can be explained with the different distribution of Pt and Pd within the NPs depending on the synthesis method. Sonochemistry in this system has the advantage of concentrating the more precious Pt on the surfaces of the NPs, an economic advantage for applications.

Winjobi and co-workers [44] studied carbon nanotube supported Pt-Pd nanoparticles for formic acid oxidation. Small Pt, Pd and Pt_xPd_y alloy nanoparticles with uniform dispersion supported on CNTs were prepared through a modified ethylene glycol method. The results show that the mass activity of FAOR on these CNTs supported catalysts increases with more Pd amount of the catalyst, although the particle size gets larger. The CV study indicates a direct oxidation pathway of FAOR occurred on the Pd surface while on the Pt surface, the FAOR goes through CO_{ads} intermediate pathway.

1.7 Methods

The research will describe a new approach to address both the activity and stability issues synergistically by using Au and Pd metal nanoparticles alloyed with Pt catalysts. A good catalyst for anode fuel cell should have small particles (typically ≤ 4 nm) with a good dispersion on functionalized MWCNTs. By adapting method developed for the preparation of small tatrakis(hydroxymethyl)phosphonium chloride (THPC) Au nanoparticles [45], The research also report the preparation of small Pd and Pt metal nanoparticles using THPC as both reducing agent and stabilizing ligand. Sodium L-ascorbate was used as reducing angent to decorate Pt nanoparticles on Pd-

based [28,45]. A variety of analytical techniques were employed to charaterize the size, distribution, morphology and chemical composition of these metal nanoparticles.

Kim and co-workers [45] studied the preparation of Pd-shell nanoparticles having various core types and sizes. Their describes the structural and optical properties of core-shell particles in which the outer shell is composed of Pd and the inner core is composed of either Au (conducting) or silica (dielectric). Monodispersed Au-core particles having ~ 75 nm diameters were prepared by using THPC as reducing agent; silica-core particles having diameters ranging from 100 to 500 nm were prepared by the Stober method. The silica-core particles were functionalized with amine groups and seeded with small Au nanoparticles (~ 2-3 nm). Both types of core particles were then coated with Pd (Pd-shell were prepared by using L-ascorbic acid as reducing agent) to afford controllable sizes of core-shell particles ranging from ~ 100 to 600 nm in overall diameter (i.e., the Pd shell thickness could be varied from 10 to 60 nm).

Obradović and co-workers [28] reported the synthesis of Pt-Au nanoparticles supported on high area carbon by simultaneous reduction of Au and Pt precursors and by reduction of Pt precursor on already prepared Au nanoparticles. The first method (Pt-Au/C were prepared by microwave-assisted polyol method) produced a solid solution of Pt in Au containing ~ 5% Pt with the remaining Pt on the nanoparticles' surface. For the Pt:Au precursor ratio of 1:4 and 1:9, the surface ratio was found to be 0.70:0.30 and 0.55:0.45, respectively. By the second method (Pt-Au nanoparticles was prepared by decoration of Au nanoparticles with Pt by using ascorbic acid ($C_6H_8O_6$)

as the reducing agent) with the Pt:Au precursors ratio of 1:12, the surface ratio was 0.30:0.70.

Tsai and Hong [52] reported the electrochemical deposition of Pt nanoparticles in MWCNTs-Nafion composite for methanol electrooxidation. A Pt(IV) complex was reduced to platinum nanoparticles on the surface of MWCNTs. The Pt-MWCNT-Nafion nanocomposite film-modified glassy carbon electrode had a sharp hydrogen desorption peak at about -0.2 V vs Ag/AgCl (3 M) in a solution of 0.5 M H_2SO_4, which is directly related to the electrochemical activity of the Pt nanoparticles presented on the surface of MWCNTs. The electrocatalytic properties of the Pt-MWCNT-Nafion nanocomposite-modified glassy carbon electrode for methanol electrooxidation were investigated by cyclic voltammetry in a 2 M CH_3OH in 1 M H_2SO_4 solution. The Pt-MWCNT-Nafion nanocomposite-modified glassy carbon electrode has higher electrocatalytic ability for electrooxidation of methanol than the Pt-coated glassy carbon electrode and the Pt-Nafion-modified electrode.

1.8 Characterization and structure analysis

The catalysts were characterized their physical properties by using XRD, TEM and EDX techniques to observe the formative phase, particle size and also the distribution of particle. The electrocatalytic activity and stability of the prepared catalyst toward methanol oxidation, ethanol oxidation and formic acid oxidation were examined by CV and amperometric current density - time technique.

1.9 Objectives

The aim of this research were to prepare PtAu binary catalysts supported on functionalized MWCNTs (PtAu-MWCNTs) by THPC reduction method and electrodeposition, and PdPt binary catalysts supported on functionalized MWCNTs (PdPt-MWCNTs) by THPC and sodium L-ascorbate reduction methods. The electrocatalytic activity of PtAu and PdPt binary cathode catalysts toward methanol, ethanol and formic acid oxidations by CV will be investigated. The stability of the PdPt binary cathode catalysts toward the formic acid oxidation by amperometric current density - time will be investigated.

On approach to avoid the difficulty for preparation and under the condition of minimization of metal loading to lower cost of catalyst, this research has a promising potential application to functionalize MWCNTs and prepare metal nanoparticles on MWCNTs for DMFCs, DEFCs and DFAFCs.