Novel electrodes with enhanced performance for proton exchange membrane fuel cell applications

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2013

Li, B. (2013). Novel electrodes with enhanced performance for proton exchange membrane fuel cell applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54959>

<https://doi.org/10.32657/10356/54959>

**NOVEL ELECTRODES WITH ENHANCED
PERFORMANCE FOR PROTON EXCHANGE
MEMBRANE FUEL CELLS APPLICATIONS**

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**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

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A thesis submitted to Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2013

ABSTRACT

As a promising substitution to conventional power sources rely on combustion of fossil fuels, proton exchange membrane fuel cells (PEMFC) have attracted plenty of interest for various applications such as power sources for portable electronics, stationary power generation, and onto mobiles. At the present time, PEMFCs are still facing the challenges of cost as well as performance issues before they can be largely commercialized. One of the high cost factors comes from the significant amount of platinum (Pt) used in the PEMFC, especially at the cathode side due to the sluggish kinetic towards oxygen reduction reaction (ORR).

The objective of this study is focus on understanding factors limiting the efficient use of the electrocatalyst in PEMFCs, and more importantly developing and optimizing new methods to prepare electrodes that are able to overcome cost and cathode kinetic limitations. More technically and specifically, this study is focused on reducing cathode Pt loading without sacrificing the fuel cell performance due to the sluggish kinetic and high Pt usage at the cathode.

In state of the art PEMFCs, Pt supported on carbon black is used as an electrocatalyst. Catalyst support strongly affects the electrical properties of the catalyst layer. In order to reduce the Pt loading as well as improve the catalyst performance, carbon nanofibers (CNFs) directly grown on carbon paper is produced to act as novel catalyst support. This structure ensures that all the catalyst particles are in firm electrical contact with the carbon paper backings. Furthermore, CNFs possess higher electric conductivity, larger surface area and better corrosion resistance compared with

conventional carbon black catalyst supports. Due to these advantages the use of CNFs as catalyst support can improve the Pt catalyst utilization efficiency; the mass transfer properties of the catalyst layer and the durability.

In the single cell test, Pt/CNFs electrode is able to produce 50% (0.14 mgPt/cm^2) and 70% (0.07 mgPt/cm^2) higher cathode Pt mass power output than that using Pt/Carbon black catalyst (0.4 mgPt/cm^2).

To further reduce the cathode Pt loading and improve the performance, a pulse current electrodeposition (PCE) based three-step method was developed and utilized to fabricate membrane-electrode assemblies (MEAs) cathodes with ultra low platinum loading. The purpose of this study is to improve the catalytic activity of platinum by alloying it with transition metals on oxygen reduction reaction occurred at cathode side and to investigate the electrochemical and electrocatalytic characteristics of ternary alloys in PEMFCs.

This approach involves an electrodeposition process to establish an improved catalyst layer structure with better catalyst utilization efficiency, followed with a galvanic displacement and electrochemical dissolution process to produce core shell structured Pt-based alloy to improve the catalyst mass activity. The control of catalyst distribution uniformity on a $5 \times 5 \text{ cm}^2$ electrode prepared by this novel three step process was studied. It was found that density and porosity of the carbon black substrate affect the catalyst layer thickness and thus influence the performance, PtFeNi catalyst prepared on a dense carbon black substrate produces a catalyst layer thickness of 3-5 μm , while catalyst prepared on a loose carbon black substrate exhibits a

thickness of about 10 μm . The MEA prepared with a loose carbon substrate cathode performs twice higher than that with a dense carbon substrate in a single cell test.

Different Pt loadings of 0.02, 0.035, 0.05, and 0.1 mgPt/cm^2 were prepared and tested in MEA cathodes, the results demonstrate that the best performance was obtained at a cathode catalyst loading of 0.05 mgPt/cm^2 . The comparison of a 0.05 mgPt/cm^2 PtFeNi cathode with a 0.4 mgPt/cm^2 commercial Pt cathode was also studied, indicating a comparable performance for the two electrodes. In terms of mass power output the PtFeNi cathode exhibits a 8 times higher performance than that of Pt cathode, while preliminary durability test was also carried out on the PtFeNi MEA, a good stability of the catalyst was proven.

ACKNOWLEDGEMENTS

I would like to express the sincerest gratitude and appreciation to my supervisor, Prof Chan Siew Hwa, for his guidance in my Ph. D research. His kindness warms me when I make mistakes; his patience clears my mind when I am messed; his strictness stimulates me to make progress step by step and do not act rush; his diligence encourages me to continuously devote on the right directions.

I would like to thank the school and the laboratory for providing me with a convenient environment to study and an international circumstance to learn from others. My friends acquainted here not only help me in the study, but also enrich my learning about the world.

I sincerely thank my dearest parents and relatives. Their love and tolerance provide me a warm and safe haven. My countless thanks would be given to all the good friends. Their understanding, encouragement and timely help accompany me on the way to growth.

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CHAPTER 1. Introduction

1.1 Background

Energy and environment are the major subjects of research in the 21st century. Unfortunately the present energy options still rely highly on the combustion of fossil fuels, while industry products on the combustion of fossil fuels (combustion engine, *etc.*) are major sources of air pollution nowadays. The combustion engines are the most important causes for the increase of carbon dioxide in our atmosphere, which lead to global warming through the green-house effect. Globally, the demand for energy is expected to continually increase due to the fast development of several developing countries. Thus there would be the combustion of more fossil fuels per year if no clean technology is introduced into the industry. With regard to the transportation sector; the number of vehicles in developing countries such as China and India are projected to reach 31% of the total global light-vehicle market by 2014 [1]. This will certainly aggravate the air pollution and global warming problem if these vehicles are entirely fed with petroleum derived fuels.

Our humanity is facing immense challenges to decrease the air pollution and carbon emissions, especially when there is a significant increase in energy consumption projection. Therefore, new clean technologies for energy conversion and power generation are urgently needed. So far, the automotive companies worldwide have put a lot of effort to develop electrical vehicles, which will certainly minimize if not eliminates the urban air pollution problem. While the drawbacks of electrical power

based vehicles are also conspicuous; the poor energy storage capacity of batteries means that this type of electric cars have very poor range between charges, and recharging of batteries always takes time.

In this regard, fuel cells are receiving increased recognition as promising candidates to the present less clean power sources due to their advantages such as high efficiencies, high energy density and remarkable environmental acceptability [2-8]. There are several types of fuel cells and among them proton exchange membrane fuel cells (PEMFC) are considered to be most suitable for automotive applications owing to their fast start up, compact and lightweight, high power densities, and almost zero emission. Several companies such as Honda Motor Company, Ltd have successfully developed concept cars driven by PEMFCs.

Although the technological viability of fuel cells has been demonstrated, its commercial application demands that the cost must be significantly reduced while concurrently increasing its lifespan without compromising the electrochemical performance [9, 10]. One of the high cost factors comes from the significant amount of platinum (Pt) used in the PEMFC, especially at the cathode side due to the sluggish kinetic of four electrons involved transformation towards oxygen reduction reaction (ORR) [11-15]. The price of Platinum is quite high of around 1500 USD/Oz, and what's worse is that there is not enough platinum in the earth to product fuel cell electric vehicles. Hence, researchers are highly motivated to investigate and develop improved process in order to substantially lower the Pt loading of the PEMFC without sacrificing the fuel cell performance.

In brief, two approaches below are used to achieve the objective: the first approach is the improvement of catalyst activity, which is realized by alloying Pt with other metal to form Pt-M binary/ternary catalyst and to reduce the average particle size of the catalyst [16-28]. The other approach is the optimization of the microstructure of three-phase boundary in the catalyst layer in order to reduce the kinetic overpotential [7, 29-31]. There are mainly two ways that are investigated to improve the catalyst utilization efficiency in the catalyst layer. Firstly is the introduce of new catalyst supports such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) [32-43], and secondly is the use of new process such as sputter deposition, electrodeposition, and thin film methods to gain an improved catalyst layer structure [44-51].

The conventional catalyst support is carbon blacks XC-72 with high mesoporous content. Ideal supports for electrocatalysts in PEMFCs should have the following characteristics [52, 53]:

- Provide a high electrical conductivity,
- Allow good reactant gas access to the electrocatalyst,
- Good water management,
- Good corrosion resistance.

Driven by the aim to increase catalyst utilization, a series of methods have been investigated and developed to improve the effective surface area of platinum in a MEA environment; either by reducing the catalyst particle size and/or increasing of the three phase interface between the catalyst, electrolyte and reactants. In the past few

decades, a mass of patents have also been granted investigating the importance of such methods and developing processes in related to the field of PEMFC.

Deposition methods of Pt-based catalysts on carbon support mainly including two categories: powder type and non-powder type. With regards to a powder type process, a Pt ions containing solution is first reduced by a reducing agent that converts the Pt ions into Pt nanocrystals. After that, Pt nanoparticles will be adsorbed on various carbon supports and thus carbon supported Pt catalysts are produced. However, there are some drawbacks for conventional powder-type method; first and foremost, it is very difficult to increase the platinum-carbon ratio to beyond 40 wt.% and at the same time freezing Pt nanoparticle size [54]. As is well known, the sluggish kinetic of oxygen reduction reaction (ORR) at the cathode are directly dependent on the effective surface area of the electrocatalyst in the catalyst layer and, therefore on the platinum particle size. Thus it is important to produce small catalyst particle size. In addition, as it is hard to improve the ratio of Pt to carbon black in a conventional powder type process, the efforts to decrease the catalyst layer thickness will be limited.

With regard to non-powder type processes, the catalyst nanoparticles are prepared directly onto the surface of the carbon electrode or membrane. Among these processes, physical sputter deposition technique is a well-known process to produce an ultra-thin catalyst layer ($< 1\mu\text{m}$). There has been some publications demonstrated that this process is able to prepare MEAs with high platinum utilization at ultra-low Pt loading ($< 0.02\text{ mgPt/cm}^2$) [55, 56]. Although ultra low Pt loading the catalyst mass power output is greatly improved, the specific power output is still lower than commercial

MEAs. Besides, further increase the Pt loading wouldn't increase the fuel cell performance. What is more, physical sputtering deposition technique needs a very high initial investment due to the expensive high vacuum apparatus.

Another method is electrodeposition, which composed of two different processes of direct current electrodeposition (DCE) and pulsed current electrodeposition (PCE). The investigations on electrodeposition begin from DCE, improved catalyst utilization efficiency was obtained but the specific power output is not good due to large catalyst particle size (20-50 nm) [35]. Recently, PCE was intensively studied as a promising method to prepared electrodes with improved catalyst utilization efficiency and overall performance, PCE is able to produce smaller catalyst particle size than DCE [46-49, 57-61]. Compared to the ultra-thin catalyst layer produced by sputter deposition ($< 1\mu\text{m}$); electrodeposition is able to produce a thicker catalyst layer thickness of 5-10 μm , which means that it is possible to use a higher catalyst loading ($> 0.05\text{ mgPt}/\text{cm}^2$) and therefore to obtain higher specific power output and improved physical stability.

1.2 Motivations and research objectives

In a conventional PTFE-bonded catalyst process, the catalyst utilization efficiency is very low due to the fact that a large portion of Pt nanoparticles decorated on these carbon blacks are trapped inside the pores of the carbon supports, where the three-phase boundary among reactants, electrolyte, and electrode cannot be established. What is more, the agglomeration of carbon blacks also conceals a fraction of Pt catalysts in between them. Thus the catalyst utilization efficiency of a

conventional Pt/carbon black electrode is rather low.

There are a lot of methods such as brushing, rolling and spraying Pt/carbon black slurry to prepare the catalyst layer, however these methods have been verified to be hard to obtain a high Pt utilization efficiency, therefore the objective of reducing of Pt loading in order to reduce cost is a formidable task by using conventional methods. In this work, the primary objective of this study is to develop and optimize novel processes to attain high Pt utilization efficiency and thus decrease the Pt loading and hence the cost. Catalyst layer is the critical components in a MEA, at the anode hydrogen molecules were split into protons and electrons while at the cathode oxygen molecules were transformed into water. Optimization of the catalyst layer to obtain higher catalyst utilization efficiency is a multi-parameter case, the reaction rate especially at the cathode need to be improved while at the same time better transport pathways for protons, electrons, reagents and by-products should be also be promoted.

Carbon nanofibers (CNFs) with small diameters (20-100nm) posses quite large surface areas but low porosity, so it should be better supports for Pt nanoparticles. Besides being completely devoid of micro-porosity that may trap Pt catalysts as carbon blacks does, CNFs also show good electrical conductivity , high tensile strength , excellent resistance to electrochemical corrosion , and are expected to have a high gas permeability. As carbon paper is used in fuel cells as charge-collecting electrodes, it is proposed to grow CNFs *in situ* on carbon paper, and then decorated the CNFs with highly dispersed Pt nanoparticles to obtain a desired PEM fuel cell electrode. Such a 3D unique structure may warrant that every Pt particles is in electrical contact with the carbon backing and will further improve the catalyst utilization efficiency.

Despite investigating on novel catalyst supports, a novel electrodeposition based three-step technique was also developed to selectively deposit Pt-M (M=transitional metals) alloy nanoparticles onto carbon-based substrates where both electronic and ionic pathways exist. This process will ensure not only the existence, but also the expansion of the three-phase interface and therefore lower the noble metal loading. Furthermore, the use of Pt alloys will accelerate the sluggish kinetic at the cathode.

In brief, the objective of this project is to design novel electrodes with high performance, good stability and reduced Pt loading. To achieve this goal, most of the efforts have been devoted to the following scope:

- a. Investigation of *in-situ* grown CNFs as novel catalyst support for the improvement of catalyst utilization efficiency, in particular
 1. Study the growth of CNFs or CNTs on carbon paper.
 2. Study the deposition of Pt particles onto the *in situ* grown CNFs; try to obtain as smaller Pt particles as possible.
 3. Characterize the performance of Pt/CNF/carbon paper electrodes in a MEA environment.
- b. Development and optimization of a novel electrodeposition-based three step process to prepare electrodes with ultra-low loading and excellent performance.
 1. Design a process to produce Pt-alloys nanocatalysts with improved catalyst layer structure; specifically, firstly electrodeposit transitional metal particles

to the substrate, than a Pt containing solution was added on the substrate to form Pt-transitional metal alloy, lastly excess and unalloyed transitional metal atoms will be removed by a electrochemical dealloy process.

2. Study the effect of different Pt loadings, catalyst layer thickness, and uniformity on the electrode performance in a MEA environment.
3. Study the effect of different alloy compositions such as PtFe, PtNi, and PtFeNi on the catalyst morphology, catalyst size, and therefore the performance.

CHAPTER 2. Literature review

2.1 Overview of PEMFCs

2.1.1 Introduction

A proton exchange membrane fuel cell (PEMFC) is a device that converts the chemical energy of reactants directly into electrical energy through electrochemical reactions. PEMFC was first developed in the 1960s, and since 1980s numerous researches on PEMFCs have greatly accelerated as new fabrication methods to reduce the cost issue remarkably [62]. Because of a string of advantageous features including high energy density, low operating temperature, low weight and compactness, long stack life span, fast start-ups, and excellent environmental acceptability [63-65]; PEMFC is considered to be one of the most promising and attractive candidates for both industry and home applications such as stationary power generation, power sources for portable electronics and automobiles. Over the past decade, portable electronics or prototype vehicles adopting PEMFCs as the power source have been released from several companies.

2.1.2 Working principle of PEMFCs

In the most common case, a PEMFC is made of a planar configuration. The core component of a PEMFC is called a membrane-electrode-assembly (MEA), which has

3 parts: an anode, a cathode and an ion conducting membrane in between anode and cathode. Both the anode and cathode are made of carbon paper backings with a catalyst layer on its working side. The current state of the art catalyst used in a MEA is nanosized Pt nanoparticles (2-5 nm) supported on carbon blacks; and the membrane is made of Nafion for low temperature PEMFC ($< 100\text{ }^{\circ}\text{C}$), which is a good proton conductor in humidified condition. Hydrogen fed PEMFC is a type of fuel cell that uses hydrogen as the anode fuel and oxygen/air as the cathode oxidant to produce electricity. The only by-product for this type of PEMFC is water and some heat thus it is almost zero emission.

Fig 2.1. The cross-sectional schematic diagram of a planar MEA for a PEMFC

Fig 2.1 presents an illustration of the cross section of hydrogen fed PEMFC. At the anode, hydrogen molecule is split into protons and electrons, then the protons are transported to the cathode through Nafion electrolyte and at the same time those electrons are conducted to the cathode via an outside circuit in order to supply power. At the cathode, oxidants such as oxygen or air will be injected to combine with the

electrons and protons to produce the only by-product of water.

Water management is an important problem, if the cathode structure is not properly designed, water flooding will block the transport pathways of oxidants and thus cause the decrease of fuel cell performance. While a good cathode structure can produce a proper water balance.

The reactions at the electrodes are listed as follows:

All in a word, PEMFCs is able to produce electricity from hydrogen and oxidant (air or oxygen) during an electrochemical conversion. Specifically is the hydrogen oxidation reaction (HOR) that occurs at the anode and the oxygen reduction reaction (ORR) that takes place at the cathode, respectively. The only by-products generated by PEMFC are water and some waste heat coming from the chemical reactions; the operating temperature range of PEMFC using Nafion as the membrane is from room temperature to no more than 100 °C.

2.1.3 Technical challenges for PEMFCs

Although there are so many advantages for a PEMFC over other power generators, PEMFC is still not able to be widely commercialized. Economic factor is the primary

limitation for the widely-scale commercialization of PEMFCs, the use of platinum catalyst or other precious metals is one of the major factors causing the high cost of PEMFCs. Among all the major components in a fuel cell stack, the contribution to cost from electrode catalyst i.e. Pt, is 77%, membrane i.e. nafion, is 6%, bipolar plate is 5% and gas diffusion layer i.e. carbon paper, is 5% [66]. The total Pt resources on the earth is very limited, moreover the cost of Pt electro-catalysts is very high. Therefore the total Pt loading used in the electrodes need to be substantially reduced, according to the 2012 DOE reports, a total Pt loading of 0.125 mg/cm^2 is expected before 2017, in order to realize the widely commercialization of PEMFCs. The high cost of a PEMFC can be reduced by several means, such as reducing the Pt loadings especially at the cathode or by improving its electrochemical performance and stability.

Despite cost barrier, there also have other technological challenges in PEMFCs. In detail, it is the development of an anode electrocatalyst that has high CO tolerance beyond the level of 50 ppm, as well as a cathode electrocatalyst that can reduce the large overpotential encountered under open circuit conditions [67-75].

Another important issue that is urgently needed to be addressed for PEMFCs before it's widely commercialization is durability. The Pt catalyst has been proven that they have a tendency to grow larger due to aggregation and grow larger during the fuel cell operating [16, 24, 76-84], which will lead to the decrease of efficient Pt active surface area. Due to this reason after long time operation there will be significant fuel cell performance degradation. Furthermore, due to the poor electrochemical corrosion resistivity of carbon blacks supports, the degradation of electrodes will be more severe.

They will suffer from electrochemical oxidation under the operating conditions, especially at the start up of a fuel cell due to the relatively high voltage of ~ 1 V.

2.2 Fuel Cell Performance

Polarization curve is the primary evaluation technique of a PEMFC. The current response of a PEMFC is recorded as its voltage varies (or by measuring its voltage response to current) to obtain a polarization curve. An electrochemical test station was used to measure polarization, when the fuel cell is connected to a test station there will be a simulated load that mimic a particular electrical waveform.

The as-measured current-voltage (VI) curve is the most commonly used profile to evaluate PEMFC performance. Fig 2.2 displays a typical polarization profile of a proper prepared PEMFC. To facilitate the comparison of MEAs performance with different size, the current density can be normalized to the active area. In addition, power output curve as a function of current density could be obtained by calculates from the result of the voltage and the current density. Several important values could be extracted from the power output density curve, i.e., a peak power output could be observed at the high current region. However, the power output density at high voltage region (0.55-0.65 V) is of the most interest as it is expected to be the ideal working voltage. More importantly, the current density and power output density that normalized to Pt loading on the cathode are considered to be the most important parameters as the aim to reduce Pt loading and cost, which is also called cathode specific mass activity (A/mg Pt).

ΔE_{eq} means the theoretical voltage determined by the Gibbs energy and the number of total electrons n that transferred in the electrochemical reaction taken place in a PEMFC. It is the ideal maximum value between the anode and cathode. It is described in the equation below:

$$\Delta E_{eq} = E_{cathode} - E_{anode} = -nF\Delta G \quad (2.1)$$

where F represents the Faraday constant, ΔG means the Gibbs energy of the cell reaction. This ideal theoretical maximum fuel cell voltage requires that equilibrium be established at both electrodes. In a real fuel cell the voltage is described by the following equation:

$$\Delta E_{cell} = \Delta E_{eq} - |\eta_{cathode}| - |\eta_{anode}| - \Delta E_{ohmic} \quad (2.2)$$

where $\eta_{cathode}$ and η_{anode} represent the overpotential at the cathode and anode, respectively. With regard to a hydrogen fed PEMFC, anode overpotential is negligible due to the simple kinetic and fast reaction speed of the HOR catalyzed by Pt nanoparticles. The cathode overpotential is however very high due to the sluggish kinetic of the four electrons involved ORR, reducing the cathode overpotential will largely improve the fuel cell performance.

Either PEMFC anode or cathode overpotential is composed of two parts: the reaction overpotential η_k and the concentration overpotential η_{conc} . The reaction overpotential arises from electrode reaction kinetics while the concentration overpotential is affected by the mass transport properties of the electrodes.

The ohmic overpotential (ΔE_{ohmic}) is composed of the aspects shown below:

- (1) the contact resistance between the electrodes and the flow-field plates,
- (2) the proton conduction resistance in the membrane,
- (3) the resistance between the catalyst layers and gas diffusion layers.

Among them the membrane resistance plays the key role in a properly prepared MEA.

Fig 2.2 Current–voltage characteristic obtained in a 50-cm² dihydrogen/air fuel cell at 353 K at a total pressure of 150 kPa. Circles, experimental data; triangles, mass-transport-free ΔE_{cell}; squares, mass-transport-free and ohmically corrected ΔE_{cell}.

The theoretical maximum cell voltage and other overpotentials that affected a MEA performance were illustrated in Fig 2.2. The efficiency of a PEMFC is calculated by divided the cell voltage (ΔE_{cell}) over ideal maximum voltage (ΔE_{eq}). From equation

(2.2) and Fig 2.2 we can deduced which loss is in domination at different current density region, thus to improve the fuel cell efficiency by minimizing the dominant loss.

From Fig 2.2 we can see that at low current densities region the cathode overpotential (η_{ORR}) is in domination of the total losses, while at high current densities region the mass transport losses in the catalyst layer and gas diffusion layer bring the dominating losses.

The concentration overpotential η_{conc} is highly affected by the structure such as thickness, porosity, wettability, *et al.* in the catalytic layers and gas diffusion layers. The reduce of electrode overpotential by optimizing the catalyst layer structure and using better catalyst composition to speed up the electrode kinetics is the primary interest in this thesis.

Despite electrode overpotential, ohmic losses may also highly affect the fuel cell performance significantly if the PEMFC is not properly designed and assembled.

2.3 Recent works on reducing Pt loadings and increasing Pt utilization

At the present time, PEMFCs still face cost as well as performance issues before its commercialization; high cost issue mainly comes from the high amount Pt usage while the performance limitations are mainly caused by sluggish kinetics from the cathode where molecular oxygen and protons are converted to water by the oxygen reduction reaction (ORR) . Hence researchers are highly motivated to find out ways to

substantially lower the Pt loading especially at the cathode but still high performance; lots of efforts have been contributed mainly on the following two approaches:

The first approach is the improvement of catalyst activity, which is realized by alloy Pt with other metal to form Pt-M binary/ternary catalyst and reduce the catalyst size [16, 24, 85-96]. Various Pt-alloys has been proved to have improved mass activities both in liquid electrolytes and in PEMFCs. Among them Pt_3Ni was studied of the primary interest [97-102], Pt_3Ni (111) single-crystal surface exhibited 10-fold more active Pt-mass activity improvements compared to pure-Pt (111) surface; although it was realized in liquid electrolytes and its realization in real MEAs remains challenging. Alternative catalyst supports such as CNTs or CNFs have been demonstrated to have the ability to enhance the electro-catalyst activity due to their unique properties such as high surface area, good electron conductivity, and good corrosion resistance [34, 103-110]. These characteristics of CNFs/CNTs enable better catalyst dispersion with uniform distribution and smaller size; furthermore they supply better longtime stability so as to enhance the catalyst mass activity.

The other approach is the optimization of catalyst layer structures so that the effect of reducing the cathode Pt-loading is only restricted to its kinetic voltage loss. A catalyst decaling method has been demonstrated to produce a thin and uniform catalyst layer [111-118]. Wenzhen Li etc. use a filtration process to prepare a thin catalyst film a super-hydrophobic polycarbonate filter, then the catalyst layer was transferred directly onto membrane; the thickness of the catalyst layer can be controlled accurately by altering Pt loadings of the catalyst and electrode [119]. Electrodeposition has been proved as another effective method to obtain better catalyst layer structure [44, 47, 57,

120-126], by this method one can establish a unique catalyst layer structure with super high catalyst density at the most surface of the electrode, while the catalyst density decrease as far away from the electrode and membrane interface. One dimensional catalyst structures such as Pt nanowires, Pt nanotubes, cross-linked Pt nanostructure have also been reported to present much higher mass specific activity [127], as these structures facilitate easy electron as well as gas transport.

Recent works focused on both methods to lower the Pt loading but maintain the performance will now be introduced.

2.3.1 Enhanced catalytic activity catalysts

Nanosized Pt particles (2-5nm) supported on carbon blacks supports is currently commercialized catalyst for both electrodes to catalyze the anode hydrogen oxidation reaction and/or cathode oxygen reduction reaction. As a face-centered cubic (fcc) structured crystal, Pt has a lattice parameter of 3.92 Å [128]; and for those nanosized Pt particles they usually expose only low-index facets such as Pt {110} and Pt {111} and a thermodynamically favored spherical shape. The order of surface energies (γ) for these low-index crystallographic planes follows: $\gamma(111) < \gamma(100) < \gamma(110)$ [129, 130]. The surface orientation of Pt crystals has been found to strongly affect the catalytic property; high-index facets have been reported to possess higher catalytic activity with regard to ORR [86, 131, 132].

Driven by the enhanced catalytic activity provided by Pt high-index facets, many

works have been reported on the synthesis of Pt nanostructures that expose high-index facets [93, 99, 133-139]. Wang et al. reported that nanocube-shaped Pt presents four times catalytic activity in a 0.5 M H₂SO₄ solution than Pt nanoparticles [140]. The high performance is explained by the high exposure Pt {100} facets of Pt nanocube. Tian et al. [141] reported the synthesis and characterization of Pt tetrahexahedra which expose lots of high-index crystallographic planes including Pt {730}, Pt {210}, and Pt {520}. This kind of Pt catalyst exhibit 2-4 times better reaction efficiency than Pt/C catalyst. Pt nanostructures that are rich of high-index facets possess numerous unsaturated atomic steps, edges or kinks; such steps and edges are demonstrated to have improved catalytic activity than low-index facets that are exposed by commercialized Pt/C catalysts.

Although such high-index crystallographic planes possess enhanced catalytic properties, their use in PEMFC remains challenging. The primary barrier for commercialization of these high-index facets is their quite unstability during the PEMFC running. Thus other method that is able to enhance the catalytic property and provide good stability was desired, alloying Pt with other metal has been proved to be such a way that can solve the problem.

Alloying Pt with other non-precious metals has been the hottest area that investigated by researchers and scientists. After alloying Pt with other metal(s) surface electronic structure of Pt catalyst was changed and therefore improved performance of Pt-alloys has been reported in both liquid electrolytes and PEMFCs [85, 89, 90, 92, 142-144]. Three general approaches have been investigated regarding Pt-based alloy catalysts: Pt alloy nanoparticles, Pt core-shells and Pt alloy 1D nanostructures.

2.3.1.1 Pt alloy catalysts

Since the late 1970s, Pt based alloys has been well know as their ability to produce higher oxygen reduction activity in acid electrolytes [145]. In the 1980s, strong commercial interest in the phosphoric acid fuel cell led to an extensive investigation and development of various Pt-based alloy catalysts. Since 1990s, emerging interest has been drawn in PEMFCs due to their high efficiency, low emission, quick start-up and compactness. Thus Pt-based binary and/or ternary alloys were intensively studied towards ORR, which is the reason that caused the high cathode overpotential in a PEMFC. ORR that occurred at a PEMFC cathode has sluggish kinetics due to the complex four-electron involved process, thus lead to high cathode overpotential. Therefore the investigation and better understanding of the ORR mechanism catalyzed by Pt-based catalysts is important in order to supply guidance for the searching of new catalysts with high cathode activity.

In the work carried out by Norskov *et al.*, the strength of adsorption of O and OH additives on the catalysts surface is considered to be the most important factor in predicting the oxygen reduction activity [146-148]. The d-band center is a concept that represent the first moment of the density of states (DOS) projected onto the d-orbital for the surface atoms interacting with the adsorbate; it can be measured and/or calculated as a guidance to predict the capability of an atom to adsorb an adsorbate. The relaxation of d-band will lead to a weak M-OH_{ads} interaction and therefore easy reduction in –OH coverage. The reduction of –OH adsorbate cover layer strongly

affect the catalytic activity as it promotes the O_2 adsorption, dissociation, and reduction by supplying more available active sites.

Fig. 2.3 shows oxygen reduction catalytic activity vs. oxygen binding energy, a classic volcano-shaped curve was observed [149]. The plot of different metals predicts that Pt is not at the peak, which implies catalyst surfaces with better activity could exist. Fig. 2.3 (b) shows the dependency of different Pt_3M alloys, in this result better oxygen reduction activity was calculated from different kinds of Pt_3M alloys.

Fig 2.3 Trends in calculated oxygen reduction activity plotted as a function of the oxygen binding energy on (a) different metal surfaces and (b) Pt_3M alloy surfaces [146, 149].

Experimentally, many kinds of Pt-based alloys (PtCo/C [150-152], PtNi/C [86, 153, 154], PtV/C [86], PtFe/C [25, 155, 156], PtCu/C [16, 27, 157, 158], PtCr/C [159, 160], PtMn/C [161], PtAu/C [162-167], PtIr/C [168-170], and so on) have been prepared and tested in both dilute acid and MEA environments. Their electro-catalytic activity

towards oxygen reduction reaction was of the primary interest, most Pt alloys exhibited better ORR activity as well as stability. These investigations reveal that the ORR activity of Pt-based alloys is affected by several parameters such as the alloy compositions and the atomic ratio of third party metal. In order to study the effects of Pt to other metal atomic ratio, PtM alloy catalyst on carbon blacks supports with different atomic ratios were investigated. It was demonstrated that PtM alloys are able to generate much better catalytic activity and stability when the atomic ratio of Pt to M is 3:1. For example, in a single fuel cell environment, Pt₃Co/C showed much better activity and stability as the cathode catalyst than PtCo/C [171].

Pt alloyed with one or more transition metals have been proved to produce excellent ORR activity, however the drawbacks of using Pt-transition metal alloys as catalyst in PEMFCs is the leaching of transition metals during fuel cell operation; these transition metals may penetrate into the Nafion membrane and cause severe contamination and fuel cell degradation [172]. The dissolution probability of transition metals in Pt-alloys has been demonstrated to be related to the particular metal as well as the atomic ratio. With the increase of transition metal contents, it will be easier for these transition metals to be dissolved during operation. Antolini et al. studied the relationship of transition metal content and its stability in accelerated degradation test (ADT) for Pt_{1-X}M_X (M = Fe, Ni, and Co) [173], demonstrated that when X was small enough, the alloyed PtM is very stable and only unalloyed transition metals will be dissolved. However, when this X value raise up to beyond 0.6, even those alloyed transition metals is not again stable and will be dissolved.

Post treatments of PtM alloys have been proved to be able to increase their stability

[26, 174], such as chemical and electrochemical leaching, heat treatment, et al. It is believed that post heat treatment of Pt-alloys will raise the degree of alloying and bring more crystallized structure; which explains the improved stability after heat treatment. However heat treatment will bring a severe side effect of increased particles size, which will cause the decrease of electrochemical active surface area (ECSA). Other research suggested that Pt-alloys (such as PtCo) possess better sintering resistance with compared to pure Pt, thus heat treatment is still an available method with carefully chosen heating temperature and heating time. Roques et al. investigated the effect of chemical leaching on the improvement of PtCo/C stability [175]. A Part of the PtCo/C catalysts was soaked in 1 M HClO₄ solution for 48 h at room temperature, and then both acid-treated and untreated PtCo/C catalysts were *in-situ* studied by X-ray absorption near-edge structure (XANES) under a potential of 0.9 V vs. RHE. Better stability was observed for acid-treated specimen after 6-10 h of testing, evidenced by the unchanged surface Co oxidation state for acid-treated PtCo/C; however for untreated sample the surface Co oxidation state was changed after the test.

2.3.1.2 Pt core-shell catalysts

Besides the improvement of intrinsic activity of catalyst, engineering Pt alloys by arranging Pt atoms to only the surface and near surface layers has drawn great interests to reduce the cost, improve the catalytic activity and avoid dissolution of other metals in Pt alloy. Such a method will substantially reduce the Pt loading.

Adzic et al. at Brookhaven National Laboratory in the United States proposed the idea of Pt-monolayer on other metal particles as the electrocatalyst [176-184], due to the argument that only surface Pt atoms will participate in the catalysis. Furthermore the structure of Pt monolayer supported on other metals will bring modification of the d-band status of Pt monolayer, which will also help to improve its ORR activity. In their study, 10 times higher mass activity versus ORR were found for Pt/Pd/C core-shell composite than pure Pt catalyst [176], although the size of Pt monolayer on Pd/C substrates is 9 nm and is much higher than Pt nanoparticles of 3.5 nm. In another paper the preparation of Pt monolayer supported on either Ir or Pd₃Co/C and tested the electrochemical activity towards ORR [185], in terms of mass Pt specific activity they produced 1.01 and 0.57 A/mgPt for Pt/Ir and Pt/Pd₃Co/C, respectively. Both of the two values meet the target of 0.44 A/mgPt set by US Department of Energy (DOE).

Strasser *et al.* reported another method to prepare various Pt-alloys such as PtCo [186-188], PtCu [157, 189-191], PtFe [192], PtNi [193, 194], *et al.*. In their process Pt alloys were prepared by an impregnation/freeze drying route and the following annealing and electrochemical dealloying. Commercial Pt/C catalyst were impregnated with aqueous solutions containing other metals, then they were freeze dried in liquid N₂ and annealed to form Pt alloys. At last the catalysts were dealloyed in an electrochemical process to remove the surface non-precious metal atoms to form a core-shell structure with a Pt-poor core and a Pt-rich shell. As reported Pt-Cu alloy was prepared by following the introduced method, the catalysts were characterized using RDE to determine their ORR activities. At 0.9 V an improvement of 4-6 times was reported for dealloyed PtCu catalysts.

Zhang et al. studied Pt monolayer on various supports and they claimed that the composition and structure of the core affect the ORR activities of Pt monolayer strongly [177]. In their studies, Pt monolayer supported on Au/Ni, Pd/Co and Pt/Co nanoparticles were prepared and their ORR activities were characterized using rotating disk electrode (RDE). The ORR activity were compared at 0.85 V, in terms of Pt mass activity it is in the order of [195] > Pt/PdCo/C > Pt/PtCo/C, while in terms of total noble metal mass activity the order is Pt/PtCo/C > Pt/AuNi/C > Pt/PdCo/C.

In summary, Pt based core-shell structure provide a strategy that is promising to reduce the Pt usage and improve the intrinsic activity for PEMFC applications. However most of the processes reported are quite complicated and not easy to be applied into large scale production. Besides, in most cases the size of Pt alloys obtained are still too big (>8 nm) to have a good mass electrocatalytic property. Although Pt-based core-shell structures has shown much better ORR activity in acid solutions, the use of Pt-based core-shell catalyst in a MEA environment is hardly reported.

2.3.1.3 One dimensional Pt and Pt-alloy nanostructures

In the synthesis of Pt nanostructures, by using different metal precursors, reducing agents, and dispersing agents the kinetic and thermodynamic status could be controlled in order to product different Pt morphologies such as Pt nanowire [127, 196, 197], nanodendrites [198-204], nanorods [205-207], *et al.* The use of a strong reduction agent may produce polyhedral nanocrystals, while a mild reduction agent

will facilitate the growth of one dimensional structure. For example, as reported Pt nanowires were produced by using formic acid as the reduction agent, Pt nanodendrites were synthesized when the reduction agent is ascorbic acid, while with the use of NaBH_4 as a strong reduction agent, Pt nanocubes were prepared. The reaction temperature will also affect the reduction rate and nucleation rate of the precursors thus affect the morphology of Pt nanostructures.

Some ions such as Ag^+ , Br^- , Fe^{2+} , Fe^{3+} , and OH^- were found to play an important role in controlling the morphology of Pt nanostructures. These ions will slightly change the surface energy of some specific facets, thus to affect the morphology of metal nanostructures. The surface energy of low-index Pt facets is in the order of $\{111\} < \{100\} < \{200\}$, thus most 1D Pt nanostructures will grow along the $\{111\}$ direction. It was reported that Br^- could reduce the surface energy of $\{100\}$, which will led to a growth of Pt nanostructures grow along both $\{100\}$ and $\{111\}$ direction in a controlled ratio [208]. By adding Ag^+ ions into the solution, a growth of Pt nanostructures along $\{100\}$ direction was also reported [209].

Sun *et al.* [127, 210] produced Pt nanowires on both carbon nanospheres and Nitrogen-doped carbon nanotubes using a simple room temperature long time reduction process, in this process formic acid was utilized as the reducing agent. After a 72 hrs reduction, Pt nanowires were prepared on both carbon nanospheres and CNTs; the Pt nanowires were confirmed to be in single crystalline structure with the growth axis along $\{111\}$ direction. The diameter of Pt nanowires grown on carbon nanospheres were around 4 nm, by controlling the weight ratio of Pt precursor to carbon nanospheres the loadings of Pt nanowires on carbon supports were controlled.

The surface area of Pt nanowires is affected by the diameter of them; Pt nanowires with smaller diameter will expose larger surface area. As reported by Sun *et al.*, nitrogen-doped carbon nanotubes have a very rough surface [210], which will supply a high density of nucleation sites for the growth of Pt nanowires and thus reduce the diameter of Pt nanowires grown on them. Pt nanowires with diameter of about 2.5 nm were produced on nitrogen-doped carbon nanotubes which are much smaller than that grown on carbon nanospheres (4 nm).

Pt and Pt alloy nanotubes were successfully produced and their reaction activity and stability towards ORR were demonstrated to be much better than Pt/C catalysts. Chen *et al.* [211] grown Ag nanowires first and follows a galvanic displacement process to produce a nanocable structure with an Ag core and Pt or PtPd shell. At last the Ag core was removed in acid solutions to form hollow structured Pt or PtPd nanotubes. Pt/C, Pt nanotubes, and PtPd nanotubes were characterized in O₂-saturated H₂SO₄ solution using RDE technique, at 0.85 V PtPd nanotubes shows 5-6 times and Pt nanotubes shows 3 times higher specific activity than Pt/C catalysts. The stability of Pt nanotubes and Pt/C catalysts were also compared in an accelerated degradation test (ADT). After 1000 CV cycles in the potential range of 0 - 1.3 V vs. RHE in Ar-saturated H₂SO₄ solution at 60 °C, a ECSA loss of 20% was observed for Pt nanotubes; which is much better compared to the loss of 90% for Pt/C catalyst. This result reveals that Pt nanotubes possess quite good stability. The synthesis of Pt-alloy nanowires were also reported, PtFe nanowires with length of 200nm and diameter of 2-3 nm were prepared using oleylamine and octadecene as reducing agents.

One dimensional Pt and Pt alloy nanostructures offers better ORR activity and

stability as reported in lots of papers; however most of the works are only tested in acid solution environment. There are very few works on the study of the performance of these one dimensional structures in a MEA, theoretically one dimensional structures could supply better electrons transport and better mass transport, however the design of a MEA using 1D structure as the catalyst should be different from the ways to prepare a MEA using Pt/C catalyst. Thus the design of MEAs using 1D structures as the catalyst to produce good performance need to be addressed in future.

2.3.2 Improved catalyst layer design

The commercialized process to prepare an electrode is the thin film method, in this process proper amount of Pt/C, solvent, and nafion were thoroughly mixed together using ultrasonic treatment. The obtained ink/slurry will be brushed onto the gas diffusion layer, following the hot press process to sandwich a nafion membrane in between two of such electrodes. The catalyst utilization efficiency of MEAs prepared by such a process is quite low. In the past decades a decaling process was intensively studied as a better method to prepare an MEA, in this process catalyst ink will be firstly sprayed on a piece of PTFE thin paper, the catalyst layer will be transferred directly on the membrane by a hot press method. Catalyst utilization efficiency of MEAs prepared by such a decaling process was reported to be in the range of 22% to 45%, which is still very low. Improved thin film method of coating the catalyst ink directly onto the membrane using spraying method is believed to provide better ionic conduction and thus better catalyst utilization.

In order to control the thickness of the catalyst layer prepared by a thin film method, Pt on carbon black with high catalyst loading is needed. As well known when the Pt loading goes higher than 50 wt.%, the Pt particles will suffer from agglomeration and the size will be large. Furthermore, the use of nafion in the ink will isolate some Pt/C catalysts and inhibit the electron conduction pathway of such isolated catalysts. The mass transport pathway in such a catalyst layer is also considered to be quite long.

In order to improve the catalyst utilization efficiency some new methods were proposed to prepare the catalyst layer. Sputtering is a well known method to be able to produce thin and uniform metal layer, extensive efforts have been dedicated to investigate the use of sputtering to prepare an electrode [55]. Another method of electrodeposition has also attracted lots of attention as a new method to prepare electrodes [212, 213]; it is believed that the *in-situ* formed catalyst layer by electrodeposition has better catalyst utilization efficiency in MEAs.

Novel catalyst supports such as CNTs and CNFs have also been studied as their unique properties such as high electron conductivity, high surface area, good corrosion resistance, and excellent thermal and mechanical properties. As the 1D structure, the use of CNTs and CNFs as catalyst supports is considered to facilitate the mass transport as well as electron conduction in the MEA operation.

Recent works on the preparation of improved catalyst layer structure will be reviewed as follow.

2.3.2.1 Modified thin-film methods

The normally used solvent to prepare a catalyst ink is isopropanol, Xiong et al. [214] however mixed water, Pt/C and nafion together to prepare the ink, without use any organic solvents. In this process the nafion membrane was first treated in a solution containing 5% H_2O_2 and 0.2 M NaOH for 1 hr and then let it dry at 60 °C for 15 min. The catalyst ink was painted directly onto both sides of pre-treated membrane. They claimed that as the whole process is carried out at temperatures no more than 80 °C, there is no distortion of the painted area and the membrane, however in conventional process a high temperature of more than 130 °C was used to hot press the electrode and membrane together, at such a high temperature distortions of the catalyst layer and membrane is a common problem that will cause delaminating at the catalyst layer and membrane interface. High performance with Pt loadings of only 0.05 mg/cm² on both the anode and cathode was obtained.

Park et al. [215] studied the effect of various swelling agents with different boiling points including ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TEEG), and glycerol. Catalyst slurry were painted on pre-swollen nafion membrane with these solutions and tested for both PEMFC and direct methanol fuel cells (DMFCs). The use of EG was found to produce the best result. The use of dimethyl sulfoxide (DMSO) as a dispersing agent was found to offer a smooth and dense catalyst layers on the EG pre-swollen membrane, due to the optimal drying rate of EG.

Li *et al.* [31] utilized a simple filtration method to prepare a thin layer of Pt/CNFs, Pt

nanoparticles were deposited on stacked-cup CNFs using ethylene glycol (EG) as the reducing agent. The as-prepared Pt/CNFs will be dispersed in ethanol solution with controlled amount, than this ink was drawn through a 0.2- μm -pore polycarbonated filter paper. After filtration proper amount of nafion was sprayed on this catalyst layer. At last the catalyst layer was transferred to both sides of membrane using a hot pressing method. By this method a thin and uniform Pt/CNFs catalyst layer was produced. The peak power density of Pt/CNFs MEA prepared by filtration method reach around 900 mW/cm^2 , while that of commercial E-TEK based MEA is about 750 mW/cm^2 .

2.3.2.2 CNTs and CNFs as catalyst supports

In the past two decades, under the strong driving force of fuel cell cost reduction and performance optimization in order to achieve the widely commercialization of PEMFCs; CNTs and CNFs have attracted plenty of investigations as the novel catalyst supports for increasing Pt utilization; due to their unique properties such as high surface area, high electric conductivity and good corrosion resistance. The main purposes for using CNT- and CNF-supported Pt catalyst are to reduce Pt loading through increasing the catalyst utilization as well as improving the catalyst activity and stability [216].

In recent years several catalyst supports have been tried for Pt catalyst in PEMFCs in order to replace carbon black. For example, Chai *et al.* [217] proposed spherical carbon capsules with hollow mesoporous core and mesoporous shell structures as

potential catalyst supports . Saha *et al.* [218] reported the fabrication of a 3D core/shell heterostructure consisting tin nanowire core and carbon nanotube shell (SnC) grown directly onto carbon paper as Pt catalyst support. They also studied Tungsten oxide nanowires grown on carbon paper as Pt electrocatalyst support [219]. Ryoo *et al.* [220] proposed nanoporous carbon with high surface area and uniform pore structure as Pt support. Su *et al.* [87] proposed the use of nitrogen-adopted carbon sphere as Pt support with enhanced performance. Conducting polymers such as polyaniline have also been used as Pt support as reported in the papers. Most of this work focused on using a specific morphology and/or high surface area materials for catalyst support to either increase porosity, improve catalyst dispersion or to enhance mass transfer properties.

However, CNFs- and CNTs-supported Pt and Pt alloy electrocatalysts attracted the most active research in terms of catalytic supporting strategies. In comparison with the most widely used Vulcan XC-72R carbon support which has an electronic conductivity of 4.0 S cm^{-1} and specific surface area of $237 \text{ m}^2 \text{ g}^{-1}$, CNT and CNF have significantly higher electronic conductivities of 104 and $103\text{--}104 \text{ S cm}^{-1}$, respectively and extremely high specific surface areas of $200\text{--}900 \text{ m}^2 \text{ g}^{-1}$ [221].

Since CNT and CNF are relatively inert, it is necessary to modify the nature and concentration of surface functional groups in order to deposit Pt particles on their surface. Therefore their pretreatment process and Pt deposition methods could affect the Pt catalyst dispersion and catalytic activity for fuel cell reactions.

Yu *et al.* [222] reported the functionalization of CNTs by oxidation in HNO_3 and $\text{H}_2\text{SO}_4\text{--HNO}_3$. The latter show a relatively higher capability in producing surface functional groups such as carbonyl, carboxyl and hydroxyl. These groups can act as specific nucleation sites for a well-dispersed deposition of smaller Pt nanoparticles on the surface of CNTs.

Yang *et al.* [223] reported the pretreatments of MWCNTs in an acidic mixture of 69% HNO_3 and 98% H_2SO_4 solutions in ultrasonic condition followed with the Pt deposition. Xing [224] reported a sonochemical process to treat CNTs in nitric and sulfuric acids to create surface functional groups for metal nanoparticles deposition. CNTs treated in the sonochemical process were shown to lead to the deposition of uniformly dispersed high loading of Pt nanoparticles. Pt nanoparticles of a size less than 5 nm and loading up to 30 wt% with little aggregation were synthesized on the sonochemically treated carbon nanotubes. Cyclic voltammetry measurements in 1.0 M H_2SO_4 showed that the Pt nanoparticles on carbon nanotubes are more than 100% active in the electrochemical adsorption and desorption of hydrogen than the Pt nanoparticles supported on carbon black.

2.3.2.3 Sputter deposition

Sputter deposition is well known to be able to produce a uniform and ultra-thin (< 10nm) metal layer, thus the use of sputter deposition as a method to produce thin catalyst layer on either the electrode or membrane have attracted numerous investigations. Early study of using sputter deposition technique to prepare MEAs was

conducted by Hirano *et al.*. In their investigation Pt nanocatalysts were sputter deposited on an uncatalyzed carbon black electrode with a loading of 0.1 mgPt/cm^2 . The catalyst layer was confirmed to have a thickness of $1 \text{ }\mu\text{m}$, while another electrode prepared by a conventional method with a loading of 0.4 mgPt/cm^2 was prepared for comparison, the catalyst layer thickness of conventional electrode was $32 \text{ }\mu\text{m}$. At the high current density area, the sputter deposited electrode shows lower power output, they claimed that it was because sputter deposited electrode has lower loading and thus smaller total Pt active surface area. However with regard to the low current density area, sputter deposited electrode shows higher ORR potential than that of conventional electrode. This result suggested that sputter deposited electrode shown higher catalyst utilization, and this technique was promising to prepare electrodes with ultra-low loading.

One of the advantages of sputter deposition technique is that it allows the Pt deposition on a series of substrates, by using different substrates the Pt catalyst layer structure can be optimized. Kim *et al.* [225] compared the deposition of Pt on three different substrates of carbon blacks substrate, CNTs substrate, and a blend of carbon blacks and CNTs substrate. The ECSA of Pt supported on different substrates were measured, Pt/CNTs shown an ECSA value of $16.1 \text{ m}^2/\text{g}$, which is about 2 times higher than Pt/carbon blacks ($9.1 \text{ m}^2/\text{g}$). They claimed that the use of CNTs as substrate allows deeper penetration of Pt catalysts and thus able to produce a more three-dimensional structured catalyst layer structure. The use of a blend of CNTs and carbon blacks (1:1) as substrate display even higher ECSA value of $20.6 \text{ m}^2/\text{g}$, which is 50% higher than CNTs substrate, demonstrated a better catalyst layer structure.

The prime limitation of using sputter deposition technique to prepare MEAs is that it can't deposit Pt deeply into the substrate, thus it is impossible to create electrodes with large Pt active area compared to other methods. When the Pt loading is smaller than 0.05 mgPt/cm^2 , this technique can produce a thin and uniform catalyst layer, however with the increased catalyst loading it can only bring larger Pt particles size and decreased performance. Gruber et al. [55] sputter deposited Pt nanoparticles on gas diffusion layer with different Pt loadings, the polarization performance were tested at ambient temperature and pressure with H_2/O_2 as fuel and oxidant. At the Pt loading of 0.05 mgPt/cm^2 the peak power output was 132 mW/cm^2 , when the catalyst loading was increased to 0.011 mg/cm^2 the peak power output increased to 156 mW/cm^2 . Decreased Pt utilization was observed from this result. The best performance was obtained at the loading of 0.05 mgPt/cm^2 , when the loading was further increased the power output substantially decreased. From this paper we can conclude that although sputter deposition method brings much better mass activity in MEA environment at ultra-low loading, it is still hard to prepare MEAs with specific activity and longtime stability that is comparable to MEAs prepared by thin film method.

In order to obtain a deeper penetration of Pt catalyst, novel substrate of CNTs or CNFs grown directly on carbon paper as the substrate was studied by various labs. Chen et al. [226] prepared CNTs on carbon cloth by a microwave-assisted CVD method, in this process the loadings of CNTs could be improved by adjusting the negative bias voltage. Pt nanoparticles with diameters of around 2 nm were then deposited on the CNTs/carbon cloth substrate. Sun et al. [227] first grown nitrogen-containing CNTs on a silicon substrate by microwave-plasma-enhanced CVD method, after that Pt

nanoparticles with 2 nm diameter were also prepared using sputter deposition technique. Tang et al. [41, 228] grown CNTs directly on carbon papers, follows the sputter deposition of Pt nanoparticles. The Pt/CNTs/carbon paper electrode was tested in a single cell as the cathode, a remarkable improvement of Pt mass activity compared to a commercial Pt/VXC72R-based electrode was observed. The electrochemical stability of both Pt/CNTs and Pt/VXC72R electrodes were tested in an accelerated degradation test, after 100 oxidation cycles between 0.6 and 1.8 V, the Pt/VXC72R electrode lost 80% of its performance while Pt/CNTs based electrode lost only 50% percent of its original performance. The better electrochemical corrosion resistance might be attributed to the novel CNTs/carbon paper substrate.

Remarkable improvement in mass activities were reported in a lot of investigations with the use of sputter deposition method, especially at low Pt loadings below 0.05 mgPt/cm², however the specific activity is still lower than electrodes prepared by commercial thin film method. The specific power output is as important as mass power output, so the specific power output need to be largely improved before sputter deposition technique could be adopted as a commercial process for the production of electrodes.

2.3.2.4 Electrodeposition

Electrodeposition is another method that able to create thin catalyst layer, this method is believed to produce higher catalyst utilization than other methods as the catalyst is deposited at those sites that are in contact with both electronic and ionic pathways.

The catalyst layer created by this method has very high Pt to C ratio at the surface of the electrode; with larger distance away from the electrode surface this Pt to C ratio become smaller. Compared with sputter deposition technique, electrodeposition is able to produce a catalyst layer with a thickness of more than 10 μm , which is about 10 times thicker than that created by sputter deposition. The utilization of electrodeposition method to prepare Pt nanoparticles on various carbon substrates has been intensively studied to improve the catalyst utilization efficiency and reduce Pt loading.

Taylor *et al.* [229] explored the use of pulse electrodeposition to prepare electrodes with low Pt loading. In this process nafion bonded uncatalyzed carbon black electrode was used as the substrate, this substrate was dipped into a Pt-containing solution and used as a working electrode, a pulse wave was used to deposit Pt nanoparticles on nafion-bonded carbon blacks. It was claimed that this method supply good ion and electron conduction of the electrode. Pt nanoparticles of 2-4 nm were found to be formed on the nafion-bonded carbon black electrode at a low loading of 0.5 mgPt/cm^2 . ORR activity of such electrode was characterized in acid solution, compared with a conventional E-TEK electrode, the electrodeposited electrode presented 10-fold higher mass activity. The remarkable result was attributed to the large improvement of Pt utilization efficiency. Antoine *et al.* [230] proposed a different electrodeposition process to prepare carbon supported Pt catalysts. In this method Pt containing solution was first impregnated in carbon supports, and then a pulsed current was applied to deposit the pre-impregnated Pt ions. Pt particles with diameter of 2-4 nm were prepared at a loading of 20 wt.%.

There are several studies focused on the optimization of electrodeposition process to obtain smaller Pt size, better Pt dispersion, and better electrochemical activity. Kim *et al.* [47] explored the effect of pulse electrodeposition parameters on the cell performance of as-prepared MEAs. In this study, an organic solvent treated carbon black layer was used as the catalyst support. The carbon black electrode was loaded on a copper plate-coupled sample holder and used as the working electrode in a Pt salt-containing electrolyte. A pulse wave was then applied to the electrode to deposit Pt nanoparticles, different parameters such as current densities, on time and off time, and total charge density were investigated in order to optimize the catalyst deposition. Using a current density of 400 mA/cm^2 , a duty cycle of 2.9% and a total charge of 8 C/cm^2 , a $\sim 6 \text{ }\mu\text{m}$ thick catalyst layer was obtained with a high Pt to carbon ration up to 75 wt.% near the surface of the electrode, a current output of 380 mA/cm^2 was obtained at 0.8 V.

Chen *et al.* investigated the effect of different additives in the electrolyte [57], different amount of glycerol was added into the electrolyte to increase the viscosity. In this work a CNTs modified carbon fiber was used as the substrate, pulse electrodeposition was used to deposit Pt catalysts, it was demonstrated that Pt nanoparticles size was controlled with different amount of glycerol in the electrolyte. Pt nanoparticles in the range of 2-3 nm diameters were successfully deposited on CNTs/CF. Saminathan *et al.* [231] electrodeposited catalysts on *in situ* grown CNTs on carbon paper, a direct current electrodeposition at various voltages of -0.3, -0.6, -1.2, -2.4, and -3.6 V vs SCE were used, at -0.6 V a highly uniform Pt nanoparticles on CNTs/carbon paper was obtained, while at other voltages Pt dispersion were

non-uniform. These as-prepared electrodes were also tested in single cell environment; a peak power output of 441 mW/cm^2 was obtained with a Pt loading of 0.13 mg/cm^2 at -0.6 V . The Pt particles size calculated by XRD was 6.18 nm .

Pt catalysts electrodeposited on CNTs and CNFs have been reported on several papers, Wang *et al.* [35] first produce a CNTs layer on carbon paper by a CVD method, then Pt nanoparticles in the range of about 25 nm diameter was decorated on CNTs by direct current electrodeposition. This electrode presented higher catalyst utilization efficiency compared with an E-TEK conventional electrode, however due to the large Pt particles size the power output is low. Guo *et al.* [232] used a three-step process to electrodeposit Pt catalysts on single wall carbon nanotubes (SWCNTs). In the first step, SWCNTs were electrochemically cycled between the potential ranges of -0.4 and 1.8 V (vs. SCE) in 0.5 M NaSO_4 solution to incorporate functional site groups includes carboxylate, carbonyl, and hydroxide on the surface of SWCNTs. After that the activated SWCNTs were cycled in a $2.5 \text{ mM K}_2\text{PtCl}_6$ solution between 0.3 and 1.3 V (vs. SCE), after this operation Pt ions were adsorbed on those functional groups. At last, these adsorbed Pt ions were reduced to Pt nanocrystals by an electrochemical cycling between the potential range of -2.5 and 1.6 V (vs. SCE) in $0.1 \text{ M H}_2\text{SO}_4$. The as-prepared Pt/SWCNTs presented a uniformly distributed particle with size in the range of $4\text{-}6 \text{ nm}$, the catalysts showed good electrocatalytic activity towards methanol oxidation reaction (MOR).

Electrodeposition is able to produce ultra high Pt to carbon ratio at the surface of the electrodes with a catalyst layer thickness of $\sim 10 \text{ }\mu\text{m}$, thus it is possible to improve the catalyst utilization efficiency at a practical Pt loading. Compared to sputter deposition,

which is only able to improve the catalyst utilization efficiency at ultra-low catalyst loading ($\sim 0.04 \text{ mgPt/cm}^2$), electrodeposition shows brighter future as a constitution process for the mass production of fuel cell electrodes.

2.4 Introduction of pulse electrodeposition

In order to obtain uniformly distributed PtFeNi catalyst nanoparticles on the electrode, it's very important to first produce a uniform FeNi distribution during the electrodeposition process. In an electrodeposition process, the metal ions are first transferred to the cathode as adatoms by the charge transfer reaction. Then these adatoms will either form new nucleation or just keep growing on the existing crystals. The whole process is controlled by the rate of charge transfer and the surface diffusion rate of adatoms. When the charge transfer rate is fast and in domination, the nucleation rate will increase and form a finer crystal grain. However, when the surface diffusion is relatively faster and dominate the electrodeposition process, the crystals will grow larger.

Fig 2.4. Illustration of a typical pulse electrodeposition waveform

Pulse electrodeposition is composed of repeated current on and current off intervals compared to direct current deposition. Pulse electrodeposition enables higher current density, as the current off intervals supply higher concentration of metal ions to the surface of the electrode. Higher current density brings faster charge transfer rate, and thus finer crystal structure. Fig 2.4 shows the illustration of pulse electrodeposition waveform. Several operating parameters can be changed in pulsed electrodeposition, such as current on-time (T_{on}), current off-time (T_{off}), current density at on-time (J_p). Thus it is possible to control the pulse deposition by changing these parameters to vary the mass transport, crystallization, and particles size. To direct current deposition, there are only two parameters, i.e., current density and deposition time can be varied.

Pulse electrodeposition has been demonstrated as the most promising method to prepare metal thin films and other nanostructures like nanodots, nanowires, and

nanodendrites, etc. Devaraj et al. used electrodeposition to prepare copper thin film [233]. In their work, pulse electrodeposited copper film shown finer grain and denser structure. As reported by Ibl et al. [234], denser gold film with less porosity was produced using pulse electrodeposition. Finer grained nickel structures were also produced by Kim et al. using pulse electrodeposition method [235]. Hydrogen evolution reaction is one of the major problems that decrease the mechanical property of electrodeposited metal films. A decrease of hydrogen content and therefore a denser metal structure observed in pulse electrodeposited palladium have also been reported by Yoshimura et al [236]. Investigations of the production of various metal films with finer grain and less porosity by pulse electrodeposition have also been reported [58, 237, 238].

Pulse electrodeposition of metal nanoparticle has attracted plenty of interest in use for PEMFCs applications. Chen et al. reported the synthesis of Pt nanoparticles with size in the range of 2-3 nm on CNTs using pulsed electrodeposition [57]. In their work, glycerol was added into the electrolyte as additives to produce a viscous electrolyte, which is able to help deposit smaller Pt particles size.

2.4.1 Limiting factors of Pulse electrodeposition

With the advancing of electrochemical equipments, it is now possible to use some extreme pulse electrodeposition parameters, i.e., ultra-short pulse-on, pulse-off time, and high voltage. However, it is unfortunately that the usable range of these parameters is not unlimited. In a real operation if the pulse wave parameters are

beyond the suitable range, adverse effects will come along. The existing limiting factors mainly attributed to two parts: (1) double-layer capacitance and (2) mass transport property.

When there is a voltage applied to the electrode, the total current (J_t) generated can be decomposed into two parts: the first one is faradic current (J_f) and the second one is capacitive current (J_c). J_c is a current that charges the double layer. After a short time that is required to charge the electrode, J_c is becoming negligible. Puippe et al. suggested that the charge time must be longer than the pulse-on time, otherwise the pulse waveform will be seriously distorted [234]. Due to the same reason, pulse off time should also be longer than the discharge time. The charge/discharge time is closely related to the current density as well as the physical and chemical nature of the electrode (diffusivity, roughness, wettability, cleanliness, etc.) and the electrolyte (conductivity, concentration, etc.).

The double layer charge/discharge time could be calculated out by numerical methods, but such numerical methods are rather complicated. In order to have a quick acquiring of the charge/discharge time, Puippe et al. provided a very simple empirical formula as follows [239].

$$T_c = 17/J_t$$

$$T_d = 120/J_p$$

where T_c and T_d are charge and discharge times, respectively, in microseconds and in A/cm^2 for J_p .

Apart from the operating parameters limitation caused by double layer capacitance, ions transportation either in the electrolyte or on electrode/electrolyte interface also reduce the usable range of electrodeposition parameters. In detail, when a current on-pulse is applied on an electrode, metal cations near the electrodes will suddenly be consumed and therefore form a cation depletion layer. Such a cation depletion layer resulted that a high current density/voltage is not able to be used. Ibl *et al.* explained the ions transportation limitation in a double diffusion-layer model, in which the cation depletion layer is divided into two sublayers [234]:

(1) The pulsating diffusion layer (δ_p) located nearby the cathode surface, in this sublayer the concentration pulsates with the frequency of the pulse current waveform. In detail, the ion concentration in this layer decreases during the current on-pulses, and replenished in the current off-times,

(2) The stationary outer diffusion layer (δ_s) that shows a steady concentration gradient which extends well into the electrolyte.

Fig 2.5 presents the concentration profiles in diffusion layers when there is a current on-pulse applied onto the electrode. At where near the electrode surface, the concentration of metal cations was depleted after the current on-pulse, therefore to form a pulsating diffusion layer. As the distance being even farther away from the electrode surface, another stationary diffusion layer will also be formed during the whole electrodeposition period.

The limitations caused by these two different diffusion layers are quite different and will be described below:

- (1) The depletion of metal cations in the pulsating diffusion layer limits the use of maximum peak current density,
- (2) The depletion of metal cations in the stationary diffusion layer limits the average current density.

Fig 2.5 Concentration profiles of the diffusion layers in pulse electrodeposition immediately after a current pulse was applied to the electrode

2.4.2 Effect of operating parameters on the catalyst size and structure

The discussion and investigation of how the pulse parameters such as peak current density, pulse-on time, and pulse-off time affect the final structure (grain size, porosity, uniformity, etc.) have been intensively reported [240-242]. In the following discussions, the influence of these parameters will be reviewed and summarized. It should be noted that the results reported by different researchers for a similar

electrolyte-electrode system are often in contradiction, which are ascribed to many reasons as described below:

(1) The complexity of the electrodeposition process which will be affected by many parameters involved in the electrode, electrolyte, and the operating environment.

(2) The experimental variables in electroplating are too large thus it is very hard to control.

(3) The lack of standardized procedure in investigating the general effect of a certain pulse parameter.

In general, a common area that studied by researchers is the influence of duty cycle or pulse frequency on the final structure and physical/chemical properties of electrodeposits. However, because these parameters are only mathematical quantities that extracted from the real pulse parameters (i.e., T_{on} and T_{off}), so they cannot explain the effect of T_{on} and T_{off} accurately. For example, Sun *et al.* [243] investigated the effect of pulse frequency on nickel electrodeposition by fixing a constant duty cycle and peak current density. However, in real operation with the increasing of frequency, there will also be simultaneously decrease of other important parameters that will affect the results, i.e., the pulse on-time and off-time. Thus it is rather difficult to accurately resolve the effect of a single parameter separately.

2.4.2.1 Influence of peak current density

Electrodeposited particles size distribution is of the primary interest in many areas, especially in catalysis field. Peak current density has large influence on the deposited particles size, in general, smaller particles size could be obtained with large peak current density. There has been many researches to study the influence of peak current density on the structure and morphology of deposits. For example, Pippe *et al.* [234, 244] use pulse electrodeposition method to prepare gold, cadmium, palladium and copper structures, in this study finer deposits structure were obtained with the use of higher peak current densities. In other works, finer Ni nanostructure were also produced when higher peak current densities were used in the pulsed electrodeposition of Ni [237, 245].

The smaller crystal size obtained with the use of a higher peak current density could be attributed to the higher overpotential generated in the electrode surface. It is believed that higher overpotential on the electrode surface is able to substantially increase/decrease the free Gibbs energy needed for the form of new nucleis, which means higher nucleation rate and therefore finer grain structure and/or smaller crystal size.

2.4.2.2 Influence of current on time

The current on time is another important parameter that will affect electrodeposit structures and morphology. The influence of pulse on-time have been reported in

many papers and scientific reports. Rehrig et al. [246] use a constant peak current density and duty cycle, while a changed pulse on time to investigated the effect of pulse on-time on gold electrodeposits. In this paper, smaller gold particles size with longer pulse on time was observed. The decreased particles size was explained by more available nucleation sites with longer pulse on-time. What's more interesting is that the preferred crystal growth direction also changed from (111) to (100) orientation with longer pulse on-time. Puippe and Ibl [247] however use constant peak current density and pulse off-time, in this study larger cadmium crystal size was observed with the use of longer pulse-on time from 0.03 to 1 millisecond. It was explained that during the off-time growth centers are blocked, thus new crystal nucleis are only formed at a new pulse. Therefore, longer pulse on-time will build up the existing nuclei to larger size. In other reports, Knödler [248] prepared refined silver crystal structure with the use of increased pulse on-time. It was claimed that longer pulse on-time brings higher overpotential which attributes to the finer crystal structure. Yoshimura et al. [236] also reported that there is an increase tendency of overpotential by using longer pulse on-time.

The increase tendency of electrodeposits particles size with longer pulse on-time can also be found in other papers. Devaraj et al. [233] reported such an increase tendency of copper crystal particles size with the use of longer pulse on-time. Kim et al. [235] investigated the use of different current on-time ranged from 1 to 1000 milliseconds for nickel electrodeposition, an increase tendency of nickel grain size with the use of longer current on-time was observed. They explained that with the use of longer pulse on-time there will be smaller overpotential on the electrode and therefore larger grain

size.

In summary, the study of pulse on-time factor is closely related to the time range as well as the electrode-electrolyte system used, otherwise there would be some contradictory results that obtained. In particular, when a too long pulse on-time is used (> tens of milliseconds), an increase tendency in the grain size were reported consistently in almost all literatures.

2.4.2.3 Influence of current off-time

Pulse off-time has been reported as another important factor that affect the electrodeposits structure in a series of literatures [238, 249]. During the pulse off-time, the pulsating diffusion layer will be compensated. Despite this compensation, there are still three other processes will also present to affect the whole process, which are listed as below:

- (1) recrystallization or grain growth,
- (2) adsorption/desorption of ions or addition agents,
- (3) corrosion.

Puippe et al. [244] studied the effect of current off-time at constant peak current density and current on-time for the pulse electrodeposition of cadmium, gold, and copper. The study revealed different result for different species. Cadmium grain refinement was observed with longer current off-time, while gold and copper shown

grain growth with longer current off-time. Copper and gold grain growth was explained by their recrystallization in the off-time. The authors claimed that larger grains are thermodynamically more stable, and therefore, longer off-time will supply more times for the crystal to stabilize with grain growth. The contrasting behavior observed for cadmium was explained in terms of deactivation of growth centers due to adsorption of grain growth inhibiting species, probably sulfate ions, during the off-time. Knödler [250] reported the electrodeposition of silver from ethylenediamine, ammonia and thiocyanate baths. An increase in pulse off-time resulted in an increase in the grain size of the deposits obtained from the ammonia and thiocyanate baths, but the opposite trend was observed in the case of ethylenediamine bath.

Kolliar et al. [245] studied the influence of pulse parameters on nickel electrodeposited on a rotating disc electrode from an additive-free Watts bath. Nickel electrodeposits were obtained at constant frequency of 10^{-2} Hz, but for two different duty cycles, 95% and 2% (i.e., $T_{\text{off}} = 9.8$ and 0.5 seconds, respectively). An increase in the pulse off-time was found to yield finer grain size deposits. The authors attributed the decrease in crystal size with prolonged off-time to possible poisoning of growth sites due to adsorption of anions or other foreign species from the bulk solution. In another study, Sun et al. [243] reported that nickel electrodeposits from an additive-free bath pulse-plated at constant duty cycle and peak current density showed a decrease in crystal size with increasing off-time. This behavior was also attributed to deactivation of the growth centers as a result of oxide formation and/or adsorption of a metal-impurity.

From the previous discussion it is clear that a general trend for the influence of pulse

on-time and off-time on the deposit characteristics cannot be predicted, a priori, from the experiments. Indeed, Puipe and Ibl [181] pointed out that the on-and off-time do not always influence the structure in the same direction. This is because the electrocrystallization process is strongly affected by adsorption and desorption processes which are system-dependent.

2.5 Conclusion

In this chapter, the working principle of PEMFCs and its technical challenges for commercialization were reviewed. Cost issue is the primary barrier that limits its commercialization, thus reduced use of noble Pt catalyst has been the hot topic in PEMFCs community. The detailed description of fuel cell performance was discussed in this chapter in order to have guidance on how to reduce the Pt loading at the cathode, especially. Most of the works on reducing Pt loading were contributed in two ways: either by enhancing the catalyst electrocatalytic activity or by optimizing the catalyst layer structure.

Those works on reducing the Pt loading were systematically reviewed, the use of Pt alloys catalyst, Pt core-shell alloy catalyst, and Pt one dimensional structures are able to improve the intrinsic catalytic properties. On the other hand, various methods aimed to provide an enhanced catalyst layer structure that is able to improve catalyst utilization efficiency as well as electrons, protons, and mass transport efficiency are reviewed. Most of these works can be categorized into the following methods: modified thin-film method, novel catalyst supports such as CNTs and CNFs, sputter

deposition, and electrodeposition.

Based on the review, reduced use of noble Pt catalyst will be studied in this thesis to address the cost issue through two ways: either by improving its intrinsic catalytic properties or by improving catalyst utilization efficiency.

CHAPTER 3. Carbon Nanofibers *in situ* Grown on Carbon Paper as Catalyst Support for PEMFCs Cathodes

3.1 Introduction

A new MEA design is studied as to improve the PEMFC performance from the three following aspects:

1. Improve the Pt catalyst utilization and distribution;
2. Mass transfer problems in the catalyst layer;
3. Durability problems in the catalyst layer.

In this new MEA design, carbon nanofibers (CNF) were directly grown on carbon paper backing by a chemical vapour deposition (CVD) process. After that the CNFs/CP composites were functionalized by citric acid. Pt nanodots are deposited on to these CNFs by an impregnation-reduction method. The Pt reduction is performed in Ar/H₂ stream at 140 °C for 40min.

Carbon nanofibers (CNFs) based three dimensional hierarchical micro-porous layer was prepared on one side of carbon paper by a chemical vapor deposition process. Platinum nanoparticles with an average diameter of around 2 nm were deposited on CNFs/carbon paper by a simple impregnation method. Cyclic voltammetry was used to measure the electrochemical active area. The Pt/CNFs/carbon paper electrodes with catalyst loading of 0.07 and 0.14 mgPt/cm² were tested as the cathodes in PEMFC

environment using humidified H_2 and O_2 at room temperature and atmosphere pressure. The Pt/CNFs membrane electrode assemblies (MEAs) exhibit 50% (0.14 mgPt/cm^2) and 70% (0.07 mgPt/cm^2) higher cathode Pt mass power output than that using Pt/C (0.4 mgPt/cm^2) MEA.

3.2 The problem of low Pt utilization in a conventional PEMFC

The largely use of Pt in PEMFCs is the major barrier for its commercialization, because Pt is the major contributor to its high costs. Thus, method to reduce the Pt loading and at the same time maintaining the fuel cell performance is of the primary interest to PEMFC community. In a conventional PEMFC, the catalyst is well dispersed nanosized Pt particles decorated on Vulcan X-72 carbon blacks. One of the most important parameters for such Pt/C catalyst is the active Pt surface area, which is determined by its size. Smaller size will bring larger Pt surface area and therefore better Pt mass power output. It can be described as total Pt surface area per gram of Pt.

Most of the efforts were contributed to lower the cathode Pt loading by improving the oxygen reaction reduction (ORR) catalytic activity and optimizing the cathode catalyst layer structure. The hydrogen oxidation reaction (HOR) happen at the anode is fast, and the anode overpotential is negligible compared with the cathode overpotential. It is much easier to obtain low anode Pt loading and many works have been reported on the successfully decrease of anode Pt loading [251].

In order to make clear the principles of reducing Pt loading and to improve the catalyst

utilization efficiency, the detailed description of the ORR occurred at the cathode was introduced as follows:

The major processes happening inside the cathode catalyst layer can be summarized into the following four sub-steps:

1. Firstly is the diffusion of reaction agents of oxygen or air through the gas diffusion layer into the catalyst layer, in this step the multi-pore structure of the catalyst layer provides gas transport pathways.

2. Secondly is the oxygen dissolution at electrolyte structures interface: The oxygen molecules dissolve into the Nafion structures and become part of the ionomer phase.

3. After the dissolution of oxygen species into the ionomer networks, these oxygen species will diffuse to the catalyst-Nafion interface.

4. Lastly is the ORR on the catalyst surface: those oxygen species that arrived at active catalyst site will react with protons that come from the anode and electrons to form water.

Any of the four steps have strong influence in the overall ORR that taken place in the cathode catalyst layer. It should be noted that each steps may cause limitations on the fuel cell performance, therefore it is also helpful to have a clear understanding of the detailed catalyst layer micro-structure.

In terms of the anode process, after the fast HOR those electrons will be conducted out

to a circuit through Vulcan X-72 carbon supports and the carbon paper backing, and at the same time protons conducted to the cathode through a proton conduction electrolyte of Nafion membrane.

In summary the active catalyst surfaces are those located at the 3-phase boundary of Pt-C-Nafion. In detail, the utilized Pt catalyst should be in good connection with the carbon paper backing to provide electronic transport pathway, while the good connection with Nafion networks will enable the transportation of protons. Furthermore, a good transportation of chemical species and final products are also very important. This is the low Pt utilization problem which is the primary problem in a conventional catalyst layer shown in Fig 3.1.

Fig 3.1 Cross section of a membrane electrode assembly representing its low Pt utilization

In order to better understand this problem, the catalyst layer structure in a

conventional PEMFC and its preparation process is described in the following section.

The PEMFC catalyst layer is made of Pt/carbon blacks and Nafion ionomer; it is presented in a porous structure. Usually, the platinum particles are formed in a thermodynamically favored spherical shape with diameter of 2-5 nm, and the most commonly employed carbon support, Vulcan XC-72, is 20-50 nm diameters in size. Pt to carbon weight ratio is an important parameter. A high Pt to carbon ratio is favorable in order to make a thin catalyst layer that will promote better electrons, protons and mass transports. However, the increase of Pt to carbon ratio will usually lead to the increase of Pt particles size.

Carbon supported Pt catalysts resulted a 10-100 fold increase in Pt surface area as compared to the unsupported Pt particles that used in the very early PEMFCs. The Nafion networks in the catalyst layer acts as a binder of Pt/carbon blacks as well as supplying the pathway for protons conduction. A commonly used Nafion loading in both anode and cathode has been reported to be around 1-2 mg/cm² varies as different carbon supports and catalyst layer structures.

As stated earlier, typical thickness of catalyst layers range from 10 micros to 50 microns. The catalyst layer thickness varies as the change of the catalyst ink/slurry composition, catalyst loading, and the catalyst layer fabrication process. The fabrication process has strong effect on the catalyst layer structure and thickness, and therefore determine the final performance.

Agglomerate structures have been described to interpret the catalyst layer structure of the catalyst layer prepared with Pt/carbon black supports, especially in the

mathematical modeling works [252, 253]. Actually, the study on the detailed catalyst layer structure and the reactions processes occurred in the electrodes were driven by the efforts that have been done on the mathematical modeling.

The agglomerate model of catalyst layer emphasize that the catalyst layer structure was composed of spherical Pt/carbon blacks agglomerates with multi-pores in-between the space of such agglomerates. The spaces in between the agglomerates are occupied by either Nafion electrolyte or with water, while the agglomerate is considered to be covered with a film of ionomer. The catalyst layer (CL) is then a porous structure made of random aggregates of the agglomerates.

In the catalyst layers, the reaction only occurs at where transportation pathways for conduction of electrons, protons and reaction agents (oxygen, hydrogen, and/or air) exist. More specifically, the anode HOR and cathode ORR happens only at those catalyst particles surface covered with Nafion electrolyte, which is able to dissolve the gaseous reaction agents. Furthermore, all components involved in the PEMFC electrochemical reaction such as electrons, protons, reactants (O_2 /air, H_2), and by-products (H_2O) must be transported to the active catalyst surface as facile as possible. In brief, both the anode and cathode reactions take place at atomistic and nanoscale in the catalyst layer including the micro-scale and nano-scale transport of charged and chemical species.

In a conventional process, the electrode is prepared on a carbon paper. The preparation of a micro-porous layer before applying the catalyst layer has been proven to be able to largely improve its performance [254] [255, 256]. Gas diffusion slurry/ink is

prepared by thoroughly mix carbon black particles together with PTFE and isopropanol. This ink/slurry is applied onto PTFE treated carbon paper using an either brushing or micro-spraying method. After that, the catalyst layer will be added on this gas diffusion layer. Similarly, the catalyst ink is prepared by thoroughly mix Pt/carbon blacks and Nafion in isopropanol solvent by an ultrasonication treatment. The isopropanol solvent will be removed in the following hot pressing treatment.

The loading of Pt, Nafion and PTFE will affect the structure, porosity, hydrophobicity, gas permeability, mass transport and electron conduction of the catalyst layer and thus affect the performance. Furthermore, the application process of applying catalyst ink also affects the dispersion and uniformity as well as performance. Finally a Nafion membrane is sandwiched by two of such electrodes by a hot pressing method to form a conventional MEA as shown in Fig 3.1.

As mentioned before, in order to catalyze the reaction, pathways for both proton and electron from the catalyst are needed. However, because of agglomeration not all Pt particles are in electrical contact with both the carbon backing and Nafion membrane. As show in Fig 3.1, Pt particles in white circles are detached from either protonic or electronic path in the catalyst layer. This is the main drawback of conventional PTFE-bonded electrodes, thus the Pt utilization is low. The utilization of Pt is defined as the surface area of Pt that is used for electrochemical reaction as compared to the total surface area of Pt in the catalyst layer.

3.2 New MEA structure design

Here a new structure of the catalyst layer is proposed and is shown in Fig. 3.2. This alternative microstructure consists of CNFs supported well dispersed platinum on its outer surface and covered by a thin layer of Nafion.

Fig 3.2 Illustration of (a): conventional catalyst structure and (b): new CNFs based catalyst structure

In this approach CNFs were grown directly onto the carbon paper and then Pt particles are deposited on CNFs, to ensure that every Pt particles is in electrical contact with the carbon paper backing. So, after applying Nafion in the right place and form a channel to the membrane the proton conduction problem is solved. In this structure (Fig 3.2 (b)) the oxygen diffusion length is short in comparison to agglomerate structure shown in Fig 3.2 (a). This results in less resistance to diffusion and potentially a more utilized catalyst. Furthermore, some studies reported that CNF support would also help to

reduce the rate of degradation since CNFs are more stable than carbon black.

A schematic of the whole preparation process of new designed MEA is presented in Fig 3.3. The whole procedure includes the following steps;

1. Prepare the metal particles (Fe, Co, Ni or alloy etc.), which will catalyze the growth of CNFs on carbon paper by means of physical sputtering deposition or electrodeposition.
2. *In situ* growth of carbon nanofibers (CNF) directly on carbon paper by chemical vapor deposition (CVD) method.
3. Functionalization of the as-synthesized CNFs/carbon paper composites and then deposit Pt catalyst particles on the surface of functionalized CNFs.
4. Apply appropriate amount of Nafion onto the above-prepared electrode.
5. Finally prepare the MEA by sandwiching a Nafion membrane between a commercial anode and a novel designed cathode using a hot press method.

Fig 3.3 Description of the whole process to prepare a new designed MEA

3.3 Preparation of CNFs directly on carbon papers

Carbon nanofibers preparation is the first major step in the new designed MEA approach. There are two key processes for the growth of nanofibers: first is the

catalyst preparation, second is the CVD growth.

Carbon nanofibers and carbon nanotubes grown directly on the fibers of carbon paper has been intensively investigated these years, such as Dodelet *et al.* at The University of Western Ontario [257]; Yan *et al.* at University of California, Riverside [35]; and Dai *et al.* at The University of Dayton [257, 258]. Dodelet *et al.* produced carbon nanotubes by an ohmic heating method. To the catalyst was prepared by dipping carbon paper in solution containing silica and group VIII metal salts. While Yan *et al.* electrodeposited Co particles onto the carbon paper and produced carbon nanotube by a CVD method, and then Pt particles were also electrodeposited onto the surface of carbon nanotubes. Dai *et al.* successfully synthesized aligned carbon nanotubes on carbon fibers via pyrolysis of iron (ii) phthalocyanine (FePc). They first prepared a SiO₂ coating which was used to facilitate the growth of aligned carbon nanotubes.

3.3.1 Electrodeposition of catalyst

In the work of Dodelet *et al.* [257], although they obtained MWCNTs on carbon paper, electrical contact between MWCNTs and carbon paper could be hindered due to the use of silica. So here two other different ways were tried for the preparation of catalyst, sputtering and electrodeposition; which can ensure that the catalyst particles and subsequent CNFs formed are in electrical contact with the carbon paper backings. Thus, it secures the electronic pathway for every CNFs and hence every Pt particles to the carbon paper backings.

It is well known that the morphology of the as prepared catalyst will greatly affect the morphology of the CNFs or CNTs obtained, especially the diameter. Larger catalyst particles will produce CNFs or CNTs with larger diameters, and vice versa. CNTs or CNFs with smaller diameter will have larger surface area with respect to their mass. So catalyst deposited with smaller size is studied. There have been several other efforts in literature to study the yield of CNFs or CNTs by controlling the reaction conditions such as temperature, gas phase compositions and so on. There were many investigations with regard to the effect of catalyst. Many scientists have found that alloy catalysts of transition metals (Fe, Co, Ni and Mo) can produce higher yield and good purity of carbon nanotubes. So, the electrochemically deposited alloy catalysts of Fe and Ni are adopted.

The first method used to prepare the catalyst is electrodeposition. The catalyst preparation is achieved by a three-electrode dc method in a nickel and iron containing electrolyte (every litre of the electrolyte contain 30g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 200g $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 50g H_3BO_3 , 60g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1g Ascorbic Acid). Potentiostatic electrodeposition method is used with a potential of -0.9 vs AgCl/Ag (1M KCl).

Fig 3.4 Fe/Ni alloy particles deposited onto carbon paper by potentiostatic electrodeposition method with different loadings; (a) is 1 coulombs/cm⁻², (b) is 2 coulombs/cm⁻², (c) is 6 coulombs/cm⁻², insert picture in (a) is the raw carbon paper

Fig 3.4 shows the result of Fe-Ni particles deposited onto carbon paper. By assuming that the yield of electrodeposition is 100%, the total loading of Fe/Ni can be easily controlled by adjusting the total charges transferred. The total charges transferred for

Fig 3.4 (a) is 1 coulombs cm^{-2} , Fig 3.4 (b) is 2 coulombs cm^{-2} , and Fig 3.4 (c) is 6 coulombs cm^{-2} , which is corresponding to about 0.3 mg cm^{-2} , 0.6 mg cm^{-2} and 1.8 mg cm^{-2} , respectively. By comparison one can see clearly that higher loading induced larger catalyst particles, thus theoretically it should produce CNFs or CNTs with larger diameter.

Fig 3.5 SEM and optical images of CNFs grown on carbon papers with 0.6 mg cm^{-2} Fe-Ni alloy catalysts. (a) Image of CNFs as grow on raw carbon paper (upper one) and activated carbon paper (lower one); (b) is the back side of CNFs grown on activated carbon paper; (c) is the SEM image of CNFs grown on activated carbon paper, (d) is the cross section of CNFs grown on activated carbon paper

The direct CVD growth of CNFs on carbon paper with Fe-Ni alloy catalyst does not

give any good results. The growth of CNFs is not uniform and the productivity is quite low.

Activation of the carbon paper before applying electrodeposition has been found to be very important. Activated carbon fibers on carbon paper will have a highly microporous surface and better wettability than raw carbon fiber; these properties will help to obtain a uniform dispersion of the electrodeposited Fe-Ni catalyst metal particles. Fig 3.5 (a) shows the image of CNFs as grown on raw carbon paper (upper one) and activated carbon paper (lower one). From the image one can see that without activation of carbon paper, the distribution of as grown CNFs is not uniform. So here a pretreatment process is adopted before the electrodeposition. The standard activation process is described as follows:

- (1) Immerse the raw carbon paper into ethanol to evacuate the air inside the carbon paper;

- (2) Insert the carbon paper into a solution contain H_2O_2 (0.1 M) and H_2SO_4 (0.1 M); ultrasonication is then applied for 60 min; after that put the carbon paper into a furnace and raise the temperature to 300 °C for 30 min.

- (3) Carefully brush one side of the carbon paper with dilute paraffin wax in order to obtain one side catalyst electrodeposition in the following process. Selective side deposition of catalyst will bring only one side growth of CNFs; this will make the further selective side deposition of Pt particles easier. Fig 3.5 (b) shows the back side of CNFs grown on activated carbon paper; demonstrate that CNFs are only produced on one side of the carbon paper.

Fig 3.5 (c) shows the result of CNFs grown on activated carbon paper decorated with 0.6 mg cm^{-2} Fe-Ni alloy catalyst particles. A uniform CNFs distribution yet high yield can be observed here. Fig 3.5 (d) is the cross-section of CNFs grown on activated carbon paper with 0.6 mg cm^{-2} Fe-Ni alloy catalyst particles. A thick layer of CNFs can be observed one side of the carbon paper.

In the CVD process for the growth of CNFs or CNTs, many other key factors such as temperature, gas condition, and pressure also play important role on the morphology of the produced CNFs or CNTs as well as the catalyst. So here every factor is kept the same except the loading of Fe-Ni catalyst. Carbon papers with Fe-Ni catalyst were put into a CVD system. The furnace of this CVD system is kept at ambient pressure and flushed with a gas flow of Ar ($142.5 \text{ ml min}^{-1}$) and H_2 (7.5 ml min^{-1}) for 30 min, then the temperature was heated to 550°C and then held at this temperature for 20 min under the same gas flow as before. This stage can reduce the oxidized Fe-Ni catalyst. After that the temperature was increased again to 760°C , whereupon ethylene (C_2H_4) was introduced for 30 min, at the gas flow of Ar ($142.5 \text{ ml min}^{-1}$), C_2H_4 (150 ml min^{-1}) and H_2 (7.5 ml min^{-1}) for the growth of the carbon nanofibers. Finally, the ethylene was turned off, while the Ar ($142.5 \text{ ml min}^{-1}$) and H_2 (7.5 ml min^{-1}) were continuously flushed through the furnace until the temperature was less than 100°C .

Fig 3.6 SEM images of (a) is the raw carbon paper and (b) is the high magnification, (c) and (d) are the low magnification and high magnification of CNFs grown on carbon paper with 0.3 mg cm⁻² Fe-Ni alloy catalyst; (e) and (f) are the low magnification and high magnification

of CNFs grown on carbon paper with 0.6 mg cm^{-2} Fe-Ni alloy catalyst; (g) and (h) are the low magnification and high magnification of CNFs grown on carbon paper with 1.8 mg cm^{-2} Fe-Ni alloy catalyst

Fig 3.6 shows the SEM images of the produced CNFs on carbon paper with different loadings of Fe-Ni alloy catalyst particles. Fig 3.6 (a) and (b) are the low magnification and high magnification SEM images of raw carbon papers before the deposition of CNFs. The pristine carbon paper consisting of numerous graphite fibers has a weave structure with large holes and gaps present. Clean and smooth surface is shown in the image and the diameter of carbon fibers are mostly in the range of 7-8 μm . Fig 3.6 (c) and (d) show the low magnification and high magnification SEM images of CNFs deposited on carbon paper with about 0.3 mg cm^{-2} Fe-Ni alloy catalyst. A thick layer of CNFs covers the surface of pristine carbon fibers with an extremely high density and high porosity by curling and coiling together. The diameter of CNFs coated carbon fibers are in the range of 20-25 μm , thus the thickness of CNFs is estimated to be 6.5-8.5 μm . The diameters of these CNFs are very small. As a result, the large holes and gaps were greatly diminished by the *in situ* grown CNT layer, and a high surface roughness was also obtained due to its highly porous structure.

Fig 3.6 (e) is the SEM image of CNFs deposited on carbon paper with about 0.6 mg cm^{-2} Fe-Ni alloy catalyst and (f) is an enlarged view. Fig 3.5 (c) and (d) show the lower magnification and cross-section of the same sample. From the image one can see a very thick layer of CNFs cover the surface of pristine carbon paper. Almost all the big holes and gaps have been covered. It is hard to distinguish the cylindrical shape of raw carbon fibers on pristine carbon paper. The other unique feature of these

CNFs is that their diameters are only slightly larger compared to CNFs deposited on carbon paper with about 0.3 mg cm^{-2} Fe-Ni alloy catalyst.

Fig 3.6 (g) and (h) show the SEM images of CNFs deposited on carbon paper with about 1.8 mg cm^{-2} Fe-Ni alloy catalyst. From the low magnification, one can see very densely packed CNFs covered the surface of carbon paper. However, from the high magnification we can see that the diameter of these CNFs are very large, even up to 300-500 nm. This result has confirmed that large catalyst particles will produce CNFs with large diameter. As the diameter of these CNFs is too large, the total surface area of these CNFs will be quite small compared to CNFs deposited on carbon paper with about 0.3 and 0.6 mg cm^{-2} Fe-Ni alloy catalyst.

Fig 3.7 (a) TEM images of carbon nanofibers grown on carbon paper with 0.6 mg cm^{-2} Fe-Ni alloy catalyst; (b) is the enlarged view

Fig 3.7 displays a TEM close-up of the CNFs grown on carbon paper with 0.6

mg cm⁻² Fe-Ni alloy catalyst; indicating that these CNFs have a diameter of 30-50 μm. The surface is also quite rough.

3.3.2 Catalyst prepared by magnetron sputtering method

Magnetron sputtering is well-known to be one of the most effective and robust deposition techniques for thin film deposition. It has excellent control over film thickness and uniformity, and is therefore an essential tool in the semiconductor and hard disk industries. It is another famous method for the preparation of thin catalyst layer. Ni₅₀Ti₅₀ was selected as the catalyst for the growing of CNFs on carbon paper. In this work, CNTs were directly grown on Toray™ carbon paper TGPH-090 through a thermal chemical vapor deposition (CVD) process, which has a suitable growth temperature and is easy to scale up. Carbon paper sputtered with a thin layer of Ni₅₀Ti₅₀ was placed into a furnace at ambient pressure. First flush the furnace with a gas flow of Ar (142.5 ml min⁻¹) and H₂ (7.5 ml min⁻¹) for 30 min, then the temperature was heated to 550 °C and then held at this temperature for 20 min under the same gas flow as before. This stage was to reduce the oxidized Fe-Ni catalyst. After that the temperature was increased again to 760 °C, whereupon ethylene (C₂H₄) was introduced for 30 min, at the gas flow of Ar (142.5 ml min⁻¹), C₂H₄ (150 ml min⁻¹) and H₂ (7.5 ml min⁻¹) for the growth of the carbon nanofibers. Finally, the ethylene was turned off, while the Ar (142.5 ml min⁻¹) and H₂ (7.5 ml min⁻¹) were continuously flushed through the furnace until the temperature was less than 100 °C.

Fig 3.8 SEM images of carbon paper surface with different magnifications for CNFs insitu grown on carbon paper with magnetron sputtered $\text{Ni}_{50}\text{Ti}_{50}$ catalyst, insert of (c) is a typical image of the as grown CNFs

Typical SEM images of CNFs grown on the fibers of a carbon paper are shown in Fig 3.8. From the image one can see that a high density of CNFs with very small diameter of 20-30 nm is firmly anchored on the carbon paper. Fig 3.8 (c) shows the enlarged

view and some bright points are shown in the image. These points are identified as catalyst particles (Ni) from EDAX analysis. Insert of Fig 3.8 (c) is the TEM image of a typical CNF.

3.4 Deposition of Pt nanodots onto the surface of as prepared CNFs

The utilization of CNFs as catalyst support for PEMFCs has sparked enormous interest due to their unique properties such as high chemical and oxidative stability, strong mechanical strength, good electronic conductivity and high surface area [259, 260]. CNF based electrodes for PEMFCs have shown increased catalyst utilization and performance compared to conventional carbon black support [64]. However the preparation of highly dispersed and controllable loading of Pt on CNFs still remains a big challenge to the research community.

In the present study, a very simple process to obtain uniformly distributed Pt nanoparticles with narrow distribution of particles on the *in-situ* grown CNFs on carbon paper substrate has been developed.

3.4.1 Functionalization of CNFs followed by Impregnation Method

In this process the CNFs were functionalized in 0.1M citric acid as its hydrophobic nature. Citric acid route is a well-accepted functionalization process for CNFs and CNTs. It can incorporate carboxyl and hydroxide groups to the surface of CNFs and

CNTs. Poh [261] *et al.* compared the Pt deposition on citric acid modified MWCNTs/XC-72 and H₂SO₄-HNO₃ modified MWCNTs/XC-72. Better Pt dispersion was obtained on citric acid modified MWCNTs/XC-72. They explained that citric acid can facilitate higher density of functional groups than H₂SO₄-HNO₃. Kannan *et al.* [262] also confirmed that citric acid treatment is a mild yet effective surface modification method. The standard functionalization process in this work is described as follows:

(1) First the CNFs/CP composite was soaked in ethanol under stirring for 10 min, in order to evacuate all the air bubbles.

(2) The composite was placed into 0.1M citric acid and ultrasonically treated for 10 min, and then it was kept immersed in the solution for 1h.

(3) Finally the sample was put into a furnace and heated to 300 °C for 30 min.

The Pt depositions on functionalized CNFs (enriched carboxyl and hydroxide groups on the surface) were then performed by carefully dropping the Pt containing solution onto the surface of carbon paper followed by in-situ Pt reduction at 150 °C with a gas flow of Ar (142.5 ml min⁻¹) and H₂ (7.5 ml min⁻¹) for 60 min. H₂PtCl₆·6H₂O dissolved in three different solvent were studied. 10 mM H₂PtCl₆ in ethanol, 10 mM H₂PtCl₆ in deionized water, 10 mM H₂PtCl₆ in acetone were carefully dropped onto the functionalized CNFs/CP surface with controlled amount. The loadings of Pt are then estimated by assuming totally Pt applied regardless of possible loss in the manual process.

Fig 3.9 (a) Transmission electron micrographs of Pt nanodots deposited on CNFs, (a), (b) and (c) are deposited from $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ precursor in different solutions; (a) is 0.1M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in ethanol, (b) is 0.1M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in deionised water, (c) is 0.1M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in acetone; (d), (e) and (f) compare the effect of CNFs diameter on Pt particles' size, (d) is Pt nanodots deposited on CNF with 20nm diameter and (f) is the enlarged view, (f) shows Pt nanodots deposited on CNF with 60nm diameter

Fig 3.9 (a) shows the TEM image of the Pt deposited on 7cm² CNF/CP composites with 0.25 ml 10 mM H₂PtCl₆ in ethanol. This is equal to 0.07 mg cm² by assuming that there is no Pt loss in the following operation.

The particles size distributions of the Pt nanodots on the surface of functionalized CNFs were obtained by directly measuring the size of 100 randomly chosen particles in the highly magnified TEM images. The mean particles size is 1.56 nm as shown in the histogram of Fig 3.10 (a). Fig 3.9 (b) shows the TEM image of the Pt deposited on 7cm² CNFs/CP composites with 0.25 ml 10 mM H₂PtCl₆ in deionized water. The size distribution is broader and some big particles appear as compared to Fig 3.9 (a). The mean particles size is 2.35 nm as shown in Fig 3.10 (b). Fig 3.9 (c) shows the TEM image of the Pt deposited on 7cm² CNFs/CP composites with 0.25 ml 10 mM H₂PtCl₆ in acetone. The Pt particles agglomeration is observed.

Fig 3.10 (a) Size distribution histograms of fig 3.9 (a); (b) size distribution histograms of fig 3.9 (b)

All in all, the above results show that good Pt dispersion on CNFs using 10 mM H_2PtCl_6 in different solvents is in this order: ethanol > deionized water > acetone. Among them the use of ethanol and deionized water can achieve more homogeneous dispersion. Ethanol can achieve much better homogeneous dispersion and smaller particles size than water. The use of acetone cannot achieve homogeneous dispersion. This should be explained by the better wettability of ethanol on the surface of CNFs. As the presence of carboxyl and hydroxide functional groups on the surface of CNFs, the use of water can also have a homogeneous dispersion of Pt particles.

3.4.2 Effects of CNFs Diameter

Fig 3.9 (d) and (f) compares the effects of CNFs diameter on the deposited Pt size. In the experiment it is observed that the Pt particles size is slightly different on CNFs with different diameter. To investigate the effect of CNFs diameter/surface area on Pt deposition; typical CNF samples with different diameter of 20 nm and 60 nm were chosen for comparison. In this experiment the Pt particles is deposited by dropping 0.25 ml 10 mM H_2PtCl_6 in ethanol onto 7cm^2 CNFs/CP composites. In the case of Pt/CNFs-60nm the mean Pt particles size is 1.67nm and in the case of Pt/CNFs-20nm the mean Pt particles size is 1.34nm as shown in Fig 3.11 (a) and (b). Tian *et al.* [263] have also studied this effect and they attributed the effect to the higher surface area of MWCNTs with smaller diameter. They used three different MWCNTs samples with tube diameter of <10nm, 20-40nm, and 40-60nm to synthesize Pt/MWCNT nanocomposited by a microwave-assisted method. The surface area of MWCNT-10nm,

MWCNT-30nm, and MWCNT-50nm was 310.5, 86.5, and 41.0 m² g⁻¹, respectively. Higher surface area will offer larger number of functional groups/sites for the absorption of H₂PtCl₆ precursor and for the accommodation and nucleation of PtO_x/Pt crystallites. However, in the case of the MWCNT support with low surface area (MWCNT-50nm), there would be competition between the nucleation and crystallite growth of PtO_x/Pt nanoparticles due to the limited sites on the MWCNT surface, resulting in relatively larger particle size and cluster formation.

It is considered that surface area should be a key reason for the diameter effect; and curvature should also be counted as another important reason. CNFs with smaller diameter possess larger curvature, which confines the growth of PtO_x/Pt nanoparticles, while for CNFs with large diameter; this geometrical effect will be weaker and thus produce larger particles size.

Fig 3.11 Size distribution of Pt particles deposit on (a) CNFs with diameter of 60 nm and (b) CNFs with diameter of 20 nm

3.4.3 Effects of Pt Loading

Saha *et al.* [264] deposited Pt onto MWCNTs using different concentrations of Pt precursor and chemical reduction with glacial acetic acid. They found that higher concentrations of Pt precursor would produce larger Pt particles.

In this work, the effect of Pt loadings on particles size was also studied. Two CNFs/CP composites with the same size of 7cm^2 were dropped 0.25 ml and 0.5 ml 10 mM H_2PtCl_6 in ethanol, respectively, which is equal to 0.07 and 0.14 mg cm^{-2} Pt loadings.

Fig 3.12 TEM images of Pt nanodots deposited on CNFs with different loadings at different magnifications: (a and c) Pt loading of 0.14 mg cm^{-2} , (b and d) Pt loading of 0.07 mg cm^{-2}

Fig 3.12 shows the TEM images of Pt nanodots deposited on CNFs with two different loadings of 0.07 and 0.14 mg cm⁻². It can be seen from the images that Pt nanodots are homogeneously dispersed over the entire surface (big particles with 20-30 nm diameter is Ni catalyst encapsulated in CNFs), the density of Pt particles increases with the Pt loading. The average size of Pt nanodots on CNFs was obtained by measuring 100 randomly chosen particles in the magnified TEM images and shown in Fig 3.13, It is clearly seen that the Pt nanodots with narrow particle size distribution have the mean nanoparticle sizes of 2.41 and 1.63 nm, respectively, which correspond to the Pt loadings of 0.14 and 0.07 mg cm⁻².

Fig 3.13 Particles size distribution of Pt nanodots on CNFs with different loadings of (a) 0.14 mg cm⁻² and (b) 0.07 mg cm⁻²

3.4.4 CV performance and durability

Cyclic voltammetry is a simple but very useful technique that is used widely to;

- (1) Measure specific surface areas of supported metal nanoparticles;
- (2) Provide information about their surface crystallography, composition, and purity;
- (3) Characterize the surface functionalities present on the surface of carbon supports.

The Pt area was determined electrochemically according to the following formula:

$$S_{\text{ESA}} \left[\frac{\text{m}^2 \text{Pt}}{\text{mgPt}} \right] = \frac{\text{charge} [\mu\text{C} \cdot \text{cm}^{-2}]}{210 [\mu\text{C} \cdot \text{cm}^{-2} \text{Pt}] \times \text{Ptloading} [\text{mg} \cdot \text{cm}^{-2}]} \times 10^4 \quad (4.1)$$

When the average size of Pt particles is known, it is also possible to estimate the actual Pt surface area, S_{actual} , according to the following formula:

$$S_{\text{actual}} = 60\,000 / (\rho d) \quad (4.2)$$

where d is the mean Pt particles size in Å and ρ is the density of Pt metal (21.4 g cm⁻³).

Fig 3.14. Cyclic voltammograms of Pt nanodots deposited on CNFs use 10 mM H_2PtCl_6 in ethanol

The cyclic voltammetry of Pt particles supported on CNFs (10 mM H_2PtCl_6 in ethanol) is represented in Fig 3.14. It shows three characteristic potential regions: the hydrogen adsorption and desorption potential region $-0.25 < E < 0.1$ V followed by the double layer region $0.1 < E < 0.5$ V (on the anodic scan), and the oxygen adsorption and desorption region for potentials greater than 0.5 V vs Ag/AgCl (1M KCl). The features observed in the cyclic voltammogram of Pt catalysts are characteristic of their surface crystallography and their cleanliness.

Fig 3.15. Cyclic voltammograms of Pt nanodots deposited on CNFs use (a) 10 mM H_2PtCl_6 in acetone and (b) 10 mM H_2PtCl_6 in ionized water

The electrochemical active surface area of the two different loadings were $70.2 \text{ m}^2 \text{ g}^{-1}$ (ethanol, 0.14 mg cm^{-2}) and $85.5 \text{ m}^2 \text{ g}^{-1}$ (ethanol, 0.07 mg cm^{-2}), respectively, which are 30% and 60% higher than commercialized 50wt. % Pt/XC-72 (Johnson Matthey, 3.5 nm, $S_{\text{ECSA}}=53.6 \text{ m}^2 \text{ g}^{-1}$).

The cyclic voltammograms of Pt particles supported on CNFs (10 mM H_2PtCl_6 in acetone and deionized water) is represented in Fig 3.15. The electrochemical active surface area was calculated to be $49.1 \text{ m}^2 \text{ g}^{-1}$ (acetone, 0.14 mg cm^{-2}) and $65.5 \text{ m}^2 \text{ g}^{-1}$ (deionized water, 0.14 mg cm^{-2}), so the ECSA of Pt dispersion on CNFs use 10 mM H_2PtCl_6 in different solvents is in the order: ethanol > deionized water > acetone (see Table 3.1). This result is tally with that observed from TEM images.

Table 3.1 The electrochemical active surface area of Pt catalyst deposited with different precursors

	Ethanol	Deionized Water	Acetone	Commercial
0.14 mg cm^{-2}	$70.2 \text{ m}^2 \text{ g}^{-1}$	$65.5 \text{ m}^2 \text{ g}^{-1}$	$49.1 \text{ m}^2 \text{ g}^{-1}$	$53.6 \text{ m}^2 \text{ g}^{-1}$
0.07 mg cm^{-2}	$85.5 \text{ m}^2 \text{ g}^{-1}$	$79.0 \text{ m}^2 \text{ g}^{-1}$	$63.5 \text{ m}^2 \text{ g}^{-1}$	

To evaluate the durability of Pt/CNFs electrode, both Pt/CNFs and Pt/Carbon blacks electrodes were subject to 3000 cyclic voltammetry cycles in 0.5M H_2SO_4 solution with a scan speed of 50 mV s^{-1} . As shown in Fig. 3.17 (a) and (b), standard hydrogen adsorption/desorption peaks between -0.22 and 0.1 V can be observed with a decreasing tendency after thousands of cycles. The decreasing hydrogen adsorption/desorption area indicates the loss of Pt surface area, which is due to the corrosion of catalyst support as well as the grow up of Pt particles. Fig. 3.17 (c) and (d) show the calculated ECSA after cycling in acidic solution, Pt on CNFs retain 76% of its original ECSA, however Pt on carbon black only retain 19.4% of this value.

Therefore, Pt on CNFs is much more stable than commercial Pt/carbon black catalyst under the same test condition.

Fig. 3.16. CV curves from the 1st cycle to 3000 cycles in 0.5 M H₂SO₄ at 50 mVs⁻¹ of (a) Pt on *in situ* grown CNFs and (b) Pt on carbon blacks; (c) shows the comparison of normalized ECSA after thousands of CV cycles; (d) shows ECSA of Pt on CNFs before and after 3000 cycles, the data for Pt on carbon black was also shown for comparison.

3.5 Single cell performance characterization

Cyclic voltammetry (CV) curves were obtained for Pt dispersed on CNFs with

loadings of 0.14 mgPt/cm^2 and 0.07 mgPt/cm^2 . CV curve for 50 wt.% Pt/C from Johnson Matthey was also obtained for comparison. The ECSA of Pt catalysts can be estimated by integrating the charge in the hydrogen adsorption/desorption region of the CVs. By using the total charge passed for H-desorption Q_H , ECSA can be calculated following $\text{ECSA} = Q_H / L_{\text{Pt}} \times 0.21$, where L_{Pt} represents the platinum loading. As shown in Fig 3.16 (a), The ECSA is 70.2 and $85.5 \text{ m}^2/\text{g}$ for Pt/CNFs/carbon paper with loadings of 0.14 and 0.07 mgPt/cm^2 , which is 30% and 60% higher than Pt/C commercial catalyst ($53.6 \text{ m}^2/\text{g}$). The higher ECSA has proven that the as-synthesized Pt/CNFs/carbon paper electrodes are promising for use in MEA.

Fig. 3.17. (a) Cyclic voltammograms for commercial Pt/carbon black, Pt/CNFs/carbon paper with loadings of 0.14 mgPt/cm^2 and 0.07 mgPt/cm^2 , (b) Polarization curves of MEAs made with Pt/carbon black (0.5 mgPt/cm^2), Pt/CNFs/carbon paper (0.14 mgPt/cm^2 and 0.07 mgPt/cm^2) as the cathode, anodes were Pt/carbon black with a Pt loading of 0.4 mgPt/cm^2 .

The as-prepared Pt/CNFs/carbon paper electrodes were tested as PEMFC cathodes. The anodes for all MEAs are made of 50 wt.% Pt/C with a catalyst loading of 0.4 mgPt/cm^2 . At room temperature and atmosphere pressure, fed with humidified H_2 and

dry O₂, the polarization curves for Pt/CNFs/carbon paper cathodes with different catalyst loadings are shown in Fig 3.16 (b). Power output at 0.6 V are 162 and 286 mW/cm² for cathode loading of 0.07 and 0.14 mgPt/cm², respectively. For comparison, a Pt/C cathode (0.4 mgPt/cm²) was also tested and a power output of 545 mW/cm² was obtained at 0.6 V. With respect to cathode Pt mass specific power output, Pt/CNFs MEAs offer 2.31 (0.07 mgPt/cm²) and 2.04 (0.14 mgPt/cm²) kW/gPt at 0.6 V, which are 112% and 87% higher than Pt/C of 1.09 kW/gPt (0.5 mgPt/cm²). Strictly speaking, it is more accurate to conduct the comparison of mass specific power output under the same Pt loading. The reason of using 0.5 mgPt/cm² on Pt/C is because this is the most commonly used loading in the fuel cell market. From the economic point of view, higher mass specific power density is a big advantage, i.e., the higher mass specific power density for Pt/CNFs is attributed to the higher ECSA as well as better catalyst utilization efficiency.

3.6 Conclusion

As discussed in Chapter 2, reduced Pt usage could be obtained by improving either its intrinsic catalytic activity or utilization efficiency. CNFs *in situ* grown on carbon paper ensure that all Pt particles were in firm electrical contact with carbon backing, which can largely improve the catalyst utilization efficiency. What is more, CNFs possess better corrosion resistance, electron conductivity, and higher surface area; makes it an ideal catalyst support. Therefore in this Chapter, CNFs *in situ* grown on carbon paper was used as a novel catalyst support to study its performance. *In situ*

grown fishbone-type CNFs on carbon paper were used as the catalyst support for PEMFC cathode. Pt nanoparticles in the size range of 1-2 nm was obtained by a simple impregnation process. With the use of Pt/C catalyst (0.4 mgPt/cm^2) as the anode for all MEAs, fuel cell performance of MEAs with Pt/CNFs as the cathode catalysts showed 87% (0.14 mgPt/cm^2) and 112% (0.07 mgPt/cm^2) higher mass specific power output than Pt/C (0.5 mgPt/cm^2) catalyst. The improved performance of CNFs electrode is attributed to its 3D hierarchy structure, which improves electron transfer and catalyst utilization efficiency. The higher ECSA calculated from CV curves also explains the improvement in performance. Better durability performance was also proved for this new type of catalyst support structure.

CHAPTER 4. Pulse electrodeposition based three-step method to prepare PtFeNi ternary catalyst for the use in PEMFC cathodes

4.1 Introduction

In this chapter, a three step method to prepare nanoengineered PtFeNi alloy catalyst based electrodes with ultra-low Pt loading is demonstrated for proton exchange membrane (PEM) fuel cell applications. This method involves firstly the electro-deposition of FeNi alloy onto porous carbon electrode substrate, and then follows the galvanic displacement process to form PtFeNi alloy. At last, excess Fe and Ni surface atoms are selectively dissolved in a chemically coupled electrochemical process. Core-shell structured PtFeNi alloy composed of a multi-layer Pt-rich shell and a Pt-poor core is finally produced and characterized by various methods. Scanning electron microscopy (SEM) of electrode surface reveals that carbon blacks are covered with extremely high density of nano-catalysts. Electron dispersive X-ray detector (EDX) confirms that these catalysts are PtFeNi. The as-prepared PtFeNi ternary alloy electro-catalyst based electrodes were used as cathodes in fuel cell testing and present good performance with a Pt loading of only 0.05 mgPt/cm².

4.2 Experimental Methods

The key process to prepare an electrode with ultra-low-Pt-loading and enhanced

performance is shown in Fig 1. The detailed processes are described as follows;

Fig 4.1. Illustration of the synthesis process

4.2.1 Functionalization of XC-72

In this process certain amount of XC-72 powders were add into 0.1 M citric acid solution and ultrasonically treated for 1 hr. The resulting suspension was centrifuged and then heat treated at 300 °C for 30 min. After this process the CA-modified XC-72 is now in hydrophilic nature. Citric acid route is a well-accepted functionalization process for carbon blacks and carbon nanotubes. It can facilitate the growth of high density of functional groups like carboxyl and hydroxide.

4.2.2. Preparation of uncatalyzed carbon electrode

The above pretreated XC-72 carbon blacks were thoroughly mixed in ultrasonic bath with well-defined masses of Nafion solution (weight ratio of Nafion over XC-72 carbon black is 1/3). This hydrophilic solution is then sprayed onto a hydrophobic carbon paper to form a dual layer structure which is hydrophilic for one side but

hydrophobic for the other. This hydrophilic layer will act as the catalyst support, while the hydrophobic side will act as the gas diffusion layer.

In this study, the as-prepared carbon ink was directly sprayed onto Avcard 1120 carbon papers from Ballard power systems. These kinds of carbon papers were fabricated based on P50 carbon fiber paper substrate which was treated with PTFE to make it hydrophobic. A micro-porous layer for better control of permeability, diffusivity and conductivity was applied on one side of the carbon paper.

Appropriate amount of citric acid treated carbon blacks (Vulcan XC-72) were ultrasonically mixed together with proper amount of 5 wt.% Nafion solution and isopropanol to prepare inks. The as prepared inks will be applied on the carbon paper using a micro spraying technique. By changing the operating parameters such as spray pressure, spray angle and ink flow rate, the porosity of this catalyst substrate layer could be controlled. The addition of Nafion in the ink provides an adhesive function to the carbon ink for carbon particles to adhere stronger to the carbon paper backing. Furthermore, it also offers ion conduction pathway inside the electrode catalyst layer.

In the preparation of catalyst inks, it is important to obtain uniformly distributed carbon blacks in the solvent. In the ultrasonically treatment process, the solution was brought to high frequency ultrasound (20 kHz) agitation at 20% amplitude for 5 minutes shown in Fig. 4.2 (a). After which, the solution was cooled with lower frequency ultrasound agitation for 3 minutes (Fig. 4.2 (b)). To dilute the solution for suitable application of carbon ink, some isopropanol was added. This solution was then brought to both high and low ultrasonic processes again at 5 minutes and 3

minutes, respectively.

Fig 4.2. (a) High frequency ultrasound equipment and settings, (b) low frequency ultrasound

The as-prepared carbon black ink was applied to the carbon fabric by air brushing (Badger Model 100-LG, Fig. 4.3 (a)) with compressed nitrogen (Fig. 4.3 (b)) in a fume box (LABCONCO Protector Laboratory Hood) (Fig. 4.3 (c)). The use of air brush allowed pressure from the gas tank to be transmitted to the carbon black ink for deposition. By changing the air flow rate and pressure, the density and porosity of catalyst substrate layer could be controlled. Lower pressure nitrogen (10 – 30 psi) was favored over higher pressures to prevent excessive release of ink.

The spraying process must be done at a slow speed and air brush should be angled at 45° in order to get a good substrate, approximately 6cm away from the carbon fabric surface (Fig. 4.3 (d)) to ensure a uniform distribution of the carbon support layer (Fig. 4.3 (e)). The completed GDL was then left to dry for 1 hour at room temperature of

approximately 23°C.

Fig 4.3. Detail operating process of air-brushing to prepare uncatalyzed carbon substrate.
Digital images of (a) micro spray gun, (b) compressed air and nitrogen, (c) fume hood, (d)
operating angle and distance of the spray gun, (e) sprayed uncatalyzed electrode

4.2.3. Pulse electrodeposition of FeNi

There is only one side of the electrode substrate need to be deposited with electrocatalyst. Therefore in the electrodeposition process the back side should be isolated from the electrolyte. In the above steps a dual layer electrode substrate was prepared, a hydrophobic gas diffusion layer and a hydrophilic carbon black substrate. To achieve one side electrodeposition, following steps were taken to make sure that no

catalyst will be deposited on the back side.

In order to achieve this, a simple yet practical apparatus was assembled (Fig. 4.4). The small slits at the sides of the acrylic container ‘locks’ the GDL in place and hydrodynamic pressure from catalyst solution prevents itself from sipping to the back of the GDL. It could be shown in Fig. 4.5 that the container has successfully prevented the catalyst solution from sipping to the back surface.

Fig 4.4. Assembled and explosion view of electrodeposition apparatus

Fig 4.5. Digital images of the electrodeposition apparatus in operation

Electrodeposition of FeNi was performed on a Solartron PS 1470E station in a nickel and iron containing acidic electrolyte at room temperature. The electrolyte is composed of 30 g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 200 g/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$; and 50 g/L H_3BO_3 ; 1 g/L ascorbic acid is also added into the solution as additives.

Pulse electrodeposition was used to allow usage of higher current density without compromising on desired small particle size. Pulse electrodeposition is composed of repeated current on and off cycles. A galvanic square pulse wave was applied at 0.1 A/cm^2 for 0.05 s and 0 A/cm^2 for another 0.5 s. This current pulse will continue and only be stopped until certain amount of total charges has been transferred. The total charges applied is 3 Coulombs/cm^2 .

4.2.4. Galvanic displacement deposition of Pt

The galvanic displacement mechanism is shown in Fig 4.6. In this process 10 mM H_2PtCl_6 solution was dropped onto the FeNi covered electrode to form PtFeNi ternary alloy by a galvanic displacement reaction. The amount of Pt containing solution is precisely controlled in order to control the loading of Pt. After galvanic displacement for 15 minutes the solution was collected and tested by an inductively coupled plasma-mass spectrometer. Only trace Pt amounts was detected, thus one can assume that the loading of Pt on the electrode equals to the Pt contained in the precursor solution.

Fig 4.6. Illustration of the galvanic mechanism

4.2.5. Selective electro-dissolution of surface Ni and Fe atoms

PtFeNi alloy was dealloyed by chemically coupled electrochemical method in a typical three electrode cell. The as prepared PtFeNi electrode was immersed into 0.5 M H_2SO_4 solution as a working electrode, Ag/AgCl (1M KCl) was used as a reference

electrode and a piece of Pt mesh was used as the counter electrode. Cyclic voltammetry (CV) was performed to selectively dissolve the surface Fe and Ni atoms (-0.25-1.25 V vs Ag/AgCl (1M KCl), room temperature), Around 10 cycles of cyclic voltammetry were applied to the working electrode.

Fig. 4.7 (a) presents the first five cycles of the CV profiles for PtFeNi electrode in 0.5 M H₂SO₄ between the voltage of -0.25 – 1.25 V. From the image, one can see that there are two broad and large peaks located at 0.43 V and 0.77 V, which demonstrated the dissolution of Fe and Ni atoms. This exhibited that the transition metal atoms were removed in H₂SO₄ at a high rate right from the start. It also meant that dissolution could not be carried out for too long as it may destroy the binary and ternary alloy structure causing Pt lost due to dissolution. Among Fe, Ni and FeNi, Fe corroded at the fastest rate followed by Ni and then FeNi alloy [265].

The first few cycles involved dissolution of non-noble metal, cleaning up unalloyed transitional metal atoms and leaving a Pt enriched shell. The shifts in Pt reduction peak towards higher potentials in the first few cycles account for Pt enrichment with increase of Pt catalytic surface area. This electrochemical dissolution process was continued for about 10 cycles until a stable CV profile was obtained.

First 4.7 (a) First five CV cycles for the electro-dissolution of unalloyed Fe, Ni atoms, (b) CV profile of PtFeNi ternary electro-catalyst after dissolution

Fig 4.7 (b) displays the final CV profiles of PtFeNi ternary electro-catalyst in 0.5 M H₂SO₄. It shows three characteristic potential regions: (1) the hydrogen adsorption and desorption potential region at the voltage range between -0.25 and 0.1 V, followed by (2) the double layer region from 0.1 to 0.5 V (on the anodic scan), (3) the oxygen adsorption and desorption region for potentials greater than 0.5 V vs Ag/AgCl (1M KCl). From this CV profile a Pt electrochemical active surface area (ECSA) was calculated out to be 33.5 m²/g. The peak for oxygen reduction is also very sharp which indicates that this electrode might have good electro-catalytic activity towards ORR.

After all the above processes, the as-obtained PtFeNi ternary alloy based cathode and a pure Pt based anode (prepared with carbon-supported 50 wt.% Pt from Johnson Matthey) were hot pressed onto each side of a commercial Nafion 112 membrane (EW1100, DuPont) for 2 min at 140 °C with a pressure of 40 kg/cm² to form a membrane-electrode-assembly (MEA). Room temperature humidified H₂ (8 sccm/cm²)

and dry air (20 sccm/cm^2)/ O_2 (5 sccm/cm^2) were fed into the anode and cathode as fuel, respectively. All single cells testing in this study was operated at room temperature of around 22°C and atmosphere pressure.

4.3 Evolution of the electro-catalyst at each steps: morphology, composition, and structure

The XC-72 carbon black catalyst support is first functionalized with Citric Acid to create high density of functional groups like carboxyl and hydroxide; which can provide more nucleation sites for the adatoms, higher nuclei density with more uniform distribution and finer particles size. Furthermore, the carboxyl and hydroxide groups would inhibit surface diffusion and as described before lower surface diffusion rate would induce finer particle size.

The other reason why the catalyst support is first functionalized before electrodeposition is related to the hydrogen evolution reaction (HER). HER is inevitable in metal electrodeposition process and it will significantly harm the electrodeposited structure when large bubbles are formed. Large hydrogen bubbles will cover the XC-72 carbon black catalyst support and induce the fall off of FeNi metal particles. Citric acid treatment makes the catalyst support hydrophilic thus the electrolyte can penetrate into the electrode to form a catalyst layer with enough thickness.

Fig 4.8. SEM images of FeNi alloy deposited on: (a) Citric acid pretreated carbon black, and (b) untreated carbon black. The total charge passed is 3 Coulombs/cm² for both cases

Fig 4.8 presents SEM images of electrodes prepared by pulse electrodeposit FeNi alloy onto citric acid treated and untreated carbon black support. The total charge applied is 3 Coulombs for both cases. Fig 4.8 (a) shows the result for citric acid treated electrode, which displays a very fine and uniform structure, and the surface of carbon black is smoothly covered with FeNi alloy. Fig 4.8 (b) presents the surface morphology of FeNi deposited on unmodified carbon black electrode, which shows a rough surface and the crystal size is much larger. By comparing these two images, one can see that there is larger amount of FeNi alloy deposited onto untreated carbon black electrode. This is due to better hydrophilic nature for citric acid treated electrode, thus the electrolyte can penetrate deeper into the electrode. However, for untreated electrode due to its hydrophobic nature, the electrolyte is unable to penetrate into the electrode effectively and thus most of the FeNi alloys will only be deposited on the outer surface.

4.3.1 Evolution of composition

Fig 4.9 (a1), (b1), and (c1) present the SEM images of electrode surface morphology at different stages. Fig 4.9 (a1) shows the electrode surface structure after the electrodeposition of FeNi alloy, and carbon blacks are covered with a uniform layer of FeNi. Some dark area seen in this image represents Nafion. Fig 4.9 (a2) presents its corresponding EDX results, indicating a composition of $\text{Fe}_{23}\text{Ni}_{77}$ alloy. After the electrodeposition proper amount of H_2PtCl_6 solution was dropped onto the electrode. Fig 4.9 (b1) shows the surface morphology at this step. Fig 4.9 (b2) displays its EDX result, presenting a composition of $\text{Pt}_{23}\text{Fe}_{34}\text{Ni}_{43}$. Compared with the composition before galvanic displacement, the atomic ratio of Fe remains almost constant while the content of Ni decreases significantly. One can deduce that Ni atoms play the most important role in the galvanic displacement with Pt^{4+} ions. Ni atoms show much faster galvanic displacement activity compared with Fe atoms. Pt alloyed with transitional metals have been widely reported as constitute catalysts due to their improved ORR activity. However the dissolution of transitional metal atoms remains a problem as it may contaminate the Nafion membrane causing degradation of fuel cell performance. To dissolve the surface and unalloyed transitional metal atoms, a chemically coupled electrochemical dissolution process was used. Fig 4.9 (a3) display this SEM image of electrode surface after this electrochemical dissolution process. As one can see from this image, the surface morphology undergoes some visible changes, i.e., the metal particles which cover the carbon black surface is brighter, which indicate that the surface atoms are precious metal. Fig 4.9 (c2) presents the EDX result for PtFeNi alloy after electrochemical dissolution; a composition of $\text{Pt}_{75}\text{Fe}_{20}\text{Ni}_5$ was

demonstrated.

Fig 4.9. SEM images of electrode surfaces: (a1) after PtFe alloy deposition, (b1) after the Pt galvanic displacement, and (c1) after electrochemical dissolution. (a2), (b2), and (c2) are EDX results of catalyst compositions correspond to (a1), (b1), and (c1); respectively

4.3.2 Evolution of the morphology

Highly magnified SEM images of electrodes surface at different steps are shown in Fig. 4.10 to illustrate the change of surface morphologies. Fig 4.10 (a1) and (a2) present the highly magnified SEM images of electrode surface after the pulse electrodeposition of FeNi alloys. From this two images, one can see that carbon blacks are covered with a uniform thin layer of FeNi alloy, and the surface of FeNi alloy is quite smooth. Fig 4.10 (b1) and (b2) present the highly magnified SEM images of electrode surface after the Pt galvanic displacement. As compared with Fig 4.10 (a1)

and (a2), an obvious change in the surface structure can be observed and the alloy that cover the surface of carbon blacks become rougher. The change in surface morphology also indicates the successful galvanic displacement to form PtFeNi ternary alloy. As mentioned before, the Fe and Ni atoms may contaminate the membrane and cause degradation of fuel cell performance. As reported from some papers, when Pt is alloyed with other transitional metals, the latter will be quite stable even under severe chemical and electrochemical environment when the atomic ratio of transitional atoms is less than 20%. However when the atomic ratio of second transitional metals is above 20% or it has not been in alloyed state, these second transitional metal atoms are easily dissolved and become contaminants.

As shown in Fig 4.10 (b2), a composition of $\text{Pt}_{23}\text{Fe}_{34}\text{Ni}_{43}$ was obtained after the galvanic displacement, showing a rich content of transitional metals. Thus a chemically-coupled electrochemical process was used to dissolve the unalloyed Fe and Ni atoms to prevent contamination in fuel cell environment. The electrodes were inserted into a acid solution contains 0.5 M H_2SO_4 and a standard three compartment cell was used for the electrochemical dissolution process. The as-prepared electrodes were used as the working electrodes, a piece of Pt mesh was used as the counter electrode, and a Ag/AgCl (1 M KCl) electrode was used as the reference electrode. 10 cycles of cyclic voltammogram waveforms were applied to the working electrode in the range of -0.25 to 1.25 V vs Ag/AgCl (1M KCl).

Fig 4.10 High magnified SEM images of electrode surfaces at different steps of (a1), (a2): carbon black electrode after the pulse electrodeposition of FeNi alloy, (b1), (b2): electrode after Pt galvanic displacement, (c1), (c2): electrode after dissolution of surface and unalloyed Fe, Ni atoms

Fig 4.10 (c1) and (c2) display the high magnification SEM images of the electrode surface after electrochemical dissolution process. Compared with the surface morphology shown in Fig 4.12 (b1) and (b2), obvious differences can be observed. The alloy surface is become rougher and the ternary catalysts with uniformly dispersed particles size in the range of 2-3 nm were demonstrated. The density of catalysts nanoparticles is quite high, Fig 4.10 (c3) confirms that the catalyst loading is about 60 wt.% at the surface of the electrode.

4.3.3 Evolution of catalyst structure

To appreciate the structure of the catalysts at each step, XRD patterns were obtained to study the catalyst structure. Fig 4.11 present the XRD profiles for electrodes at each steps, including the electrode after FeNi alloy deposition, electrode after galvanic displacement and electrode after electrochemical dealloy. A XRD profile of commercial pure 50 wt.% on carbon black was also shown in the image for comparison.

Pt and Ni single crystals have a face-centered cubic (fcc) structure, while pure Fe possess a body-centered cubic (bcc) and a hexagonal structure. After the electrochemical de-alloy process, a composition of $\text{Pt}_{75}\text{Fe}_{20}\text{Ni}_5$ was obtained according to the EDX result shown in Fig 4.9 (c2). Accordingly, as shown in Fig 4.11, an fcc structure with shifts of the diffraction peak positions to smaller lattice constant was obtained. No peaks assigned to $\langle 100 \rangle$ or $\langle 110 \rangle$ crystal planes can be observed in the 2θ region lower than 40° , demonstrating that Pt and Fe, Ni atoms form alloy with solid

solution phases or disordered crystallite structures.

After electrochemical de-alloy, the lattice parameter of Pt decrease from 3.92 to 3.88 Å. The decreasing of lattice parameter results from the interpenetration of transition metals which have smaller atom radius compared with platinum.

Fig 4.11. XRD profiles of the electrode at different steps includes: electrode after the electrodeposition of FeNi alloy, electrode after the galvanic displacement process to form PtFeNi alloy, electrode after the cleanup of surface and unalloyed Fe, Ni atoms

4.3.4 Final catalyst morphology and its comparison with commercial catalyst

After FeNi deposition, appropriate Pt containing solution was then dropped onto FeNi

electrode to form PtFeNi alloy by galvanic displacement and chemically coupled electrochemical dissolution was then used to dissolve excess surface Fe and Ni atoms as these transition metals may harm the Nafion membrane.

Fig 4.12 (a) presents the SEM image of an as-prepared PtFeNi electrode. From this image, one can see that the electrode surface is covered uniformly by a layer of nanocatalysts. Fig 4.12 (c) shows its higher magnification. One can clearly distinguish that there are very large amount of nanoparticles covering the carbon black surface.

Fig 4.12 (d) displays the surface morphology of another electrode using commercial Johnson Matthey 50% wt Pt/carbon black as catalyst. By comparison, one can judge that the in-house prepared PtFeNi electrode has clearly higher catalyst loading on the electrode outer surface.

Fig 4.12 (f) shows the EDX result of the in-house prepared PtFeNi electrode. It confirms that the composition of the electrocatalyst is $\text{Pt}_{75}\text{Fe}_{20}\text{Ni}_5$, with a catalyst loading of 60 wt.% on carbon black. Fig 4.12 (e) presents an even higher magnification SEM image. From this image one can distinguish that the catalyst size is around 3 nm with uniform catalyst size distribution.

Fig 4.12 (b) displays the backscattered SEM image of the electrode. The brighter area represents catalysts and the darker area represents carbon blacks or Nafion. The large contrast between carbon black and catalysts reveals more clearly that carbon blacks were coated with a dense shell of precious metal, which is $\text{Pt}_{75}\text{Fe}_{20}\text{Ni}_5$ as confirmed by the EDX result in Fig 4.12 (f).

Fig 4.12. (a), (c), and (e) are SEM images of the obtained electrode at different magnifications; (b) is the back scattered image of the electrode, (f) is the EDX result for the electrode; (d) is commercial 50% wt Pt/carbon black from Johnson Matthey.

4.4 Fuel cell performance

Fuel cell testing is carried out on the as-synthesized PtFeNi on carbon black electrodes as it is the most straight forward method to determine the performance of an electrode. Compared to the fast anode hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR) at the cathode is a highly irreversible, complex, and its kinetics is rather sluggish. For this reason a lowering of cathode Pt loading is the mainly pursued research topic. In this study, in-house developed electrode with 0.05 mg/cm^2 Pt loading of $\text{Pt}_{76}\text{Fe}_{19.5}\text{Ni}_{4.5}$ trimetallic electrocatalyst is used as the cathode, while the anode is a standard electrode with 0.4 mg/cm^2 50% wt Pt on carbon black commercial catalyst from Johnson Matthey.

Fig 4.13 presents a representative set of fuel cell performance data for as-prepared MEAs. The testing was conducted at room temperature (22°C) under atmosphere pressure. O_2 at 5 sccm/cm^2 or air at 20 sccm/cm^2 was used for the cathode, while the anode fuel was humidified H_2 at 8 sccm/cm^2 . As shown in the polarization curves, the MEAs exhibit current values of 396 mA and 740 mA at 0.6 V for air and O_2 , respectively. This value is very comparable to those reported results under the similar operating conditions with cathode Pt loading of around 0.4 mg/cm^2 or higher, which proves that the in-house developed $\text{Pt}_{76}\text{Fe}_{19.5}\text{Ni}_{4.5}$ catalyst is suitable for use in a PEMFC cathode.

To better understand the cathode kinetics, impedance spectra were recorded at 0.8 V for PtFeNi MEA with both O_2 and air. The results were collectively shown in Fig 4.13 (b). MEAs with pure Pt cathodes were also tested for comparison. These plots show

semi-circles kinetic loops, the intercepts at the high frequency domain represent the membrane resistance (R_m), while the intercepts at the low frequency domain depict charge transfer resistance for ORR (R_{ct}).

Fig 4.13 (a) Polarization V-I curves and power densities of the MEAs with Pt₇₆Fe_{19.5}Ni_{4.5} as cathode catalyst at room temperature, no backpressure, the fuel is H₂ for anode and O₂ or Air at the cathode, respectively. (b) Impedance spectra obtained at 0.8 V for fuel cells with normal pure Pt cathode and PtFeNi ternary alloy cathode, insert in the image shows the equivalent circuit.

The mass transfer resistance is negligible at this high voltage. MEA with a PtFeNi cathode shows R_m value of $0.14 \Omega \cdot \text{cm}^{-2}$ for both air and O_2 , while the results of R_{ct} were 0.76 and $1.32 \Omega \cdot \text{cm}^{-2}$ for O_2 and air, respectively. The R_{ct} value for pure Pt MEA were 1.15 and $1.4 \Omega \cdot \text{cm}^{-2}$, which are higher than PtFeNi MEA. The results demonstrate that PtFeNi cathode possess better ORR activity than the pure Pt cathode.

In addition, the preliminary stability assessment of the single cell was evaluated at room temperature, fueled with humidified H_2 (8 sccm/ cm^2) and dry O_2 (5 sccm/ cm^2) under atmosphere pressure. Fig 4.14 (a) shows the stability result; with a constant input current density of $1 \text{ A}/\text{cm}^2$. The cell voltage exhibits relatively stable at around 0.5 V, which equals to a specific power output of about $0.5 \text{ W}/\text{cm}^2$.

During the durability test, the cell was self heated up to around 40°C , but the anode was humidified only at 22°C . The cell voltage shows a tendency of declining slowly, which is attributed to the lack of humidification at the anode. In order to confirm that such voltage decrease is not related to the catalyst activity, the cathode input and output gas pipe were exchanged during the testing in order to pull more water back to the anode. From Fig 4.14 (a), one can see that after this swapping the cell voltage reverts back to even higher than 0.5 V, because higher cell temperature with sufficient humidification improves the reaction efficiency.

Fig. 4.14 (b) displays the comparison of I-V polarization curve before and after the durability test. Although there is a decrease tendency as shown in Fig. 4.14 (a), the I-V curve reveals a slightly better performance after this long time operation, which further confirms that there is no catalyst activity loss after the testing.

Fig 4.14. (a) Long time stability of the MEA. (b) I-V polarization curves of the single cell before and after long time running

Electrodeposition provides a gradually changed catalyst loading in the catalyst layer. At the surface of the electrode the catalyst loading is quite high. The high density of electrocatalysts at the surface improves the reaction efficiency. However as the increase of depth into the electrode, the catalyst loading decreases which offers an optimized catalyst layer structure.

4.5 Comparison of fuel cell performance with conventional electrodes

To have a better understanding of the fuel cell performance prepared with PtFeNi cathode, pure Pt electrodes prepared by 50 wt.% Pt/XC-72 with a loading of 0.4 mgPt/cm² was also characterized under the same operating condition to compare. While the catalyst loading for PtFeNi cathode is 0.05 mgPt/cm².

Fig 4.15 (a) presents the comparison of fuel cell performance for pure Pt and PtFeNi cathodes. Surprisingly, even though the catalyst loading for pure Pt cathode is 8 times higher than PtFeNi cathode, it produced comparable polarization profiles. PtFeNi cathode shows higher open circuit voltage than the pure Pt cathode, demonstrating reduced cathode overpotential than Pt catalyst. This result is in coincidence with the EIS results shown in Fig 4.15. The reduced cathode overpotential should be attributed to the better electro-catalytic activity of PtFeNi ternary catalyst towards ORR.

Fig 4.15 (b) shows the comparison of current density output of the two cathodes at 0.8 and 0.6 V. At 0.8 V, PtFeNi cathode exhibits a current density of 0.16 A/cm², which is 50% higher than pure Pt cathode of 0.107 A/cm². However with regard to the mass current density output, which is normalized to the Pt loading; PtFeNi cathode shows 3.2 A/mgPt, which is 12 times higher than pure Pt cathode of 0.268 A/mgPt. At 0.6 V, MEA with PtFeNi cathode exhibited mass current density of 14.8 A/mgPt, which is 8 times higher than the pure Pt cathode. In brief, PtFeNi cathode shows about 10 times improved mass power output than commercial Pt catalyst, which indicates its potential for commercial application.

Fig 4.15 (a) Polarization profiles of MEAs prepared with both pure Pt cathode and PtFeNi cathode, (b) Comparison of the specific current density output and mass current density output at 0.8 and 0.6 V for pure Pt and PtFeNi electrodes

4.6 Characterization of the MEA cross section

To investigate the catalyst layer structure, the cross section of a as-prepared MEA was studied by SEM. Fig 4.16 (a) shows the SEM image of the cross section and (b) is the corresponding back scattered image. The two bright portions between the Nafion membrane (the middle dark portion) present heavier elements such as Pt, the left bright portion presents the catalyst layer of PtFeNi cathode with a Pt loading of 0.05 mg/cm², while the right side displays the catalyst layer of pure Pt anode with a loading of 0.4 mg/cm². Fig 4.16 (c) is the higher magnification image of the cathode and Fig 4.16 (d) is the image of anode. By comparison we can see that both electrodes have a catalyst layer thickness of around 10 μ m. However, the catalyst distribution is different.

Unlike the even catalyst distribution at anode, catalyst distribution at the cathode is uneven in terms of indepth direction. At the outer surface of cathode the catalyst density is rather high which has also been demonstrated in Fig 4.16 (a), (c), and (d); while it decays with increasing distance from the surface into the catalyst layer. This new type of functional graded catalyst layer structure has also been observed in others papers with electrodeposition method .

It is believed that this unique uneven structure plays a very important role in high performed cathode with ultra low Pt loading, as this *in situ* formed catalyst layer by electrodeposition improves the catalyst utilization efficiency.

Fig 4.16 (a) is the SEM image of the MEA cross section, (b) is the corresponding back scattered image; (c) and (d) are the high magnifications for the PtFeNi cathode and Pt anode, respectively

4.7 Conclusion

In conclusion, a three-step electrodeposition based process has been demonstrated for the fabrication of PtFeNi electrodes. This process includes the electrodeposition of FeNi alloy, galvanic displacement to form PtFeNi alloy catalyst, and the electrochemically coupled chemical dissolution of surface Fe and Ni atoms to form a core shell structured PtFeNi catalyst. Functionalization of the carbon black substrate

was found to be important in order to acquire a better FeNi distribution. These as-prepared PtFeNi based electrodes shows good ORR activity in a fuel cell with an ultra-low Pt loading of 0.05 mgPt/cm^2 . The reason for its good performance is attributed to the following aspects:

1. The in-situ formed catalyst layer structure by electrodeposition process improves reaction efficiency due to its functionally graded catalyst distribution. This in-situ formed catalyst layer has high catalyst loading at the electrode surface and membrane interface where the catalyst utilization is relatively higher. However, the catalyst loading decreases when away from the electrode surface where the reaction activity is relatively lower.

2. In conventional powder type processes to prepare electrodes, a large portion of catalyst particles are hide in-between the catalyst supports (i.e., XC-72 carbon blacks). While in this process all catalyst are in contact with the mass transport channels, which brings higher catalyst utilization efficiency.

3. Due to the use of electrodeposition, all metal catalysts have firm connection to the electrode thus ensure that each catalyst particles is in electrical contact with the carbon paper backing.

4. PtFeNi alloy has improved electrocatalytic ORR activity as compared to pure Pt. Furthermore, the core shell structure with a Pt poor core helps to reduce the overall Pt loading.

CHAPTER 5. Control of the parameters in electrodeposition based three-step process to prepare Pt-alloy electrodes

5.1 Introduction

A three-step process is described in this chapter, which involves firstly the electrodeposition of FeNi nanoparticles to act as the seeds to form PtFeNi nanoparticles. The electrodeposition of FeNi also determines the uniformity of the catalyst distribution and the catalyst layer thickness. Secondly, a galvanic displacement process is implemented to form PtFeNi ternary alloys. In this process the loading of Pt is controlled by changing the amount of Pt containing solution. Lastly, those unalloyed and excess surface Fe, Ni atoms were dissolved in a 0.5 M H_2SO_4 solution in repeated CV waveforms between -0.25 – 1.25 V. After these three processes, core-shell structured PtFeNi ternary alloy catalysts with a FeNi core and PtFeNi shell is obtained.

In this chapter, the control of catalyst uniformity, catalyst layer thickness, the loading of noble Pt catalyst, and different alloy catalyst compositions were investigated and discussed in order to have a better understanding and to optimize the electrodeposition-based three step process.

5.2 Control of the uniformity

Uniformity of the catalyst distribution is one of the major concerns with respect to the commercialization of the new process. In this study, the in-house designed experiment setup ensures that catalyst will only be electrodeposited on only one side of the electrode with an effective area of $5 \times 5 \text{ cm}^2$.

During the electrodeposition of Fe, Ni, or FeNi some minor bubbles were observed on the electrode. In the process of the electrochemical dissolution of excess and unalloyed Fe and Ni atoms, minor bubbles were also observed. One can judge the uniformity of catalyst deposition is related to the uniformity and size of these bubbles. Fig 5.1 shows the image of minor hydrogen bubbles breaking away from the electrode surface during the process of electrochemical dissolution of Fe and Ni atoms. From this image, one can see that these bubbles are tiny in size and uniformly distributed on the electrode surface, showing that the electrodeposited Fe and Ni atoms are also uniformly distributed on the electrode surface.

In the electrodeposition process, the current density of the pulse should be well controlled. A small current density will lead to a more uniform catalyst distribution and deeper penetration of electrodeposition. However, as illustrated in the last chapter, small current density in electrodeposition will produce relatively larger metal particles size, thus a larger current density is preferred in order to obtain a smaller catalyst size. In this case, a current density of 100 mA/cm^2 would not produce hydrogen bubbles that were too large; hence, it was kept constant throughout the experiments.

Fig 5.1. Hydrogen bubbles breaking away from the electrode surface in the process of electrochemical dissolution

Based on visual inspection, the stagnant bubbles first covered the bottom part of the GDL before covering the whole exposed surface of the GDL. Also, minute hydrogen bubbles escaped from all areas of the exposed surface of the GDL. This implied that by using this set-up for a larger GDL, deposition would still be well distributed and the non-noble metal electrodeposited would be uniform.

There tends to be edge effects in electrodeposition that causes non-uniformity where there is accumulation of charge density at the edges as compared to the parallel electrode surface. As shown in Fig 5.2, if a piece of carbon paper is directly immersed into the electrolyte, there will be current accumulation along the edges and cause unwanted high deposition at the edges.

Fig 5.2. Poor arrangement of electrodes favors deposition on the edges

This will cause more deposition at the edges of the GDL. However, the design of this acrylic electrodeposition bath eliminated this effect, by isolating the edges of the carbon fabric with the electrolyte.

The samples were allowed to dry after electrodeposition. After the deposition of metal nanoparticles, the color of the electrode surface turns from dark black to a lighter color. The colors of the deposited layer offer another means to judge the uniformity of electrodeposited catalyst by visual inspection. Fig 5.3 (a) and (b) present the images of electrode surface after the electrodeposition of Ni with total charges of 1.5 and 3.0 C/cm^2 , respectively. It was obvious and understandable that there were more Ni nanoparticles electrodeposited at charge density of $3\text{C}/\text{cm}^2$ due to their more intense colour as compared to $1.5\text{C}/\text{cm}^2$. The author also confirmed that edge effects of electrodeposition were not an issue here, as the edges of the carbon support layer do not show any intense color.

Fig 5.3. Electrodeposited GDLs prepared total charges of (a) $1.5\text{C}/\text{cm}^2$, (b) $3\text{C}/\text{cm}^2$, red line cropped area indicate the effective area for electrodeposition

5.3 Control of catalyst layer thickness

The thickness of catalyst layer has strong effect on the transport of electrons, gas and water in the electrodes during fuel cell operation, thus affecting the final fuel cell performance. A thinner catalyst layer will be in favor of better mass and electrons transportation [7]. As the catalyst used is Pt or Pt alloys supported on carbon supports,

thus a high Pt to carbon ratio will lead to a thinner catalyst layer thickness with respect to a proper catalyst loading. However, there are still technical limitations for the Pt to carbon ratio, with the increase of Pt to carbon ratio it is also harder to control the Pt catalyst particles size and uniformity.

In this study, transitional metals (Fe, Ni, and FeNi) were first electrodeposited on the electrode before the Pt galvanic displacement process. The thickness of the catalyst layer is controlled by the thickness of electrodeposited transitional metal layer. In this pulsed electrodeposition process, electrolyte will penetrate into the electrode, when the pulse current is on, the metal ions in the electrolyte near carbon substrate will be momentarily transferred to the carbon substrate and induce a metal ion depletion layer. Then, the current was off to allow replenishing of ions into the depletion layer to ensure the use of a higher overpotential in order to obtain smaller metal particles size.

After repeated current on and off waveforms, a high metal loading will be formed on the outmost surface of the electrode, and the metal loading will decrease with increased indepth into the electrode. In this study, it was that if one use a hydrophobic substrate, the metal nanoparticles will only be deposited on the very surface of the electrode due to its hydrophobic nature. Thus the carbon paper substrate with hydrophilic side facing the electrolyte was used.

A micro-porous layer composed of CA-treated carbon blacks, proper amount of Nafion sprayed on PTFE-treated carbon paper to act as the hydrophilic layer was used. A spray gun (Badger Model 100-LG) assisted by compressed air was used to prepare this micro-porous catalyst support layer. In this process, the density and porosity of

this layer was affected by the pressure and flow rate of compressed air. High air pressure and flow rate will bring to a denser structure.

Fig 5.4 shows the SEM images of micro-porous carbon layer sprayed on PTFE-treated carbon paper at different air flow rate and pressure. By comparison, one can see that as shown in Figs 5.4 (b1) and (b2), when the air pressure and flow rate is high, the structure is quite dense and the porosity is relatively low, and the surface of this hydrophilic layer is smooth. However, when the air flow rate and pressure is low, this micro-porous layer presents a rough and polyporous structure as shown in Figs 5.4 (a1) and (a2). This kind of structure will allow deeper penetration of electrolyte into the electrode and help to produce a thicker catalyst layer in the process of pulse electrodeposition.

Fig 5.4 SEM images of hydrophilic micro-porous carbon layer sprayed on PTFE treated carbon paper at (a1), (a2): low air pressure and flow rate, (b1), (b2): high air pressure and flow rate

Both the carbon substrate prepared with high and low air flow rate and pressure were used as cathodes for MEAs preparation. Either dense or loose carbon substrates were placed into the slit of the experiment setup and FeNi alloy was electrodeposited on both electrodes. Then proper amount of Pt containing solution was carefully dropped onto the surface of the two electrodes to prepare PtFeNi alloy electro-catalyst with a catalyst loading of 0.05 mgPt/cm^2 . Excess and unalloyed Fe and Ni atoms were cleaned up in $0.5 \text{ M H}_2\text{SO}_4$ solution under 10 cycles of CV waveforms between -0.25

- 1.25 V.

Figs 5.5 (a) and (b) display the back scattered images of the cross section of MEAs prepared with dense and loose catalyst support layer. Back scattered image can easily distinguish atoms with large atomic number from low atomic number atoms. The bright portion in these two images represents precious metal atoms of Pt, while the dark area on the right side of the two images represents Nafion membrane, and the dark area on the left side shows the carbon substrate.

As one can see from Fig 5.5 (b), when the catalyst support layer is sprayed with low air flow rate and pressure, a catalyst layer with a thickness of more than 10 μm was obtained. At the interface of cathode and membrane, the catalyst loading is rather high, and the catalyst loading gradually decreases the away from the outmost cathode surface. The cathode adheres firmly with membrane and no gap between the electrode and the membrane can be observed.

For comparison, Fig 5.5 (a) present the back-scattered image of the cross section of MEA prepared with dense catalyst support layer. Compared to Fig 5.5 (b), the catalyst layer thickness is only around 3-5 μm . At the electrode-membrane interface, ultra-high catalyst loading can be observed from the image, while the catalyst loading decreases abruptly when away from the electrode surface. Some gaps can be observed between the electrode and the membrane, indicating a relatively poor adhesion between the electrode and the membrane.

Fig 5.5 Back-scattered image of the cross section of MEAs prepared with (a) electrode prepared on dense hydrophilic carbon layer, (b) electrode prepared on a loose hydrophilic carbon layer

To study the effect of carbon substrate density and porosity on the performance in a real single cell environment, two PtFeNi electrodes synthesized with dense and loose carbon substrate with catalyst loading of 0.05 mgPt/cm^2 were used as the cathodes of two MEAs. The anodes for both MEAs were prepared by brushing 50 wt.% Pt/carbon black catalyst slurry on PTFE-treated carbon paper, and the loading was 0.4 mgPt/cm^2 for both anodes.

Fig 5.6 (a) and (b) show the polarization curves and power output profiles for the two as-synthesized MEAs, respectively. The PtFeNi electrode prepared by relatively loose carbon black substrate show much better fuel cell performance than that prepared by dense carbon black substrate. At the working voltage of 0.6 V, catalyst prepared on loose substrate exhibited a current density of 660 mA/cm^2 , which is about twice higher than the current density produced by electrode prepared on dense substrate (320 mA/cm^2).

Usually, a thinner catalyst layer is pursued in conventional PTFE-bonded method or thin film methods. As the catalyst loading of commercial electrodes are around $0.3 - 0.5 \text{ mgPt/cm}^2$, the catalyst layer thickness prepared by conventional methods is in the range of $10\text{-}30 \text{ }\mu\text{m}$. Inversely, when the catalyst loading is 0.05 mgPt/cm^2 , a thickness of $10 \text{ }\mu\text{m}$ has been proved to be better than that of $3 - 5 \text{ }\mu\text{m}$.

Fig 5.6 Comparison of the (a) polarization profiles and (b) power output profiles of MEAs prepared with different cathodes: PtFeNi catalysts prepared on loose and dense carbon substrates

5.4 Influence of catalyst loading

In the last section, the performance of PtFeNi ternary electro-catalyst prepared on loose and dense carbon substrate we compared; demonstrating that a relatively looser carbon black substrate will produce a catalyst layer thickness of around $10 \text{ }\mu\text{m}$ and improve the fuel cell performance twice at the working voltage of 0.6 V .

In this section, PtFeNi ternary catalysts were prepared on the loose carbon black substrate with different Pt loading to investigate the relationships of fuel cell performance with Pt loading.

PtFeNi electrodes with four different Pt loading were prepared, their use as MEA cathodes were also characterized and compared. Fig 5.6 (a), (b), (c), and (d) display the SEM images of PtFeNi electrodes surfaces with different electro-catalyst loadings of 0.02, 0.35, 0.05, and 0.1 mgPt/cm², respectively. These electrodes were prepared based on electrodeposited FeNi alloy with total charges of 3 C/cm². After the Pt galvanic displacement process, excess and unalloyed Fe and Ni atoms were dissolved in 0.5 M H₂SO₄ under 10 cycles of CV waveforms between -0.25 – 1.25 V.

From Fig 5.6 (a), one can see that at the low Pt loading of 0.02 mgPt/cm², some Pt nanoparticles were formed on the carbon blacks with well dispersed particles size of about 2-3 nm. As shown in Fig 5.6 (b), when the loading of Pt catalyst rise to 0.35 mgPt/cm², there are more PtFeNi nanoparticles decorated on the carbon blacks supports, but the particles size distribution is still in the range of 2-3 nm. When the Pt loading rises up to 0.05 mgPt/cm², higher density of Pt nanoparticles was found to cover the carbon blacks substrate.

Fig 5.6 (c) shows the SEM image of PtFeNi electrode surface with Pt loading of 0.05 mgPt/cm². As shown in the image, PtFeNi nanoparticles cover most of the surface of carbon supports, and the size distribution of ternary alloy catalyst remains uniform with an average diameter of 3 nm. The ultra-high electro-catalyst loading and yet small catalyst size indicates that this electrode possess good electro-catalytic activity

in a real MEA environment. As shown in Fig 5.6 (d), when the Pt loading was further increased to 0.1 mgPt/cm^2 , all carbon blacks surface were buried in PtFeNi nanoparticles. At such loading, these ternary catalysts agglomerate together with an average diameter of 4-5 nm.

Fig 5.7 SEM images of PtFeNi electrodes surface with different catalyst loadings of (a) 0.02 mgPt/cm^2 , (b) 0.35 mgPt/cm^2 , (c) 0.05 mgPt/cm^2 , (d) 0.1 mgPt/cm^2 , respectively

These electrodes at different Pt loadings were used as the cathodes in MEAs to compare their electro-catalytic activities towards ORR. The anodes for all MEAs were

synthesized by brushing 50 wt.% Pt/carbon black slurry on PTFE-treated carbon paper.

Fig 5.8 (a) and (b) compares the polarization and power output profiles for different cathode Pt loadings, respectively. From the result, one can tell that the cathode Pt loading of 0.05 mg/cm² produce the best performance. When the cathode Pt loading was increased to 0.1 mg/cm², the catalyst size also increases from 3 nm to 4 – 5 nm, inducing a drop in fuel cell performance. As seen from Fig 5.7 (d), the catalyst grains agglomerate together to induce the block of mass transport pathways, which might be another reason for the decrease of fuel cell performance at 0.1 mgPt/cm².

Fig 5.8 Comparison of the (a) polarization profiles and (b) power output profiles of MEAs prepared with different Pt loadings.

However, at the loading of 0.05 mgPt/cm² the catalyst particles size is no difference with lower loadings of 0.035 and 0.02 mgPt/cm². Thus, with the increase of Pt loading,

the fuel cell performance would improve as expected. Table 5.1 summarizes the peak power density, current density and mass power output at 0.6 V for different Pt loadings. The results confirm that 0.05 mgPt/cm² is the best loading in this study.

Table 5.1 Comparison of the peak power density, current density and mass power output at 0.6 V for different cathode Pt loadings.

Catalyst Loading	Peak power density	Current density at 0.6 V	Mass power output at 0.6 V
0.1 mgPt/cm²	> 427 mW/cm ²	520 mA/cm ²	3.12 W/cm ²
0.05 mgPt/cm²	> 533 mW/cm ²	760 mA/cm ²	9.18 W/cm ²
0.035 mgPt/cm²	277 mW/cm ²	320 mA/cm ²	5.49 W/cm ²
0.02 mgPt/cm²	217 mW/cm ²	164 mA/cm ²	5.05 W/cm ²

5.5 Influence of alloy catalyst composition

Despite the electrodeposition of FeNi alloy, pure Fe and Ni nanoparticles were also electrodeposited on the uncatalyzed electrodes, thus different compositions of PtFe, PtNi, and PtFeNi were synthesized to compare their electro-catalytic performance towards ORR in MEA environments. The study found that the use of Fe, Ni, and FeNi as the different substrates to synthesis Pt-alloy catalyst in the galvanic displacement process produced different Pt-alloy catalyst nanoparticles size. The detail characterization and comparison of PtFe, PtNi, and PtFeNi catalysts will be described

below.

5.4.1 PtFe alloy catalyst

Back scattered electron images were captured to give a quick and better idea of the existence and distribution of Pt catalysts on the electrode surface. Fig. 5.9 shows the back-scatter image of a PtFe sample after dissolution of excess and unalloyed Fe atoms. As mentioned before, the brighter area correlates with higher mean atomic number while darker area represents lower mean atomic number in the sample. As one can see from Fig 5.9, brighter spots that represent Pt particles were wrapped around the darker areas, which represent carbon blacks support or Nafion structures. The distribution of Pt was uniform which also prove that pulse current electrodeposition has created good distribution of non-noble metal for the galvanic displacement of Fe surface atoms by Pt particles from the Pt salt.

Fig. 5.9. Back-scatter image of PtFe electrode surface with Pt loading of 0.05 mg/cm^2

Fig 5.10 (a) and (b) display the SEM images of PtFe electrodes with different Pt loadings after the electrochemical dissolution process of excess and unalloyed Fe atoms. As shown in both the two images, PtFe alloy nanoparticles can be observed decorating on the surface of carbon blacks supports. These PtFe nanoparticles were formed on the carbon blacks side by side and show bunches morphology. Each PtFe nanoparticle is composed of a core-shell structure, which is made up by a non-noble metal core and a Pt-poor outer shell. There have been many works reported on the dissolution of the transition metals in Pt-based alloy that leading to the formation of Pt enriched skin; leaving a “transition metal-rich core” and a “Pt-rich shell” combined structure which is similar in this case. This phenomenon of Pt enrichment after dissolution produced well-defined, individual core-shell structured PtFe nanoparticles. Within this core-shell structure, the mismatch of crystal lattice between surface and core elements causes additional lattice strain on the surface, shifting the d band center of the surface Pt layer and therefore altering the electronic properties of the surface Pt layer. This phenomenon reduces the adsorption energy of oxygenated intermediates, leading to enhancement in ORR kinetics.

Fig 5.10. SEM images of PtFe electrode surface with different Pt loadings after the electrochemical dissolution of excess and unalloyed Fe atoms, (a) 0.03 mgPt/cm², (b) 0.05 mgPt/cm²

From the comparison of electrode surface with different Pt loadings in Fig 5.10 (a) and (b), it was noticeable and reasonable that a higher Pt loading demonstrates higher density of PtFe nanoparticles decorated on carbon blacks supports and exhibited better distribution. There were significantly more Pt particles at 0.05mg/cm² loading and the particles also showed a better spread over the surface.

Particle size distribution was also studied for various FESEM samples for a randomly selected small area of $2.4 \times 10^{-13} \text{ m}^2$. The particle size distribution could be assumed to be similar for the fabricated electrode area $3.3 \times 10^{-5} \text{ m}^2$ due to uniform distributions of Pt-M alloy catalysts. Higher magnification of Pt clusters and its corresponding size histograms of PtFe electrodes with different Pt loadings are shown in Fig 5.11 and Fig 5.12. The size distribution histograms were obtained by counting 100 randomly selected nanoparticles from the high magnified FESEM images.

Pt electrodeposits prefer to deposit on the existing Pt particles when the Pt loading is high; thus leading to the growth of the Pt particles size. As reported in many papers [35, 266], a major drawback of electrodeposition is the large Pt particles size (20-70 nm). In these cases, although electrodeposition process was proved to be able to improve the catalyst utilization efficiency, the large Pt particles size induced to a poor fuel cell performance. There is no advantage for a catalyst with large sizes of 20-70nm even if every Pt particle was utilized [9]. Thus, means were taken by researchers to reduce Pt particle sizes close to commercial size of ~3 nm.

Fig. 5.11. SEM image of PtFe electrode with a Pt loading 0.03 mgPt/cm^2 and its corresponding particle size distribution

Fig. 5.12. SEM image of PtFe electrode with a Pt loading 0.05 mgPt/cm^2 , and its corresponding particle size distribution

FESEM image and its particle size distributions histogram appear in Fig 5.11 revealed that lower Pt loading of 0.03 mgPt/cm^2 produced PtFe particles with a mean size of 5.54nm. However, a slightly higher loading of 0.05 mgPt/cm^2 produced Pt particles with an only slightly larger mean size of 6.08nm.

Even the Pt loadings are already very low in this project, a higher loading 0.05 mg/cm^2 compared to 0.03 mg/cm^2 indeed gave larger sized Pt particles. However, the author concluded that both loadings did not give significantly difference in Pt particle size (5.54nm vs. 6.08nm) while the sizes are too big. Take account into the deviation, it can be considered that both electrodes have more-or-less identical PtFe nanoparticles size. Since the sample with a 0.05 mg/cm^2 loading had a significantly better distribution and dense spread of Pt particles, the surface area of Pt available for chemical reactions would be larger even though the Pt particles were a little bigger. Hence, it would be

reasonable to predict that performance of a higher loading and better distributed electrode will produce a fuel cell with better performance.

Fig 5.13. TEM result of PtFe nanoparticles and its corresponding particles size distribution histogram

The morphology of Pt particles was observed by TEM as well. The PtFe sample with 0.05 mgPt/cm^2 loading was characterized with TEM. As shown in Fig 5.13, the PtFe particles were overlapping on one another, making it difficult to identify one Pt particle from another. This fabrication method of electrode was unlike the commercially available Pt/C where the Pt particles were very well defined and may take an elliptical or spherical shape. Hence, the size histogram in Fig 5.13 was based on the more defined particles around the edge of the Pt cluster. Based on FESEM and TEM comparison, the mean particle size of Pt is in agreement.

Once again, the dense and well-distributed Pt particles (for $0.05\text{mg}/\text{cm}^2$ loading) coupled with their small mean particle size suggested a large surface area of Pt available for the chemical reactions to occur. These findings obtained from FESEM and TEM characterizations gave a positive prediction on the performance of the PtFe fuel cell.

5.2.2 PtNi alloy catalyst

Fig 5.14 presents the back scattered image of a PtNi electrode surface with a Pt loading of $0.05\text{ mgPt}/\text{cm}^2$. As observed from this image, a group of bright areas representing precious metal atoms were uniformly dispersed in the image. In comparison to the back-scatter image of PtFe with the same Pt loading in Fig 5.7, PtNi catalysts show a higher degree of blending with the darker areas that representing carbon blacks and Nafion structures. A lower Pt to carbon ratio on the outmost electrode surface may be responsible for this difference.

Fig 5.14. Back scattered image PtNi electrode surface with a Pt loading of $0.05\text{mg}/\text{cm}^2$

Fig 5.15 shows different magnifications of SEM images of PtNi electrode surface. It was also evident that at the electrode surface, PtNi particles were as many as PtFe presented in Fig 5.10 (b). A worthy point to note from FESEM results was that the morphology of PtNi structures was unlike that of PtFe structures. With the same loading of $0.05\text{ mgPt}/\text{cm}^2$, the lesser PtNi catalyst density than PtFe catalyst on the outmost electrode surface could be explained by the difference in galvanic displacement process. In the galvanic displacement process, Fe atom reacts faster with Pt^{4+} ions than Ni atoms to form Pt atoms, resulting that more Pt atoms were formed on the PtFe electrode surface; while the slower reaction speed of Ni atoms with Pt^{4+} ions causing more Pt^{4+} penetrate into the electrode and form PtNi alloy inside the electrode. It is believed that higher catalyst density on the surface is favorable in a MEA

environment, because of higher reaction efficiency on the electrode surface. On the electrode surface, the proton conductive resistance is smaller and therefore improve the reaction efficiency. An ideal electrode should have as high Pt loading as possible at the surface if the catalyst size and distribution can be well controlled.

Fig 5.15. SEM images of PtNi electrode surface with different magnifications at the loading of 0.05 mgPt/cm²

In order to have a better understanding of the PtNi catalyst structure and size distribution, TEM characterization was conducted and the result was presented in Fig 5.16. A particle size distribution histogram was also shown in Fig 5.16 by counting

100 randomly selected PtNi nanoparticles. As shown in Fig 5.16, PtNi nanoparticles were formed on the surface of carbon black supports, a mean particle size of 3.28 nm was calculated for PtNi catalysts. By comparison to the TEM results of PtFe catalysts shown in Fig 5.13, PtNi catalysts (3.28 nm) exhibit a much smaller mean size than that of PtFe alloy (5.52 nm).

Fig 5.16. TEM image of PtNi particles at a Pt loading $0.05\text{mg}/\text{cm}^2$ and its corresponding particle size distribution histogram

Overall, PtFe electrode shows a higher catalyst loading and better distribution at the outmost surface, which is a big advantage for the use in a MEA environment as compared PtNi electrode. However, with regard to the mean particles it is an inverse story, i.e., the mean Pt particle size of PtNi alloy was 40% of that in PtFe alloy. One of them possesses better catalyst layer structure and another shows smaller catalyst particles size: both aspects are the primary issues in preparing an improved electrode,

thus PtNiFe ternary electrocatalyst is studied in the following section.

4.2.3 *PtFeNi alloy catalyst*

Fig 5.17 displays a representative back scattered image of PtFeNi electrode surface. The brighter areas representing PtFeNi electro-catalysts are uniformly distributed over the whole surface, indicating a uniform distribution of catalyst. The proportion of bright area is identical with PtFe electrode shown in Fig 5.7, which is higher than PtNi electrode as shown in Fig 5.14. Several large gray areas that circled in the image demonstrate the distribution of Nafion. Other small gray areas could be observed on the side of almost every bright spots, indicating that all the catalysts are in good contact with Nafion electrolyte. Take into consideration that all the catalysts were in electrical contact with the carbon paper backing and the thin catalyst layer (around 10 μm), most of the PtFeNi catalysts were expected to expose to electrons pathway, protons pathway, and reaction agents, and therefore ultra-high catalyst utilization efficiency should be obtained for such an electrode.

Fig 5.17. Back scattered image of PtFeNi electrode surface at a loading of 0.05 mgPt/cm²

Fig 5.18 (a-d) display the SEM images with different magnifications from 6000 $\times$ to 800000 $\times$ of PtFeNi electrode surface. As seen from the low magnified image of Fig 5.18 (a), PtFeNi electrocatalysts cover the electrode surface with excellent uniformity and high density. The high PtFeNi catalyst to carbon support ratio at the surface with well controlled size is favorable for the application in a MEA environment. Some gray areas show the present of Nafion, which is also identified in the back scattered image of Fig 5.17.

Figs 5.18 (b) and (c) display the higher magnifications of PtFeNi catalysts. From the images, one can have a clearer view on the catalyst morphology. High density of PtFeNi nanoparticles were observed covering carbon blacks supports. These catalyst

nanoparticles were packed on carbon black surface side by side and leaving no more rooms on the surface of carbon supports. Refer to the EDX result in Fig 5.15 (f), a very high catalyst loading of 60 wt.% was obtained for PtFeNi catalyst at 0.05 mgPt/cm² on the electrode surface. Fig 5.18 (d) shows the highly magnified (800000 $\times$) SEM image. It is able to distinguish individual electrocatalyst particles from one another. The particles sizes of most catalysts are in the range of 2-3 nm with a uniform size distribution, proving that this kind of PtFeNi electrode with both high catalyst density on the surface and well controlled catalyst size should be ideal for the use in a MEA environment.

Fig 5.18 Different magnification of SEM images of PtFeNi electrode surface at 0.05 mgPt/cm²

Fig 5.19 displays the TEM results of PtFeNi ternary electrocatalysts. In order to have a further investigation on the catalyst morphology and size, a high catalyst to carbon black ratio was confirmed from this image as the whole carbon black surface was loaded with PtFeNi catalyst particles. The densely packed catalysts particles on the surface make it hard to distinguish one particle from another. Luckily, one is still able to count the catalysts particles size from the area near the edge of carbon blacks support. The catalyst size distribution histogram was obtained by counting 100 randomly selected catalyst particles from several TEM images (only one typical TEM image was shown here). A mean particles size of 2.98 nm was obtained. The TEM results further confirmed that the sizes of these catalysts are well controlled.

Fig 5.19 TEM results of PtFeNi catalysts and its size distribution histogram

5.2.4 Fuel cell performance comparison of Pt-M (M=Fe, Ni, FeNi) alloys

In the last sections, the surface morphology and catalyst size of different Pt-M (M=Fe, Ni, and FeNi) alloys were investigated. It was found that the catalyst size is quite different with different compositions. The preparation process was composed of three steps: the first process is electrodeposition of transition metals; the second step is the impregnation of Pt containing solutions to form PtM (M=Fe, Ni, and FeNi) alloys by a galvanic displacement process; at last process is that excess and unalloyed transition metal atoms were removed by a electrochemical dissolution process. Thus the use of different transition metal components can cause the difference of particles size in the electrodeposition process. Among the catalysts, PtNi and PtFeNi are able to produce well controlled particles size of around 3 nm. However, PtFe catalyst has a much larger catalyst size of 5-6 nm. With regard to the second galvanic displacement process, different catalyst layer structures were obtained due to the varied reaction speed of different transition metals with Pt^{4+} ions. PtFe and PtFeNi are able to achieve quite a high catalyst loading on the electrode surface, while PtNi electrode has a much lesser catalyst density on the electrode surface.

Figs 5.20 (a) and (b) present the comparison of polarization and power output profiles for different Pt-based alloy compositions, respectively. It is clear to see that PtFeNi outperforms both PtFe and PtNi catalysts at higher voltage region or low voltage region. The peak power density, current density output and mass power output at working voltage of 0.6 V were summarized in Table 5.2. At 0.6 V, PtFeNi electrodes exhibits 239% and 548% of better performance compared with those of PtFe and PtNi electrodes, respectively.

Fig 5.20 Comparison of the (a) polarization and (b) power output profiles for different Pt-M (M=Fe, Ni, and FeNi) alloys

Table 5.2 Comparison of the peak power density, current density and mass power output at 0.6 V for different cathode Pt-M (M=Fe, Ni, and FeNi) composition.

Composition	Peak power density	Current density at 0.6 V	Mass power output at 0.6 V
PtFe	277 mW/cm ²	320 mA/cm ²	3.84 W/cm ²
PtNi	203 mW/cm ²	140 mA/cm ²	1.68 W/cm ²
PtFeNi	>532 mW/cm ²	765 mA/cm ²	9.20 W/cm ²

5.6 Conclusion

To improve and optimize the electrode performance prepared by electrodeposition-based three step process, the influence of several conditions such as

catalyst layer thickness, catalyst loading, and catalyst compositions on the performance in MEA cathode environment was investigated and discussed. The conclusions of are drawn below:

- (1) In the spraying process to prepare carbon substrate layer, varying the air flow rate and pressure would affect the carbon substrate structure either in loose or dense form. PtFeNi catalyst prepared on a loose carbon substrate produces twice the performance of that on a dense carbon substrate. The catalyst layer thickness formed on a loose carbon substrate is around 10 μm , while on a dense carbon substrate it is about 3-5 μm .
- (2) PtFeNi ternary catalyst prepared on a loose substrate with different loadings of 0.02, 0.035, 0.05, and 0.1 mgPt/cm^2 were tested in a MEA cathode environment. The Pt particles sizes are about 3 nm for 0.02, 0.035, and 0.05 mgPt/cm^2 . However, when the Pt loading was increased, the particle sizes increase to about 4-5 nm. In a single cell test, the best performance achieved was at 0.05 mgPt/cm^2 .
- (3) In the three-step process to prepare Pt-based alloy catalysts, the composition was found to have significant impact on the Pt-M alloy particles size. PtNi and PtFeNi catalysts are formed with catalyst size of around 3 nm, while PtFe catalysts particles size were about 5-6 nm. At 0.6 V, PtFeNi electrodes exhibits 239% and 548% higher in performance than those obtained on PtFe and PtNi electrodes, respectively.

CHAPTER 6. Conclusions and future recommendations

6.1 Conclusions

In this thesis, novel processes were developed to prepare Pt, Pt-alloy electrodes with improved catalyst utilization efficiency. The work is mainly devoted to the following two methods:

A process based on the impregnation of Pt nanoparticles onto *in situ* grown CNFs on carbon paper was developed to prepare novel electrodes. Such method ensures that all Pt catalysts are in electrical contact with the carbon backing. Furthermore, the use of CNFs as catalyst supports provide better mass transport property and durability compared with carbon blacks.

Another process of a three-step method to prepare nanoengineered PtFeNi alloy catalyst based electrodes with ultra-low Pt loading was investigated and optimized. This method involves firstly the electro-deposition of FeNi alloy onto porous carbon electrode substrate, then follows by galvanic displacement process to form PtFeNi alloy; and finally the excess Fe and Ni surface atoms were selectively dissolved in a chemically coupled electrochemical process. In this process, an improved catalyst structure with better catalyst utilization was formed. The use of Pt-alloy also possesses better ORR activity over pure Pt catalyst.

More detailed conclusions summarizing from this thesis are listed below;

(1) With a CVD process, CNFs with diameters in the range of 20-50 nm were successfully produced directly onto the carbon paper with a loading of about 0.3-0.5 mg/cm². Higher yield of CNFs up to 2 mg/cm² was also obtained. In this case the whole surface of the carbon paper is covered by CNFs, but the diameter of CNFs is larger. The CNFs with thinner diameter is used as catalyst support to study the deposition of Pt.

(2) Firstly, CNFs were functionalized by citric acid, which can introduce carboxyl and hydroxide groups to the surface of CNFs to improve the hydrophilicity. Then, Pt precursor were dropped onto the surface of carbon paper followed by an in-situ reduction with a gas flow of Ar (142.5 ml/min¹) and H₂ (7.5 ml/min¹) for 60 min at 150 °C. H₂PtCl₆·6H₂O dissolved in ethanol, deionized water, and acetone were used as precursor and compared. Ethanol shows the best performance, with the obtained Pt particles mean size of 1.63-2.41 nm and narrow particle size distribution for two different loadings of 0.07 and 0.14 mg/cm², respectively. Cyclic voltamograms were performed for the two electrodes, and the electrochemical active surface area of the two different loadings were 70.2 m²/g (0.14 mg/cm²) and 85.5 m²/g (0.07 mg/cm²), which are 30% and 60% higher than that of commercial one with 50wt. % Pt/XC-72 (Johnson Matthey, 3.5 nm, S_{ESA}=53.3 m²g⁻¹).

(3) With the use of Pt/C catalyst (0.4 mgPt/cm²) as the anode for all MEAs, fuel cell performance of MEAs with Pt/CNFs as the cathode catalysts showed 87% (0.14 mgPt/cm²) and 112% (0.07 mgPt/cm²) higher mass specific power output than Pt/C (0.5 mgPt/cm²) catalyst. The better performance of CNFs electrode is attributed to its

3D hierarchy structure, which improves electron transfer and catalyst utilization efficiency.

(4) A three-step electrodeposition based process has been demonstrated for the production of PtFeNi electrodes. This process includes the electrodeposition of FeNi alloy, galvanic displacement method to form PtFeNi alloy catalyst, and the electrochemically coupled chemical dissolution of surface Fe and Ni atoms to form a core-shell structured PtFeNi catalyst. Functionalization of the carbon black substrate was found to be important in order to acquire a better FeNi distribution. These PtFeNi electrodes show good ORR activity in a fuel cell environment with an ultra-low Pt loading of 0.05 mgPt/cm^2 . The reason for its good performance is attributed to the following aspects:

- a). The in-situ formed catalyst layer structure by electrodeposition process improves reaction efficiency. This in-situ formed catalyst layer has high catalyst loading at the electrode and membrane interface where the catalyst utilization is relatively higher. However catalyst loading decreases in the direction away from the interface but into the electrode where reaction activity is relatively lower.
- b). Electrodes prepared by this process will have no catalyst particles hide between the catalyst supports due to agglomeration; which is a very common issue for other process.
- c). Due to the use of electrodeposition all metal catalysts has firm connection to the electrode thus ensure that each catalyst particles is in electrical contact

with the carbon paper backing.

- d). PtFeNi alloy has improved electrocatalytic ORR activity as compared to pure Pt. Furthermore, the core shell structure with a Pt poor core helps to reduce the overall Pt loading.

(5) In order to improve and optimize the electrode performance prepared by electrodeposition-based three-step process. The influence of several conditions such as catalyst layer thickness, catalyst loading, and catalyst compositions on the performance in MEA cathode environment was investigated and discussed. The conclusions of how these parameters influence the performance were summarized as follows:

- a) In the spraying process to prepare carbon substrate layer, varying the air flow rate and pressure can prepare the carbon substrate either in loose or dense condition. PtFeNi catalyst prepared on a loose carbon substrate produces twice the performance of that prepared on a dense carbon substrate. The catalyst layer thickness formed on a loose carbon substrate is around 10 μm while on a dense carbon substrate it is about 3-5 μm .
- b) PtFeNi ternary catalyst prepared on a loose substrate with different loadings of 0.02, 0.035, 0.05, and 0.1 mgPt/cm^2 were tested in a MEA cathode environment. The Pt particles sizes are about 3 nm at 0.02, 0.035, and 0.05 mgPt/cm^2 , but when the Pt loading was increased further, the size is increased to around 4-5 nm. In the single cell testing, the best performance was obtained at 0.05 mgPt/cm^2 .

- c) In this three-step process to prepare Pt-based alloy catalysts, the composition was found to have significant impact on the Pt-M alloy particles size. PtNi and PtFeNi catalysts are formed with catalyst size of around 3 nm, while PtFe catalysts particles size were about 5-6 nm. At 0.6 V, PtFeNi electrodes exhibits 239% and 548% better performance than that obtained on PtFe and PtNi electrodes, respectively.

6.2 Recommendations and future works

The following subjects are suggested for further development:

- (a) In chapter 3, the use of CNFs *in situ* grown on carbon paper as catalyst support was proved to improve single cell performance by improving catalyst utilization efficiency; while in chapter 4, Pt based alloys on carbon black shown much better intrinsic catalytic property. Therefore, Pt-based alloy catalysts with well controlled catalysts size deposited on CNFs/carbon paper may further improve the electrode performance, which deserved to be further studied.
- (b) In chapter 4, PtFeNi catalyst produce comparable single cell performance with commercial electrodes with only one-tenth of Pt loading. Durability test with tens of hours was conducted. With regard to commercial use, endurance fuel cell test with thousands of hours for PtFeNi electrodes need to be carried out.

(c) PtFeNi electrodes show good performance for the application in low-temperature PEMFC. In the past decades, high-temperature PEMFCs draw plenty attention due to its advantages of CO-tolerance. Thus it is worthy to investigate the use of PtFeNi catalysts in PEMFC at different temperatures such as 80 °C, 150 °C or even 200 °C.

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