SYNTHESIS, CHARACTERIZATION AND PERFORMANCE TESTING OF Pt-
BASED ELECTROCATALYSTS FOR LOW TEMPERATURE PEM FUEL
CELLS

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ABSTRACT

The oxygen reduction reaction (ORR) activity on the cathode plays a significant role in deciding the overall performance of proton exchange membrane (PEM) fuel cells. Dramatic effort has been devoted to the attempt to enhance the catalytic activity and reduce the overpotential caused by the irreversible oxygen reduction reaction on the cathode side of PEM fuel cell. To reduce the electrode overpotential and increase cell performance, the exploration of new catalytic materials as substitutes for the traditionally preferred platinum-only catalyst has been extensively carried out in recent decades. Applying transition metal modified Pt bimetal electrocatalyst instead of Pt is one of the main approaches for this purpose.

The objectives of this research are to identify potential Pt-modified electrocatalysts for the cathode in hydrogen and methanol PEM fuel cells and provide better understanding of the promoting effect of the synthesized electrocatalysts as a function of material atomic ratio, particle distribution and alloying composition.

The physical properties and ORR activity of carbon supported PtFe and PtCr electrocatalysts were studied extensively. All the electrocatalysts were prepared by colloidal method and subsequent catalytic properties and performance were studied. Catalyst surface area was determined by BET nitrogen adsorption and electrochemical methods. Particle size and their distribution were studied by transmission electron microscopy (TEM). X-ray diffraction characterization (XRD) measurements were conducted to determine the crystallite structure. Electrocatalyst activity was evaluated by rotating disc electrode (RDE) and single cell measurements.
It can be concluded from the experiment results that PtFe/C and PtCr/C electrocatalysts could be better replacements for conventional Pt/C as the cathode of PEM fuel cell. The Pt$_{9}$Fe$_{1}$/C and Pt$_{4}$Cr$_{1}$/C gave the best catalytic activity which was demonstrated both on RDE and single cell measurements. For H$_{2}$ PEM fuel cell testing, both of Pt$_{9}$Fe$_{1}$/C and Pt$_{4}$Cr$_{1}$/C showed comparable ORR results with Pt/C; for methanol PEM fuel cell, they displayed a dramatically enhanced oxygen reduction capability and methanol tolerance, compared to Pt/C.

In addition, it was found that the catalytic activity of the studied PtFe and PtCr electrocatalysts varied dramatically at various chemical compositions; also, alloy structure may not be the predominant factor in deciding the enhanced electrocatalytic activity of bimetal electrocatalysts.
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Chapter 1

Introduction

1.1 Background

Fuel cell technology is categorized as one of the techniques that apply electrochemical principles. Fuel cells are electrochemical energy conversion devices which consume fuel and oxidant inside a reactor with the help of electrocatalysts on electrodes, the anode and the cathode. In a fuel cell, electricity is continuously produced as long as reactants are provided and the device converts chemical energy directly into electrical energy, without other stages in between that may cause efficiency loss. The most attractive advantage of fuel cell technology is the high efficiency for overall energy conversion.

1.1.1 History of fuel cell technology and the main classification of fuel cell types

The spontaneous working fuel cell was discovered in the 19th century. The prototype of the invention was simple. However, with R&D efforts, the fuel cell devices have received significant improvements. Many previous technical problems that impeded progress of this technology including water flooding, stack sealing, and fuel distribution are not critical problems anymore. Nowadays, the cost of fuel cell, which was prohibitively high in the past, has been dramatically reduced when compared to about
twenty years ago, but it is still a significant hurdle to be overcome for the successful implementation of the technology.

According to operating temperature, the fuel and electrolyte in fuel cells, fuel cells can be classified in three types as shown in Table 1-1.

1.1.2 Fuel cell applications

Fuel cell technologies can be widely used for different applications. For example, fuel cell technique on Gemini and Apollo airspace for power generation and other auxiliary utilization were the first “demonstrations” of practical fuel cells and those real applications inspired people’s enthusiasm to explore the possible uses of fuel cells. Based on the abundant research efforts placed on fuel cells, the current and potential fuel cell uses have been extended to transportation, stationary, and portable electronic devices. Proton exchange membrane fuel cells (PEMFCs) which are classified as low temperature fuel cells in Table 1-1 are the most promising fuel cells to be mass-marketed in the nearest future.
1.2 Basic aspects of PEM fuel cells

1.2.1 Components of PEM fuel cell

Proton exchange membrane fuel cell is made up of a fuel cell stack and an external load. Membrane electrode assembly (MEA), schematically shown in Figure 1-1,
is the core component of a proton exchange membrane fuel cell which consists of an anode (gas diffusion layer and electrocatalyst), a cathode (gas diffusion layer and electrocatalyst) and a membrane (solid electrolyte) sandwiched in between. The external load could be any electricity consumption device. In fact, the components and structure of fuel cells are more complicated than the one mentioned above. However, those are not the focus of this research since the electrode material, especially electrocatalyst, is the main topic in this study.
1.2.2 Working principle of PEM fuel cell

Proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) are classified as low operating temperature fuel cells. They are very similar systems with close operating principle and operating conditions; even through the cell efficiencies of these two are different. Both of them are based on proton exchange membrane fuel cell technologies. The most significant difference between these two systems is fuel fueling system: H$_2$ fuel for PEMFC and diluted methanol for DMFC. Both of them are among the most promising fuel cells to be commercialized for various applications [1, 2] .

Even though the advantages of PEM fuel cell including high efficiency and low emission are very attractive, there are still unsolved barriers to reaching the goal to truly realize the commercialization of fuel cell technologies in real life: cost is the main issue. Moreover, the two important technical barriers that need to be overcome are related to sluggish electrode kinetics and membranes. For membranes, water retention capability and proton conductivity need to be improved [3-5] since water is the necessary material inside the membrane that enable the movement of protons from one side to the other side. However, the details about the membrane are beyond the discussion in the present research. In this study, improving the sluggish electrode kinetics is the main objective, where the electrode kinetics is directly impacted by the electrocatalytic material used for the electrode reaction.

The theoretical single cell potential is 1.23 V for H$_2$ PEM fuel cell, and 1.19 V for direct methanol PEM fuel cell (DMFC). However, for practical operation, the obtained
single cell potentials are much lower than those expected. For instance, the single cell working potential of PEMFC is usually about 0.7 V and the obtained single cell working potential is only about 0.3 – 0.4 V for DMFC.

What are the reasons that account for the significant differences between the theoretical value and the obtained value? For hydrogen PEM fuel cell, on the anode side, the potential loss due to hydrogen oxidation reaction is trivial and usually can be neglected. However, on the cathode side, the potential losses are mainly due to the overpotential caused by the high irreversibility of oxygen reduction reaction (ORR) (~80%); the overpotential of 200-400 mV explains the primary reason of this low practical working potential. Moreover, for direct methanol fuel cell, in addition to the anodic overpotential due to multiproton dissociation from methanol, the cathodic overpotential due to ORR is significant. The overpotentials produced on both of the electrodes explain the even lower overall working potential of methanol PEM fuel cell compared to hydrogen PEM fuel cell.

More than a decade ago, the idea of utilizing reforming gas directly in PEM fuel cell was very popular. For automobile application, for example, people were excited about using on-board reformer to produce hydrogen to be utilized on PEM fuel cell directly. However, as we know, there is always a strict concentration limit (less than 10ppm) of CO existing in the feeding gas. Once the CO concentration exceeds this level, Pt catalyst is poisoned and fuel cell working function could be fatally destroyed. Unfortunately, it looked like no big progress was achieved on reducing the CO concentration in reformate to a level lower than the acceptable level by PEM fuel cell. Later, this attempt was given up and another option of on-board pure hydrogen supply is
selected as the method for anodic gas feeding for hydrogen PEM fuel cell until now. This decision actually simplified hydrogen fuel cell research progress since there was no need to worry about CO-poisoning of the anode electrocatalyst.

Currently, because of the highly reversible hydrogen reaction, we always treat potential losses on anode of $\text{H}_2$ PEM fuel cells as trivial;

The mechanism of $\text{H}_2$ oxidation is relatively simple, by using Pt as electrocatalyst as example:

\[
\text{H}_2 + \text{Pt} \rightarrow \text{Pt-H}_2 \quad [1-1]
\]
\[
\text{Pt-H}_2 \rightarrow \text{Pt-H} + \text{H}^+ + e^- \quad [1-2]
\]
\[
\text{Pt-H} \rightarrow \text{Pt} + \text{H}^+ \quad [1-3]
\]

Total overall reaction at the anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$ \[1-4]\]

For direct methanol fuel cell, the potential losses from anode could not be neglected since it is almost as important as the losses from the cathode.

The anodic reaction of methanol PEM fuel cell is much more complicated than hydrogen PEM fuel cell as shown below [6]:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6 e^- \quad [1-5]
\]
\[
\text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{Pt-(CH}_3\text{OH)}_{\text{ads}} \quad [1-6]
\]
\[
\text{Pt-(CH}_3\text{OH)}_{\text{ads}} \rightarrow \text{Pt-(CH}_3\text{O)}_{\text{ads}} + \text{H}^+ + e^- \quad [1-7]
\]
\[
\text{Pt-(CH}_3\text{O)}_{\text{ads}} \rightarrow \text{Pt-(CH}_2\text{O)}_{\text{ads}} + \text{H}^+ + e^- \quad [1-8]
\]
\[
\text{Pt-(CH}_2\text{O)}_{\text{ads}} \rightarrow \text{Pt-(CHO)}_{\text{ads}} + \text{H}^+ + e^- \quad [1-9]
\]
\[
\text{Pt-(CHO)}_{\text{ads}} \rightarrow \text{Pt-(CO)}_{\text{ads}} + \text{H}^+ + e^- \quad [1-10]
\]
M + H₂O → M-(H₂O)_{ads} \quad [1-11]

Pt-(CO)_{ads} + M-(H₂O)_{ads} → Pt + M + CO₂ + 2H^+ + 2e^- \quad [1-12]

Pt is an example electrocatalyst; M stands for the metal element and it could be the same or different from Pt. Here reaction [1-5] is the overall anodic half cell reaction and step [1-6] to [1-12] show the complicated mechanism of electrochemical methanol dissociation. This mechanism is widely accepted as the rational explanation of the anodic mechanism.

On the cathode of hydrogen PEM fuel cell, the mechanism of ORR is considerably more complicated than the one for hydrogen oxidation.

An ideal 4-electron transfer can be written as [7]:

O₂ + Pt → Pt-O₂ \quad [1-13]

Pt-O₂ + H^+ + e^- → Pt-HO₂ \quad [1-14]

Pt-HO₂ + Pt → Pt-OH + Pt-O \quad [1-15]

Pt-OH + Pt-O + 3H^+ + 3e^- → 2Pt + 2H₂O \quad [1-16]

Overall reaction at the cathode: O₂ + 4H^+ + 4e^- → 2H₂O \quad [1-17]

The complexity of the oxygen reduction reaction compared to the hydrogen oxidation could be attributed to a couple of possible reasons: (1) multielectron transfer reaction (2) strong O-O bond during reactions (3) side reaction producing H₂O₂ and (4) formation of strongly bonded Pt–O or Pt–OH species during intermediate steps.

The mechanism of ORR for methanol PEM fuel cell is more complicated than the one above because of methanol crossover from anode side to cathode. This complication
leads to even worse catalytic activity performance on the cathode of direct methanol PEM fuel cell.

1.3 Electrocatalysis studies of PEM fuel cells

For fuel cell technique to be accepted by industrial companies, the kinetic performance needs to be improved. Thermodynamic studies have proved the feasibility of fuel cell reactions. However, kinetic studies of fuel cell reactions, especially the electrocatalysis of the ORR electrode reactions need to be further explored and understood. Fuel cell reactions based on different electrodes have dramatically different performances, which mean the discovery of new electrode material with enhanced electrocatalytic performance is one of the keys to the development of fuel cell technologies. Unfortunately, the fundamental research so far on electrocatalytic materials have not explained clearly the principle of how electrode materials contribute to fuel cell reactions.

1.4 Electrocatalytic material studies of PEM fuel cells

For decreasing the electrode overpotential and increasing overall cell performance, the exploration of new catalytic materials instead of the traditionally preferred platinum-only catalyst was carried out extensively in recent decades. Different approaches of exploring the potential electrocatalysts have been developed and different categories of electrocatalytic materials were extensively studied for both the anode and
cathode [8-11]. A significant breakthrough in discovery new electrocatalytic material for PEM fuel cell was the introduction of combinatorial technique for quickly testing and screening electrocatalysts [12]. The combinatorial technique was first time introduced for the application of discovering anodic electrocatalysts for DMFC. The quartnary combination of $\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5$ was found to be most active electrocatalyst in their study. Later, this technique was extensively applied to the research of heterogeneous electrocatalysts by other research groups [13, 14].

For cathodic studies, the main categories of material studied include:

(1) Transition metal modified noble metal alloys or bi-metal and multimetal electrocatalysts. Pt - transition metal alloy and bimetal catalysts have shown good ORR and methanol tolerance capability including supported Pt-Ni, Pt-Rh, Pt-Ir, Pt-Co, Pt-Cr, Pt-Fe, for low temperature PEM fuel cells [10, 14-19]. Bonakdarpour et al. [14] studied the $\text{Pt}_x\text{Fe}_{1-x}$ and $\text{Pt}_x\text{Ni}_{1-x}$ electrocatalysts by combinatorial method. They found that for $\text{PtM}$ binary electrocatalysts, the $\text{Pt}_3\text{M}$ could be the most favorable alloy composition for obtaining the most stable catalytic activity in PEM fuel cell.

PtIr binary electrocatalysts were investigated by Ioroi et al.[15]. The oxygen reduction reaction (ORR) kinetic studies were conducted both on rotating disk electrode (RDE) and PEM single cell. The catalytic activity of ORR was enhanced by a factor of more than 1.5 at 0.8 V vs RHE (reversible hydrogen electrode) at various Ir compositions of 5 -20% in PtIr alloy.

Recently, the application of ternary electrocatalyst of PtCoMn both on anode and cathode for PEM fuel cell was extensively studied by 3M Company [20]. The PtCoMn electrodes, with Pt loading of $0.1 \text{mg Pt/cm}^2 - 0.2 \text{ mg/cm}^2$, showed a substantial
enhancement of fuel cell activity and durability, when compared to Pt/C with higher Pt loading. In addition, the cathodic catalytic studies on RDE showed PtNiFe to be the most active electrocatalyst in the finished measurements: the half wave potential was 0.95 V on PtNiFe vs 0.91 on Pt/C. The catalytic activity was 10 times more active with good stability as demonstrated by cyclic voltammetry (CV) and thermal cycling studies.

Pt based multimetal electrocatalysts with ultra-low Pt mass content was investigated for ORR in PEM fuel cell [21]. Pt-metal monolayer catalysts PtAuNi/C and transition-metal core/precious-metal shell catalysts of PtAuNi/C were studied. With as low as 6 ug/cm\(^2\) Pt loading and at the same produced current density, a 80 mV ORR half-wave potential advantage was obtained on PtAuNi/C electrode, in comparison with Pt/C electrode (with Pt loading of 6 ug/cm\(^2\)) on RDE measurements. In addition, more than 16 times Pt mass activity improvement was acquired on PtAuNi/C electrode as well.

(2) Macrocyclic derivatives of transition metal compounds, mainly for the application of cathode transition metal complexes with porphyrin and non-porphyrin ligands have been extensively studied. One of the approaches is the discovery of non-Pt electrocatalysts: The oxygen reduction activity of Fe and Co metalloporphyrins were investigated extensively [22 - 24]. Jiang et al. tested the catalytic activities of synthesized binary metalloporphyrin through the steady state voltammetry on rotating disk electrode. The heat-treated binary metalloporphyrin of CoTPP/FeTPP and CuTPP/FeTPP (tetraphenylporphyrin) showed better oxygen reduction activities in acidic electrolytic solution in the presence of 1 mol methanol, compared to Pt black electrode; iron phthalocyanine was studied as well for the application of ORR [25]. Lalande et al. found
in their study that iron phthalocyanine (FePc) and tetracarboxylic iron phthalocyanine (FePcTc) showed some degree of ORR activity but with weak stability. The catalytic stability was improved after pyrolysis but the mechanism was not clear.

(3) Other studies on non-Pt electrocatalysts include Ru-based chalcogenides, metal carbide, etc [26-28]. A group of Ru-based bimetallic electrocatalysts (RuCrNx/C, RuTiNx/C, RuPbNx/C, RuCoNx/C and RuFeNx/C) were tested. The RuFeNx/C catalyst showed the onset potential for ORR as high as 0.9 V (NHE) which is comparable to that of the Pt/C catalyst. The maximum obtained power density was 0.18 W/cm² which still needs to be improved [29]. Meng et al reported a 100 mV more positive potential was achieved by tungsten carbide nanocrystal cathodic electrode compared with that obtained from traditional Pt/C cathodic electrode and the exchange current density was two orders of magnitude larger than that on Pt/C [28]. However, the conclusion was based on rotating disk electrode (RDE) measurement only, and the real application on fuel cell was not reported in their research.

The main focus in the current study is on the investigation of fuel cell performance enhancement by first row transition metal modified Pt bi-metal electrocatalysts, mainly including carbon supported PtFe and PtCr as cathodic electrocatalysts. The motivation of working on these materials was based on the assumptions that the addition of first row transition metals to Pt enhances the oxygen reduction reaction and methanol tolerance; the second metal acting as promoter of Pt assists the active catalytic-sites to work at their maximum capacity.
1.5 Objectives of this research

The primary research objective of this work is to identify and exploit high performance transition metal modified Pt-based electrocatalysts which will show better performance at the cathode side than that obtained from Pt-only electrocatalyst when applied to PEM fuel cell, both for hydrogen PEM fuel cell and methanol PEM fuel cell.

The second objective of this work is to provide better understanding of the promoting effect of the synthesized electrocatalysts as a function of material atomic ratio, particle distribution, alloying composition.

1.6 Summary

Significant effort has been placed on the development of fuel cell technology. As one of the technical barriers, the electrode kinetic performance needs to be largely improved. Compared to anodic reaction in both H₂ and methanol PEM fuel cell, more attention needs to be paid on cathodic reaction since it is the significant reason of total efficiency loss. Different approaches have been explored on the investigation of practical cathode material as substitute for Pt. Pt-first row transition metal combinations seem to be a promising approach. The aim of this thesis is to identify, exploit and produce high performance transition metal modified Pt-based electrocatalysts and use them to provide better understanding of the promoting effect of the synthesized electrocatalysts as a function of material atomic ratio, particle distribution and alloying composition.
References:


Chapter 2

Experimental methods

2.1 Introduction

In this chapter, the experimental methods used to enhance the understanding of the catalytic working function of low operating temperature fuel cells, especially PEM fuel cells, are introduced. These methods include electrocatalyst fabrication; electrode preparation; techniques for physical characterization of material surface properties and crystallite structures; and techniques for electrochemical studies of electrocatalysts including rotating disk electrode (RDE) measurement and single fuel cell measurements.

2.2 Synthesis methods

Electrocatalyst performance is affected by several factors. Synthesis route plays an important role in determining the catalyst performance in a fuel cell, especially with respect to catalytic activity and reaction rate. It was found that even by applying the same operating conditions, e.g. T, P, humidity, electrocatalyst and electrocatalyst loading, and electrocatalyst-support composition, fuel cell performances are largely different when different synthesis methods are used [1, 2].

Different methods used for catalyst synthesis include impregnation methods, colloid solution method and electrochemical deposition methods. In the present study, the
The colloidal solution method was chosen to satisfy most of the criteria for obtaining high performance electrocatalysts.

A good method for making electrocatalysts should provide: (1) highly dispersed electrocatalyst on support, (2) narrow particle size distribution and uniform particle composition, (3) multi-metal electrocatalyst structure with preferred atomic ratio, and (4) preferred crystallite structure.

The Bönnemann method, which is one of the colloidal methods, was selected in the current research for electrocatalyst synthesis for the purpose of satisfying most of the criteria above for producing high performance electrocatalysts. The synthesis procedure is presented in Figure 2-1 and the details are explained as below:

- **Me** stands for metals
- All reactions were under inert gas protection

Figure 2-1: The overall route of electrocatalyst synthesis

\[
N(\text{Oct})_4\text{Br} + KHB(\text{Et})_3 = N(\text{Oct})_4HB(\text{Et})_3 + KBr \tag{2-1}
\]

\[
\text{MeCl}_n + nN(\text{Oct})_4HB(\text{Et})_3 = \text{Me}^* (\text{N}[ (\text{Oct})_4^{+} ]_n + n\text{B}(\text{Et})_3 + n/2\text{H}_2 + n\text{Cl}^{-} \tag{2-2}
\]

MeCl\textsubscript{n} stands for metal chloride(s); Me\textsuperscript{*} stands for nanoscaled metal or metal alloys
A series of Pt-based electrocatalysts were prepared by the modified Bönnemann colloidal method [3-5]. The synthesis process was carried out under anhydrous and inert gas conditions. Appropriate amounts of tetraoctylammonium triethylhydroborate, N(Oct)_4HB(Et)_3, were produced by dissolving tetraoctylammonium bromide, N(Oct)_4Br, in tetrahydrofuran (THF). Stoichiometric amount of potassium triethylhydroborate, KHB(Et)_3, was then slowly added to the above solution. After the mixture had been stirred for 2 hours, it was cooled for 6 hours and filtered. The anhydrous metal chlorides, MeCl_n, were dissolved in THF based on the metal atomic ratio in the total. The obtained N(Oct)_4HB(Et)_3 in Reaction [2-1] was added dropwise at 45°C to the dissolved metal chloride(s) in THF to produce metal colloids (Me*). The obtained colloidal solution was added slowly to carbon powder suspension (Vulcan carbon XC-72R from Cabot Corp.) in THF with strong stirring. The supported metal colloid suspension was filtered after 12 hour stirring, then washed with ethanol and dried under high vacuum. Excess protective surfactant surrounding the catalyst surface was eliminated by placing the product into a Lindberg tube furnace and heat treating for 4 hours at 350 ºC with continuous flow of 15% H_2 in N_2. After this treatment, the catalyst was ready to be used.

The electrocatalyst synthesized by this method has the advantages of small average particle size and narrow particle distribution. Moreover, the method is very suitable to producing metal alloys with any atomic ratios as long as the physical solubility is allowed for the prototype of metal chloride(s) in solution.

The preliminary synthesis work done earlier was previously reported [6]. The surface areas of the synthesized supported catalysts were significantly higher than that of
unsupported catalysts which were synthesized by other method from earlier reports [7]. The particle sizes distributed in a narrow range around 3 nm.

2.3 Surface area determination

2.3.1 BET surface area measurements

In the past, especially at the early developing stage of the fuel cell technology, Pt noble metal black was selected as the electrocatalyst for both the anode and cathode. At that time, the loading of Pt metal had to be kept up to several grams per square centimeter to maintain acceptable catalytic activities. The high noble metal loading made the fuel cell device prohibitively expensive. Later, this situation was improved dramatically by introducing catalyst support.

To increase the surface area of catalytic material and potentially increase the material catalytic activities, introducing appropriate catalyst support to the electrocatalyst is one of the effective methods. Carbon supported platinum has higher surface area since the active catalytic sites are largely increased when compared to unsupported platinum. The surface area of supported catalysts have been measured effectively by the method of Brunauer-Emmett-Teller or so called BET method.

However, even though the surface area can be determined using BET method, for supported electrocatalysts, the measured surface area through BET is the sum total of the areas of the catalyst support and catalyst itself. So, the active surface area of the supported electrocatalyst can not be measured properly by this method.
In our earlier studies, the surface area measurements were conducted mainly through BET method; however, realizing the BET measurement may not be very helpful in determining the effective surface area of electrocatalyst, BET measurement wasn’t carried out much during the later research.

### 2.3.2 Chemical surface area determination

As explained earlier in the discussion of BET characterization method, for supported electrocatalysts, the measured surface area is not the active surface area of electrocatalysts themselves but the combination of electrocatalyst support and electrocatalyst. However, with the help from TEM measurement, the more precise active surface area of electrocatalysts (the chemical surface area) can be obtained. The method is described below:

First, find the average particle sizes through TEM measurement; second, assume particles with a spherical geometry; then the estimated particle size is substituted into the formula below [8, 9]:

\[
S_{\text{CSA}} = \frac{6 \times 10^3}{\rho_{\text{pt}} \times D}
\]

[2-3]

Where

- \(S_{\text{CSA}}\) stands for chemical surface area (m\(^2\)/g),
- \(\rho_{\text{pt}}\) stands for density of metal or metal alloys (g/cm\(^2\)), and
- \(D\) stands for the mean diameter of particles (nm).
2.3.3 Electrochemical surface area determination

Electrochemical surface area (ESA) is defined as the actual active chemical surface area that participates in the electrode reactions. Cyclic Voltammetry (CV) electrochemical measurement in conjunction with Transmission Electron Microscopy (TEM) measurement was used to find out the electrochemical surface area of active electrocatalysts.

2.4 TEM characterization

Electrocatalyst particle size and catalyst particle distribution are important parameters in determining catalyst catalytic performance [10] as the Pt electrocatalytic performance is largely affected by various catalyst particle sizes. The particle sizes of electrocatalysts could be characterized by other methods like XRD from which the metal particles can be calculated by Scherer’s formula below:

\[
L = \frac{0.9 \lambda_{\text{Ko}}}{B_{(2\theta)} \cos \theta_{\text{max}}} \tag{2-4}
\]

Where

\(L\) stands for the metal particle size; \(\lambda_{\text{Ko}}\) stands for the X-ray wavelength; \(B_{(2\theta)}\) stands for the half peak broadening; and \(\theta_{\text{max}}\) stands for the maximum angle of diffraction peak of interest.

The XRD method is not straightforward. However it is a very helpful method on crosscheck the particle sizes measured through TEM. To explore the correlation of
particle sizes and catalytic activities, the particles on TEM images can be counted and the particle distribution range is easily determined.

In this study, TEM images of synthesized catalysts were obtained by a Phillips 420T microscope. The operating voltage was 120 kV. The characterized samples were prepared by placing one drop of homogenous catalyst slurry in methanol on the 200 mesh copper lacey carbon film (from Electron Microscopy Sciences). The histograms of measured particle size distribution were obtained by measuring the particle sizes in TEM images.

2.5 EDX measurement for elemental analysis

After the aimed Pt based bi-metal electrocatalysts have been synthesized for a predetermined atomic ratio, the actual atomic ratio of the different elements needs to be confirmed through an instrumental method. The technique of EDX, Energy Dispersive X-ray Analysis, was utilized for such elemental analysis.

EDX analysis is based on the fact that each element of the periodic table has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be uniquely distinguished from each other. However, the EDX has the limitation which is not good for detecting the elements in a small amount in specimen and is not good for detecting a few elements, H for example.

In this study, EDX elemental analysis was carried out on a FEI Quanta 200 ESEM equipped with EDX. The operation was conducted at 20 kV with high beam mode. The samples for EDX measurement were prepared as following: a small piece of double
coated adhesive carbon tape was placed on a sample holder (aluminous cylindrical mount). A thin layer of sample power was spread on the carbon tape. Then the tape surface was sprayed with canned air to remove loose material from the top. The prepared sample was then ready to be characterized.

2.6 XRD measurements

As mentioned earlier, the electrocatalysts that were worked on are Pt-based bi-metal materials. X-ray diffraction measurement (XRD) is very helpful in exploring the fundamental of the effect of material structure on catalytic activities.

To better understand the fundamental working function of electrocatalysts, the metal crystallite size and metal lattice parameter need to be determined. By determining the trend of how electrocatalytic activities change with the variation of crystallite sizes, one obtains an idea of what particle size range of electrocatalysts would be the better choice for achieving higher catalytic activity.

In addition, for the Pt-based bi-metal electrocatalysts, the correlation of the metal crystallite structure and the catalytic activities need to be investigated. XRD is an important technique in detecting metal lattice parameter, which is a strong indication of the degree of alloying of metals.

Current XRD studies were conducted on a Sintag Powder diffractometer using Ni-Filtered Cu $K_{\alpha}$ radiation. The tube current was 30 mA and tube voltage was 35 kV. The scan rate was set as 0.1 deg /min with 0.020° steps. The scans were conducted between the range of 10 - 90 degree. The diffraction pattern analysis was done on the Jade
8.0 software. The Pt fcc reflection patterns were fitted to Gaussian line shapes on a linear background. Scherrer’s formula and Bragg’s equation were then applied to obtain the average particle sizes and lattice parameters, respectively.

## 2.7 Electrochemical measurements

### 2.7.1 RDE measurement

Rotating Disk Electrode (RDE) electrochemical measurement is typically an important method for the electrocatalytic study of catalytic materials. The testing results from RDE can be used to prescreen and evaluate the activity of different electrocatalysts and to select the potential electrocatalyst candidates for fuel cells.

The catalyst performance evaluation in a fuel cell is a complex issue. To evaluate the prepared material, the electrocatalysts need to be combined and tested together with membrane to make membrane electrode assembly (MEA). The catalytic activity obtained from fuel cell measurement may be attributed to factors including electrocatalyst itself, membrane material, and the method of making the MEA. With the same electrocatalyst loaded on MEAs, the tested MEAs could show significantly different power outputs. The RDE measurement can be an efficient method to isolate and determine the relative activity of various electrocatalysts without the influence of membrane and other factors.

The electrochemical activities were evaluated by rotating disk electrode sweep voltammetry and cyclic voltammetry measurements, which were conducted on the RDE-2 instrument (from BASi) in conjunction with the Gamry computer controlling system.
equipped with a PCI-4 potentiostat. The three electrode RDE system consists of a working electrode, a counter electrode and a reference electrode. Platinum coil was used as counter electrode and Ag/AgCl electrode was used as reference electrode. The measured potential was referenced to a reversible hydrogen electrode (RHE). The working electrodes were made by spreading a thin layer of carbon-supported catalyst on the surface of a glassy carbon electrode. The geometric working surface area of the working electrode was 0.07 cm$^2$.

The details of making the working electrode are described elsewhere [11-13]. Briefly, certain amount of electrocatalyst of interest was weighed and added to 1 ml pure ethanol and then mixed with 10 µl diluted 10% Nafion solution (original 20% Nafion from Dupont Company). The catalyst suspension was ultrasonically stirred for one hour until a homogeneous solution was obtained. Then 10 - 15 µl (depending on the interested electrocatalyst loading) of the made solution was then carefully spread on the effective working area of glassy carbon electrode. The electrode was ready for use after being dried in an oven at 60 ºC for about 10 minutes.

To eliminate surface contamination from the Nafion thin film (introduced during electrode making), a cyclic voltammetry with fast scan was applied with a scan range of 0.0 V to 1.0 V for 1 min. Then the electrode was pretreated by placing it into 0.1 M perchloric acid and running three cyclic voltammetry (CV) measurements between -0.1 V to 0.35 V at a rate of 5 mV/s to stabilize the electrode [14]. Electrolytes in this study were 1 M perchloric acid with and without 1 M methanol (Sigma-Aldrich) by diluting high purity concentrated perchloric acid (Sigma-Aldrich) with deionized water (Millipore). The measurements were carried out at room temperature over scan
ranges from 0.2 V to 1.2 V vs RHE for the CV measurements and from 1.0 V to 0.1 V vs RHE for the sweep voltammetry cathodic oxygen reduction measurements at a scan rate of 5 mV/s. The electrolyte was saturated by oxygen for at least 24 hours before the measurements. The glassy carbon electrode used for the substrate of electrocatalyst was polished before each experiment.

The image in Figure 2-2 shows the setup of rotating disk electrode (RDE- 2 from BASi) which was used for RDE measurement. More detail about working principle is described in [15]. RDE was used to evaluate the activities of different electrodes and also used for screening the potential electrocatalytic material.

Linear sweep voltammetry and cyclic voltammetry are the two techniques used for the current studies. Linear sweep voltammetry was used in assessing the electrocatalytic
activities of synthesized electrocatalysts for oxygen reduction activity and methanol tolerance by comparing the polarization curves obtained on studied Pt-transition metal electrodes to the one obtained on conventional Pt electrode.

In addition, by obtaining the hydrogen adsorption and desorption peak areas and OH intermediate adsorption and oxide formation region, cyclic voltammetry (CV) can be a very helpful technique on determining electrocatalytic behavior of different electrocatalysts and identifying the intermediate species produced during electrode reactions. The electrochemical surface areas of different Pt-based electrocatalysts were determined by cyclic voltammetry method in this study. By conducting CV measurement on the electrode of interest in acid electrolyte, the hydrogen adsorption and desorption peaks were obtained. Assuming the active Pt sites is covered by monolayer of hydrogen atom, the charge measurement related to hydrogen adsorption or desorption corresponds to the actual Pt surface area participating in the electrode reaction [16].

2.7.2 Single cell measurements

The fuel cell testing was conducted on a homemade single cell testing station. The schematic is shown in Figure 2-4. The system was designed both for H₂ PEM fuel cell and methanol PEM fuel cell measurements.
A single fuel cell unit was used for all the measurements. Operating temperature was controlled by two small heaters attached on each side of fuel cell metal plates. Operating pressure was controlled by backup pressure valves. The working current and potential were collected through an Agilent 6060B system DC electronic load, and the open circuit potential was measured and collected through Keithley 617 programmable electrometer. The anode gas flowed horizontally and the cathode gas flowed vertically into the gas distribution channels. Both of the outlet gas water mixtures condensed at the exits with the aid of water condensers. All experiments were carried out without external humidification. Data collection including the cell potential, gas flow rate, and fuel cell inlet and outlet gas temperatures was monitored and controlled using a data acquisition
unit. The fuel cell (from Electrochem. Inc) has a nominal geometry reaction area of 5 cm²; however, excluding the area preoccupied by the wall of gas distribution channels, the calculated actual reaction area is 2.9 cm². This number was used for the calculation of all the current and power densities in this study if not specified.

2.8 Error bar determination

To make the experimental data more reliable, multiple parallel measurements were conducted to assure the repeatability of experimental results. Experimental error was calculated using the standard derivation of obtained values from the following equation [2-5] to estimate the spread of experimental value.

\[ \sigma = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \bar{x})^2} \]  [2-5]

Where \( \bar{x} = \frac{1}{N} \sum_{i=1}^{N} x_i \) is the mean value of experimental data.

All the plots shown in this thesis represent the mean value of the collected data from repeating measurements. Error bars were plotted on the curve to show the overall distribution range of the data (Figure 3-12 and Figure 4-5 as examples). Since multiple performance curves of different electrodes were included in one diagram for most of the plots, the error bars were not marked on every diagram to make the plot easier to read.
2.9 Summary

This chapter provides a description of experimental methods, including the synthesis method, electrocatalyst characterization methods and performance testing methods, used for conducting electrocatalyst studies for low temperature PEM fuel cells.

The Bönnemann colloidal method was selected for electrocatalyst synthesis; BET, TEM, XRD, EDX were chosen for physical property characterization; RDE and single fuel cell was conducted for catalytic activity measurements. Detail explanations were given for each of the techniques to clarify the contribution to better understand the fundamental material properties.

References


Chapter 3

Platinum-Iron Alloy Electrocatalysts for Cathodic Reaction

3.1 Introduction

Previously in Chapter 1, the basic working principle of low temperature PEM fuel cell was discussed. It was clearly explained that the catalytic material is one of the main determining factors for cell performance. It is well known that the catalytic material on electrodes plays a significant role in deciding current density, electrode overpotential and cell performance [1, 2].

To reduce the electrode overpotential and increase cell performance, the exploration of new catalytic materials as substitutes for the traditionally preferred platinum-only catalyst has been extensively carried out in recent decades. As mentioned earlier in Chapter 2, different approaches of exploring the potential electrocatalysts have been developed and different categories of electrocatalytic materials were extensively studied both for the anode and cathode [1, 3].

Current research is focused on the study of carbon supported electrocatalysts, which is mainly about bimetal electrocatalysts formed of Pt and transition metals with different atomic ratios. In this chapter, the carbon supported PtFe or PtFe/C electrocatalysts were investigated with respect to synthesis, characterization, and performance testing.
All the catalysts were prepared by colloidal method and subsequent catalytic properties and performance were studied. Catalyst surface area was characterized by BET nitrogen adsorption method. Particle size and their distribution were studied by transmission electron microscopy (TEM). X-ray diffraction characterization (XRD) measurements were conducted to determine the degree of Pt-Fe alloying and catalyst performance was evaluated by rotating disc electrode (RDE) sweep voltammetry and cyclic voltammetry (CV) operated in acidic media with and without methanol. The performance evaluation of PtFe/C was conducted on hydrogen PEM fuel cell to test the oxygen reduction reaction (ORR) activity and on methanol PEM fuel cell to test the ORR activity under the influence of the presence of methanol.

3.2 Experimental results and discussion

3.2.1 Preparation of electrocatalysts

A series of PtFe electrocatalysts were prepared by a modified Bönnemann colloidal method [4-6]. The main synthesis process was carried out by two step reactions as shown in reactions [3-1] and [3-2] below, under anhydrous and inert gas conditions. Details about material usage during synthesis are shown in Table 3-1.

N(Oct)$_4$Br + KHB(Et)$_3$ = N(Oct)$_4$HB(Et)$_3$ + KBr \hspace{2cm} [3-1]

PtCl$_2$ + FeCl$_3$ + 5N(Oct)$_4$HB(Et)$_3$ = PtFe$^+$[(Oct)$_4$$^+$]$_5$ + 5B(Et)$_3$ + 5/2H$_2$ + 5Cl$^-$ \hspace{2cm} [3-2]
3.2.2 Electrocatalyst surface area measurement

The BET total surface areas of synthesized carbon supported Pt and PtFe catalysts are shown in Table 3-2. The measured total surface area and pore volume have a standard derivation of ±3%. The catalyst support is Vulcan Carbon XC-72R with a measured surface area of 216 m²/g. Since heterogeneous electrocatalysis is normally a surface reaction, effective dispersion of catalytic active phase on inert carbon support is the best way to obtain the maximum catalytic active sites. The Pt/C had a surface area of 141 m²/g, and the other PtFe/C composites had surface areas of about 110 m²/g. The

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>Metal chloride (g)</th>
<th>N(Oct)₄Br (g)</th>
<th>1M KHB(Et)₃ (ml)</th>
<th>Vulcan carbon XC-72R (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>PtCl₂ 0.137</td>
<td>1.120</td>
<td>2.051</td>
<td>0.40</td>
</tr>
<tr>
<td>PtₓFeᵧ/C</td>
<td>PtCl₂ 0.132</td>
<td>1.267</td>
<td>2.319</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>FeCl₃ 0.010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PtₓFeᵧ/C</td>
<td>PtCl₂ 0.125</td>
<td>1.532</td>
<td>2.805</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>FeCl₃ 0.025</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt₁Fe₁/C</td>
<td>PtCl₂ 0.106</td>
<td>2.161</td>
<td>3.960</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>FeCl₃ 0.064</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Twice stoichiometric amount of N(Oct)₄Br and KHB(Et)₃ was added to insure the completion of reaction.
synthesized supported catalysts had several times the surface area of the unsupported catalysts [7], around 30 m$^2$/g. It is generally assumed that catalysts with large surface areas potentially have better catalytic activity. However, that does not take into account such factors as poisoning by specific materials and limitations of the working media. For the cathodic reaction of methanol PEM fuel cell, for example, the Pt catalytic activity is severely limited by methanol crossover from the anode side. PtFe catalysts showed better performance in this environment as shown later from the RDE and CV measurements.

Table 3-2: BET surface areas of carbon support and synthesized catalysts

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>BET Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan Carbon XC72</td>
<td>216</td>
<td>NA</td>
</tr>
<tr>
<td>20wt% Pt/C</td>
<td>141</td>
<td>0.27</td>
</tr>
<tr>
<td>20wt% PtFe/C = 1:1</td>
<td>110</td>
<td>0.25</td>
</tr>
<tr>
<td>20wt% PtFe/C = 3:1</td>
<td>113</td>
<td>0.24</td>
</tr>
<tr>
<td>20wt% PtFe/C = 9:1</td>
<td>114</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Recent research strongly supports the fact that metal alloys have good methanol and CO-intermediates tolerance capability while keeping acceptable ORR activity [8-10].

In our study, it was observed the physical structure of Pt was modified by alloying with Fe. The reduced Pt-Pt distance, which was characterized by XRD, was found to lead to enhanced oxygen reduction activity as observed by others[11, 12]. Furthermore, the PtFe alloy structure suppresses the methanol oxidation reaction. For methanol oxidation to happen, adjacent Pt active sites for methanol chemisorption are needed. Since the Pt
active sites are surrounded by Fe active sites, which are methanol insensitive [13, 14], the methanol oxidation is largely restricted.

3.2.3 Confirmation of the nominal atomic composition of electrocatalysts

PtFe electrocatalysts were synthesized with a variety of predetermined atomic compositions. Figure 3-1 and Figure 3-2 show the energy dispersive X-ray (EDX) Spectra of synthesized Pt$_9$Fe$_1$/C and Pt$_1$Fe$_1$/C, respectively. The carbon peaks in all the EDX diffraction patterns show the existence of carbon support and an unexpected Al peak introduced by the background noise from the sample holder. The actual compositions of the synthesized material were confirmed to be very close to the predetermined atomic compositions. In addition, EDX analysis of the electrode material after fuel cell testing was conducted. Figure 3-3 shows the EDX spectrum of the Pt$_1$Fe$_1$/C electrode (after fuel cell testing at various operating temperature). It could be extracted from the comparison of Figure 3-2 and Figure 3-3 that the Fe content changes significantly after the application. The presence of a small amount of potassium (about 0.1-0.3 percent) was also observed in the EDX diffraction patterns. This probably indicates that some of the intermediate produced during synthesis was not completely washed away from the end products of the electrocatalysts. However, after fuel cell operation, the potassium was completely removed (Figure 3-3). More detailed discuss about the EDX analysis is given in a later section.
Figure 3-1: EDX spectrum of synthesized Pt₉Fe₁/C
Figure 3-2: EDX spectrum of synthesized Pt$_{1}$Fe$_{1}$/C
Figure 3-3: EDX spectrum of Pt$_1$Fe$_1$/C after fuel cell test
3.2.4 Crystallite structure determination of electrocatalysts

X-ray diffraction characterizations were performed to explore the crystallite structures of the synthesized catalyst composites. Figure 3-4 shows the diffraction pattern of synthesized carbon supported Pt_{9}Fe_{1} (20 wt %) with diffraction peaks at about 40.3°, 47.1°, 68.8°, 82.8°, 87.9°, corresponding to (111), (200), (220), (311), and (222) diffractions. Compared to Pt/C diffraction peaks at 39.7°, 46.3°, 67.5°, 81.3°, 86.8°, all peaks shifted because of the introduction of metal Fe.

![Platinum, ferroan, syn - (Pt,Fe)](06009PtFe9-1.raw) 06009 PtFe=9:1

Figure 3-4: X-ray diffraction patterns of PtFe/C alloy composite

Also, the diffraction pattern shown in Figure 3-1 exactly matches the diffraction pattern of PtFe in the XRD reference database (PDF# 00-029-0718) linked by Jade8.0 software. This strongly supports the fact that the synthesized catalysts are the preferred...
metal alloys instead of being simple metal mixtures since no diffraction peaks appear for
the single metal platinum and iron. Figure 3-5 shows the X-ray diffraction pattern of
synthesized carbon supported PtFe electrocatalysts. The crystallite sizes calculated from
Scherrer’s formula are 3.1 nm, 3.7 nm and 4.1 nm respectively which are larger than
what were observed in the TEM images, probably because of some of the large crystallite
particles, which were formed during heat treatment, detected by XRD may not have been
counted in the particle statistical computation from the TEM images. The average lattice
parameters, which are 3.920 Å ± 0.003 for Pt/C and 3.890 ± 0.009 Å for PtFe/C were
obtained from Bragg’s equation. The reduced lattice parameters after introducing Fe
further suggests that the synthesized electrocatalysts are alloy structures.
Figure 3-5: X-ray diffraction patterns of Pt/C and PtFe/C with different atomic ratios
3.2.5 Determination of particle size distribution

Transmission electron microscopy (TEM) studies were carried out to find out the particle size and particle size distribution of the synthesized carbon supported catalysts. Figure 3-6 shows clearly the small dark PtFe particles supported on the large grey carbon powders. The statistic histograms of metal particle distributions for 20 wt% carbon supported Pt\textsubscript{9}Fe\textsubscript{1} and Pt\textsubscript{1}Fe\textsubscript{1} are shown in Figure 3-7. Both (a) and (b) in Figure 3-6 show that most of the particles, more than 80%, fall into the range of 2.0 - 3.9 nm with a mean particle size 3.2 nm for Pt\textsubscript{9}Fe\textsubscript{1} and 2.6 nm for Pt\textsubscript{1}Fe\textsubscript{1}. The average particle size of Pt\textsubscript{3}Fe\textsubscript{1} is around 3.0 nm. These results show that the adopted modified Bönnemann method provides a highly desired route for catalyst synthesis since recent research have demonstrated that catalyst activity is the highest by using catalysts with particle size distributed within such a range [9, 15-17].

3.2.6 ORR activity measurement of Pt electrocatalyst on RDE

Rotating disk electrode sweep voltammetry and cyclic voltammetry measurements were conducted to test and evaluate the catalytic activities and methanol tolerance of the synthesized PtFe/C electrocatalysts.

Pt/C which is considered the most state-of-the-art cathode electrocatalyst has been applied for H\textsubscript{2}/O\textsubscript{2} fuel cells for many years; however, this cathode has poor electrocatalytic activity for DMFCs [18-20] due to methanol fuel crossover.
Figure 3-6: Bright-field TEM image of (a) PtFe/C with atomic ratio 9:1; (b) Pt:Fe/C with atomic ratio 1:1

Figure 3-7: Histograms of metal particles distribution of (a) Pt:Fe = 9:1 with carbon support and (b) Pt:Fe = 1:1 with carbon support
The reaction of the methanol at the cathode is not only a waste of fuel for the reason of no electron transfer along external load, it also reduces the cell voltage dramatically because of the poisoning caused by intermediates produced during methanol dissociation. Figure 3-8 shows the comparison of cathodic polarization behavior (Pt/C electrode) of oxygen reduction reaction (ORR) with and without methanol (1 M) in 1 M perchloric acid as electrolyte at different rotating speeds of 400rpm and 2500rpm. The catalytic activity of Pt/C has a significantly higher electrocatalytic activity when no methanol exists in the acid solution. Comparing the two group polarization diagrams of cathodic reaction under different rotating speeds, the open circuit potential was around 1.0 V with no methanol present in the acid solution. However, high overpotential was observed once the Pt electrode was tested with methanol present in the electrolyte. The open circuit potential steeply dropped down to around 0.65 V after 1 M methanol was added to the acid solution. Also, the kinetic processes dramatically slowed down as observed in the two diagrams. At 400 rpm, for example, if the potential is fixed at 0.4 V, the produced current density is about 1.70 mA/cm² without methanol present in the acid solution; however, the current density is only about 0.76 mA/cm² for the reaction with 1 M methanol present. A likely explanation is that the intermediates produced during methanol oxidation, which are not easily released from the Pt surface, occupy part of the active Pt catalyst site for oxygen reduction reaction. Because of this, the Pt catalytic kinetic rate of oxygen reduction reaction was significantly suppressed by the presence of methanol in the working media.
Figure 3-8: Polarization curve for ORR at Pt electrode in oxygen saturated 1M HClO₄ and polarization curve for ORR at Pt electrode in oxygen saturated 1M HClO₄ + 1M CH₃OH, 25°C
Clearly, Pt/C is not an ideal cathodic catalyst for direct methanol fuel cells. The high overpotential and slow reaction kinetics are serious shortcomings to DMFCs commercialization in addition to the high electrode material cost. To address this problem, we investigated the cathodic catalytic activity of the synthesized PtFe/C by RDE measurements. Table 3-3 shows the measured onset potentials and current densities of Pt electrode and PtFe electrodes with various atomic compositions under the same operating condition.

Table 3-3: Onset potentials and current densities at various electrodes, 400 rpm, 25°C

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Pt</th>
<th>Pt₁Fe₁</th>
<th>Pt₃Fe₁</th>
<th>Pt₀Fe₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Current Density mA/cm²</td>
<td>Onset potential V</td>
<td>Current Density mA/cm²</td>
<td>Onset potential V</td>
</tr>
<tr>
<td>1M HClO₄</td>
<td>1.70</td>
<td>1.02</td>
<td>3.95</td>
<td>0.89</td>
</tr>
<tr>
<td>1M HClO₄ + 1M CH₃OH</td>
<td>0.76</td>
<td>0.66</td>
<td>4.07</td>
<td>0.83</td>
</tr>
</tbody>
</table>

All currents were measured at the corresponding applied potential equals to 0.4 V. All the error bar of current density was in the range of about 2.5% of above data for repeating measurements and all the error bar of potential was in the range of about 1%. Pt₀Fe₁ as example.
3.2.7 Evaluation of ORR performance of PtFe catalysts on RDE

Two important electrochemistry features can be extracted from Figure 3-9. By applying the new PtFe electrocatalysts, the onset potentials of the ORR shifted slightly from ca. 900 mV to ca. 850 mV even with 1 M methanol present in the working solution of 1 M oxygen saturated perchloric acid electrolyte. This is a significant improvement compared to the open circuit potential shift of 350 mV (from ca.1.0 V to ca. 0.65 V) under the same working conditions for Pt/C electrode. The other observation is that at the same rotating speed, the performance curve of the electrolyte solution without methanol is very close to the performance of that with methanol. This shows that the PtFe electrocatalysts are weakly impacted by the presence of methanol in the electrolyte and the electrocatalysts have better selectivity to oxygen reduction reaction than to methanol oxidation reaction in a Pt/C system. The cyclic voltammetry measurement was also conducted in 1 M perchloric acid electrolyte with and without methanol. Figure 3-10 shows that the PtFe/C catalysts are effective oxygen selective catalysts since it appears no obvious methanol adsorption and desorption peaks were observed. As noted earlier, it is well known that the reaction of methanol oxidation taking place on the cathode is extremely undesirable from the viewpoint of high overpotential and low fuel efficiency.
Figure 3-9: Polarization curves of Pt$_9$Fe$_1$ electrode at various rotating speeds in O$_2$ saturated 1 M HClO$_4$ with and without 1 M methanol at 25ºC
Figure 3-10: Cyclic voltammetry curves of PtFe/C electrode in 1 M perchloric acid with and without 1M methanol, 25°C
Figure 3-11 presents RDE polarization results of ORR performance of Pt/C, Pt$_3$Fe$_7$/C, Pt$_{11}$Fe$_1$/C, Pt$_9$Fe$_1$/C with methanol present. All the three PtFe/C electrodes showed enhanced catalytic activity than Pt/C electrode. Compared to the PtFe/C polarization behaviors, and in view of the experiment error of ± 0.03V, the onset potential of Pt/C catalyst was ca. 0.2 V lower, and the Pt/C polarization curve reached a much lower limiting current under the same operating condition. The reason is due to the high insensitivity of the effective catalytic sites of PtFe to methanol poisoning resulting in enough active catalytic sites to support oxygen reduction. Pt$_9$Fe$_1$/C showed the best catalytic activity compared with the other two since the obtained current density from Pt$_9$Fe$_1$/C electrode is the highest during the scan range from 0.9 V - 0.2 V.

One of the interesting observations from Figure 3-11 is that the onset potential for O$_2$ reduction reaction is almost the same for the PtFe catalysts with various atomic components. This may be due to significant changes in the microstructure of Pt-Pt bond resulting from the addition of Fe. The other observation is that the electrocatalyst with 10 percent Fe has the highest activity. However, the catalytic activity declined very fast when the Fe content increased to 25 percent. When the Fe content reached 50 percent, the activity increased again but to below the activity of the 10 percent Fe containing electrocatalyst. Thus, the atomic ratios of Pt and Fe have a significant affect on the catalyst activity, although further research is required to explain in detail the effects of the component ratio on the catalytic activity.

Toda et al. [12] reported, using PtFe (50% Fe) electrode, a current density of ca. 20 times larger than that obtained for pure Pt electrode for ORR reaction. However, they only reported the catalytic activity of ORR without methanol present. In our study, we
measured the catalytic activity in acid solution with 1 M methanol, and the acquired
current densities were 3-5 times larger than of that achieved from Pt/C electrode.

From this observations we confirmed that, in accordance with the research results
showed earlier [21, 22], compared to Pt/C catalyst, PtFe/C not only has significant better
ORR capability in the absence of methanol, but also has better tolerance to methanol
presence. However, the research results reported by Bonakdarpour et al. [23] and Toda et
al.[12] showed some quantity of Fe metal was removed from the surface of Pt$_{1-x}$Fe$_x$
alloys during acid treatment and measurement. Further tests of the synthesized
electrocatalysts need to be conducted on both H$_2$ PEM fuel cell and methanol PEM fuel
cell.

### 3.2.8 Single cell measurements

The single cell measurements were carried out on two types of cells, hydrogen
PEM fuel cell and methanol PEM fuel cell. The electrocatalysts were evaluated based on
both of the testing results.

#### 3.2.8.1 MEA fabrication

The commercialized E-TEK electrode, 20 wt % Pt/C, was employed as anodic
electrodes for all the fabricated MEAs, with a electrocatalysts loading of 0.5mg/cm$^2$. The
homemade 20 wt % Pt/C and 20 wt % PtFe/C were applied as cathodic electrodes with
the same electrocatalyst loading of 0.5mg/cm$^2$. 
Figure 3-11: Polarization curves of Pt/C and PtFe/C performance with 1M methanol in 1 M O$_2$ saturated HClO$_4$, 400 rpm, 25°C
The membrane electrolyte assembly was prepared by a modified hot press method which is described elsewhere [24-26] and the procedure is described below as four steps:

1. Membrane treatment  
2. Ink preparation  
3. Ink painting  
4. Hot press

Nafion 117 (perfluorinated membrane, thickness of 0.007 inch, from Aldrich Chemical Company, Inc.) was selected for this study. The raw membrane was cut into small squares with 6 cm x 6 cm dimension, and the membranes were placed into 3% H₂O₂ and boiled for 1 h. Then the membranes were rinsed in distilled water and placed into Milli-Q water to continue boiling. After 1 h, the membranes were placed into 5% H₂SO₄ and boiled for 1 h. Then the membranes were rinsed and boiled in Milli-Q water for 1 h. The treated membranes were de-wrinkled on a vacuum bench and were ready for use.

The anode of MEA was prepared by cutting E-TEK Pt electrode (Pt loading of 0.5 mg/cm²) to a square shape with the area of 5 cm².

The cathode of MEAs was prepared by mixing carbon supported electrocatalyst with water, isopropanol and 5% Nafion solution. Details are shown in Table 3-4, where the cathode of MEA01, MEA02, MEA03, MEA04 and MEA05 were made of carbon supported Pt, Pt₉Fe₁, Pt₃Fe₁, Pt₁Fe₁, and E-TEK Pt, respectively. The MEA side of this gas diffusion layer (GDL) type has a thicker microporous layer (MPL) coating than the coating on the other side. The catalyst ink was ultrasonically stirred for 1 h to make a homogeneous ink. The ink was painted on 5 cm² carbon cloth (E-TEK, ELAT v 2.1 hand fabricated double sided coating). The painted carbon cloth was heated in an oven at 60°C for 30 minutes.
The prepared anode and cathode were hot pressed on the Nafion 117 membrane, with the catalyst sides against membrane face to face, at 260ºF and 600 pounds for 40 seconds, by a Carver press (hydraulic unit model #3912). After cooling down, the MEA was removed gently from the Carver press and was ready to be used for fuel cell measurements.

Table 3-4: Composition of MEAs for single cell measurements

<table>
<thead>
<tr>
<th>MEAs</th>
<th>Anode</th>
<th>Cathode</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA 01</td>
<td>E-Tek Pt/C catalyst</td>
<td>Homemade Pt/C catalyst</td>
<td>Dupont Nafion 117</td>
</tr>
<tr>
<td></td>
<td>wt 20 %</td>
<td>wt 20 %</td>
<td></td>
</tr>
<tr>
<td>MEA 02</td>
<td>E-Tek Pt/C catalyst</td>
<td>Pt_{0.1}Fe_{0.9}/C catalyst</td>
<td>Dupont Nafion 117</td>
</tr>
<tr>
<td></td>
<td>wt 20 %</td>
<td>wt 20 %</td>
<td></td>
</tr>
<tr>
<td>MEA 03</td>
<td>E-Tek Pt/C catalyst</td>
<td>Pt_{0.2}Fe_{0.8}/C catalyst</td>
<td>Dupont Nafion 117</td>
</tr>
<tr>
<td></td>
<td>wt 20 %</td>
<td>wt 20 %</td>
<td></td>
</tr>
<tr>
<td>MEA 04</td>
<td>E-Tek Pt/C catalyst</td>
<td>Pt_{0.1}Fe_{0.9}/C catalyst</td>
<td>Dupont Nafion 117</td>
</tr>
<tr>
<td></td>
<td>wt 20 %</td>
<td>wt 20 %</td>
<td></td>
</tr>
<tr>
<td>MEA 05</td>
<td>E-Tek Pt/C catalyst</td>
<td>E-Tek Pt/C catalyst</td>
<td>Dupont Nafion 117</td>
</tr>
<tr>
<td></td>
<td>wt 20 %</td>
<td>wt 20 %</td>
<td></td>
</tr>
</tbody>
</table>

3.2.8.2 \textit{H}_2 \textit{PEM fuel cell measurement}

In this section, the catalytic activities of fabricated PtFe/C electrocatalysts were investigated by varying the \textit{H}_2 fuel cell measurements at different conditions.

The fuel cell measurements were conducted at different temperatures of 25ºC and 70ºC; and at different pressures of 1 atm and 2 atm. The data shown in all the power vs. current (P-I) and potential vs. current (V-I) figures were the averages of parallel measurements.
In Figure 3-12, the V-I and P-I responses of single cell measurements of PtFe/C cathodes are compared to homemade Pt/C cathode.

It is found at 25ºC and 1 atm that the catalytic performance of Pt$_9$Fe$_1$ was the best over others including Pt, Pt$_3$Fe$_1$, and Pt$_1$Fe$_1$ electrodes at low current density. However, when the produced current density passed over 0.4 A/cm$^2$, Pt electrode showed better performance, and the performance was in the order of Pt > Pt$_9$Fe$_1$ > Pt$_1$Fe$_1$ > Pt$_3$Fe$_1$.

It could be read from the P-I curves in Figure 3-12 that the maximum power output of Pt$_9$Fe$_1$ was 0.25 W/cm$^2$; which was lower than the power output obtained from Pt, from which the obtained maximum power output was 0.28 W/cm$^2$. It can be deduced from above that the Pt is still the higher performance electrode as cathode for hydrogen PEM fuel cell at such working condition, compared to PtFe electrodes as cathode; the power output of Pt is around 10% higher than that obtained from Pt$_9$Fe$_1$. In addition, comparing the performance of all the PtFe electrodes, Pt$_9$Fe$_1$ had a closer performance with Pt$_1$Fe$_1$/C as cathode; however, the performance of Pt$_3$Fe$_1$ was obviously lower than the other two. The results match the outcomes we got from RDE measurements.

It is observed that the maximum power output of Pt$_3$Fe$_1$ was the smallest, 0.20 W/cm$^2$, which is about 20% less than the maximum power achieved from Pt$_9$Fe$_1$. The V-I curve of Pt was above the performance curves of Pt$_9$Fe$_1$, Pt$_3$Fe$_1$, and Pt$_1$Fe$_1$, indicating a better performance.
Figure 3-12: H₂ PEM single cell performances at 25°C, 1atm. [Pt(A), Pt9Fe1(A), Pt3Fe1(A), Pt1Fe1(A) in diagram stand for the V-I curves and Pt(B), Pt9Fe1(B), Pt3Fe1(B), Pt1Fe1(B) in diagram stand for P-I curve. Anode: E-TEK 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt9Fe1/C, Pt3Fe1/C, Pt1Fe1/C for MEA01, MEA02, MEA03 and MEA04, respectively. Loading: 0.5mg/cm²]
The cathode of MEA05 was made of E-Tek 20 wt% Pt/C electrocatalyst. Compared to E-Tek electrocatalyst (the performance curves of MEA05), the performance of homemade Pt/C electrocatalyst was slightly inferior. However, it is difficult to treat them as comparable since catalytic activities are significantly affected by material source, synthesized methods, post-treatment et al.[27]. Even though the catalyst loadings are the same on both MEAs, these two electrocatalysts were made by different methods and the raw materials for making electrocatalysts might come from different sources. In this study, all the discussion was explored among homemade catalytic materials. The data obtained from E-Tek cathode was mainly for reference.

While temperature was increased to 70°C and the pressure still was kept at 1 atm, the activity, as shown in Figure 3-13, of Pt was relatively weak at low current density. However, it went up quickly at high current density, and P-I performance curves show a close performance of Pt₀Fe₁ and Pt. It could be deduced from Figure 3-13 that the power density obtained for MEA01 (Pt/C cathode) was 0.48 A/cm² at 0.4 V, which was very close to the power density of 0.49 A/cm² at 0.4 V acquired from Pt₀Fe₁. This observation indicates a comparable performance of Pt₀Fe₁ to Pt and Pt₀Fe₁ could be a potential replacing material of Pt/C for cathode of PEM fuel cell.
Figure 3-13  H₂ PEM single cell performances at 70°C, 1atm. [Pt(A), Pt₉Fe₁(A), Pt₃Fe₁(A), Pt₁Fe₁(A) in diagram stand for the P-I curves and Pt(B), Pt₉Fe₁(B), Pt₃Fe₁(B), Pt₁Fe₁(B) in diagram Stand for P-I curve. Anode: E-TEK 20 wt % Pt/C. Loading: 0.5 mg/cm²; Cathode: 20 wt % home made Pt/C, Pt₉Fe₁/C, Pt₃Fe₁/C, Pt₁Fe₁/C for MEA01, MEA02, MEA03 and MEA04, respectively. Loading: 0.5 mg/cm²]
Another interesting thing is the Pt$_9$Fe$_1$ performed differently at room temperature and 70ºC. The V-I curves of Pt$_9$Fe$_1$ show similar trend both at low and high temperature and the performance of Pt$_9$Fe$_1$ was as stable as the one obtained from Pt. The activity enhancement of Pt$_9$Fe$_1$ to oxygen reduction was significant as temperature increased: at 25ºC, the Pt had a 20% higher power output than Pt$_9$Fe$_1$ as the cathode; however, when the operation took place at 70ºC, the V-I and P-I curves obtained from Pt$_9$Fe$_1$ were very close to the corresponding curves obtained from Pt, which means the activity of Pt$_9$Fe$_1$ “catches up” with the activity of Pt very quickly at elevated working temperature, and it indicates Pt$_9$Fe$_1$ might be more sensitive to temperature due to the introduction of Fe promotes active catalytic-sites to work at their maximum capacity.

The performance of Pt$_1$Fe$_1$ was different from Pt$_9$Fe$_1$. At 25ºC, the performance curve of Pt$_1$Fe$_1$ was just below the performance curve of Pt (Figure 3-12). However, while the operating temperature was changed to 70ºC and the other working condition was kept unchanged, the V-I curves (Figure 3-13) performed very differently: at higher current density, the Pt$_1$Fe$_1$ showed worse performance compared to all others. The performance of the MEAs was in the order of Pt$_9$Fe$_1$ > Pt > Pt$_3$Fe$_1$ > Pt$_1$Fe$_1$.

This observation is partially consistent with what we concluded from the rotating disk electrode measurements conducted at 25ºC. The reason is probably due to the fact that at higher temperature, the reaction in fuel cell is enhanced and this strong reaction creates a more acidic environment on the surface of the electrode which makes Pt$_1$Fe$_1$/C relatively unstable because of the loss of Fe from the surface/bulk of PtFe/C.
It is suspected that the Pt\textsubscript{1}Fe\textsubscript{1} partially lost alloyed Fe while reaction occurred at high temperature, especially from the catalyst surface. This suspicion was confirmed from the EDX measurement by comparing the elemental composition of catalytic material before and after reaction (Figure 3-2 and Figure 3-3). The loss of Fe affects not only the crystal structure of the PtFe alloy, but also the total metal loading of catalytic material. The reduced electrocatalyst loading eventually causes the big drop in the V-I performance. Although the Pt\textsubscript{1}Fe\textsubscript{1} showed an easily degrading performance at high temperature, the Pt\textsubscript{0}Fe\textsubscript{1} electrode however showed a very stable performance. The ORR activity of Pt\textsubscript{0}Fe\textsubscript{1} electrode even was enhanced at high temperature when one compares the performance curves of Figure 3-12 and Figure 3-13, indicating a stable crystal structure of the material of Pt\textsubscript{0}Fe\textsubscript{1} at various conditions.

Figure 3-14 and Figure 3-15 show the performance of the same fuel cell tested at 2 atm, with the same other operating conditions as above.

It is observed from Figure 3-14 that at room temperature, the MEA performance was in the order of MEA02 (Pt\textsubscript{0}Fe\textsubscript{1})>MEA01 (Pt) >MEA04 (Pt\textsubscript{1}Fe\textsubscript{1})>MEA03 (Pt\textsubscript{3}Fe\textsubscript{1}). All the performance curves of different PtFe/C in Figure 3-14 are closer to the performance curve of Pt/C if compared to the trend of applicable curves in Figure 3-12, which indicates a sensitive response of catalytic activities of PtFe/C electrodes to an increased pressure. It also can be found that the V-I performance curve of Pt\textsubscript{0}Fe\textsubscript{1} is very close to that of Pt. The V-I of Pt\textsubscript{0}Fe\textsubscript{1} is always above the V-I curve of MEA01. When current density was larger than 0.8 A/cm\textsuperscript{2}, the performance curve of Pt\textsubscript{0}Fe\textsubscript{1} dropped down to below the performance curve of Pt. However, the drop was trivial compared to the
overall performance. In addition, the maximum power density obtained from MEA02 (Pt$_9$Fe$_1$) was 0.355 A/cm$^2$, and the maximum power density obtained from MEA01 (Pt) was 0.341 A/cm$^2$.

Figure 3-15 shows the measurement at 70°C and 2 atm. The V-I curve of MEA02 (Pt$_9$Fe$_1$) is slightly above the V-I curve of MEA01 (Pt). Even though the difference is very small (which was in the range of experimental error), it indicates at least an equivalent performance of Pt$_9$Fe$_1$ as cathode for ORR in fuel cell compared to Pt.
Figure 3-14: H₂ PEM single cell performances at 25°C, 2 atm. [Pt(A), Pt9Fe1(A), Pt3Fe1(A), Pt1Fe1(A) in diagram stand for the V-I curves and Pt(B), Pt9Fe1(B), Pt3Fe1(B), Pt1Fe1(B) in diagram stand for P-I curve. Anode: E-TEK 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt9Fe1/C, Pt3Fe1/C, Pt1Fe1/C for MEA01, MEA02, MEA03 and MEA04, respectively. Loading: 0.5mg/cm²]
Figure 3-15: H₂ PEM single cell performances at 70°C, 2atm. [Pt(A), Pt₉Fe₁(A), Pt₃Fe₁(A), Pt₁Fe₁(A) in diagram stand for the P-I curves and Pt(B), Pt₉Fe₁(B), Pt₃Fe₁(B), Pt₁Fe₁(B) in diagram Stand for P-I curve. Anode: E-TEK 20 wt % Pt/C. Loading: 0.5 mg/cm²; Cathode: 20 wt % home made Pt/C, Pt₉Fe₁/C, Pt₃Fe₁/C, Pt₁Fe₁/C for MEA01, MEA02, MEA03 and MEA04, respectively. Loading: 0.5 mg/cm²]
3.2.8.3 Methanol PEM fuel cell measurement

The methanol PEM fuel cell measurements were carried out on the same MEAs and same fuel cell system as above. The measurement was conducted at 1 atm and at different temperatures of 25°C, 50°C and 70°C.

Figure 3-16 to Figure 3-21 show the V-I and P-I performance curves of MEA01(Pt), MEA02(Pt₀Fe₁), MEA03(Pt₃Fe₁), and MEA04 (Pt₁Fe₁) at different operating conditions by feeding 1M methanol. All the measurements clearly indicate that Pt₀Fe₁ had the best performance compared to all other MEAs when applied in methanol PEM fuel cell. Pt₁Fe₁ had a better performance than Pt at room temperature and 50°C. However, its activity was exceeded by Pt at 70°C. Both of the measurements on hydrogen PEM fuel cell and methanol PEM fuel cell show unstable performance of Pt₁Fe₁.

Table 3-5 lists the summary of direct methanol fuel cell measurements for all PtFe/C and Pt/C MEAs. Pt₀Fe₁/C showed a significant improvement over Pt/C when applied to cathodic electrode for methanol PEM fuel cell. The other PtFe/C also showed an improved performance when compared to Pt/C. The open circuit potential (OCP) of Pt₀Fe₁ was about 0.45 V at different operating temperatures. This is about 50 mV higher than the one obtained from Pt. In addition, the maximum power densities produced from Pt₀Fe₁ were significantly larger than those produced from Pt. It can be found that at room temperature for instance, the maximum power with Pt was only 3.52 mW/cm² and
Figure 3-16: Methanol PEM single cell performances, 1mol methanol, 25°C, 1atm. [Pt(A), Pt9Fe1(A), Pt3Fe1(A), Pt1Fe1(A) in diagram stand for the V-I curves; Anode: E-TEK 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt9Fe1/C, Pt3Fe1/C, Pt1Cr1/C for MEA01, MEA02, MEA03 and MEA04 respectively. Loading: 0.5mg/cm²]
Figure 3-17: Methanol PEM single cell performances, 1mol methanol, 25°C, 1atm. [Pt(B), Pt9Fe1(B), Pt3Fe1(B), Pt1Fe1(B) in diagram stand for the P-I curves; Anode: E-TEK 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt9Fe1/C, Pt3Fe1/C, Pt1Cr1/C for MEA01, MEA02, MEA03 and MEA04 respectively. Loading: 0.5mg/cm²]
the maximum power density from Pt9Fe1 was 6.21 mW/cm², which was a 75% power output increase; at high temperature, 70ºC for instance, a large enhancement of 20% more power output was produced.

Table 3-5: Summary of methanol PEM fuel cell performance with different cathodic electrodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Open circuit potential</th>
<th>Current density at maximum power density</th>
<th>Maximum power density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>25ºC</td>
<td>1 atm</td>
<td>0.38 V</td>
<td>41.38 mA/cm²</td>
<td>3.52 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>50ºC</td>
<td>1 atm</td>
<td>0.40 V</td>
<td>82.76 mA/cm²</td>
<td>11.59 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>70ºC</td>
<td>1 atm</td>
<td>0.40 V</td>
<td>151.72 mA/cm²</td>
<td>19.88 mW/cm²</td>
</tr>
<tr>
<td>Pt9Fe1</td>
<td>25ºC</td>
<td>1 atm</td>
<td>0.44 V</td>
<td>62.07 mA/cm²</td>
<td>6.21 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>50ºC</td>
<td>1 atm</td>
<td>0.45 V</td>
<td>127.59 mA/cm²</td>
<td>4.03 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>70ºC</td>
<td>1 atm</td>
<td>0.45 V</td>
<td>186.21 mA/cm²</td>
<td>24.21 mW/cm²</td>
</tr>
<tr>
<td>Pt2Fe1</td>
<td>25ºC</td>
<td>1 atm</td>
<td>0.39 V</td>
<td>41.28 mA/cm²</td>
<td>3.41 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>50ºC</td>
<td>1 atm</td>
<td>0.42 V</td>
<td>79.31 mA/cm²</td>
<td>11.1 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>70ºC</td>
<td>1 atm</td>
<td>0.41 V</td>
<td>96.55 mA/cm²</td>
<td>16.41 mW/cm²</td>
</tr>
<tr>
<td>Pt1Fe1</td>
<td>25ºC</td>
<td>1 atm</td>
<td>0.39 V</td>
<td>48.28 mA/cm²</td>
<td>4.34 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>50ºC</td>
<td>1 atm</td>
<td>0.42 V</td>
<td>124.14 mA/cm²</td>
<td>12.41 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>70ºC</td>
<td>1 atm</td>
<td>0.42 V</td>
<td>151.72 mA/cm²</td>
<td>18.21 mW/cm²</td>
</tr>
</tbody>
</table>
Figure 3-18: Methanol PEM single cell performances, 1mol methanol, [50°C, 1atm. Pt(A), Pt9Fe1(A), Pt3Fe1(A), Pt1Fe1(A) in diagram stand for the V-I curves; Anode: E-TEK 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt9Fe1/C, Pt3Fe1/C, Pt1Cr1/C for MEA01, MEA02, MEA03 and MEA04 respectively. Loading: 0.5mg/cm²
Figure 3-19: Methanol PEM single cell performances, 1mol methanol, 50°C, 1atm. [Pt(B), Pt9Fe1(B), Pt3Fe1(B), Pt1Fe1(B) in diagram stand for the P-I curves; Anode: E-TEK 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt9Fe1/C, Pt3Fe1/C, Pt1Cr1/C for MEA01, MEA02, MEA03 and MEA04 respectively. Loading: 0.5mg/cm²]
Figure 3-20: Methanol PEM single cell performances, 1mol methanol, 70°C, 1atm. [Pt(A), Pt9Fe1(A), Pt3Fe1(A), Pt1Fe1(A) in diagram stand for the V-I curves; Anode: E-TEK 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt9Fe1/C, Pt3Fe1/C, Pt1Cr1/C for MEA01, MEA02, MEA03 and MEA04 respectively. Loading: 0.5mg/cm²]
Figure 3-21: Methanol PEM single cell performances, 1mol methanol, 70°C, 1atm. [Pt(B), Pt9Fe1(B), Pt3Fe1(B), Pt1Fe1(B) in diagram stand for the P-I curves; Anode: E-TEK 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt9Fe1/C, Pt3Fe1/C, Pt1Cr1/C for MEA01, MEA02, MEA03 and MEA04 respectively. Loading: 0.5mg/cm²]
3.3 Summary

In this chapter, 20 wt% Fe modified Pt based electrocatalysts, which were supported on Vulcan XC-72R carbon black, were synthesized by the Bönnemann colloidal method. The catalyst particles distributed in a narrow range with an average of around 3 nm. The alloy crystal structure of the catalyst was confirmed through XRD diffraction patterns and crystal-lattice parameters. Rotating disk electrode measurement showed that PtFe/C displayed dramatically enhanced oxygen reduction capability in acidic media in the presence of methanol. The produced current density was 3-5 times larger than those obtained from traditional Pt/C. Compared to the significant potential decline of about 350 mV in Pt/C electrode, the open circuit potential shift, about 50 mV, in PtFe/C electrode was slight before and after the presence of 1 M methanol in 1 M HClO₄ working solution. The fuel cell performance evaluation was conducted using a single cell system at various operating condition. The PtFe/C electrocatalysts demonstrated comparable catalytic activity when compared to Pt/C as cathode for H₂ PEM fuel cell and significantly enhanced catalytic activity for methanol PEM fuel cell. Pt₀Fe₁/C catalyst showed a promising potential to be a good cathode catalyst for low temperature PEM fuel cells. Pt₁Fe₀/C did not demonstrate a high activity due to Fe loss at elevated temperature even though it showed a good performance at room temperature.
References:


Chapter 4

Platinum- Chromium Electrocatalysts for Cathodic Reaction

4.1 Introduction

The oxygen reduction activity plays a significant role in deciding the overall performance of proton exchange membrane fuel cells. Dramatic effort has been devoted to the attempt to enhance the catalytic activity and reduce the overpotential caused by the irreversible oxygen reduction reaction on the cathode side of PEM fuel cell. Applying transition metal modified Pt bimetal electrocatalyst instead of Pt is one of the main approaches for this purpose. In this study, the ORR activity of carbon supported Pt-Cr electrocatalysts was explored extensively.

Introducing first row transition metal(s) to Pt to form Pt-transition metal alloy and Pt-transition bi-metal electrocatalyst is always of the interest. Compared to Pt electrode, Pt - transition metal combinations show better performance when applied to cathodic electrode on PEM fuel cell. By applying a variety of PtNi electrocatalyst as cathodic electrode for ORR on RDE, a 1.5-3 times mass activity and 1.5-4 time specific activity was achieved when compared to Pt electrode [1]; Toda et al. studied the electocatalytic activity of PtFe, PtCo, PtNi with regard to the ORR activity in perchloric acid solution by RDE. A significant ORR enhancement was obtained in their study on all of the tested material [2].
Carbon supported PtCr alloy electrocatalyst with atomic ratio of PtCr= 1:1 was prepared via the method of carbonyl by Yang et al. [3]. The ORR catalytic activity of the above electrocatalyst was tested by RDE system. A large enhancement of specific activity (SA) of above electrocatalyst in acidic solution without methanol was detected. A large enhancement of both specific activity (SA) and mass activity (MA) in acidic solution with methanol presence was determined as well.

Antolini et al. [4] reported better performance of alloyed PtCr electrocatalyst with atomic composition of PtCr = 9:1. The ORR study was conducted via RDE in 1M acid solution with and without methanol. The lowest methanol oxidation and highest ORR was detected on the proposed PtCr Electro catalyst.

Unalloyed carbon supported PtCr electrocatalysts were synthesized and investigated by Koffi et al. [5] via Rotating disk electrode (RDE) measurements. The PtCr electrocatalyst with atomic ratio close to 0.8:0.2 showed higher activity for ORR in methanol-free oxygen saturated acidic solution. The PtCr electrocatalyst with atomic ration close to 0.7:0.3 showed higher activity for ORR at low overpotentials in oxygen saturated acid solution containing 0.1 M methanol. Overall, enhanced ORR catalytic activity was obtained from the unalloyed PtCr/C electrocatalysts as well.

In this chapter, Cr was introduced to Pt to form a bimetal electrocatalyst for two reasons: firstly, reduce the total amount of Pt usage; secondly, Cr has an active valence state with large 3d vacancy which may contribute to better adsorption of O$_2$ to the Pt active catalytic sites PtCr/C and better reduction of the bonding strength of O-O. The PtCr/C could potentially help to prompt the electrochemical kinetics of the low temperature PEM fuel cells as cathodic elecrocatalysts. The enhanced ORR performance
of PtCr/C cathodic electrode in comparison to the one obtained from Pt/C cathodic electrode has been discussed based on the obtained results both through half cell study on RDE and single cell study on H\textsubscript{2} PEM fuel cell and methanol PEM fuel cell at various conditions.

### 4.2 Experimental results and discussion

#### 4.2.1 Preparation of electrocatalysts

A variety of carbon supported PtCr electrocatalysts were prepared by the modified Bönnemann colloidal method [6-8]. The procedure was the same as described in Chapter 3. Anhydrous metal chlorides of chromium chloride, CrCl\textsubscript{3} and platinum chloride, PtCl\textsubscript{2}, were dissolved in anhydrous tetrahydrothuran (THF) based on the predetermined Pt to Cr atomic ratio of 4:1, 2:1 1:1, 1:2, and 1:4. Details are summarized in Table 4-1. The synthesis proceeded mainly through two steps as shown in reaction [4-1] and [4-2].

\[
N(\text{Oct})_4\text{Br} + K\text{HB(Et)}_3 = N(\text{Oct})_4\text{HB(Et)}_3 + K\text{Br} \tag{4-1}
\]

\[
\text{PtCl}_2 + \text{CrCl}_3 + 5N(\text{Oct})_4\text{HB(Et)}_3 = \text{PtCr}^* (N[(\text{Oct})_4]^+)_5 + 5\text{B(Et)}_3 + 5/2\text{H}_2 + 5\text{Cl}^- \tag{4-2}
\]

Twice the stoichiometric amount of N(Oct)_4HB(Et)_3 was supplied to reaction [4-2] to ensure completion of reaction.
The obtained colloidal solution was added to carbon powder suspension (Vulcan carbon XC-72R from Cabot Corp.) in THF to produce the carbon supported PtCr electrocatalysts. The catalysts were heat-treated to eliminate the protective surfactant surrounding the catalysts surface.

<table>
<thead>
<tr>
<th>Electrocatlsys</th>
<th>Metal chloride (g)</th>
<th>N(Oct)_4Br (g)</th>
<th>1mol KHB(Et)_3 (ml)</th>
<th>Vulcan carbon XC-72R (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>PtCl_2 0.137</td>
<td>1.12</td>
<td>2.05</td>
<td>0.40</td>
</tr>
<tr>
<td>Pt_2Cr/C</td>
<td>PtCl_2 0.128</td>
<td>1.44</td>
<td>2.60</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>CrCl_3 0.019</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt_2Cr/C</td>
<td>PtCl_2 0.120</td>
<td>1.73</td>
<td>3.20</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>CrCl_3 0.035</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt_3Cr/C</td>
<td>PtCl_2 0.108</td>
<td>2.21</td>
<td>4.05</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>CrCl_3 0.064</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt_3Cr/C</td>
<td>PtCl_2 0.089</td>
<td>2.93</td>
<td>5.40</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>CrCl_3 0.106</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt_3Cr/C</td>
<td>PtCl_2 0.066</td>
<td>3.82</td>
<td>6.99</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>CrCl_3 0.157</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Twice the stoichiometric amount of N(Oct)_4Br and KHB(Et)_3 was added to ensure the completion of reaction.

### 4.2.2 Confirmation of particle composition of synthesized electrocatalysts

Carbon supported PtCr electrocatalysts were synthesized with a variety of nominal atomic compositions (Pt: Cr = 4:1, 2:1, 1:1, 1:2, and 1:4). Energy dispersive X-ray (EDX) analysis was conducted to confirm if the actual atomic ratios of PtCr bi-metal electrocatalysts are in agree with the predetermined atomic ratios.
Figure 4-1: EDX spectrum of synthesized Pt/C

Figure 4-2: EDX spectrum of synthesized PtCr/C with atomic ratio of 2:1
Several EDX spectra of the synthesized electrocatalysts of Pt/C, Pt$_2$Cr$_1$/C, Pt$_1$Cr$_1$/C are shown in Figure 4-1 to Figure 4-3, respectively. The first large peak from left in each figure indicates the element carbon. The Al spectral peaks appearing in all the figures were due to background noise introduced by the sample holders. The intensity of diffraction peak of Pt decreases with respect to the decrease of Pt concentration in PtCr electrocatalysts. The analysis results of metal composition are summarized in Table 4-2. It is clear from Table 4-2 that the actual atomic ratios of as-prepared PtCr electrocatalysts are close to the nominal atomic ratios that were desired. A small oxygen peak was detected from EDX spectrum of Pt/C in Figure 4-1, indicating the possible existence of platinum oxide which formed during the stage of synthesis or sample treatment.

Figure 4-3: EDX spectrum of synthesized PtCr/C with atomic ratio of 1:1
However, the crystallite structure, alloyed or unalloyed, degree of alloying etc., can not be determined by EDX.

Table 4-2: Physical characterization of lattice parameter, material atomic ratio and particle size through the instruments of XRD, EDX, and TEM.

<table>
<thead>
<tr>
<th>electrocatalyst</th>
<th>XRD Lattice parameters</th>
<th>EDX PtCr atomic ratio %</th>
<th>TEM Average particle size nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt:Cr = 1:4</td>
<td>3.8993</td>
<td>28 : 72</td>
<td>2.8</td>
</tr>
<tr>
<td>Pt:Cr = 1:2</td>
<td>3.9068</td>
<td>68 : 32</td>
<td>2.8</td>
</tr>
<tr>
<td>Pt:Cr = 1:1</td>
<td>3.9141</td>
<td>52 : 48</td>
<td>3.0</td>
</tr>
<tr>
<td>Pt:Cr = 2:1</td>
<td>3.9163</td>
<td>64 : 36</td>
<td>3.1</td>
</tr>
<tr>
<td>Pt:Cr = 4:1</td>
<td>3.9188</td>
<td>72 : 28</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt Only</td>
<td>3.9226</td>
<td>100</td>
<td>3.4</td>
</tr>
</tbody>
</table>

4.2.3 Crystallite structure determination of electrocatalysts

X-ray diffraction characterizations (XRD) were performed to explore the crystallite structures of synthesized carbon supported PtCr electrocatalyst composites. Figure 4-4 shows the X-ray diffraction patterns of synthesized carbon supported PtCr electrocatalysts (20wt %) with atomic composition of Pt<sub>1</sub>Cr<sub>4</sub>, Pt<sub>1</sub>Cr<sub>2</sub>, Pt<sub>1</sub>Cr<sub>1</sub>, Pt<sub>2</sub>Cr<sub>1</sub> Pt<sub>4</sub>Cr<sub>1</sub> and Pt only, from top to bottom, respectively. The peak at around 26° on each of the diffraction spectrum suggests the graphite carbon support. The XRD patterns show clearly the characteristic peaks of Pt at 39.7°, 46.3°, 67.5°, 81.3°, 87.9°. With Cr contents decrease in PtCr electrocatalysts, all the characteristic peaks turns sharper, indicating
electrocatalyst crystallite size may increase with the decrease of Cr content in PtCr
elecotrocatalysts.

To judge a material to be alloy structure, the lattice parameter for bulk alloys
should decrease when the content of chromium increases and the characteristic
diffraction peaks of the platinum shift towards higher $2\theta$ values.

Lattice parameters of the synthesized Pt/C and PtCr/C electrocatalysts are shown
in Table 4-2. The lattice parameters of PtCr/Cs were reduced compared to the lattice
parameter of Pt/C. All peaks in XRD image shifted slightly because of the introduction of
metal Cr. However, the contractions are relatively small in comparison with reported data
in other literature about the lattice parameters of PtCr electrocatalyst with the same
atomic composition [3, 4], indicating partially alloys were formed during electrocatalyst
preparation. However, the degree of alloy was not determined. The change of lattice
parameters with respect to the change of Cr concentration in bulk materials is presented
in Figure 4-5. No pure Cr diffraction peak was detected by XRD, probably due to some
of the Cr present with the amorphous formation or with other different formations in PtCr
bulk. This explanation is partly supported by the observation of weak overall diffraction
peaks at high Cr content. Other study of oxidation state of metal in bulk electrocatalysts,
which was not carried out in this study, would be helpful for further explanation. In
addition, Koffi et al. reported the unalloyed structure of synthesized PtCr electrocatalysts
through Bönnemann colloidal method [5]. They attribute the unalloyed structure of the
synthesized PtCr bi-metal electrocatalysts to the applicability of synthesis methods to
different materials. The characterization results from our studies show partially alloyed
PtCr were synthesized by Bönnemann colloidal method.
Figure 4-4: XRD diffraction patterns of PtCr/C electrocatalysts
4.2.4 Determination of particle size and particle distribution

Transmission electron microscopy (TEM) studies of synthesized PtCr/C electrocatalysts were carried out to determine the particle size and particle size distribution. Figure 4-6 to Figure 4-9 present some of the TEM images of Pt/C and PtCr/C electrocatalysts. The statistic histograms of metal particle distributions of each figure was obtained by measuring 200-300 randomly selected particles from TEM
images of each type of the carbon supported electrocatalyst. The small dark particles (Pt or PtCr with different atomic ratio) are supported on the large grey particles (carbon powders) with a good dispersion, as observed from TEM images. No Pt and Cr distinction was found. As shown in Table 4-2, the average particle sizes of synthesized PtCr electrocatalysts decreased with the Cr contents increase. The statistic histograms of metal particle distributions show the metal particles have relatively narrow particle distributions of 1-5 nm as expected, with an average of around 3 nm. No obvious agglomeration was found after heat treatment at 350°C. These results show that the adopted modified Bönnemann method provides a desired route for catalyst synthesis since recent research have demonstrated that catalyst activity is the highest by using catalysts with particle size distributed within such a range [9-12].
Figure 4-6: TEM image of Pt/C and histograms of particle distributions of Pt

\[ d = 3.4 \pm 0.7 \text{ nm} \]
Figure 4-7: TEM image of Pt₄Cr₁/C and histograms of particle distributions of Pt₄Cr₁
Figure 4-8: TEM image of Pt₄Cr₁/C and histograms of particle distributions of Pt₂Cr₁
Figure 4-9: TEM image and histograms of particle distributions of Pt$_1$Cr$_2$
4.2.5 Electrocatalyst chemical surface area determination

The overall chemical surface areas (CSA) of synthesized Pt/C, PtCr/C can be calculated using the equation of:

$$S_{\text{total}} = \frac{6 \times 10^3}{\rho_{\text{ave}} \times D}$$  \[4-3\]

Where $S$ Stands for surface area (m$^2$/g); $\rho_{\text{ave}}$ Stands for the average density of metal Pt or metals PtCr (g/cm$^3$); $D$ Stands for the mean diameter of particles (nm)

Assuming the chemical surface areas of Pt in PtCr is proportional to the atomic ratio of Pt in total components; the chemical surface area of Pt was calculated by the equation of

$$S_{\text{Pt}} = \gamma \times S_{\text{total}}$$  \[4-4\]

Where $\gamma$ stands for the atomic proportion of Pt in the total

The calculated chemical surface areas (CSA) from above are summarized in Table 4-3. Due to the obviously smaller density of Cr compared to Pt, the average densities of PtCr electrocatalysts decrease with respect to the increasing of Cr content. The total chemical surface areas of PtCr varied from 83 m$^2$/g to 214 m$^2$/g while Cr contents in electrocatalysts increase from none to 80 percent. However, the Pt chemical surface areas decrease from 83 m$^2$/g to 43 m$^2$/g with increasing Cr contents from none to 80 percent.
4.2.6 Determination of electrochemical surface area (ESA) and Pt utilization efficiency

The active electrochemical surface area was determined by cyclic voltammetry (CV) technique operated on rotating disk electrode (RDE). This technique is described elsewhere.\[13-16] The CV was conducted in 1M HClO\(_4\) solution; the solution was purged with argon gas to remove dissolved oxygen before measurements, in addition, argon gas flowed through the surface of solution during the measurements to isolate the solution from air; sweep rate was controlled at 100 mV/s. The obtained CV plots are shown in Figure 4-10. Knowing the hydrogen adsorption constant of 0.21 mC/cm\(^2\) Pt and Pt loading on electrode, the active platinum surface areas of Pt in all the electrocatalysts were calculated based on columbic charge associated with hydrogen desorption. The

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Average particle size nm</th>
<th>Average density g/cm(^3)</th>
<th>CSA(_{total}) m(^2)/g</th>
<th>CSA(_{Pt}) m(^2)/g</th>
<th>ESA(_{pt}) m(^2)/g</th>
<th>Pt utilization efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>3.4</td>
<td>21.4</td>
<td>83</td>
<td>83</td>
<td>78</td>
<td>94</td>
</tr>
<tr>
<td>PtCr = 4:1</td>
<td>3.2</td>
<td>18.6</td>
<td>101</td>
<td>81</td>
<td>63</td>
<td>77</td>
</tr>
<tr>
<td>PtCr = 2:1</td>
<td>3.1</td>
<td>16.7</td>
<td>116</td>
<td>77</td>
<td>58</td>
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<tr>
<td>PtCr = 1:1</td>
<td>3.0</td>
<td>14.3</td>
<td>140</td>
<td>70</td>
<td>48</td>
<td>69</td>
</tr>
<tr>
<td>PtCr = 1:2</td>
<td>2.8</td>
<td>11.9</td>
<td>180</td>
<td>60</td>
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<td>53</td>
</tr>
<tr>
<td>PtCr = 1:4</td>
<td>2.8</td>
<td>10</td>
<td>214</td>
<td>43</td>
<td>22</td>
<td>51</td>
</tr>
</tbody>
</table>
columbic charge was obtained by integrating the total area of hydrogen desorption peak in each of the CV curves. The calculated electrochemical surface areas are shown in Table 4-3.

The electrochemical active surface area (ESA) is the actual Pt active surface which participates in electrochemical reaction. So Pt utilization efficiency ($\beta$) was used in this study to specify how much of the applied Pt was utilized in electrocatalytic reaction. The calculated values are also listed in Table 4-3.

$$\text{Pt utilization efficiency (}\beta\text{)} = \frac{S_{\text{ESA}}}{S_{\text{CSA}}} \times \%$$ [4-5]

The measured electrochemical active surface of Pt/C varies with different electrocatalyst loading. With loading increases, the thickness of electrode layer increases. Some of the active chemical surface area is blocked from participating in the electrocatalysis reaction. With the current electrocatalyst loading in this study, the Pt utilization efficiencies of synthesized Pt was above 90%, indicating most of the active Pt surface are able to participate in reaction; the Pt utilization efficiencies were around 70% while the PtCr ratios change from 4:1 to 1:1. And at lower PtCr ratios of 1:2 and 1:4, the Pt utilization efficiencies were reduced to around 50%.
Figure 4-10: Electrochemical surface area measurement of Pt and PtCr electrocatalysts through cyclic voltammetry method
4.2.7 ORR activity measurement of PtCr electrocatalyst on RDE

Rotating disk electrode (RDE) in conjunction with Gamry data acquiring system was employed in conducting linear sweep voltammetry to test and evaluate the catalytic activities and methanol tolerance of the synthesized PtCr/C electrocatalysts, compared to Pt/C electrode.

In Chapter 3, the ORR activity of Pt/C electrocatalyst was tested and evaluated in O$_2$ saturated 1 M HClO$_4$ electrolyte. Through the comparison of Pt/C polarization behaviors at the condition of with methanol and without methanol in the electrolyte, it is found catalytic activity of Pt/C was largely limited by the presence of methanol in electrolyte, which is in agree with many early literatures studies [17-19]. Comparing the two group polarization diagrams of cathodic reaction under different rotating speeds, the open circuit potential was around 1.0 V with no methanol present in the acid solution. However, high overpotential was observed once the Pt electrode was tested with methanol present in the electrolyte. The open circuit potential steeply dropped down to around 0.65 V after 1 M methanol was added to the acid solution, indicating Pt/C as a non-ideal selection for the cathode of direct methanol fuel cell.

Figure 4-11 shows the ORR activities of synthesized PtCr electrocatalysts which were tested through linear sweep voltammetry which was conducted on RDE in 1 mol HClO$_4$ at room temperature.
Figure 4-11: Polarization curves of various PtCr electrodes in O$_2$ saturated 1 M HClO$_4$ solution at 25º, 400rpm
Compared to the Pt electrode, the Pt₄Cr₁ and Pt₂Cr₁ electrodes showed higher activity performance; a close performance of Pt₁Cr₁ was observed. However, the Pt₁Cr₂ electrode performed lower. The better or equivalent performance of Pt₄Cr₁, Pt₂Cr₁ and Pt₁Cr₁ indicates the addition of transition metal of Cr to Pt could enhance the ORR kinetic, and Pt₄Cr₁ could be a better atomic composition in all the tested material. The low performance of Pt₁Cr₂ electrode indicates this atomic combination is not desired in improving ORR reaction kinetic.

Open circuit potentials of ORR were around 0.93 V for PtCr and 1.01 for Pt. An 80mV difference between these two types of electrocatalysts was observed, which indicates higher overpotential was produced on PtCr electrode in comparison with Pt electrode.

A methanol tolerance measurement was carried out for the PtCr electrodes of Pt₄Cr₁, Pt₂Cr₁, Pt₁Cr₁ and Pt₁Cr₂ in 1M HClO₄ acid media with 1M methanol in presence. Figure 4-12 Shows the PtCr electrode ORR polarization curves with PtCr (A) stands for the performance curve in 1 M HClO₄ solution and PtCr (B) stands for the performance curve in 1 M HClO₄ solution with methanol. Unlike Pt/C electrode, on which the kinetic processes was dramatically slowed down by the introduction of methanol in electrolyte, the performance curve of the same PtCr electrode in the electrolyte solution without methanol was very close to the performance of that with methanol. This observation indicates that the PtCr electrocatalysts are weakly impacted by the presence of methanol in the electrolyte and the PtCr eletrocatalysts may have good selectivity to oxygen reduction reaction than to methanol oxidation reaction. It also can be summarized from Figure 4-12 that catalytic activity declined with the Cr concentration increasing.
Figure 4-12: Polarization curves of various PtCr electrodes in O2 saturated 1 M HClO$_4$ solution with and without 1M methanol at 25°, 400 rpm
The Pt-based electrocatalyst with 20 percent Cr produced the highest activity. The catalytic activity did not change much when the Cr content increased to 33 percent. However, when the Cr content reached 50 percent, the activity significantly declined but still was equivalent to that obtained on Pt electrode. With the Cr content increasing to 66 percent, the catalytic activity declined further. It can be concluded from above that the atomic ratios of Pt to Cr have a significant affect on the catalytic activity. The change of catalytic activity with different atomic ratio can be explain by the combination of promoting effect of secondary metal and effective electrochemical surface area, although further research is required to explain the results in detail.

It had been observed on Pt electrode that a significant drop of the open circuit potential of 350 mV (from ca.1.0 V to ca. 0.65 V) in the working electrolyte with methanol. However, the potential drop was limited to around 50 mV on PtCr electrode while conducting the measurements at the same working condition.

4.2.8 Electrocatalytic activity measurements on a single fuel cell

The electrocatalytic activity measurements of synthesized Pt/C and PtCr/C electrocatalysts as cathode for ORR were conducted both on hydrogen and methanol PEM fuel cell. Electrocatalytic activities of MEAs were measured by repeating measurements. The data shown in all the P- I and V- I figures was the averages of the measurements.
4.2.8.1 MEA fabrication

The MEAs were prepared by similar procedure which was described in Chapter 3.

The commercialized E-tek electrode, with 20 wt % Pt/C, was employed to make anodic electrodes for all MEAs, with an electrocatalysts loading of 0.5 mg/cm². The homemade 20 wt % Pt/C and 20wt % PtCr/C were applied as cathodic electrodes with the same electrocatalyst loading of 0.5 mg/cm².

Details on the MEA components are shown in Table 4-4, where the cathode of MEA01, MEA02, MEA03, MEA04 MEA05, and MEA06 was made of carbon supported Pt, Pt₄Cr₁, Pt₂Cr₁, Pt₁Cr₁, Pt₁Cr₂, and Pt₁Cr₄, respectively.

<table>
<thead>
<tr>
<th>MEAs</th>
<th>Anode</th>
<th>Cathode</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA 01</td>
<td>E-Tek Pt/C catalyst wt 20 %</td>
<td>Homemade Pt/C catalyst 20 wt %</td>
<td>Dupont Nafion 117</td>
</tr>
<tr>
<td>MEA 02</td>
<td>E-Tek Pt/C catalyst wt 20 %</td>
<td>Pt₄Cr₁/C catalyst 20 wt %</td>
<td>Dupont Nafion 117</td>
</tr>
<tr>
<td>MEA 03</td>
<td>E-Tek Pt/C catalyst wt 20 %</td>
<td>Pt₃Cr₁/C catalyst 20 wt %</td>
<td>Dupont Nafion 117</td>
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<tr>
<td>MEA04</td>
<td>E-Tek Pt/C catalyst wt 20 %</td>
<td>Pt₁Cr₁/C catalyst 20 wt %</td>
<td>Dupont Nafion 117</td>
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<tr>
<td>MEA 05</td>
<td>E-Tek Pt/C catalyst wt 20 %</td>
<td>Pt₁Cr₂/C catalyst 20 wt %</td>
<td>Dupont Nafion 117</td>
</tr>
<tr>
<td>MEA06</td>
<td>E-Tek Pt/C catalyst wt 20 %</td>
<td>Pt₁Cr₄/C catalyst 20 wt %</td>
<td>Dupont Nafion 117</td>
</tr>
</tbody>
</table>
4.2.8.2 $H_2$ PEM fuel cell measurement

The catalytic activities of fabricated PtCr/C electrocatalysts were investigated by varying the $H_2$ fuel cell measurements at different operating conditions. The fuel cell measurements were conducted at different temperatures of 25°C and 70°C; and at different pressures of 1 atm and 2 atm.

Figure 4-13 shows the P- I and V-I curves of a single cell measurement by employing the synthesized carbon supported PtCr electrocatalysts as cathodes. Operations were conducted at 25°C and 1 atm. Since the anode of MEAs was the same for all, in the text description, the compositions of cathodes were used to indicate MEA performance to easier identification of different MEAs.

The performance of applied PtCr electrocatalyst was in the order of: $Pt_4Cr_1/C > Pt_2Cr_1/C > Pt/C > Pt_1Cr_1/C > Pt_1Cr_2/C > Pt_1Cr_4/C$. The performance of $Pt_4Cr_1$ was very close to the performance of $Pt_2Cr_1$. They were almost the same taking into account the standard derivation of the measurements. It can be obtained from P- I curves that the maximum power output was 0.33 W/cm$^2$ for $Pt_4Cr_1$ and 0.32W for $Pt_2Cr_1$. The difference is within the error bar range, so it is hard to affirm that $Pt_4Cr_1$ outperformed $Pt_2Cr_1$ or visa versa; however, both of them obviously outperformed Pt since the maximum power output produced from Pt was 0.28 W/cm$^2$ at the same operating condition. Another observation is the obvious underperformance of $Pt_1Cr_2$ and $Pt_1Cr_4$ compared to Pt. V- I curves show at low current density (< 0.2 A/ cm$^2$), the performance of $Pt_1Cr_2$ was comparable with the performance of Pt and $Pt_4Cr_1$. However, it declined very fast at high current density. Also, the performance of $Pt_1Cr_4$ even declined at the
beginning with a fast pace. The obtained maximum power outputs were 0.17 W/cm$^2$ and 0.1 W/cm$^2$ for Pt$_1$Cr$_2$ and Pt$_1$Cr$_4$ respectively, which are largely less than the ones produced on Pt. This could be attribute to much limited active catalytic sites were available on Pt$_1$Cr$_2$ and Pt$_1$Cr$_4$ for oxygen reduction reaction. For the PtCr cathodic electrodes with Pt component larger than 50 percent, even though the electrochemical active surfaces were smaller than that of Pt-only (Table 4-3), those are large enough to generate better performance with the promoting help from Cr, compared to Pt cathodic electrode. In addition, open circuit potentials (OCP) obtained on all PtCr was almost the same with that obtained form Pt electrode, except the OCP was low on the electrode of Pt$_1$Cr$_4$.

When temperature was increased to 70°C with the same other operating conditions, the performance curves of P-I and V-I of tested MEAs showed the same trend as the one obtained at 25°C (Figure 4-15). The smoothly promoted performance by temperature increasing indicates good stability of all tested PtCr. So, even though the PtCr electrocatalyst were formed with weak alloy structures, which were demonstrated from XRD measurements, the promoting effect of transition metal Cr to Pt is still remarkable. From this we may tentatively conclude that the alloy structure may not be the predominant factor in deciding the enhanced electrocatalytic activity of multimetal electrocatalysts. It is also been noted that the difference of maximum power outputs between Pt electrode and Pt$_4$Cr$_1$ was reduced at 70°C, compared to the difference produced at 25°C. The Pt$_1$Cr$_4$ still gave the worst performance probably due to the reason we mentioned earlier, and it was not included in further single cell measurements.
Figure 4-13: H₂ PEM single cell performances at 25°C, 1atm. [Pt(A), Pt₄Cr₁(A), Pt₂Cr₁(A), Pt₁Cr₁(A), Pt₁Cr₂(A), Pt₁Cr₄(A) in diagram stand for the V-I curves Pt(B), Pt₄Cr₁(B), Pt₂Cr₁(B), Pt₁Cr₁(B), Pt₁Cr₂(B), Pt₁Cr₄(B) in diagram Stand for P-I curves. Anode: E-Tek 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt₄Cr₁/C, Pt₂Cr₁/C, Pt₁Cr₁/C, Pt₁Cr₂/C, Pt₁Cr₄/C for MEA01, MEA02, MEA03 and MEA04, MEA05, MEA06 respectively. Loading: 0.5mg/cm²]
Figure 4-14: H₂ PEM single cell performances at 25°C, 2 atm. [Pt(A), Pt4Cr1(A), Pt2Cr1(A), Pt1Cr1(A), Pt1Cr2(A)] in diagram stand for the V-I curves. Pt(B), Pt4Cr1(B), Pt2Cr1(B), Pt1Cr1(B), Pt1Cr2(B) in diagram stand for P-I curves. Anode: E-Tek 20 wt% Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt% home made Pt/C, Pt₄Cr₁/C, Pt₂Cr₁/C, Pt₁Cr₁/C, Pt₁Cr₂/C, for MEA01, MEA02, MEA03 and MEA04, MEA05, respectively. Loading: 0.5mg/cm²]
Figure 4-15: H₂ PEM single cell performances at 70°C, 1atm. [Pt(A), Pt4Cr1(A), Pt2Cr1(A), Pt1Cr1(A), Pt1Cr2(A), Pt1Cr4(A) in diagram stand for the V-I curves Pt(B), Pt4Cr1(B), Pt2Cr1(B), Pt1Cr1(B), Pt1Cr2(B), Pt1Cr4(B) in diagram Stand for P-I curves. Anode: E-Tek 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt₄Cr₁/C, Pt₂Cr₁/C, Pt₁Cr₁/C, Pt₃Cr₂/C, Pt₅Cr₄/C for MEA01, MEA02, MEA03 and MEA04, MEA05, MEA06 respectively. Loading: 0.5mg/cm²]
Figure 4-16: H₂ PEM single cell performances at 70°C, 2 atm. [Pt(A), Pt4Cr1(A), Pt2Cr1(A), Pt1Cr1(A), Pt1Cr2(A) in diagram stand for the V-I curves Pt(B), Pt4Cr1(B), Pt2Cr1(B), Pt1Cr1(B), Pt1Cr2(B) in diagram Stand for P-I curves. Anode: E-Tek 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt1Cr1/C, Pt2Cr1/C, Pt1Cr2/C, Pt1Cr1/C, Pt1Cr2/C, for MEA01, MEA02, MEA03 and MEA04, MEA05, respectively. Loading: 0.5mg/cm²]
Figure 4-14 shows the P- I and V- I performance curves of MEAs with Pt and PtCr cathodic electrodes. Operation was conducted at 25°C and 2 atm. All the open circuit potential was prompted higher due to the higher operating pressure. The V- I and P- I curves of Pt, Pt\textsubscript{4}Cr\textsubscript{1} and Pt\textsubscript{2}Cr\textsubscript{1} performed very closely; when operating temperature was increased to 70°C, the measured performance curves of P- I and V- I show the similar trend with those obtained at 25°C.

Table 4-3 shows the electrochemical surface area of Pt (ESA\textsubscript{Pt}) in Pt\textsubscript{1}Cr\textsubscript{2} and Pt\textsubscript{1}Cr\textsubscript{4} are 32 m\textsuperscript{2}/g and 22 m\textsuperscript{2}/g, they are much less than the ESA\textsubscript{Pt} in Pt, Pt\textsubscript{4}Cr\textsubscript{1}, Pt\textsubscript{2}Cr\textsubscript{1}, and Pt\textsubscript{1}Cr\textsubscript{1}. In addition, the Pt utilization efficiencies, which were defined as the electrochemical active surface area of Pt divided by chemical surface area of Pt in electrocatalyst, of Pt\textsubscript{1}Cr\textsubscript{2} and Pt\textsubscript{1}Cr\textsubscript{4} are much less than other PtCr combinations in this study.

4.2.8.3 Methanol PEM fuel cell measurement

The oxygen reduction activity and methanol-resistance capabilities of synthesized PtCr electrocatalysts were tested on methanol PEM fuel cell. The measurement were carried out on the same MEAs and same fuel cell system as those in H\textsubscript{2} PEM fuel cell measurements, at 1 atm and at different temperatures of 50°C, and 70°C.

Figure 4-17 and Figure 4-18 show that V-I and P-I curve of direct methanol PEM fuel cell with Pt or PtCr cathodic electrodes, at operating temperature of 50°C. It can be learned from above curves that the Pt\textsubscript{1}Cr\textsubscript{2} cathode are obviously underperforming Pt cathode; With Cr content less than 50% in total, all the tested PtCr electrodes showed a
better or equivalent performance depending on different Pt and Cr metal combination when compared to Pt electrode. The overall performance of Pt and PtCr electrodes was in

Figure 4-17: Methanol PEM single cell performances at 50°C, 1atm. [Pt, Pt4Cr1, Pt2Cr1, Pt1Cr1, Pt1Cr2 in diagram stand for the V-I curves. Anode: E-Tek 20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt4Cr1/C, Pt2Cr1/C, Pt1Cr1/C, Pt1Cr2/C, for MEA01, MEA02, MEA03 and MEA04, MEA05, respectively. Loading: 0.5mg/cm²]
the order of Pt₄Cr₁ > Pt₂Cr₁ > Pt₁Cr₁ > Pt > Pt₁Cr₂. Pt₁Cr₄ was not tested in this methanol PEM fuel cell measurement considering its obviously weak performance in H₂ PEM fuel cell measurements.

The measurements were also conducted at 70°C. The P- I and V-I curves are shown in Figure 4-19 and Figure 4-20. The overall performing curves of all tested electrodes showed a consistent trend with that obtained at 50°C with no degrading happened during operation. The maximum power output obtained from different electrodes was 19.9 mW/cm², 25.1 W/cm², 23.3 W/cm², 20.4 W/cm², and 8.9 W/cm² for Pt, Pt₄Cr₁, Pt₂Cr₁, Pt₁Cr₁, and Pt₁Cr₂. The maximum power outputs obtained from Pt₄Cr₁ and Pt₂Cr₁ are 25% and 15% higher than the one produced on Pt electrode.

The mass activity, which is defined as the power output per the weight of Pt on cathode, of actual Pt loading on cathode was also evaluated. Figure 4-21 shows by normalizing the power output per the weight of Pt on cathode, the power outputs on different electrodes were in the order of Pt₁Cr₁ > Pt₂Cr₁ > Pt₄Cr₁ > Pt₁Cr₂ > Pt, and the obtained power densities based on Pt loading on cathodes were 81.6, 69.6, 62.7, 53.6, and 39.7 mW/cm²mgPt, respectively. The order shows all the PtCr electrodes performed better than Pt electrode when applied to the cathode of direct methanol PEM fuel cell.

From above analysis we found even though the order are different when the power outputs of different electrodes were calculated and compared based on geometry
area and the weight of Pt on cathode, it can be concluded that the catalytic activities of PtCr (when Cr < 50%) are higher than Pt in the application for direct methanol fuel cells.

In addition, the results from hydrogen PEM fuel cell measurements show the obtained OCP on PtCr electrode is close to the one obtained on Pt electrode, which means no obvious enhancement on reducing overpotential was obtained on PtCr electrode; however, the open circuit potentials (OCP) obtained on PtCr electrodes are 30-50 mV higher than the one obtained on Pt electrode, indicating a promoting effect of Cr on reducing the ORR overpotential in methanol PEM fuel cell.
Figure 4-18: Methanol PEM single cell performances at 50°C, 1 atm. [Pt, Pt4Cr1, Pt2Cr1, Pt1Cr1, Pt1Cr2 in diagram Stand for P-I curves. Anode: E-Tek 20 wt % Pt/C. Loading: 0.5 mg/cm²; Cathode: 20 wt % home made Pt/C, Pt4Cr1/C, Pt2Cr1/C, Pt1Cr1/C, Pt1Cr2/C, for MEA01, MEA02, MEA03 and MEA04, MEA05, respectively. Loading: 0.5 mg/cm²]
Figure 4-19: Methanol PEM single cell performances at 70°C, 1atm. [Pt, Pt4Cr1, Pt2Cr1, Pt1Cr1, Pt1Cr2 in diagram stand for the V-I curves. Anode: E-Tek  20 wt % Pt/C. Loading: 0.5mg/cm²; Cathode: 20 wt % home made Pt/C, Pt4Cr1/C, Pt2Cr1/C, Pt1Cr1/C, Pt1Cr2/C, for MEA01, MEA02, MEA03 and MEA04, MEA05, respectively. Loading: 0.5 mg/cm²]
Figure 4.20: Methanol PEM single cell performances at 70°C, 1atm. [Pt, Pt4Cr1, Pt2Cr1, Pt1Cr1, Pt1Cr2 in diagram stand for the P-I curves. Anode: E-Tek 20 wt % Pt/C. Loading: 0.5 mg/cm²; Cathode: 20 wt % home made Pt/C, Pt4Cr1/C, Pt2Cr1/C, Pt1Cr1/C, Pt1Cr2/C, for MEA01, MEA02, MEA03 and MEA04, MEA05, respectively. Loading: 0.5 mg/cm²]
Figure 4-21: Methanol PEM single cell performances at 70°C, 1atm. Pt, Pt4Cr1,Pt2Cr1, Pt1Cr1, Pt1Cr2 in diagram stand for the V-I curves. Anode: E-Tek 20 wt % Pt/C. Loading: 0.5 mg/cm²; Cathode: 20 wt % home made Pt/C, Pt4Cr1/C, Pt2Cr1/C, Pt1Cr1/C, Pt1Cr2/C, for MEA01, MEA02, MEA03 MEA04, and MEA05, respectively. Loading: 0.5 mg/cm². The power output was normalized with respect to the Pt loading on cathode.
4.3 Summary:

In this chapter, a variety of bimetal PtCr/C electrocatalysts with different chemical compositions were studied as cathodic electrocatalysts for proton exchange membrane (PEM) fuel cells to explore how the chemical compositions affect the performance of electrocatalysts.

A series PtCr electrocatalysts with predetermined atomic ratios were synthesized by the Bönnemann colloidal method. The TEM characterization shows a good dispersion of PtCr electrocatlaysts on the surface of carbon support. In addition, the formed particles were distributed in a narrow range. The XRD diffraction patterns show the lattice parameters of PtCr/Cs were reduced compared to the corresponding lattice parameter of Pt/C. All peaks in XRD diffraction patterns shifted slightly because of the introduction of metal Cr. However, the contractions are relatively small; indicating the crystallite structure of formed PtCr is possibly partially alloyed. The RDE and single cell measurements show that PtCr/C electrocatalysts are weakly impacted by the presence of methanol in the electrolyte and the PtCr eletrocatalysts may have good selectivity to oxygen reduction reaction than to methanol oxidation reaction. It also can be summarized that catalytic activity declined when the Cr concentration increasing. Even though the PtCr electrocatlysts were formed with partially alloy structures, which were confirmed from XRD measurements, the promoting effect of transition metal Cr to Pt is still remarkable. From this it may be concluded that the alloy structure may not be the predominant factor in deciding the enhanced electrocatalytic activity of bimetal electrocatalysts.
References:


Chapter 5

Conclusion and future work

An experimental study of transition metal modified, Pt-based bimetal electrocatalysts for the cathodic application on proton exchange membrane fuel cells was carried out. The overall work in this study includes material selection, synthesis, physical characterization and electrochemical performance measurement of synthesized electrocatalytic material. The conclusions drawn below are based on the analysis of the experimental results. The primary focus of this study was electrocatalysts for cathodic application in proton exchange membrane fuel cells.

5.1 Conclusion

Transition metal modified, carbon supported PtFe and PtCr electrocatalysts with different chemical compositions for cathodic applications were investigated in this study.

The predetermined chemical compositions of both types of electrocatalysts were confirmed and the catalyst particles distributed in a narrow range with good dispersion on carbon support. It may be concluded from this study that the Bönnemann colloidal method used in this study provides a desired route for electrocatalyst synthesis.

For H\textsubscript{2} PEMFC, Pt\textsubscript{9}Fe\textsubscript{1}/C and Pt\textsubscript{4}Cr\textsubscript{1}/C gave the best catalytic activity which showed comparable results with Pt/C; for methanol PEMFC, Pt\textsubscript{9}Fe\textsubscript{1}/C and Pt\textsubscript{4}Cr\textsubscript{1}/C displayed dramatically enhanced oxygen reduction capability and methanol
tolerance, which were demonstrated both on rotating disk electrode measurement and single cell measurement.

Compared to the ones with Pt, the shifted diffraction peaks and reduced lattice parameters show an alloy crystal structure of the PtFe electrocatalysts. Rotation disk electrode measurements, which were conducted at room temperature, showed that PtFe/C displayed dramatically enhanced the oxygen reduction capability and methanol tolerance in acidic media in the presence of methanol. The observed current density was 3-5 times larger than those obtained from traditional Pt/C. Compared to the significant potential decline of about 350 mV in Pt/C electrode, the open circuit potential shift was about 50 mV in PtFe/C electrode before and after the presence of 1 M methanol in acid solution. Through the fuel cell measurements at various operating conditions, the PtFe/C electrocatalysts demonstrated comparable catalytic activity when compared to Pt/C as the cathode for H₂ PEM fuel cell and significantly enhanced catalytic activity for methanol PEM fuel cell. Pt₀Fe₁/C electrocatalyst showed a promising potential to be a superior cathode catalyst for low temperature PEM fuel cells. Pt₁Fe₁/C did not demonstrate stable activity due to Fe loss at elevated temperature even though it showed a good performance at room temperature.

A variety of bimetal PtCr/C electrocatalysts with different chemical compositions were studied as cathodic electrocatalysts to explore how the chemical compositions affect the performance of electrocatalysts. The XRD diffraction patterns show that the lattice parameters of PtCr/C were reduced compared to the one of Pt/C. The slightly shifted peaks in XRD diffraction patterns were due to the introduction of metal Cr. However, the contractions are small, indicating partial alloys were formed during electrocatalyst
preparation. Even though the crystallite structure of formed PtCr is not clearly alloyed, the RDE and single cell measurements show that PtCr/C electrocatalysts are weakly impacted by the presence of methanol in the acid electrolyte. PtCr electrodes may have a good selectivity to oxygen reduction reaction than to methanol oxidation reaction. Although the PtCr electrodes were formed with non obvious alloy structures, the promoting effect of transition metal Cr to Pt is still remarkable. It also can be deduced from the electrochemical measurements that catalytic activity declined with the Cr concentration increase. From this it may be concluded that the alloy structure may not be the predominant factor in deciding the enhanced electrocatalytic activity of PtCr electrocatalyst.

5.2 Future work

5.2.1 Extensive study of PtFe/C and PtCr/C electrocatalysts

The current study shows that for the cathode, the PtFe electrocatalyst activities largely varied with the different chemical compositions. The enhanced catalytic activities of PtFe with different atomic ratios were demonstrated both from RDE and single cell measurements. However, it was not clear why the activity decreased significantly when the atomic ratios changed from PtFe = 9:1 to PtFe = 3:1 and then increased again when atomic ratio changed to PtFe= 1:1. Further investigation to explain the observed results would be highly recommended.
The Pt\textsubscript{1}Fe\textsubscript{1}/C instability was detected during single cell measurements at high temperature (70°C). XRD studies showed clearly the chemical composition change of this material before and after measurements. More physical property investigation is suggested.

All the RDE measurements were conducted at room temperature in our study. For future study, it is recommended to conduct the RDE measurements at elevated temperatures which are closer to real fuel cell operating conditions.

5.2.2 Pt-based electrocatalyst for methanol oxidation reaction

In the previous chapters, much effort was placed on solving the technical difficulties related to the cathode electrocatalysts in proton exchange membrane fuel cell (PEMFC) including H\textsubscript{2} PEM fuel cell and methanol PEM fuel cell. The technical difficulties related to the anode electrocatalysts in methanol PEM fuel cell also need to be addressed. In hydrogen proton exchange membrane fuel cell, because of the highly reversible reaction, the kinetics of hydrogen oxidation on the anode is much faster than the one on the cathode. Therefore, the performance loss due to anode reaction is negligible; methanol proton exchange membrane fuel cell (DMFC) is in principle a thermodynamically favorable reaction. However, the multi-electron transfer performed on the anode produces significantly large overpotential on the Pt anode. In addition, the methanol dissociation on Pt electrode produces different CO intermediates which are strongly absorbed on the Pt surface.
Pt-Ru binary metallic catalyst is considered the most established electrocatalyst accepted for methanol oxidation [1, 2] so far. PtRu with atomic ratio of 1:1 was recognized as the most effective anodic electrocatalyst for methanol oxidation [3]. The promoting effect of Ru in PtRu electrocatalysts is explained by the bi-functional effect: Ru readily split water at lower potential and supplies OH$_{ads}$ species to free the CO adsorbed on Pt active sites, where Pt are the active sites for C-H dissociation.

According to the bi-functional effect, to maximize the promoting effect of the second metal in assisting Pt, high binding energy between water and the metal and low activation energy of OH bond scission are desired. From the reported values [4], the binding energy is 2.4 eV for Mo and 2.4 eV for W; the activation energy is 0.25 eV for Mo and is 0.41 eV for W. These data are relatively close to the corresponding values of Ru, indicating Mo and W the potential candidates as the second metal for making Pt-bimetal electrocatalysts with high methanol oxidation activity. Based on the fact of the chemical composition of bi-metal electrocatalysts is significant in deciding the electrocatalyst activity, a series a PtMo/C electrocatalyst were synthesized in a preliminary work to explore the best chemical composition of the above material as the anode of methanol PEM fuel cells. The synthesized PtMo electrocatalysts was with a chemical compositions of PtMo = 4:1, 2:1, 1:1. Higher Mo concentration (> 50%) was not considered in this study.

In the preliminary work, the physical properties of the synthesized PtMo electrocatalysts were characterized by different instruments of EDX, TEM and XRD. The expected small particle size of synthesized PtMo electrocatalysts was confirmed from TEM image in Figure 5-1(a). In addition, the good dispersion of metal (small dark spots)
on carbon support (large light grey spots) was observed. The alloy crystalline structure was determined from the XRD diffraction pattern in Figure 5.1(b).

5.2.3 Catalytic study through combinatorial method

Combinatorial method makes it possible to prepare and screen large number of samples simultaneously. It is a fast route in exploring new catalytic materials for fuel cells and has been successfully applied in finding and screening the quaternary
electrocatalysts of Pt, Ru, Os, and Ir and the electrocatalysts of Pt, Ru, Mo, and W for the anode of methanol oxidation [5, 6].

The conventional catalyst exploring methods was used in our study. This method is labor intensive and time consuming. It is somehow a disadvantage in discovering the correlation between chemical composition and activity which would be beneficial in testing large number of different chemical combinations.

For the future study, a more efficient combinatorial screening approach is recommended to speed up the progress of discovery of new electrocatalysts.

References:


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Yanming Gong was born on May 25, 1971, in Yining City, Xinjiang province, P. R. China. He attended the Wuhan Institute of Technology in 1990 and received a bachelor’s degree in chemical engineering in 1994. After his graduation, Yanming worked as a chemical engineer in the field of product and process innovation at Liming Research Institute of Chemical industry in 1994 – 2001. He came to US to pursue graduate studies at Clark Atlanta University in the fall of 2001. Yanming was admitted to the department of Energy and Mineral Engineering in the Pennsylvania State University in 2004. He earned his Ph.D. degree in the program of Energy & Geo-Environmental Engineering in August 2008.

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