Development of Novel Anodic and Cathodic Materials Applied in Proton Exchange Membrane, Direct Methanol, Alkaline and Phosphoric acid Fuel Cells

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By

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ABSTRACT OF DISSERTATION
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Abstract

This dissertation summarizes the author’s research effort to identify and synthesize novel electrocatalysts for application in proton exchange membrane fuel cells (PEMFCs), direct alcohol (acid and alkaline) fuel cells (DAFCs) and phosphoric acid fuel cells (PAFCs).

Electrocatalysis enables modification of rates of electrochemical reactions to achieve maximum selectivity, yield and efficiency. It is an important chemical process during the operation of fuel cells. “Electrocatalysts” is a term in the field of Electrochemistry. In fuel cells, they are various metal-containing catalysts used to enhance the rates of the half reactions that comprise the fuel cell. The behavior of state-of-the-art Pt-based electrocatalysts highly depends on the composition (nominal composition, surface composition), structure, morphology, particle size, degree of alloying, and oxide content, among other properties.

The principle of “rule-of-thumb” has been utilized for a few decades to synthesize electrocatalysts. In this work, a microemulsion method was fully studied and taken advantage to control particle size, catalyst morphology, and crystalline shape as well as to form catalyst layers. This method accelerates the conversion of new materials synthesis from “art” to “science”. As a typical example, synthesis of carbon supported PtCo using microemulsions, including simultaneous and sequential reduction procedures in both acid and alkaline media was reported. As-prepared PtCo/C catalysts showed better performance towards oxygen reduction reaction in PEMFC than commercial Pt/C catalyst. In addition, a carbon-supported PtAu alloy core with a Ru shell (PtAu@Ru/C) catalyst was synthesized using a water-in-oil microemulsion method and heated at 220°C. It was
found that gold cluster in the PtAu@Ru/C catalyst improve the stability of Pt and Ru significantly by interacting with Pt and Ru to raise their oxidation potential, which is a promising step towards resolving the problem of Ru dissolution for the practical application of PtRu/C catalyst in direct methanol fuel cells.

Pt-based binary or ternary alloy (nano) materials are still dominant and irreplaceable electrocatalysts in the field of acid fuel cells. However, more choices are available for choosing materials as electrocatalysts for alkaline fuel cell. As a series of non-Pt materials, Pd based alloy nanoparticles were prepared by a chemical reduction method. Voltammetric and chronoamperometric measurements showed higher current density and longer-term stability for ethanol oxidation in high pH environments with palladium alloy nanocatalysts than with a commercial Pt/C catalyst. Overall, the Pd-based alloy catalysts represent promising candidates for the electrocatalytic oxidation of ethanol, and Pd₄Au/C displays the best catalytic activity among them for the ethanol oxidation in alkaline media.

Phosphoric acid fuel cells (PAFCs) have been commercialized successfully and used for stationary applications with a combined heat and power efficiency of about 80%. However, there is still a lot of room for improvements in this technology through further research and development. One major factor limiting the performance of PAFCs is the sluggish ORR kinetics in H₃PO₄, which is attributed chiefly to the impeding effect of phosphate ion adsorption on ORR activity. In this study, a Pt based Ni alloy catalyst was synthesized in-house using components that may possess novel functions. Detailed electrochemical and X-ray absorption spectroscopy (XAS) investigations have been carried out on our electrocatalysts under in-situ conditions. Using the -XANES analysis, it was found that despite being smaller than the Pt/C (E-TEK) catalysts, the Pt-
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Chapter 1

Introduction

A brief review of fuel cells is provided in this introductory chapter. Furthermore, proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC) and phosphoric acid fuel cell (PAFC) as three special examples are described separately. Also, the main methods of Pt group based catalyst synthesis used in these fuel cells are illustrated. The overall outline of research covered under the ambit of this thesis is described at the end of this chapter.

1.1 General Fuel Cell Concepts

A fuel cell is an electrochemical conversion device (a galvanic cell). It converts the free energy of a chemical reaction into electrical energy with the products of heat and water, if hydrogen and air are the reactants. The components of a fuel cell consist of an anodic catalyst layer, electrolyte, a cathodic catalyst layer, bipolar plates/interconnects, gas diffusion layers at the anode and cathode, and sometimes gaskets for sealing or preventing leakage of gases between anode and cathode. A schematic representation of a fuel cell can be seen in Figure 1.1. A fuel cell system is highly efficient (with maximum theoretical efficiency as high as 83% for liquid water output at 298K), since it is not constrained by the maximum Carnot cycle efficiency as combustion engines are. Another advantage of the fuel cell is its low emission and environment-friendly properties. These features make fuel cells one of the strongest competitors of “green” power sources in the near future.
Fuel cells are most commonly classified on the basis of the type of electrolyte used in the cells, including polymer electrolyte fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). Generally, the choice of electrolyte corresponds to the operating temperature range of the fuel cell. The operating temperature and useful life of a fuel cell depend on the physicochemical and thermomechanical properties of materials used in the cell components (i.e., electrodes, electrolyte, interconnect, current collector, etc.). An overview of the key characteristics of the main fuel cell types is displayed in Table 1.1.

1.1.1 Proton Exchange Membrane Fuel Cells

A proton exchange membrane fuel cell uses a perfluorinated sulfonic acid membrane as a solid electrolyte, carbon supported Pt or Pt based alloy as electrocatalysts, hydrogen or reformate stream as fuel, air or oxygen as oxidant, and graphite or metal plates with gas flow fields as bipolar plates.

Hydrogen in the anodic catalyst layer goes through the following electrode reaction:

Anodic reaction: \( H_2 \rightarrow 2H^+ + 2e^- \) (1.1)

Electrons generated in equation 1.1 can travel to the cathode via the external circuit; protons produced at the anode electrode migrate to the cathode through a proton exchange membrane. On the cathode, oxygen reacts with hydrogen ions as well as electrons, and water is vented as the only product.

Cathodic reaction: \( \frac{1}{2}O_2 + 2H^+ +2e^- \rightarrow H_2O \) (1.2)

Net reaction: \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \) (1.3)

A picture of a typical proton exchange membrane single fuel cell of the type being used in Northeastern University can be seen in Figure 1.2.
The membrane electrode assembly (MEA) is the “heart” and most essential part of a proton exchange membrane fuel cell. Typically, anode, proton exchange membrane, and cathode are hot-pressed together, forming a “sandwich” like assembly with highly active three-dimensional interface. This technique and the use of solubilized ionomers in the catalyst layers reduces the charge transfer resistance between membrane and electrode significantly, and enables a decrease in catalyst loading to approximately 0.5-1.0 mg Pt cm\(^{-2}\) (MEA total loading). The output power density can be as high as 0.5-2 W/cm\(^2\), and volume power density and mass power density can be 1000 W/L and 700 W/kg respectively.\(^3\) The PEMFCs are very suitable for transport applications as well as for stationary and portable applications. The structures of most commonly used Nafion membrane and other novel membranes are shown in Figure 1.3.

1.1.2 Alkaline fuel cell

Alkaline fuel cells use aqueous alkaline solution as electrolyte, hydrogen as fuel, and oxygen or purified air (with CO\(_2\) removed) as oxidant. Porous gas diffusion electrodes prepared with catalysts (Pt/C, Ag, Ag-Au, Ni, etc) for the cathodic oxygen reduction reaction and corresponding, gas diffusion electrodes prepared with catalysts (PtPd/C, Pt/C, Ni etc) for the anodic hydrogen oxidation reaction with typical bipolar plates made with graphite or nickel plate serve as the current state of the art system.

Anode reaction: \(\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^- \quad \varphi^0 = -0.828 \text{ V} \quad (1.4)\)

Cathode reaction: \(\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- \quad \varphi^0 = 0.401 \text{ V} \quad (1.5)\)

The direction of ion migration in alkaline fuel cell is different from that in proton exchange membrane fuel cell. In the case of AFCs, OH\(^-\) generated at the cathode migrates
to the anode through an asbestos membrane soaked in alkaline solution.

Alkaline fuel cells have been very successfully applied in Apollo-series missions and on the Space Shuttle. However, the development of AFCs was suspended due to the competitive development of PEMFC in 1990’s and intrinsic problems such as poisoning through the conversion of KOH to potassium carbonate (K$_2$CO$_3$). Fortunately, replacement of liquid electrolytes in conventional AFCs with Alkaline Anion Exchange Membranes (AAEMs) that can transfer hydroxide ions (OH$^-$) have reinvigorated the development of alkaline fuel cells.$^4,5$ Anion exchange membranes enable the problem of carbonate formation to be surmounted, making thereby the application of small organic molecules (alcohol) as fuels feasible. Anion exchange membrane (AEM) fuel cells have the following intrinsic potential advantages as compared to their acidic counterparts.

1) Electrocatalysis of oxidation of hydrogen, methanol, and ethanol, and oxygen reduction in alkaline medium at high pH are potentially more facile than in acidic medium.

2) An alkaline medium opens the possibility of using inexpensive non-noble electrocatalysts such as MnO$_2$, nickel, silver, gold, cobalt, iron, and similar metals. This leads to more choice of catalysts for investigation and utilization. In contrast, the concept of an ‘acid stability criterion’ in the acidic environment of PEMFCs precludes the use of most non-noble metal catalysts.

3) The alkaline medium in anion exchange membrane fuel cells allows wider choices of fuel feed such as ethanol, xylitol, oxalic acid, etc., in contrast to the hydrogen and methanol that must be used in acidic environments, since the C-C bond breakage is potentially more facile in alkaline medium.
4) Transport of OH$^-$ ions and subsequent electro-osmotic drag of H$_2$O opposes the crossover of methanol or other fuels, leading to intrinsically lower crossover problems.

5) Better water management is achieved, since H$_2$O is consumed at the cathode as a stoichiometric component and is produced at the anode, leading to a decrease in flooding on the cathode side.

6) At high alkaline pH, peroxide radical generation and subsequent radical-initiated attack of the ionomer membrane is suppressed, allowing the use of hydrocarbon backbone membranes and thereby avoiding expensive fluorinated polymers.

7) Conventional liquid electrolyte alkaline fuel cells (AFC) are subject to the problem of precipitation of carbonate (CO$_3^{2-}$/HCO$_3^-$). Use of metal-cation free ion exchange membranes for OH$^-$ ions implies that the precipitation of carbonate or bicarbonate species found in liquid electrolyte alkaline fuel cell is avoided.

Prospective hydrocarbon polymer candidates for use in this proposed anion exchange membrane fuel cell are shown in Figure 1.4 and Figure 1.5. A methodology for synthesizing anion exchange membranes from this parent hydrocarbon membrane (PES) is also shown in Scheme 4 and briefly explained here, although the exact conditions (temperature/duration etc.) are subject to further optimization. This synthesis procedure involves chloromethylation of PES (Figure 1.5a) using paraformaldehyde and hydrochloric acid as chloromethylating agents and ZnCl$_2$ as catalyst, followed by amination (Figure 1.5b) of the membrane in trimethylamine solution to introduce quaternary ammonium ion exchange groups. Finally, the membrane is immersed in hydroxide salt solutions to exchange Cl$^-$ ions with OH$^-$ ions (Figure 1.5c). The final structure of the
alkaline form of quaternized poly(arylene ether sulfone) is shown in Figure 1-5d.

1.1.3 Phosphoric acid fuel cell

Phosphoric acid fuel cells have been commercialized successfully and used for stationary applications with a combined heat and power efficiency up to 80%.\(^1\) The reactions which occur in phosphoric acid fuel cell (PAFC) can be shown as following when H\(_2\) is taken as the fuel and O\(_2\) is taken as the oxidant.

\[
\text{Anode reaction: } H_2 \rightarrow 2H^+ + 2e^- \quad (1.6) \\
\text{Cathode reaction: } \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (1.7) \\
\text{Whole reaction: } \frac{1}{2}O_2 + H_2 \rightarrow H_2O \quad (1.8)
\]

Figure 1.6 shows the nature of phosphate species as a function of pH. The poor kinetics of the oxygen reduction reaction found in PAFCs due to specific adsorption of anions (mainly H\(_2\)PO\(_4^-\)) makes it necessary to operate the cell at 200 \(^0\)C. Pt and Pt based alloy catalysts are used for both anode and cathode to avoid serious corrosion. Carbon plates with ribbed channels are used in component of bipolar plates. The research and development status of PAFC to date can be seen in Table 1.2.

1.2 Electrocatalysis in fuel cells

“Electrocatalysts” is a term in the field of electrochemistry. In fuel cells, electrocatalysts are various metal-containing catalysts used to enhance the rates of the half reactions that comprise the fuel cell (see Figure 1.7).\(^6\) The behavior of the state-of-the-art Pt based electrocatalysts highly depends on the composition (nominal composition, surface composition), structure, morphology, particle size, degree of alloying, oxide content, and so forth. The best mix of these parameters is however
subject to the specifics of the intended reaction. However, a common requirement for a high performance Pt based catalysts is inclusive of the following: (1) a narrow nanoscale size distribution; (2) a uniform composition throughout the nanoparticles; (3) a high degree of alloying; (4) high dispersion on the carbon support. Electronic and structural properties of electrocatalysts have been taken as the main criteria for the discovery and optimization of electrocatalysts for a wide range of applications. On the anode, the superior performance for Pt alloyed catalysts when compared with Pt alone has been ascribed to a bifunctional effect (that is, a promoted mechanism). The bi-functional mechanism involves supplying oxygenated species at an adjacent site via promoting elements such as Ru, which activates water at lower potentials than Pt does. Thus, CO or other oxide species strongly adsorbed on Pt are easily oxidized to CO₂. The whole process can be described as follows:

\[
\text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{PtCO}_{\text{ads}} + 4\text{H}^+ + 4e^- \quad (1.9)
\]

\[
\text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru(OH)}_{\text{ads}} + \text{H}^+ + e^- \quad (1.10)
\]

\[
\text{PtCO}_{\text{ads}} + \text{Ru(OH)}_{\text{ads}} \rightarrow \text{CO}_2 + \text{Pt} + \text{Ru} + \text{H}^+ + e^- \quad (1.11)
\]

The promoter effect may also originate from an electronic effect (intrinsic mechanism) by modifying the electronic structure of Pt and lowering the potential of fuel adsorption.

On the cathode, the improvement based on Pt has been attributed to electronic and structural effects and several other factors.

The first reported systematic study of the ORR in these systems was conducted by Mukerjee et al. Five binary alloys of Pt with first row transition elements ranging from Cr to Ni were investigated. All the alloy electrocatalysts were found to enhance
ORR activity, albeit to different extents. The highest active binary alloy was found to be PtCr, where a three-fold enhancement was reported. The activation energy for ORR was reported to be on the same order of magnitude as that of Pt, and the reaction order with respect to molecular oxygen was reported to be one, same as Pt/C. Hence the conclusion was that the surface nature of these alloys kinetically favored higher ORR kinetics, with the initial adsorption geometry remaining unchanged. Comparison of ORR activity as \(iR\) corrected Tafel plots for oxygen reduction taken at 95°C (5 atm pressure) in a PEMFC environment showed lowering of the overpotential by 50 mV and concomitant enhancement of activity by greater than two fold. In addition, the results of a long-term test were also reported, where stable performance for PtCr/C was shown up to a period of 1200 hours (steady state operation at 50°C and 200 mA/cm\(^2\)). Later publications have further confirmed these earlier reports both in the PA and PEM environments. In PEMFC’s, ternary alloys have shown enhanced ORR activity with PtCr and PtCrCu electrocatalysts (2 fold enhancement); however life time tests on these electrocatalysts showed an excessive loss of Cu over a 300 hour test operating at 200 mA/cm\(^2\). Hydrodynamic voltammograms with rotating disks were used by Toda and Watanabe et. al., who reported enhancements of 10 fold using sputtered bimetallic films with Ni, Co and Fe. These have also been recently reported by Stamenkovic in their studies on thin layers of PtNi. The consensus on ORR electrocatalysis can be summarized as:

(a) The rate determining step for oxygen reduction; based on the wealth of prior data is considered to involve the initial adsorption by molecular oxygen (with or without a charge transfer step)
The principal source of overpotential loss is due to deactivation of the surface for all reactions, this effect the oxide coverage on the Pt surface at and close to the open circuit potential in a fully hydrated environment such as those in the low temperature PEMFC (below 80°C). This is distinct from the PAFCs where the largely non-aqueous environment results in low water activity at the interface, however severe surface poisoning of the surface due to anion adsorption is responsible for the poor kinetics.

Alloying with transition metals such as Co and Cr, has been shown to shift the onset of water activation and hence oxide coverage on the Pt surface. Several variants exist on the type of surface rendered after alloying, however the general consensus is of a skin effect with the outer surface being predominantly Pt and an inner core comprising the alloy.

The primary change in electrocatalysis does not involve a lowering of the activation energy, but involves the pre-exponential term which is related to the coverage of oxides on the surface.  

1.3 Main Methods for Electrocatalysts Synthesis

1.3.1 Impregnation

Impregnation is one of the most widely used and developed methods for synthesis of electrocatalysts. This simple and straightforward method has been successfully used to synthesize state-of-the-art carbon supported Pt and Pt based alloy catalysts widely used as both anodic and cathodic materials for all kinds of fuel cells. Typically, the procedure starts with an impregnation step. A Pt precursor such as H₂PtCl₆ is stirred with
high-surface-area carbon black support in water solution for certain time to form a homogeneous mixture. Then, a reducing agent such as NaBH₄, CH₂O, or N₂H₄ is introduced into the suspension slowly with stirring to begin the reduction step. The solution is filtered and catalyst is collected after complete reaction and crystallization. As an alternative for solid and liquid reducing agents, H₂ is usually used for synthesis of Pt based alloy catalysts. The synthetic conditions of impregnation, such as the nature of the carbon black and metal precursors, temperature, pressure and pH during the reaction, play a crucial role on affecting the composition, morphology and dispersion of product catalysts.

1.3.2 Ion exchange

As an example, carbon support is treated with oxidants such as KMnO₄ or concentrated HNO₃ to form active functional groups on the surface. These functional groups are exchanged with [Pt(NH₃)₄]²⁻ to prepare nano scale Pt/C electrocatalyst. The biggest advantage of the ion-exchange method is to form well dispersed metal particles enabling good control of the size of the nanoparticle on carbon support, which is the major drawback of the impregnation method.

1.3.3 Vacuum sputtering

Vacuum sputtering is a mature physical method. The sputtered metal (e.g. Pt) is taken as cathode and the acceptor (e.g. carbon paper in the diffusion layer) is used as anode. The method comprises vaporizing a catalyst, preferably platinum, in a vacuum to form a catalyst vapor. High voltage applied between the anode and cathode sputters nanometer scale Pt particles onto the carbon paper.

One outstanding advantage of the vacuum sputtering method is that it is better suited
to mass production and reduces the amount of catalyst needed for a high performance fuel cell electrode. Makino et al\textsuperscript{40} used sputter deposition to make a cathode for a DMFC, which achieved higher mass activities than that of 0.5 mg cm\textsuperscript{−2} prepared by the paste method and thereby decreased the needed amounts of the catalytic electrode metals.

1.3.4 Colloidal

Basically, the colloidal method consists of three common steps: (1) preparation of a platinum or platinum alloy containing colloid; (2) adsorption of the colloids on the carbon support; (3) chemical reduction. Several fabrication routes have been reported. Petrow and Allen reported the first patent for synthesis of Pt/C using a sulfite-complex route.\textsuperscript{41} In this patent, complex platinum sulfite acid (II) was added into water to form a colloid followed by adsorption onto the carbon black suspended in the solution. The catalyst was filtered and dried after pH adjustment and heat treatment of the colloid solution. A modified Petrow’s route based on liquid-phase reduction of H\textsubscript{2}PtCl\textsubscript{6} with Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} was successfully developed by Giodano.\textsuperscript{42} However, the Pt particle size varied over a large range from 1.8 to 12.6 nm. A novel point in the alcohol reduction method was the use of surfactant as a stabilizer.\textsuperscript{43}

A type of colloidal method, the Bönneman method (also referred to as a “precursor” concept) was developed for preparation of electrocatalysts in Professor Helmut Bönneman’s group at the Max Planck Institute.\textsuperscript{44} This new organometallic colloid route involves the preparation of nanoparticulate noble metals, resulting in easy control of particle size, structure, and the interface between the two metals during alloy synthesis.\textsuperscript{13}

In this procedure, tetrahydrofuran (THF) is usually taken as the organic phase to suspend salts of Pt or other metals. Tetraoctylammonium hydroborate (N(Oct)\textsubscript{4}[Bet\textsubscript{3}H], which is
prepared from N(Oct)₄Br and K[Be₃H], was used as the reducing agent. To make a carbon supported catalyst, the N(Oct)₄Cl-colloids were combined with a suspension of carbon black in THF and followed by a thermal treatment to remove the organic stabilizer shell. A drawback of the Bönneman method is the rigid and fixed particle size of the resulting sols, although some merits such as stable metal colloid formation and monodisperse distribution of particle size were listed.

1.3.5 Microemulsions

Recently, a water-in-oil microemulsion media method has been reported as a good route to prepare nano-scaled catalysts. A simple illustration is shown in Figure 1.8. Briefly, reverse micelle systems are suitable reaction media for the synthesis of nanoparticles, because tiny droplets of water are encapsulated into reverse micelles. The water regions of these reverse micelles act as micro-reactors for performing simple synthetic reactions, and the size of the micro-crystals produced is determined by the size of the reverse micelles. The size of the micelles is known to be controlled by the water/surfactant molar ratio in the system. Varying the water/surfactant ratio can form different sized reverse micelles, thus leading to careful control over the particle size. The most outstanding advantage of the microemulsion method is the ability to control particle size by adjusting the water/surfactant ratio.

As a typical example, a reverse micelle system of a cyclohexane solution of AOT containing required amounts of H₂PtCl₆ and AuCl₃ was mixed with another reverse micelle system containing NaBH₄. The redox reaction was completed within a few minutes. However, continuous stirring for another 4 hours was needed for nucleus formation and crystal growth. Next, a microemulsion system containing RuCl₃ was
introduced to form a Ru shell with a PtAu core. Then, the catalyst was washed with cyclohexane, acetone, ethanol, and water, and dried in vacuum at 80 °C for 24 hours.

Generally, the choice of method highly depends on the target reaction and application.

1.4 Scope of work

The focus of this dissertation is the preparation of Pt group based catalysts and thereafter study of electrocatalysis at the cathode of PEMFCs (proton exchange membrane fuel cells), the anode of DAEFCs (direct alkaline ethanol fuel cells) as well as the cathode of PAFCs (phosphoric acid fuel cells).

1.4.1 Electrocatalysts

Electrocatalysis enables modification of the rates of electrochemical reactions to achieve maximum selectivity, yield and efficiency. Interfacial charge transfer is the key to electrocatalysis. Three steps usually happen during the process of electrocatalysis. First, electroactive species are transferred from bulk solution to the electrode surface or within the double layer. Next, electrons are exchanged between the electrode and the electroactive species. Finally, the products are removed from the electrode involving desorption. In this work, the microemulsion method was used to control particle size, catalyst morphology, and crystalline shape as well as the catalyst layers. This method contributes to the conversion of new materials synthesis from “art” to “science”.49

1.4.2 Oxygen reduction reaction on cathode of PEMFC

Two of the main obstacles limiting industrial application of PEMFCs are the sluggish kinetics of the oxygen reduction reaction (ORR) and the large proportion of \( \text{H}_2\text{O}_2 \)
formation on the cathode. Our current understanding of mechanism of ORR on Pt group
based catalysts has to be improved. The relationship of Pt particle size and activity
towards the ORR as well as H$_2$O$_2$ yield was studied in this work. One essential point of
this study was the use of Pt catalysts in different particle sizes while maintaining the same
morphology as much as possible, since the ORR is a morphology sensitive reaction.$^{50}$ By
applying Pt with other transition metals, ORR kinetics can be highly improved due to the
increase of Pt d band vacancies and more facile O$_2$ adsorption on the Pt surface.$^{51}$ It is
well known that ORR only happens on the catalyst surface.$^{52}$ However, there are few
reports about how the surface composition influences the activity and H$_2$O$_2$ production.
Carbon supported PtCo alloy catalysts were synthesized with the simultaneous and
sequential microemulsion methods. The ORR was studied on these two catalysts with
different surface composition to correlate the content of Co with the activity and H$_2$O$_2$
yield.

1.4.3 Electro-oxidation of ethanol

Ethanol has shown increasingly greater advantages than methanol as the fuel for
mobile applications such as electric vehicles.$^{14, 53}$ There are a couple of reasons to use
ethanol as an alternative or strong competitor to methanol in direct alcohol fuel cells.
First, ethanol can be produced on an industrial scale from agricultural products such as
corn. Second, ethanol is environmentally friendly and not as toxic as methanol. Third, the
oxidation and transformation efficiency of ethanol is much higher than methanol since
twelve electrons are involved if carbon dioxide is the sole oxidation product. (Six
electrons are transferred in the case of methanol.)

Materials from the Pt families$^{13, 54}$ and the Pd families$^{55}$ are still the
state-of-the-art catalysts for electro-oxidation of ethanol either in acid media or basic media. However, it is well recognized that the majority of the products of ethanol electro-oxidation are species that still contain the C-C bond (acetaldehyde, acetic acid). In other words, only 2 electrons or maximally 4 electrons are transferred during ethanol oxidation on the best catalysts to date (Figure 1.2). These parallel reactions considerably reduce the capacity of the fuel to generate electricity and produce undesirable substances.14

In addition, adsorption of these side products on catalyst surface is the main cause of surface poisoning in these catalysts.13 It is crucial to develop novel catalysts or techniques to produce higher specific activity of dehydrogenation as well as C-O and C-C bond cleavage during the ethanol oxidation process.

1.4.4 Oxygen reduction reaction on cathode of PAFC

Phosphoric acid has the lowest volatility of any common acid, which makes it useful as the electrolyte in fuel cells operating at 190°C to 200°C for many thousands of hours. Nevertheless, even under the most favorable high-temperature and pressure conditions, the oxygen reduction reaction is still very slow and irreversible at the cathode of phosphoric acid fuel cell.

The objectives of the present work are:
(1) To conduct a mechanistic study of phosphate ion adsorption on the Pt surface and its influence on the oxygen reduction reaction;
(2) To prepare and evaluate novel Pt based alloy catalysts in high temperature half cell designed in house;
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Figure 1.1 A schematic representation of a fuel cell
Figure 1.2 Image of a single cell
Figure 1.3 Chemical structure of various proton conducting polymers

Sulfonated Poly Arylene Ether Sulfone
(SPES-XX, XX=30, 40, 50, 60)

Sulfonated Poly (Sulfide Sulfone)
(SPSS-XX, X=20, 40, 50)

Nafion® 117
Figure 1.4 Chemical structure of poly ether sulfone

Figure 1.5 Synthesis Methodology.
(a) poly(arylene ether sulfone) (PES)

(b) Chloromethylated PES

(c) Cl\textsuperscript{−} form of aminated PES

(d) OH\textsuperscript{−} form of alkaline anion exchange PES
Figure 1.6 Relative concentrations of different protonation states phosphate as a function of pH.
Figure 1.7 Electrocatalysts in a MEA of a PEMFC
Figure 1.8 Illustration of the formation of reverse micelles (CMC: critical micelle concentration)
Figure 1.9 Electrons transfer pathways during ethanol oxidation
### Table 1.1 Some characteristics of important fuel cells

<table>
<thead>
<tr>
<th></th>
<th>PEMFC</th>
<th>DMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary applications</strong></td>
<td>Automotive and stationary power</td>
<td>Portable power</td>
<td>Space vehicles and drinking water</td>
<td>Stationary power</td>
<td>Stationary power</td>
<td>Vehicle auxiliary power</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>Polymeric (plastic) membrane</td>
<td>Polymeric (plastic) membrane</td>
<td>Concentrated (30-50%) KOH in H₂O</td>
<td>Concentrated (100%) KOH in H₂O</td>
<td>Molten Carbonate retained in a ceramic matrix of LiAlO₂</td>
<td>Yttrium-stabilized Zirkondioxide</td>
</tr>
<tr>
<td><strong>Operating Temperature range</strong></td>
<td>50 – 100 °C</td>
<td>0 – 60 °C</td>
<td>50 – 200 °C</td>
<td>150 – 220 °C</td>
<td>600 - 700 °C</td>
<td>700 - 1000 °C</td>
</tr>
<tr>
<td><strong>Charge Carrier</strong></td>
<td>H⁺</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>CO₃⁻</td>
<td>O⁻</td>
</tr>
<tr>
<td><strong>Prime Cell Components</strong></td>
<td>Carbon-based</td>
<td>Carbon-based</td>
<td>Carbon-based</td>
<td>Graphite-based</td>
<td>Stainless-based</td>
<td>Ceramic</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td>Platinum</td>
<td>Pt-Pt/Ru</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel</td>
<td>Perovskites</td>
</tr>
<tr>
<td><strong>Primary fuel</strong></td>
<td>H₂</td>
<td>Methanol</td>
<td>H₂</td>
<td>H₂</td>
<td>H₂, CO, CH₄</td>
<td>H₂, CO</td>
</tr>
<tr>
<td><strong>Start-up time</strong></td>
<td>Sec-min</td>
<td>Sec-min</td>
<td>Sec-min</td>
<td>Hours</td>
<td>Hours</td>
<td>Hours</td>
</tr>
<tr>
<td><strong>Power density (kW/m³)</strong></td>
<td>3.8-6.5</td>
<td>0.6</td>
<td>1</td>
<td>0.8-1.9</td>
<td>1.5-2.6</td>
<td>0.1-1.5</td>
</tr>
<tr>
<td><strong>Combined cycle fuel cell efficiency</strong></td>
<td>50-60%</td>
<td>30-40% (no combined cycle)</td>
<td>50-60%</td>
<td>55%</td>
<td>55-65%</td>
<td>55-65%</td>
</tr>
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</table>
Table 1.2 Development of techniques used in the PAFC

<table>
<thead>
<tr>
<th></th>
<th>To 1965</th>
<th>To 1975</th>
<th>To date</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td>Pt black felted with PTFE</td>
<td>Pt/C Vulcan XC-72 felted with PTFE</td>
<td>Pt/C Vulcan XC-72 felted with PTFE</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td>9 mg/cm² (Pt loading) Pt black felted with PTFE</td>
<td>0.25 mg/cm² (Pt loading) Pt/C Vulcan XC-72 felted with PTFE</td>
<td>0.1 mg/cm² (Pt loading) Pt/C Vulcan XC-72 felted with PTFE</td>
</tr>
<tr>
<td>Electrode supporter</td>
<td>Tantalum web</td>
<td>Carbon paper</td>
<td>Carbon paper</td>
</tr>
<tr>
<td>Electrolyte supporter</td>
<td>fiberglass</td>
<td>SiC felted with PTFE</td>
<td>SiC felted with PTFE</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>85% H₃PO₄</td>
<td>95% H₃PO₄</td>
<td>100% H₃PO₄</td>
</tr>
</tbody>
</table>
Chapter 2

Electrocatalysis of Oxygen Reduction on Carbon Supported Pt and PtCo Catalysts Prepared by Water-in-Oil Microemulsions

2.1 Introduction

Proton exchange membrane fuel cells (PEMFCs) have received considerable attention for applications in transportation, portable electronics, and residential power sources due to their high energy density, high efficiency, relatively low operating temperature and low emission of pollutants.\(^1\)\(^,\)\(^2\) The poor kinetics of the oxygen reduction reaction at the cathode is one of main obstacles to successful application of PEM fuel cells. Carbon-supported platinum based electrocatalysts remain the current state-of-the-art catalysts for the oxygen reduction reaction (ORR) at the cathodes in PEMFCs. However, the poor ORR kinetics on carbon supported Pt catalysts leads to large overpotentials, as much as several hundred millivolts, which limited the energy conversion in PEMFCs.\(^3\) Therefore, efforts are still needed to develop more efficient Pt based catalysts.

The particle size and size distribution of Pt nanoparticles supported on carbon play very important roles in the oxygen reduction reaction kinetics. Some researchers have found that the specific activity decreases as the particle size decreases.\(^4\)\(^-\)\(^6\) This loss of catalytic activity have been attributed to significant enhancement of heats of adsorption of commonly activated species such as oxides or hydrides in aqueous media. As a result, the electrocatalyst becomes increasingly deactivated over the particle size range of 15-20 Å, as shown previously by Mukerjee et al.\(^7\) The ideal range of particle size for optimal specific activity of the ORR is therefore between
3.5-6.0 nm. This is consistent with the fact that the oxygen reduction reaction is sensitive to not only the nature of electrocatalysts but also their structure.8

As mentioned in chapter 1, a decrease of the desorption free energy ($\Delta G_{\text{ads}}$) of oxide species on Pt alloys, particularly OH, is the main reason for the enhancement of ORR activity. This fact can be associated with the following effects: (i) electronic factors9, 10 (higher Pt 5d band vacancy for the alloys in the oxidized state); (ii) geometric effects11 (shorter Pt-Pt bond distance and coordination number as well as metal particle size effects)11; (iii) OH$_{\text{ad}}$ coverage effects12 ($\theta_{\text{ad}}$ value effects, sacrificial elements oxidized leading to an increase of available sites for O$_{\text{ads}}$); (iv) other effects (ensemble effects13, surface segregation effects12, lower activity of water effect3).

However, insufficient work has been done on peroxide yield study. Peroxide can be formed as the intermediate species in the “parallel” pathway for ORR in acid medium.14 This has been attributed to be the main source of membrane degradation during the cathode reaction of fuel cells via peroxide initiated free radical attack of the membrane, especially HOO$^\cdot$ and HO$^\cdot$ radicals.15 Investigations into H$_2$O$_2$ formation remain unclear. Murthi et al13 suggested that Fe atoms on the surface of PtFe/C are the principal cause of higher H$_2$O$_2$ yields. However, the production of H$_2$O$_2$ on the Pt$_3$Ni, Pt$_3$Co and “Pt-skin” alloys was found to be the same as on pure Pt by other researchers.12 Surface composition effects on the peroxide yield were investigated on Pt based alloy surfaces.12 Also, a weak platinum particle size effect was shown in the RRDE study.16 However sintering and agglomeration of the commercial samples that were used in these investigations might have caused more complexity and
In order to elucidate the factors controlling variation of peroxide yield a method to synthesize Pt supported catalyst with control of particle size, size distribution and morphology of the individual grains or crystallites is essential.

Recently, a water-in-oil microemulsion media method has been reported as a good route to prepare nano-scaled catalysts. The method was also well established and explained in the previous paper from the same group. The most outstanding advantage of microemulsion method is the ability to control particle size via adjusting the water/surfactant ratio. This enables compartmentalized water droplets of different sizes thus leading to careful and convenient control over the particle growth and the particle size.

In this chapter, carbon supported platinum catalysts with different water/AOT molar ratios ($\omega_0$) were synthesized. Two reaction procedures associated with the microemulsion method, simultaneous reduction and sequential reduction, were used to synthesize PtCo/C catalysts. Catalysts were characterized using UV-vis, ICP-MS, QELS, TEM and XRD. The rotating ring disk electrode (RRDE) has been used to study the activity of the catalysts for the oxygen reduction reaction as well as the subsequent formation of peroxides.

2.2 Experiment

2.2.1 Chemicals

Unless otherwise stated, all chemicals were ACS reagent grade and used as received. The surfactant, sodium dioctyl sulfosuccinate (AOT), was obtained from
Fisher scientific. 35wt% Hydrazine and Sodium Borohydride (NaBH₄) were obtained from Sigma-Aldrich. Dihydrogen hexachloroplatinate(IV) hydrate (H₂PtCl₆·xH₂O) was from Sigma-Aldrich. The cobalt source was cobaltous chloride (CoCl₂) from Alfa Aesar. The Ketjen carbon (BET surface area of 800 m²/g) was dried at 100 °C in a high vacuum oven before using. Commercially available catalysts of 40wt% platinum and 30wt% platinum supported on Vulcan XC72 were obtained from E-TEK.

2.2.2 Synthesis of Pt/C and PtCo/C catalysts

All reverse micellar solutions were prepared using cyclohexane as the hydrophobic phase and AOT as the surfactant. The reverse micelle solutions containing H₂PtCl₆ were prepared by injecting the required amounts of 0.25 M H₂PtCl₆ aqueous solution into a 0.2M cyclohexane solution of AOT. In this work the concentration of AOT was referred to the total volume of the cyclohexane solution. However, the concentration of metal salts was specific to the aqueous phase. The mixtures were then sonicated to form clear and stable micellar solutions. The same procedure was used to prepare reverse micelle solutions containing a 2M aqueous hydrazine solution as the reducing agent. Then the two reverse micelle solutions were mixed and vigorously stirred at room temperature for at least 4 hours to ensure the complete reduction of H₂PtCl₆. The color of the mixture changed from pale yellow to dark brown indicating the formation of platinum nanoparticles. The size of the platinum nanoparticles was controlled by adjusting the molar ratio of water to AOT (ω₀ = [H₂O] / [AOT]).

Preparation of the simultaneous Pt-Co nanoparticles used a microemulsion
technique as described above. The required amounts of 0.25M H$_2$PtCl$_6$ and 0.25M CoCl$_2$ were mixed and injected into a 0.2M cyclohexane solution of AOT ($\omega_0 = 8$). The mixtures were then sonicated to form clear and stable micellar solutions. The same procedure was used to prepare the reverse micelle solutions containing 1M aqueous NaBH$_4$ solution as the reducing agent. Then the two reverse micelle solutions were mixed and vigorously stirred at room temperature for at least 4 hours to ensure the complete reduction of H$_2$PtCl$_6$ as well as CoCl$_2$.

Pt-Co nanoparticles were also prepared by a sequential reaction procedure. Solution (I) consisted of AOT, cyclohexane, and CoCl$_2$, producing a pink-colored solution reflecting the color of the Co$^{2+}$ ion. Solution II contained AOT, cyclohexane and NaBH$_4$. Solution III had AOT, cyclohexane and H$_2$PtCl$_6$. Solution I and half of solution II were first mixed under constant stirring, thereafter, the color of the solution changed to gray due to the suspended Co nanoparticles. Then solution III and the remainder of solution II were added to the above solution with continual stirring for another 2 hours.

An appropriate amount of Ketjen carbon was dispersed into cyclohexane and sonicated for over 1 hour and then added to the as-prepared Pt or PtCo nanoparticle solution. The slurry was vigorously stirred at room temperature for another 4 hours. To break down the reverse micelles, acetone was dropped slowly into the slurry, inhibiting the agglomeration of Pt or PtCo nanoparticles. The slurry was then filtered, washed successively with cyclohexane, acetone, ethanol, and water. The catalysts were dried in vacuum at 80 °C for 24 hours.
The carbon-supported PtCo/C prepared by the simultaneous and sequential procedures are hereafter designated as PtCo/C–S and PtCo/C-T. Temperature programmed heat treatment at 500°C was carried out on all PtCo/C catalysts. These catalysts are denoted as Pt-Co/C-SH and Pt-Co/C-TH respectively. In order to investigate the effect of pH on the redox reactions in reverse micelles and crystal growth, the same procedures were performed in basic solution by adding stoichiometric amount of Na₂CO₃ to neutralize the HCl produced. These catalysts are named as Pt-Co/C-SB and Pt-Co/C-TB respectively.

2.2.3 Characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were taken on a Rigaku X-ray Diffractometer (D-Max 2000) with CuKα radiation. The particle size of the dispersed metal crystallites is estimated from the broadening of diffraction peaks using the Scherrer formula.

A Hewlett-Packard HP 8453 UV-Vis spectrometer was used to record absorption spectra. The optical path length was 1.0 cm and 0.2M AOT solutions were used as references.

The morphology and particle size distribution of Pt and PtCo/C were examined by a JEOL JEM-1000 general purpose transmission electron microscope (TEM). The reverse micelle solutions containing Pt or isopropanol solution containing PtCo/C were applied on a copper mesh.

The Pt particles size distribution was further confirmed by Quasi Elastic Light Scattering (QELS) with 90 plus particle size analyzer of Brookhaven Instruments
2.2.4 Electrode preparation and electrochemical measurements

The electrochemical measurements were conducted in a standard three-compartment electrochemical cell at room temperature using a rotating disk electrode (RDE) setup from Pine Instruments connected to an Autolab (Ecochemie Inc. Model-PGSTAT 30). A glassy carbon disk with 5mm diameter was used as the substrate for deposition of catalyst films. All potentials were measured with respect to a sealed hydrogen reference electrode (RHE) made from the same electrolyte used in the ORR experiments. Before deposition of catalyst films, the RDE was first polished with 0.05 micron alumina slurry (Buehler, Lake Bluff, IL) and then cleaned with distilled water under sonication. All electrochemical experiments were carried out at room temperature.

The composition of the catalysts was analyzed using a VG Elemental Plasmaquad-2 (PQ2) ICP-MS. The results can be seen in Table 2.1. Seemingly, the sequential microemulsion reduction technique is easier and more accurate in controlling the composition of the mixed metal nanoparticles. The discrepancy of the Pt/Co atomic ratio from the nominal value may be caused by a “competitive effect” during the reduction process. It is difficult to control co-reduction of Co$^{2+}$ ions in the presence of PtCl$_6^{2-}$ ions in the reverse micelles solution.

The catalyst inks were prepared by dispersion of selected amounts (according to the results of ICP) of Pt/C catalyst powders into 20 ml of isopropanol and then sonicated for at least 30 minutes to reach a uniform suspension. The catalyst film was
prepared by dispersing 8 µL of the catalyst ink on the glassy carbon (GC) substrate and dried at room temperature to reach a total metal loading of 15 µg cm⁻². A dilute Nafion solution (Water : Nafion is 50:1) was then applied on the catalyst film and dried in air. The Nafion film was used as a binder to prevent the loss of catalysts from the glassy carbon substrate during ORR measurements. It has been shown that the very thin Nafion film over the catalyst films imposes negligible diffusion resistance towards ORR measurements.²¹

CVs were also taken in 1.0 mol L⁻¹ KOH with a gold disk (9mm in diameter) serving as the working electrode, while a platinum wire and Hg/HgO (KOH 1.0 mol L⁻¹) system were used as counter and reference electrode. For RRDE measurements the preparation of catalyst inks and electrodes was similar to that of RDE measurements. The RRDE (Pine Instrument Company) consisted of a GC disk (5.61mm in diameter) and a gold ring sealed in a polytetrafluoroethylene holder. The collection efficiency N determined using a solution of the [Fe(CN)₆]⁴⁻ / [Fe(CN)₆]³⁻ redox couple was 0.39. All RRDE experiments were performed in O₂-saturated 1M HClO₄. The disk electrode potential was then scanned between 1.2V vs RHE and 0.2V vs. RHE at 20mV/s with the ring electrode potential being held at 1.4V vs RHE, at which potential the H₂O₂ oxidation reaction was diffusion-limited at all rotation rates.²² H₂O₂ yield was measured for different rotation rates (ω). The ring current is proportional to ω¹/², so that only one rotation rate is presented in this paper (ω=900rpm).
2.3 Results and Discussion

2.3.1 UV-vis measurement

Small metallic particles are characterized by sensitivity of the plasmon band of the particles, which is observed as absorbance peaks in UV-vis spectra.\textsuperscript{23, 24} As can be seen in Figures 2.1(a)-(c), the microemulsions containing PtCl\textsubscript{6}\textsuperscript{2-} aqueous solution at different $\omega_0$ values ($\omega_0=5$, 8, 11) show two peaks (203-205nm, 261nm) before reduction. These peaks confirm the presence of PtCl\textsubscript{6}\textsuperscript{2-}, and are attributable to so-called “ligand-to-metal charge-transfer” absorption bands.\textsuperscript{25} After the reduction reaction, these peaks disappear and new peaks corresponding to Pt nanoparticles appear due to plasmon frequencies in the ultraviolet range or interband transitions.\textsuperscript{26} The absorption bands of Pt nanoparticles in reverse micelles are located exactly at the theoretical band position in water (215 nm)\textsuperscript{27} and near to some experimental results.\textsuperscript{28, 29} The blue shifts relative to those results may be caused by the higher PtCl\textsubscript{6}\textsuperscript{2-} concentration used in this paper, larger changes in the dielectric constant of the surface layer surrounding the particles, less interaction between Pt nanoparticles and surfactants\textsuperscript{29} and quantum size effects that arise from confinement of electrons to extremely small regions of space.\textsuperscript{30}

In Figure 2.1 (d) two peaks are observed (221nm, 261nm) corresponding to a mixture of PtCl\textsubscript{6}\textsuperscript{2-} and Co\textsuperscript{2+} in reverse micelles. After reduction, peaks analogous to the plasmon resonance in Pt particles were observed (223-225nm) confirming the presence of a Pt-Co nano-alloy produced by both the simultaneous and the sequential procedure. The peak positions of the Pt-Co nano-alloy are significantly red shifted in
comparison with a physical mixture of microemulsions containing Pt and Co (210nm), which is due to the weaker plasmon frequency in the ultraviolet range or to interband transitions in the Pt-Co nanoalloy.\textsuperscript{23, 24} Furthermore, the slight red shift of Pt-Co (T) relative to Pt-Co (S) may indicate the formation of new electronic levels caused by the perturbation of the core by the Pt shell.

\textbf{2.3.2 QELS and TEM measurements}

Quasi Elastic Light Scattering (QELS) is a quick, non-destructive and viable technique to measure the size distribution of tiny Pt particles, undergoing diffusive Brownian motion in reverse micelle solutions. A quite narrow particle size distribution can be seen in Figure 2.2 for all three microemulsions, which is consistent with the homogeneous nature of the microemulsion system. It is interesting to note that the particles do not tend to increase in size as the value of $\omega_0$ increases. This is in contrast to an earlier report,\textsuperscript{31} where an increase of Pt particle size is shown with a corresponding increase in the $\omega_0$ value. However, it seems that Pt nanoparticle size is dependent on both crystal formation rate and $\omega_0$. In the case of a low $\omega_0$ value of 5, a large number of nuclei are formed immediately after mixing the two reverse micellar solutions because many more microreactors could be retained at the low $\omega_0$ value. On the other hand, surfactant surrounding the particles indeed prohibit their growth when their formation rate is relatively low as in the case of $\omega_0=11$.

The size and shape of Pt nanoparticles in reverse micelles can be seen in the TEM images of Figures 2.3 (a)–(c). Good particle distribution is shown for the different $\omega_0$ values of 5, 8 and 11. In general, the shapes of Pt nanoparticles are irregular
polyhedra. When $\omega_0$ is increased to 11, amorphous particles begin to appear and even clusters evolve. A minimum average particle size of 5.6nm is observed when $\omega_0$ reaches 8. Pt nanoparticles are 8.0nm in size for $\omega_0=5$, and 7.5nm for $\omega_0=11$. It is hard to match the results of QELS exactly with those of TEM because of the underlying approximations of the QELS method, such as neglect of light absorption, and the assumption of spherical particles. However, the same trend ($\omega_0=5 > \omega_0=11 > \omega_0=8$) was measured in terms of the average particle size. In fact, the type of diameter obtained with QELS is the hydrodynamic diameter, which is the particle diameter plus the double layer thickness. As a result, the average particle size measured by QELS is a little larger than that measured by TEM.

Representative TEM images of PtCo/C catalysts as synthesized by the microemulsion method are shown in Figure 2.3 (d) and Figure 2.3 (e). From the histograms, a quite narrow particle size distribution can be seen for both Pt-Co/C-S and Pt-Co/C-T, which is evidence that the microemulsion method is efficient for synthesis of Pt based catalyst with predictable control over particle size, size distribution and morphology of the individual grains or crystallites. The average particle sizes in Pt-Co/C-S and Pt-Co/C-T are 3.4 nm and 2.9 nm respectively. The particles are evenly supported on the carbon in both, although some particle agglomeration on Ketjen Black EC-300J Carbon can be seen in Figure 2.3 (d). Also, the differences in particle size and the microstructure of Pt-Co/C-S and Pt-Co/C-T are due to different nucleation and growth processes in the simultaneous and sequential methods. In the latter case, Co cores with the same particle size were formed in
reverse micelles and separated first. Afterwards, Pt shells were produced surrounding the cores.

### 2.3.3 XRD Characterization

Representative powder patterns of Pt/C with different $\omega_0$ value can be seen in XRD spectrum of Figure 2.4 (a). Both the positions and intensities were normalized to the peak at 28.037° attributed to SiO$_2$. A broad peak at 2θ≈25° corresponds to diffraction of the carbon support.$^{32}$ The five major diffraction peaks marked indicate complete reduction of PtCl$_6^{2-}$ to Pt crystals.$^{33}$ From a comparison with JCPDS files (Copyright (C) JCPDS-ICDD 1997), all of the three catalysts synthesized by the microemulsion methods as well as the commercial sample have face-centered cubic lattices.

Figure 2.4 (b) shows representative XRD patterns of the various PtCo catalysts synthesized. The substitution of smaller Co atoms into the Pt lattice in PtM/C may cause a positive shift of the peaks.$^{34}$ Lower positive shifts can be seen for PtCo/C-T and PtCo/C-TB, indicating that some Co cores still remain, so that Co is enriched in the underlayer of PtCo/C-T. Chen et al.$^{35}$ drew a similar conclusion during their study of nucleation and growth mechanism for Pd/Pt in a microemulsion system, in which Pd was found not only coordinated by Cl but also by Pd after the addition of the Pt$^{4+}$ microemulsion into the system. In addition, no well defined diffraction peaks suggesting the presence of any metallic Co or oxide phases can be seen. This is probably because the Co loading was very low and any metal Co species present were highly dispersed or amorphous.$^{18}$
Together with the data from the peak positions and intensities of the Pt-Co alloy from ASTM cards, the diffraction patterns of all as-synthesized catalysts, including those after heat treatment, are in accord with a face centered cubic structure. Evidence of formation of disordered structures is indicated by the absence of superlattice reflections in the patterns of all PtCo/C catalysts synthesized by the microemulsion method at room temperature. For the samples after heat treatment, higher intensity and sharper peaks were obtained, which means more interpenetration of Co and the creation of a more highly ordered structure. Furthermore, solid solution may result from the heat treatment as indicated by the splitting of diffraction peaks.21

According to Bragg’s law, the d-spacing formula36 can be simplified for a cubic (111) lattice:

\[ \frac{1}{d_{111}^2} = \frac{3}{a^2} \]  

\[ \left( \frac{2 \sin \theta}{\lambda} \right)^2 = \frac{3}{a^2} \]  

in which, \( d_{111} \) is the perpendicular distance between planes and \( a \) is the lattice constant.

The Pt-Pt distance, \( d_1 \), can be calculated from equation (3),

\[ \left( \frac{2 \sin \theta}{\lambda} \right)^2 = \frac{3}{2d_1^2} \]  

The main diffraction peaks and lattice parameters for Pt/C (\( \omega = 5, 8, 11 \)) and PtCo/C are summarized in Table 2.2., where the degree of alloying was calculated from the expression: \( \chi = (a-a_0)/(a_c-a_0) \).65 In the expression, \( a \) is measured lattice parameter; \( a_0 \) is the lattice parameter of Pt; \( a_c \) is the theoretical lattice parameter of
PtCo assuming the Pt is fully alloyed with Co.\textsuperscript{65} All of the catalysts including Pt/C (E-TEK) contain similar crystalline parameters. This makes it possible to investigate the effect of particle size of Pt on catalytic properties and H\textsubscript{2}O\textsubscript{2} yield without the influence of other properties of catalysts. (See section 2.3.4). Regardless of reaction conditions, a lower extent of alloying could be seen for PtCo/C-T and PtCo/C-TB catalysts prepared by the sequential method since the lattice parameter and the Pt-Pt bond distance show less shrinking than in PtCo/C-S and PtCo/C-SB.\textsuperscript{34} In other words, some isolated Co phases may exist in such Pt-enriched systems. However, whether they are on the surface or surrounded by a Pt shell needs to be determined by other techniques (e.g. CVs in alkaline medium, see section 2.3.4).

The average crystallite size for Pt/C (ω\textsubscript{0}=5, 8, 11) catalysts and PtCo/C catalysts was calculated using the Debye-Scherrer equation\textsuperscript{37}:

\[ Z = C \frac{\lambda}{B \cos \theta} \]  

(2.4)

where \( Z \) is the diameter of the average particle size in Å; \( \lambda \) is the X-ray wavelength (1.5406Å) for CuK\textsubscript{a}, \( \theta \) is the Bragg angle, \( C \) is a factor (typically from 0.9 to 1.0) depending on crystallite shape, and \( B \) is the full width at half maximum. The results for Pt/C shown in Table 2.2 are about 1.2nm smaller than Pt nanoparticles in reverse micelles as measured by TEM. The larger apparent size of Pt nanoparticles in microemulsions measured by TEM may be caused by AOT surfactant surrounding the Pt nanoparticles. Also, it is intriguing to find that smaller particles could be formed by the sequential method than by the simultaneous method due to different nucleation and growth processes.
2.3.4 Electrochemical Characterization

2.3.4.1 Cyclic Voltammetry Measurements

CVs of all catalysts in Figure 2.5(a) were cycled between 0.035V and 1.1V vs. RHE in order to avoid possible changes in the Pt electrochemical area (ECA) and surface composition. Well-defined hydrogen adsorption/desorption features corresponding to typical crystal planes of Pt could be seen in all CV curves. The ECA of Pt was calculated from integration of both the hydrogen adsorption and desorption peaks. Assuming a correlation value of $210 \mu$C/cm$^2$ average results are tabulated in Table 2.3. Apparently the ECA decreases as the platinum particles increase in size. This may be evidence that there is no surfactant contamination on the Pt surface after decomposition of the reverse micelles by acetone. Additionally, it can be observed that the Hupd region and the peak potential of oxide reduction shift positively by 25mV for Pt/C ($\omega_0=5$, 11) relative to Pt/C ($\omega_0=8$) and Pt/C (E-TEK). These positive potential shifts indicate the inhibition of chemisorption of OH$^-$ on the Pt sites of Pt/C catalysts with relatively large particle size, thus affording better catalytic performance during ORR. The same conclusion was drawn in Mayrhofer’s report, in which the explanation for positive shifts in both the Hupd region and oxide species reduction is discussed in detail as a decrease in the oxophilicity of particles with increasing particle size.

From the steady-state CVs of all catalysts in Figure 2.5 (b) and Figure 2.5(c), the double layer of Pt/C (E-TEK) is the thinnest because Vulcan XC-72 carbon was used as support. However, from a technological point of view, Ketjen carbon may be more
suitable to support metal in the microemulsion method. The high surface area and porous structure may be sufficient to increase product yield despite the thicker double layer indicated by the electrochemical test. Furthermore, redox couple peaks can be seen at 0.6V on the CV of PtCo/C-TH. This could be due to migration of reduced Co to the surface after heat treatment of PtCo/C-T in a H₂/Ar mixture. Additionally, it can be observed that the H_{upd} region and the peak potential of oxide reduction shift to positive potentials to different extent for all catalysts prepared by the microemulsion method in comparison with commercial Pt/C (E-TEK 30%). It is believed that these shifts are due to higher 5d-band vacancies caused by alloying Pt with the second transition metal or to lower activity of water. This is expected to have a beneficial effect on oxygen reduction activity because of greater inhibition of adsorption of anions, in particular OH⁻. ECA results are tabulated in Table 2.4. The much smaller ECA of PtCo/C-SH and PtCo/C-TH is in line with their larger particle sizes after heat treatment. However, it is surprising to find that PtCo/C-SB and PtCo/C-TB exhibit smaller ECA than PtCo/C-S and PtCo/C-T even though they are quite similar in particle size. Considering the process of synthesis, PtCO₃, Pt(CO₃)₂ or other solid salts of platinum might precipitate out after adding Na₂CO₃ to adjust the pH of the reverse micelles solutions. These precipitates of platinum may prevent H from adsorbing on the surface Pt atoms.

2.3.4.2 ORR polarization measurements

Figure 2.6 (a) shows ORR polarization curves for as-prepared Pt/C catalysts at 1600rpm. The CV recorded in Ar-purged solution was subtracted from ORR
polarization current density at the same sweep rate to eliminate the influence of irreversible adsorption of oxides and charging of the electrical double layer on platinum.\textsuperscript{6} Three parts can be identified, namely, the diffusion-controlled region (<0.7 V), the mixed diffusion-kinetic limitation region (0.7V to 0.9V) and the Tafel region (>0.9V). The ORR current $j$ is expressed by the Koutecky-Levich equation\textsuperscript{21}:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} + \frac{1}{j_f} \quad (2.5)$$

$$j_d = 0.620nFD^{2/3}C_O\nu^{-1/6}\omega^{1/2} \quad (2.6)$$

where $j_k$ is the kinetic current density, $j_d$ is diffusion limiting current density, $j_f$ is the diffusion-limited current density through the Nafion film, $n$ is the number of electrons exchanged, $\omega$ is the angular frequency of rotation, $\omega = 2\pi f/60$, $f$ is the RDE rotation rate in rpm; $F$ is the Faraday constant (96485 C mol\textsuperscript{-1}), $D$ is the diffusion coefficient of molecular O\textsubscript{2} in 1 M HClO\textsubscript{4} solution (1.9×10\textsuperscript{-5} cm\textsuperscript{2} s\textsuperscript{-1}), $\nu$ is the kinematic viscosity (9.87×10\textsuperscript{-3} cm\textsuperscript{2} s\textsuperscript{-1}), and $C_O$ is the concentration of molecular oxygen (1.6×10\textsuperscript{-6} mol cm\textsuperscript{-3}).

The thickness of the Nafion film used to bind catalysts on the electrode is sufficiently small that its resistance can be neglected.\textsuperscript{40} As a result, equation (2.5) can be adjusted to the simpler equation (2.7) by dropping the $j_f$ term:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \quad (2.7)$$

Tafel plots corrected for Pt surface area are shown in Figure 2.6 (b) for Pt/C (E-TEK 40%) and Pt/C by the microemulsion method. Since the reaction pathway, reaction order, and the rate-determining step of the ORR are directly related to
changes in the Tafel slope, Figure 2.6 (b) and Table 2.3 show that the ORR proceeds in quite different ways on as-synthesized catalysts that have the same support, particle distribution, morphology and Pt crystal lattice parameters, and differ only in particle size. This finding is consistent with the fact that the ORR is very structure and particle size sensitive. The structure and size sensitivity of ORR is also affected by irreversibly adsorbed “oxide” in such a way that Pt with smaller particle size shows more facile adsorption of oxygenated species, as mentioned above, although the reversible adsorption of hydroxyl ions (OH⁻) on Pt(hkl) does not change the pathway of the reaction.

The specific activity based on the real surface area of Pt in all Pt/C catalysts and the kinetics parameters are summarized in Table 2.3. Pt/C (ω₀=5), with the largest particle size, has the highest specific activity and the best kinetic performance towards the ORR. It has been shown that varying the oxophilicity of Pt nanoparticles controls their catalytic activity. Also, the coverage of oxide species, particularly OH⁻, increases as the Pt particle size decreases. As a result, the enhanced adsorption of oxygenated species on Pt of smaller particle size provide greater inhibition of adsorption or splitting of O₂ and hence degrades the catalytic performance of Pt further.

The theoretical lines for the 2-electron process and the 4 electron process of ORR are included Figure 2.7 (a). The number of exchanged electrons was calculated from the slope of straight lines. The \( n \) values of various catalysts in Table 2.4 correspond to the 4 electron transfer pathway of the ORR process. Also, this plot may be evidence to
confirm that there is little isolated Co in as-synthesized catalysts, since transition metals are believed to prevent a fraction of the H₂O₂ intermediate in the ORR from being further reduced to H₂O, thereby reducing the \( n \) value.\(^{13,39}\)

Mass transport-corrected Tafel plots (\( E \) vs. \( \log|j_k| \)) are shown in Figure 2.7(b) for Pt/C (E-TEK 30%) and PtCo/C prepared by the microemulsion method. The slope of the Tafel curve is usually taken as an indicator of the ORR pathway.\(^{41}\) In their series of kinetics studies of ORR on Pt and Pt based alloy catalysts, Markovic and his coworkers\(^{12,44}\) suggested that in HClO₄, where there is minimal specific adsorption, the Tafel slopes are controlled by both “energetic effects” (Temkin to Langmuir adsorption)\(^9,45\) and “blocking effects” (surface coverage of OH⁻ controlling availability of O₂ adsorption)\(^{43}\). With regard to the Tafel plots in Figure 2.7(b) and slope values in Table 2.4, PtCo/C-T, PtCo/C-TB as well as PtCo/C-TH prepared by the sequential method show quite similar oxygen reduction processes. Probably due to relatively “conservative” procedure in the sequential method synthesis (see experimental section), no big changes to the physical structure of Pt, including Pt-Pt bond distance and coordination number, are expected, with the exception of particle size (see Table 2.2) after heat treatment or changing the pH of the microemulsion solution. In contrast to the above similarity, larger differences of Tafel slopes could be seen for PtCo/C-S, PtCo/C-SH and PtCo/C-SB. In this case, cobalt was reduced competitively with Pt by NaBH₄, which may lead to complexity in the kinetics of ORR after changing reaction conditions during the synthesis.

Mass activity and specific activity of as-synthesized PtCo/C catalysts and
commercial catalyst towards ORR are summarized in Table 2.4, and can also be seen in Figure 2.8. Some trends can be seen: in the mass activity, PtCo/C-SB > PtCo/C–S > PtCo/C-T ~ PtCo/C-TB ~ PtCo/C-TH > Pt/C (E-TEK) > PtCo/C-SH, whereas for the specific activity PtCo/C-SB > PtCo/C-TB > PtCo/C-TH ~ PtCo/C–S > PtCo/C-T ~ PtCo/C-SH > Pt/C (E-TEK). To different extents, the catalytic performance of PtCo/C catalysts synthesized by the microemulsion method exceeds that of the commercial Pt/C catalyst. Again, the reaction conditions in the synthetic process need to be emphasized. Alkaline medium seems to be more suitable for Pt and Co to coexist well, although it does lead to some insoluble salt formation. In addition, heat treatment is commonly used to achieve a good alloy of Pt and other transition metals. However, heat treatment of PtCo/C-S synthesized by the simultaneous procedure does not enhance its catalytic activity towards ORR, which suggests that Pt and Co are already in close contact close after reduction at room temperature. Notwithstanding, it is important to do the heat treatment for PtCo/C-T (synthesized by the sequential procedure) because more than one phase might be formed after Pt is coated onto the Co surface. (See results of XRD characterization in Section 3.3)

Redox-type processes involving first row transition elements alloyed with Pt may be a reason for the enhanced ORR activity on PtM (M=transition metal) alloy catalysts as mentioned in the study of surface composition effects of PtM(M=Ni,Co) alloy on the ORR by Stamenkovic et al.. They pointed out that transition metals may serve as “sacrificial” elements to be oxidized and inhibit the adsorption of OH on Pt sites. Our results confirm their plausible explanation. The reaction order (m) of the
ORR on as-synthesized catalysts was first checked from the plots of log(i) versus log(i-i/id).\textsuperscript{44} From Table 2.4, the first order dependence of the kinetics of the ORR was performed on PtCo/C prepared by the microemulsion method and commercial Pt/C. Therefore, the general rate expression can be seen in equation 2.8, assuming that the first electron transfer for the oxygen reduction (O\textsubscript{2(ad)} + e\textsuperscript{-} → O\textsuperscript{-}2(ad)) is the rate determining step:

\[
i = nFKC_{O_2}(1-m\theta_{ad})^x \exp(-\beta FE/RT) \exp(-\gamma r\theta_{ad}/RT)
\] (2.8)

where \(F\) is Farady’s constant, \(K\) is the rate constant, \(C_{O_2}\) is the concentration of O\textsubscript{2}, \(m\) is the reaction order, \(\theta_{ad}\) is the surface coverage of adsorbed intermediates, \(\beta\) and \(\gamma\) are symmetry factors, \(E\) is the applied potential, and \(r\theta_{ad}\) is a parameter related to the rate of change of the apparent standard free energy of adsorption with the surface coverage of an oxide layer.\textsuperscript{3, 12, 49} Since other parameters are identical to catalysts with different surface composition, the (1-\(\theta_{ad}\)) term (\(m=1\)) may predominantly control the entire kinetics of the ORR. The greater the number of available sites for O\textsubscript{ad}, the lower is the \(\theta_{ad}\) value. Consequently, in HClO\textsubscript{4}, the better inhibition of adsorption of OH\textsuperscript{-} on PtCo/C leads to greater access of O\textsubscript{2} to active sites on the Pt surface, and ultimately to higher mass activity and specific activity. From Table 2.4, the positive shift of both half-wave potential and peak potential of oxide reduction may confirm the role of cobalt as a “sacrificial” element that is oxidized to prevent the formation of OH\textsubscript{ad}.\textsuperscript{12}

2.3.4.3 H\textsubscript{2}O\textsubscript{2} yield measurements

The H\textsubscript{2}O\textsubscript{2} yield for the ORR on Pt/C synthesized by the microemulsion
method with different \( \omega_0 \) values is shown in Figure 2.9 (a). The relative amounts of H\(_2\)O\(_2\) formed on the catalysts are calculated on the basis of the formula:

\[
\chi_{H_2O_2} = \frac{2I_R/N}{I_D + I_R/N} \quad (2.9)
\]

where \( N \) is the collection efficiency of the ring, \( \chi \) is the mole fraction of peroxide formed, and \( I_D \) and \( I_R \) are the disk and ring currents. Again, the disk current is correlated to the real surface area of Pt. From Figure 2.9 (a), the H\(_2\)O\(_2\) yield of ORR on all catalysts is insignificant in the potential window of 0.7V to 1.1V. However, the H\(_2\)O\(_2\) yield is far from negligible when the potential of the working electrode is lower than 0.6V, and increases as the platinum particle size increases. It is hard to account for peroxide yield using only the Pt particle size effect since many variables in the reaction pathway for oxygen reduction remain undetermined. In the following simplified scheme of oxygen reduction reaction pathways,\(^{10,38,50}\) some rate constants cannot be determined yet with RRDE measurements:

\[
\text{O}_2 \text{ (solution)} \rightarrow \text{O}_2 \text{ (surface)} \quad (2.10)
\]

\[
\text{O}_2 \text{ (surface)} \rightarrow \text{Pt-O}_2\text{,ad} \quad (2.11)
\]

\[
\text{Pt-O}_2\text{,ad} + \text{H}^+ \rightarrow \text{Pt-HO}_2 \quad (2.12)
\]

\[
\text{Pt-HO}_2 \rightarrow \text{Pt-HO} + \text{Pt-O} \quad (2.13)
\]

\[
\text{Pt-HO} + \text{Pt-O} + 3\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad (2.14)
\]

\[
\text{Pt-HO}_2 \rightarrow \text{Pt-H}_2\text{O}_2\text{,ad} \leftrightarrow \text{H}_2\text{O}_2 \quad (2.15)
\]

Antoine et al.\(^{16}\) concluded that the H\(_2\)O\(_2\) yield increases appreciably when the platinum particle size increases. However, the issue of agglomeration in Pt/C catalysts
deposited on glassy carbon was not mentioned in their study, which may affect the \( \text{H}_2\text{O}_2 \) yield of the ORR.\(^\text{17} \)
Also, they assumed that bridged end-on \( \text{O}_2 \) adsorption\(^\text{38, 51} \) happens more easily on smaller Pt particles with a larger proportion of low coordination surface atoms (tops and edges).\(^\text{52} \) This would lead to more \( \text{H}_2\text{O}_2 \) production, as this mode of adsorption is not dissociative.\(^\text{16, 53, 54} \) But there may remain competitive adsorption of bridge end-on \( \text{O}_2 \) and oxygenated species, in particular –OH, which poisons Pt as discussed earlier. In other words, the eventual number of bridge end-on \( \text{O}_2 \) molecules on smaller Pt particles may still be even less than those on larger Pt particles since a large fraction of them is occupied by –OH and other oxygenated species. In general, the particle size effect on \( \text{H}_2\text{O}_2 \) yield can still be explained from the perspective of water activation and the formation of adsorbed oxygenated species (primarily Pt-OH). It has been found that both Pt/C and Pt-alloy/C show lower overpotential loss and 4 fold higher peroxide yield in 6M TFMSA as compared to 1M TFMSA.\(^\text{3} \) The high concentration (6M) TFMSA reduces water activity due to the lower ratio of water to acid. Analogously, Pt/C(\( \omega_0=5 \)) with its larger particle size shows higher specific activity and higher peroxide yield. This may be an evidence that a certain amount of \( \text{O}_2 \) reacts in the 2-electron pathway due to the much lower dissociation energy of O-O (146 kJ\( \cdot \text{mol}^{-1} \)) after protonation and formation of \( \text{H}_2\text{O}_2 \) as compared to O-O (494 kJ\( \cdot \text{mol}^{-1} \)) in the \( \text{O}_2 \) molecule.\(^\text{38} \) Considering the ORR pathway in equations (10-15) and the conclusions by Tseung,\(^\text{55-58} \) oxygen is mainly reduced via the series pathway with peroxide as the intermediate, so that Pt/C (\( \omega_0=8 \)) with smaller particle size exhibits poor ORR kinetics and gives lower \( \text{H}_2\text{O}_2 \) yield
because of larger “OH adsorption poisoning” compared to Pt/C ($\omega_0=11$) and Pt/C ($\omega_0=5$).

In addition, the differences among microreactors formed in the microemulsion systems with different $\omega_0$ influence not only the particle size but also the crystallite morphology during crystal growth. As a result, Pt/C ($\omega_0=5$), Pt/C ($\omega_0=8$) and Pt/C ($\omega_0=11$) may have different crystallite morphologies. From a previous report,$^{51, 59}$ higher amounts of peroxide were formed on Pt(100) as compared to Pt(111) and polycrystalline Pt. Further surface study is needed to understand the crystal structure effect on the pathway of oxygen reduction reaction.

The $\mathrm{H}_2\mathrm{O}_2$ yield during ORR on PtCo/C catalysts synthesized by the microemulsion method and the Pt/C (E-TEK) sample at 900 rpm are shown in Figure 2.9 (b). From Figure 2.9 (b), the $\mathrm{H}_2\mathrm{O}_2$ yield is negligible for disk currents above 0.6V for all catalysts. Comparisons were only made between samples prepared by the simultaneous procedure and their counterparts prepared by the sequential procedure, i.e. PtCo/C-S vs. PtCo/C-T; PtCo/C-SH vs. PtCo/C-TH; PtCo/C-SB vs. PtCo/C-TB. The results are tabulated in Table 2.4 and can be explained from the perspective of water activation and the formation of adsorbed oxygenated species (primarily Pt-OH). M.A. of as synthesized catalysts (PtCo/C-S > PtCo/C-T; PtCo/C-SB > PtCo/C-TB; PtCo/C-TH > PtCo/C-SH) shows the same trend as that of peroxide yield (PtCo/C-S > PtCo/C-T; PtCo/C-SB > PtCo/C-TB; PtCo/C-TH > PtCo/C-SH), which is consistent with Tseung’s conclusions$^{55-58}$ as well as what we mentioned above during the particle size study section.
Cyclic voltammograms in 1M KOH as the methodology to probe surface composition for above catalysts were shown in Figure 2.10. Redox couple in the potential window of -0.2v to -0.5v vs. Hg/HgO is involved in the redox process relative to Co which is evident in the CV of PtCo/C-S.\textsuperscript{9} Integration was made in the hydrogen UPD region (-0.78V to -0.47V vs. Hg/HgO) and oxide species of Co formation region (-0.37V to -0.16V vs. Hg/HgO). Ratios of charge of these two regions may reflect atomic ratio of Co and Pt (named R thereafter) on the surface of catalysts. Although it is definitely not actual value of molar ratio of metallic Co and Pt on the surface, comparison between as-synthesized catalysts can be taken correspondingly. The results are shown in Figure 2.11. R values of PtCo/C-T and PtCo/C-TB are lower than those of their counterparts of PtCo/C-S and PtCo/C-TB due to different synthesis procedures (see section 2.2). It is worthwhile to correlate R value with specific activity (S.A.) and peroxide yield for as-synthesized PtCo/C catalysts. It seems that PtCo/C-S, PtCo/C-TH and PtCo/C-SB with higher R values have better catalytic property towards ORR and higher H\textsubscript{2}O\textsubscript{2} yield than their counterparts’ presumably due to sacrificial Co oxidation effect on inhibition of adsorption of OH as mentioned above in the same section. However, there still remains concern that some cobalt has already existed in its oxide species which are amorphous and hidden in XRD pattern. Therefore, further XPS, Auger electron spectroscopy (AES) experiments are needed to be done for the surface composition study in detail.
2.4 Conclusions

Pt supported on carbon catalysts were synthesized in AOT/cyclohexane microemulsions with different water/AOT molar ratios ($\omega_0$) by reducing $\text{H}_2\text{PtCl}_6$ with hydrazine. In addition, PtCo supported on carbon catalysts were synthesized in AOT/cyclohexane microemulsions in both acidic and basic media by reducing $\text{H}_2\text{PtCl}_6$ and $\text{CoCl}_2$ with NaBH$_4$. A modified sequential procedure was also used to synthesize PtCo/C and achieved lower Co/Pt ratio on the surface of catalyst.

The formation of Pt and PtCo nanoparticles was confirmed clearly by UV-vis. Pt or PtCo particles of as-synthesized catalysts were nano-scale, irregular polyhedra and uniformly distributed on the support. However, the Pt particle size depends on both crystal formation rate and $\omega_0$. A minimum average particle size of 5.6nm was observed when $\omega_0$ reached 8. Derived from analysis of XRD patterns, PtCo/C-S and PtCo/C-SB by simultaneous procedure have quite similar crystal structure and lattice parameters with PtCo/C-T and PtCo/C-TB by sequential procedure. However, the latter showed smaller particle size and lower degree of alloying which led to Co migration during high temperature heat treatment.

Better kinetics performance of the ORR was shown for Pt/C and PtCo/C synthesized in reverse micellar systems in comparison with a commercial Pt/C catalyst. The particle size seems to have the greatest influence on the catalytic properties of the as-synthesized Pt/C catalysts, since other crystalline parameters of Pt/C with different $\omega_0$ are almost the same. The specific activity of Pt/C synthesized
by the microemulsion method decreases as the particle size of Pt decreases.

Smaller peroxide yield was found for the ORR on Pt/C ($\omega_0=8$) which had smaller Pt particle size. Inhibition of adsorption of oxide species and crystal structure issues may indicate a perturbation in the pathways of the oxygen reduction reaction. Insignificant peroxide yield was found for the ORR on as-synthesized PtCo/C catalysts, which suggests that the ORR was undergoing a 4 electron pathway on these catalysts. $R$ values representing surface composition were obtained from the ratio of the integral of oxidized peak related to Co and $H_{\text{upd}}$ region of Pt. The results correlated well with S.A. of different PtCo/C catalysts and $H_2O_2$ yield. Inhibition of $OH^-$ adsorption by sacrificial oxidation of Co oxidized may be an explanation for the higher catalytic properties and higher $H_2O_2$ yield of Pt based alloy catalysts.
2.5 Chapter 2 References:


8. H. Yang; W. Vogel; C. Lamy; N. Alonso-Vante, Structure and Electrocatalytic


15. Q. Guo; P. N. Pintauro; H. Tang; S. O'Connor, Sulfonated and crosslinked


22. S. L. Gojkovic; S. Gupta; R. F. Savinell, Heat-treated iron(III) tetramethoxyphenyl porphyrin chloride supported on high-area carbon as an electrocatalyst for oxygen reduction: Part III. Detection of hydrogen-peroxide during


30. S. Wang; J. Zou; B. R. Jarrett; S. Cho; A. Y. Louie; S. M. Kauzlarich, High


2.5 Chapter 2 Figures:

Figure 2.1 (a) UV-visible absorption spectra of microemulsions containing PtCl$_6^{2-}$ and Pt nanoparticles with $\omega_0=5$, $\omega_0=8$ and $\omega_0=11$. 
Figure 2.1 (b) UV-visible absorption spectra of microemulsions containing PtCl$_6^{2-}$, Co$_{2+}$ and PtCo nanoparticles by both the simultaneous (S) and sequential (T) microemulsion procedures, and a physical mixture of microemulsions containing Pt and Co.
Figure 2.2 (a) Multimodal Size Distribution of platinum nanoparticles in AOT/cyclohexane reverse micelles. $\omega_0=5$
Figure 2.2 (b) Multimodal Size Distribution of platinum nanoparticles in AOT/cyclohexane reverse micelles. $\omega_0=8$
Figure 2.2 (c) Multimodal Size Distribution of platinum nanoparticles in AOT/cyclohexane reverse micelles. $\omega_0=11$
Figure 2.3 (a) Transmission electron micrograph and size distribution of platinum nanoparticles in AOT/cyclohexane reverse micelles. $\omega_0=5$. 

<average size> 
8.0±0.3nm
Figure 2.3 (b) Transmission electron micrograph and size distribution of platinum nanoparticles in AOT/cyclohexane reverse micelles. $\omega_0=8$. 
Figure 2.3 (c) Transmission electron micrograph and size distribution of platinum nanoparticles in AOT/cyclohexane reverse micelles. $\omega_0=11$. 
Figure 2.3 (d) Transmission electron micrograph of PtCo/C-S and size distribution of platinum nanoparticles
Figure 2.3 (e) Transmission electron micrograph of PtCo/C-T and size distribution of platinum nanoparticles
Figure 2.4 (a) XRD pattern for Pt/C ($\omega_0=5$, $\omega_0=8$, $\omega_0=11$) and Pt/C (40% E-TEK)
Figure 2.4 (b) XRD patterns of Pt/C (30% E-TEK), PtCo/C-S, PtCo/C-T, PtCo/C-SB, PtCo/C-TB, PtCo/C-SH and PtCo/C-TH
Figure 2.5 (a) Cyclic voltammetry of Pt/C ($\omega_0=5$, $\omega_0=8$; $\omega_0=11$) and Pt/C (E-TEK) catalysts with 40wt% Pt loading on carbon support at room temperature in Ar saturated 1 M HClO$_4$ at 50mV/s vs. RHE.
Figure 2.5 (b) Cyclic voltammetry of Pt/C (E-TEK), PtCo/C-S, PtCo/C-SH and PtCo/C-SB at room temperature in Ar saturated 1 M HClO₄ at 50mV/s vs. RHE
Figure 2.5 (c) Cyclic voltammetry of Pt/C (E-TEK), PtCo/C-T, PtCo/C-TH and PtCo/C-TB at room temperature in Ar saturated 1 M HClO₄ at 50mV/s vs. RHE
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Figure 2.6 (b) Tafel plots of $j_k$ for the ORR obtained from disk current in the anodic sweep at 1600rpm on Pt/C ($\omega_0=5$, $\omega_0=8$, $\omega_0=11$) and Pt/C (E-TEK) (40% Pt loading on carbon for all samples) catalysts synthized by the microemulsion method. Scan rate: 20 mV s$^{-1}$. 
Figure 2.7 (a) Koutecky-Levich plots at different potentials for the ORR in the cathodic sweep on PtCo/C-S in O₂ saturated 1M HClO₄ at room temperature. Scan rate: 20mV s⁻¹
Figure 2.7 (b) Mass corrected Tafel plots of $j_k$ for the ORR obtained from disk current in the anodic sweep at 1600 rpm on PtCo/C catalysts synthesized by the microemulsion method and Pt/C (E-TEK) catalysts. Scan rate: 20 mV s$^{-1}$
Figure 2.8 (a) Specific activity of Pt/C ($\omega_0=5$, $\omega_0=8$, $\omega_0=11$) and Pt/C (E-TEK) (40 wt % Pt loading on carbon for all samples) towards ORR at different potentials
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Figure 2.8 (c) Specific activity of PtCo/C synthesized by the microemulsion method and Pt/C (E-TEK 30%) towards ORR at different potentials
Figure 2.9 (a) $\text{H}_2\text{O}_2$ yield during the ORR on Pt/C ($\omega_0=5$, $\omega_0=8$, $\omega_0=11$) in 0.5M $\text{H}_2\text{SO}_4$ at a sweep rate of 20mV/s
Figure 2.9 (b) \( \text{H}_2\text{O}_2 \) yield during the ORR at 900 rpm on all PtCo/C catalysts by microemulsions method and commercial Pt/C in 1.0M H\( \text{ClO}_4 \) at a sweep rate of 20mV/s
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Figure 2.10 (b) Cyclic voltammograms obtained for Pt/C (E-TEK), PtCo/C-T, PtCo/C-TH, PtCo/C-TB, and ketjen carbon in 1.0 mol L⁻¹ KOH at 50 mV s⁻¹
Figure 2.11 R values (integrated charge of Co oxidized /integrated charge of H\textsubscript{upd}), H\textsubscript{2}O\textsubscript{2} yield at 0.6V (RHE) and specific activity (S.A.) at 0.9V (RHE) of PtCo/C synthesized by the microemulsion method
**Table 2.1** Composition of Pt/C and PtCo/C catalysts prepared using the microemulsion method

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nominal composition</th>
<th>Composition from ICP analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt Wt%</td>
<td>Pt: M (atomic)</td>
</tr>
<tr>
<td>Pt/C (E-TEK 40%)</td>
<td>40</td>
<td>---</td>
</tr>
<tr>
<td>Pt/C (ω₀=5)</td>
<td>40</td>
<td>---</td>
</tr>
<tr>
<td>Pt/C (ω₀=8)</td>
<td>40</td>
<td>---</td>
</tr>
<tr>
<td>Pt/C (ω₀=11)</td>
<td>40</td>
<td>---</td>
</tr>
<tr>
<td>Pt/C (E-TEK 30%)</td>
<td>30</td>
<td>---</td>
</tr>
<tr>
<td>Pt–Co/C–S</td>
<td>26.4</td>
<td>67:33</td>
</tr>
<tr>
<td>Pt–Co/C–T</td>
<td>26.4</td>
<td>67:33</td>
</tr>
<tr>
<td>Pt–Co/C–SB</td>
<td>26.4</td>
<td>67:33</td>
</tr>
<tr>
<td>Pt–Co/C–TB</td>
<td>26.4</td>
<td>67:33</td>
</tr>
</tbody>
</table>
Table 2.2 XRD data of PtCo/C catalysts by the microemulsion method

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lattice types</th>
<th>Pt (111) @2θ</th>
<th>Crystallite Size/ nm</th>
<th>Lattice parameter /Å</th>
<th>Pt-Pt bond distance / Å</th>
<th>Degree of alloying (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C (E-TEK 40%)</td>
<td>fcc</td>
<td>40.09</td>
<td>4.3</td>
<td>3.89</td>
<td>2.75</td>
<td>0</td>
</tr>
<tr>
<td>Pt/C (ω₀=5)</td>
<td>fcc</td>
<td>40.04</td>
<td>6.9</td>
<td>3.90</td>
<td>2.76</td>
<td>0</td>
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<tr>
<td>Pt/C (ω₀=8)</td>
<td>fcc</td>
<td>40.34</td>
<td>4.6</td>
<td>3.87</td>
<td>2.74</td>
<td>0</td>
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<tr>
<td>Pt/C (ω₀=11)</td>
<td>fcc</td>
<td>40.04</td>
<td>6.1</td>
<td>3.90</td>
<td>2.76</td>
<td>0</td>
</tr>
<tr>
<td>Pt/C (E-TEK 30%)</td>
<td>fcc</td>
<td>39.89</td>
<td>3.4</td>
<td>3.91</td>
<td>2.77</td>
<td>0</td>
</tr>
<tr>
<td>Pt-Co/C–S</td>
<td>fcc</td>
<td>40.33</td>
<td>3.9</td>
<td>3.87</td>
<td>2.74</td>
<td>71.9</td>
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<tr>
<td>Pt-Co/C-T</td>
<td>fcc</td>
<td>40.15</td>
<td>3.2</td>
<td>3.89</td>
<td>2.75</td>
<td>42.1</td>
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<td>Pt-Co/C-SB</td>
<td>fcc</td>
<td>40.27</td>
<td>3.9</td>
<td>3.88</td>
<td>2.74</td>
<td>61.4</td>
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<td>Pt-Co/C-TB</td>
<td>fcc</td>
<td>40.13</td>
<td>3.0</td>
<td>3.89</td>
<td>2.75</td>
<td>40.4</td>
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<td>Pt-Co/C-SH</td>
<td>fcc</td>
<td>40.40</td>
<td>8.7</td>
<td>3.86</td>
<td>2.73</td>
<td>82.5</td>
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<tr>
<td>Pt-Co/C-TH</td>
<td>fcc</td>
<td>40.13</td>
<td>10.6</td>
<td>3.89</td>
<td>2.75</td>
<td>40.4</td>
</tr>
</tbody>
</table>

* degree of alloying was calculated from the expression: \( \chi = (a-a_0)/(a_c-a_0) \) \(^{11}\)
Table 2.3 Electrode Kinetic Parameters for Different Pt/C Catalysts in 1 M HClO₄ at room temperature. Scan rate: 20 mV s⁻¹, rotation rate: 1600 rpm

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ECA (m²/g)</th>
<th>Specific Activity (mA/cm²)</th>
<th>Tafel slope (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C (E-TEK 40%)</td>
<td>43.4</td>
<td>0.4115 1.475 3.81</td>
<td>145/62</td>
</tr>
<tr>
<td>Pt/C (ω₀=5)</td>
<td>22.5</td>
<td>0.6345 2.61 8.11</td>
<td>123/57</td>
</tr>
<tr>
<td>Pt/C (ω₀=8)</td>
<td>39.9</td>
<td>0.365 1.41 3.705</td>
<td>154/57</td>
</tr>
<tr>
<td>Pt/C (ω₀=11)</td>
<td>33.3</td>
<td>0.5175 1.84 4.92</td>
<td>138/61</td>
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</tbody>
</table>
Table 2.4 Electrode Kinetic Parameters for Different PtCo/C Catalysts in 1 M HClO₄ at room temperature.
Scan rate: 20 mV s⁻¹, rotation rate: 1600 rpm

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ECA (m²/g)</th>
<th>E₁/₂ (V)</th>
<th>Number of Exchanged electrons</th>
<th>Mass Activity (mA/µg Pt) @0.90V</th>
<th>Mass Activity (mA/µg Pt) @0.85V</th>
<th>Mass Activity (mA/µg Pt) @0.80V</th>
<th>Specific Activity (mA/cm²) @0.90V</th>
<th>Specific Activity (mA/cm²) @0.85V</th>
<th>Specific Activity (mA/cm²) @0.80V</th>
<th>Tafel slope (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C (E-TEK)</td>
<td>57.3</td>
<td>0.864</td>
<td>3.7</td>
<td>0.115</td>
<td>0.401</td>
<td>0.9</td>
<td>0.315</td>
<td>1.105</td>
<td>2.475</td>
<td>151/60</td>
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<tr>
<td>Pt–Co/C–S</td>
<td>37.4</td>
<td>0.876</td>
<td>4</td>
<td>0.154</td>
<td>0.64</td>
<td>1.645</td>
<td>0.583</td>
<td>2.715</td>
<td>6.98</td>
<td>137/55</td>
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<tr>
<td>Pt-Co/C-T</td>
<td>38.0</td>
<td>0.871</td>
<td>3.8</td>
<td>0.109</td>
<td>0.479</td>
<td>1.242</td>
<td>0.452</td>
<td>1.995</td>
<td>5.175</td>
<td>123/56</td>
</tr>
<tr>
<td>Pt-Co/C-SB</td>
<td>18.4</td>
<td>0.880</td>
<td>3.5</td>
<td>0.151</td>
<td>0.742</td>
<td>2.725</td>
<td>1.445</td>
<td>6.4</td>
<td>23.55</td>
<td>95/64</td>
</tr>
<tr>
<td>Pt-Co/C-TB</td>
<td>14.6</td>
<td>0.870</td>
<td>3.7</td>
<td>0.102</td>
<td>0.464</td>
<td>1.285</td>
<td>1.105</td>
<td>5.035</td>
<td>13.95</td>
<td>118/64</td>
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<tr>
<td>Pt-Co/C-SH</td>
<td>23.1</td>
<td>0.842</td>
<td>3.9</td>
<td>0.054</td>
<td>0.287</td>
<td>1.03</td>
<td>0.37</td>
<td>1.64</td>
<td>4.975</td>
<td>119/62</td>
</tr>
<tr>
<td>Pt-Co/C-TH</td>
<td>24.5</td>
<td>0.863</td>
<td>3.8</td>
<td>0.093</td>
<td>0.422</td>
<td>1.315</td>
<td>0.6</td>
<td>2.715</td>
<td>8.49</td>
<td>115/62</td>
</tr>
</tbody>
</table>
Chapter 3

Preparation of highly stable Pt-Au@Ru/C catalyst by microemulsions method for methanol electrooxidation

3.1 Introduction

Direct-methanol fuel cells (DMFCs) have been studied for long time as promising energy sources for portable devices. A few breakthroughs have been made from the perspective of both membrane and catalyst research. However, the catalyst efficiency is still limited by CO poisoning which is one of the carbonyl species derived during methanol oxidation. A PtRu alloy is still the state-of-the-art anodic catalyst for electrooxidation in DMFCs due to its effective CO tolerance. Nevertheless, one big obstacle to the highly successful application of PtRu bimetallic catalyst is the dissolution of the more oxidizable metallic component (Ru). Most significantly, Ru dissolution may cause detrimental effects such as severe decay of anodic activity and increase of the ohmic resistance. Also, Ru may penetrate the membrane and migrate to the cathode of the DMFC, where ORR kinetics is badly impacted by the presence of Ru even in the micromolar concentration range. It has been pointed out that the dissolution of Ru or Pt is mainly caused by the formation of oxidized species derived from water activation. Besides, Ru oxidation and dissolution happen much more easily than Pt according to the potential-pH diagrams shown as following:

Potential-pH Diagram for Platinum

| PtO3 | +6  |
| PtO3 | +4  |
| PtO3 | +2  |
| PtO3 | 0   |
| PtO3 | 0.98|
| PtO3 | 1.045|
| PtO3 | 2.0 |
| PtO3 | 1.188|
| PtO3 | 1.188|

| Pt2+ |
| Pt2+ |
| Pt2+ |
| Pt2+ |
| Pt2+ |
| Pt2+ |
| Pt2+ |
| Pt2+ |
To enhance the stability of the metal catalyst, Adzic et al deposited Au clusters on a Pt catalyst through galvanic displacement by Au of a Cu monolayer on Pt. The gold cluster helps to shift the Pt oxidation potential more positive, providing high stability. In addition, nanoparticles of a PtRuNi ternary alloy and PtRuRhNi quaternary alloy exhibit enhanced electrocatalytic activity and good stability for methanol oxidation as compared to a Pt–Ru catalyst. Consequently it is interesting to explore whether the stability of PtRu can be improved by doping gold.

In this chapter, sequential reduction associated with the microemulsion method was used to synthesize catalysts with a PtAu core and a Ru shell (PtAu@Ru/C). In order to achieve the best reaction conditions, PtRu/C was synthesized by the microemulsion method first and heated thereafter at different temperatures. Catalysts were characterized using ICP-MS, HRTEM and XRD. Activity test for methanol oxidation in acidic media and long term durability test were performed on these catalysts as well. Cu UPD was exploited to determine the surface composition of catalysts.
3.2 Experiment

3.2.1 Chemicals

The surfactant, sodium dioctyl sulfosuccinate (AOT), was obtained from Fisher Scientific. All other chemicals (NaBH₄, H₂PtCl₆·H₂O, AuCl₃·4H₂O, RuCl₃, CuSO₄·H₂O) and reagents were ACS reagent grade and obtained from Sigma-Aldrich. The Ketjen carbon (BET surface area of 800 m²/g) was dried at 100°C in a high vacuum oven before using. The commercial catalyst (60wt% PtRu supported on Vulcan XC-72) was provided by E-TEK.

3.2.2 Synthesis of PtRu/C and PtAu@Ru/C catalysts

The theory and procedure of the microemulsion method to synthesize nano-alloys was illustrated in the previous chapter. As a typical example, a reverse micelle system of 0.2M cyclohexane solution of AOT (ω₀ = 8) containing the required amounts of 0.25M H₂PtCl₆ and 0.25M AuCl₃ was mixed with another reverse micelle system containing 1M NaBH₄. The reduction was completed within a few minutes. However, continuous stirring for another 4 hours was needed for nucleus formation and crystal growth. Afterwards, the microemulsion system containing RuCl₃ was introduced to form a Ru shell with PtAu core. The starting ratio of metals was kept at 8:8:1 for Pt:Ru: Au. The catalyst was successively washed with cyclohexane, acetone, ethanol, and water and dried in vacuum at 80°C for 24 hours. Then heat treatment was done at 220°C under flowing H₂/Ar for 6 hours.

3.2.3 Characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were taken on a Rigaku
X-ray Diffractometer with CuKα radiation (D-Max 2000). An incident beam of X-rays of wavelength 1.5418 Å (CuKα) filtered by a nickel filter was used. The particle size of the dispersed metal crystallites is estimated from the broadening of diffraction peaks using the Scherrer formula.

The morphology and particle size distribution of PtRu/C catalysts were examined by a JEOL 2010 Advanced High Performance transmission electron microscope (TEM). The facility is capable of an ultimate point-to-point resolution of 0.19 nm.

The composition of catalysts was analyzed by a VG Elemental Plasmaquad-2 (PQ2) ICP-MS. The results can be seen in Table 3.1.

### 3.2.4 Electrochemical measurements

Instruments for electrochemical measurements and methods for electrode preparation were the same as those described in detail in the previous chapter. Cu under potential deposition (UPD) was used to determine the surface atomic ratio of Pt and Ru, and chronoamperometric experiments associated with a “Potential Step Program” were used to obtain kinetics parameters. Both methods are described in more detail in this chapter.

The Cu UPD measurement was performed in accordance with methodology originally reported by Green. All copper UPD experiments were carried out in 0.5M H₂SO₄ and 1mM CuSO₄ solution. A glassy carbon electrode modified with 120ug/cm² of catalyst was cycled (from 0.02 V to 0.85V) in 0.5M H₂SO₄ at 10mV/s. Next, the electrode was put into a 0.5M H₂SO₄ +1mM CuSO₄ solution and polarized at 0.3 V for 120s. A linear voltammetric scan was then performed from the admission
potential to a point at which all of the UPD copper had been oxidized, at a scan rate of 10mV/s. (The charge obtained after background subtraction is designated as $Q_{Pt+Ru}$).

Last, the electrode was polarized at 1.05V at which point all the Ru on the surface is oxidized for 120s. The potential of the working electrode was then stepped to 0.3V and maintained at that voltage for another 120s. A linear voltammetric scan at a scan rate of 10mv/s was conducted next. (The charge measured after background subtraction is designated $Q_{Pt}$.) As a result, the Pt ratio on the surface of the catalyst can be calculated using formula (3.1):

$$\text{Pt\% (on the surface)} = \frac{Q_{Pt}}{Q_{Pt+Ru}} \times 100\% \quad (3.1)$$

The preceding method was tested with a standard PtRu/C (E-TEK, 60%) catalyst and confirmed to be valid as shown in Figure 3.1.

Kinetic parameters during methanol oxidation on various catalysts were obtained using the potential step approach. The potential step program used in the chronoamperometric experiments was developed by Wieckowski’s group. It provides rates of the elementary processes, avoiding the complications of CO poisoning. The methanol oxidation current was measured in a sequence of several sets of constant potential. The steps were applied starting from the predetermined potential, jumping to lower and then to higher potential biases for two cycles.

The upper potential was set at 1.1V (vs. RHE) where all organic residues on the catalyst surface are removed. The lower potential was set at the hydrogen UPD region. Instantaneous current ($t=0$) was recorded during the measurement. Tafel plots can be derived by using the instantaneous current versus potential.
3.2.5 X-ray absorption spectroscopy (XAS) measurements

XAS is an element-specific atomic core level spectroscopy. When the energy $E$ of an incident X-ray is sufficient to cause excitation, a core shell electron from an atom is ejected, producing a photoelectron. Based on the wavenumber $k$ of the photoelectron defined in equation (3.2), which is proportional to its kinetic energy, the excited photoelectron may be classified into three types.

$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} \quad (3.2)$$

When $k = 0$, the electron undergoes a transition to one of the unoccupied valence states, giving rise to edge peaks (see Figure 3.2). When $0 < k < k_c = 2/R$, (where $R$ is the distance between the absorbing atom and the closest neighboring atom), the photoelectron is strongly backscattered by the neighboring atoms, resulting in a multiple scattering process. The constructive and destructive interference between the outgoing photoelectron wave and backscattered wave are reflected in the observed maxima and minima after the edge (see Figure 3.2). When $k > k_c$, a single scattering process occurs due to being weakly backscattered by only one of the neighbor atoms.

Correspondingly, XAS can be divided into three regions: the pre-edge region, X-ray Absorption Near Edge Structure region (XANES) and Extended X-Ray Absorption Fine Structure region (EXAFS), with the latter two containing the most important information.

XANES is predominantly concerned with the complex multiple-scattering resonances of the photoelectron and covers the energy range from 50eV below the
The local absorber site symmetry and electronic structure have important effects on determining the absorption peaks of XANES spectra. In the XANES investigation of titanium silicalite, the tetrahedrally coordinated Ti shows a different XANES spectrum from those with square-pyramidal surroundings (fresnoite) and octahedral coordination.\textsuperscript{16}

EXAFS is the result of interference of backscattered electron waves with the forward-propagating waves, which appears up as modulation of the X-ray absorption coefficient starting approximately from 50 eV and continuing up to 1000 eV above the edge.

EXAFS signals are modeled and interpreted according to the following equation:

\[
\chi(k) = \sum_j N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2} \frac{1}{kR_j^2} \sin[2kR_j + \delta_j(k)] \tag{3.3}
\]

where the sum is over “shells” of atoms or “scattering paths” for the photo-electron (nearly the same concept); \( f(k) \) and \( \delta(k) \) pertain to the scattering amplitude and phase shift; and \( \lambda(k) \) represents the mean free path. Measurement of these three parameters enables the determination of: \( R \), the distance to the neighboring atom; \( N \), the coordination number of neighboring atoms, \( \sigma^2 \), the mean square variation of neighbor distance.

3.3 Results and Discussion

3.3.1 Heat treatment effect on properties of the PtRu/C catalyst
3.3.1.1 XRD measurement

Well defined XRD patterns of as-synthesized PtRu/C catalysts heated at different temperatures are shown in Figure 3.3. From Figure 3.3 and the lattice parameters in Table 3.2, good alloy formation of PtRu prepared by the microemulsion method can be discerned at room temperature with face-centered cubic structure. The XRD shows evidence of right shift of Pt (111) peak relative to the position of the Pt (111) peak of Pt/C. (cf. XRD spectra in the previous chapter.)\textsuperscript{17} The diffraction peaks shift to higher angles as temperature increases, reflecting the extent of lattice contraction arising from the substitution of smaller Ru for Pt. Lattice parameters and Pt-Pt bond distance also shows greater shrinking for samples heated at progressively higher temperatures. Furthermore, the peaks from Ru phase do not evolve until the temperature of heat treatment exceeds 620°C. Ru (hcp) peaks were marked according to JCPDS files (Copyright (C) JCPDS-ICDD 1997). Heat treatment is presumed to cause surface segregation and leads to a Ru core surrounded by a Pt shell after heating, which will be confirmed by Cu UPD measurement in section 3.3.1.3.

3.3.1.2 HRTEM measurement

The structure of the PtRu/C catalysts was examined by high-resolution transmission electron microscopy. The TEM picture of PtRu/C (room temperature, microemulsion) shown in Figure 3.4 is full of disordered PtRu nano-alloy. However, a typical fcc octahedral Pt nano-crystal fringe can be seen in the TEM picture of PtRu/C (620°C heat treatment, microemulsion). This does indicate Ru migration during heat treatment of the PtRu/C sample, resulting in the evolution of a well ordered Pt
nanocrystal.

### 3.3.1.3 Cu UPD measurements

Cu UPD measurements were done with PtRu/C (microemulsion, heated at different temperatures). The result can be seen in Figure 3.5. As the temperature of the heat treatment increases, Pt coverage increases. In other words, Ru on the surface becomes more and more depleted. It is well known that the driving force is the classical one of enrichment in the element with the lower heat of sublimation (usually also the lower melting point). Because the heats of sublimation are very different for Pt and Ru (the melting point of Pt is 550 °C lower than Ru), the endothermic heat of mixing actually drives the segregation of Pt even further towards the Ru-rich end of the bulk phase diagram. The result is in accord with that obtained from XRD measurement.

### 3.3.1.4 Activity and stability test with PtRu/C samples

Figure 3.6 compares cyclic voltammetry data of the Pt–Ru/C samples obtained by the microemulsion method heated at different temperature in fresh 0.5M H₂SO₄. No typical Pt features can be seen for any of the samples, indicating the formation of a good alloy between Pt and Ru. Figure 3.7 compares linear voltammetry data of the Pt–Ru/C samples in 0.5M H₂SO₄ containing 1M methanol. PtRu/C heated at 220 °C with 80% Pt coverage on the surface shows the most negative onset potential for methanol oxidation. Together with the kinetic performance shown in Figure 3.8 and Table 3.3, it can be concluded that the optimum temperature for heat treatment on PtRu/C catalyst prepared by the microemulsion method is at about 220 °C.
Figure 3.9 compares long term chronoamperometry (CA) data from PtRu/C samples heated at different temperatures. The surface composition from Cu UPD measurement before and after CA measurement is shown in Table 3.4. The sample heated at 220°C shows the highest current density as well as the best stability. Consequently, Ru@PtAu/C was synthesized according to the same reaction conditions used for preparation of PtRu/C by the microemulsion method heated at 220°C.

3.3.2 Properties of PtAu@Ru/C

Smaller peak shifts and concomitant lattice contractions are observed in the XRD pattern of Pt8Au@Ru8/C in comparison with that of PtRu/C from Figure 3.3 and Table 3.2. These indicate that Pt8Au@Ru8/C may have a structure with a PtAu alloy core surrounded by a Ru shell. The absence of peaks from metallic Ru means that Ru exists as very small clusters or very thin layers. In addition, no well defined diffraction peaks suggesting the presence of any metallic Au can be seen. This is probably because the Au loading was very low and any metal Au species present were highly dispersed or amorphous.

Cyclic voltammograms of PtRu/C (E-TEK) and Pt8Au@Ru8/C (prepared by microemulsion, 220°C) with the same metal loading are characterized by similar capacitative current, as shown in Figure 3.10. Peaks between 0.02V to 0.2V on the anodic scan are associated with hydrogen desorption from Pt facets. The increased current after 0.6V is attributed to oxide species formation on Pt or Ru.19, 20

Figure 3.11 depicts anodic scans of the cyclic voltammogram from
electrooxidation of methanol over PtRu/C (E-TEK) and Pt₈Au@Ru₈/C. The onset potential of oxidation on Pt₈Au@Ru₈/C was shifted negatively as much as 50mV compared to that on PtRu/C (E-TEK). During the process of electrooxidation of methanol, methanol decomposes on the catalyst surface at low potential and forms intermediates such as formic acid, formaldehyde and CO. The anodic current increases due to oxidation of these intermediates as the potential goes positive and then decreases after the peak potential because of loss of Pt active sites for the adsorption of intermediates. It has been reported that the peak potential for the oxidation of adsorbed intermediates from methanol depends on the type of catalyst used. In other words, the 30mV difference found for peak potential position on PtRu/C (E-TEK) and Pt₈Au@Ru₈ indicates that different reaction pathways occur on the two catalysts. Furthermore, the oxidation of intermediates on Pt₈Au@Ru₈ may need less activation energy as a consequence of the negative peak potential shift.

More clearly, Ru coated PtAu/C catalyst shows a significant enhancement of kinetic performance for electrooxidation of methanol in acid media as shown in Figure 3.12. It has been well known that the PtRu alloy catalyst has high activity towards methanol oxidation and excellent CO tolerance based on the “bi-functional mechanism”. Specifically, Ru on the surface of the catalyst can react with H₂O to form Ru-OH, which helps to remove CO on Pt surfaces by the following reaction:

\[
\text{Pt-CO + Ru-OH = Pt + Ru + CO}_2 + H^+ + e^- \quad (2) \quad \text{(ref.} \text{26)}
\]

H. Nitani et al derived a “Pt-Ru pair” theory from the “bi-functional mechanism”. In their study, the “pairing factor” was defined as,
\[
P_{\text{Ru}} = \frac{N_{\text{Ru-Pt}}}{(N_{\text{Ru-Pt}} + N_{\text{Ru-Ru}})} 
\]

which provides information on the inhomogeneity of Pt and Ru atoms. From EXAFs data and model simulations, they claimed that the Pt core-Ru shell structured nanoparticle should have a high “\(P_{\text{Ru}}\) value” and high catalytic activity. Our results confirmed the validity of the “Pt-Ru pair” theory.

Whether a tiny amount of gold can also contribute to the enhanced activity of PtAu@Ru catalyst is unclear and needs to be studied in the future.

The stabilizing effect of Au on Pt and Ru was determined in an accelerated stability test by running chronoamperometric measurement at a constant potential of 0.55V for 24 hours. Cu UPD measurements were conducted before and after the long term CA test to determine any loss of catalytic surface area. From Figure 3.13 and Table 3.4, there is a very insignificant change of surface area on Pt8Au@Ru8/C after the CA test with even higher current density for methanol oxidation post CA test. In contrast, PtRu/C lost more than 10% of its surface area due to dissolution of Ru and to a significantly lesser extent Pt. The same experiment carried out at 50°C on Pt8Au@Ru8/C showed no loss of surface area, providing additional evidence for the stabilizing effect of Au on both Pt and Ru at elevated temperature.

The gold in the catalyst of Pt8Au@Ru8/C is believed to be gold cluster rather than gold crystal since there are no gold crystal peaks in the XRD pattern as shown in Figure 3.4. In Zhang’s study \(^9\), the gold cluster is confirmed to help decrease oxidation of Pt nanoparticles by the XANES data. They drew an analogy between coupling of
the $d$-orbitals of small Pd clusters to the Au(111) substrate to the interactions of gold clusters with a Pt substrate.\textsuperscript{9,27} They concluded that the Pt electronic structure can be modified toward a lower Pt surface energy or lower-lying Pt $d$-band states by alloying with gold. In our case, gold is supposed to be alloyed with both the Pt enriched core and the Ru enriched shell to prevent oxidation at relatively low potentials.

3.3.3 In-situ XAS results

In order to decipher the stabilization effect of Au on the PtRu catalysts, state-of-the-art \textit{in-situ} X ray absorption spectroscopy data were collected as a function of potential at the Ru K-edge.

In the XANES region, small changes in the white line intensity corresponding to the $1s \rightarrow 5p$ transition at 22117 eV occur on changing the oxidation state of Ru. Thus, by subtracting out changes that occur in the bulk of the catalyst and using an appropriate reference spectrum, the potential-dependent oxide coverage on the surface may be determined.

Assuming that a full monolayer of oxide is formed at a potential of around 1.2 V, the data are analyzed to provide the percent oxide formation on the surface of the two catalysts. From the result shown in Figure 3.14, it is observed that the oxide growth on Au stabilized PtRu is lower than that of the corresponding E-TEK PtRu catalyst suggesting an increase in Ru oxidation potential in the presence of Au. It is noted that this value is a bulk averaged value which also corresponds to subsurface oxygen and is not entirely surface-specific, whereas the surface coverage values obtained from Cu UPD experiments are entirely attributable to the surface coverage only. This
preliminary insight into the catalyst behavior has fueled additional efforts to delve into the stabilization effects of Au on Ru.

3.4 Conclusions

PtRu alloy nanoparticles supported on carbon catalysts were synthesized in AOT/cyclohexane microemulsions and heated at different temperatures. Good alloys of PtRu can be formed even at room temperature. Surface segregation happens when the temperature of heat treatment increases. It has been found that PtRu/C catalyst heated at 220°C shows the highest activity and stability towards methanol oxidation in 0.5M H₂SO₄. PtAu core-Ru shell nanoparticles were synthesized under the same reaction condition. The sample shows a stark enhancement of kinetics performance in comparison with commercial PtRu/C catalyst. Also, PtAu@Ru/C catalyst was found to be ultra stable over the long term Chronoamperometric measurement is promising for resolving the problem of Ru dissolution in the real-world application of PtRu/C catalyst in direct methanol fuel cell.
3.5 Chapter 3 References:


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12. J. Liu; J. Cao; Q. Huang; X. Li; Z. Zou; H. Yang, Methanol oxidation on carbon-supported Pt–Ru–Ni ternary nanoparticle electrocatalysts. *J Power Sources* **2008**, *175*, 159–165.


24. M. Watanabe; S. Motoo, Electrocatalysis by ad-atoms: Part II. Enhancement of
the oxidation of methanol on platinum by ruthenium ad-atoms. *J. Electroanal. chem.*


3.6 Chapter 3 Figures:

Figure 3.1 Background and UPD stripping voltammetry for copper deposited onto PtRu/C catalyst (E-TEK, 60%) bound to a glassy carbon electrode with Nafion. The blank was done in fresh 0.5M H_2SO_4. (a) stripping voltammetry at fully reduced surface to get Q_{PtRu}, (b) following polarization at 1.05 V to leave fully oxidized surface to get Q_{Pt}. (Pt% = 69.4%)
Figure 3.2 Three types of excited photoelectrons
Figure 3.3 XRD patterns for PtRu/C (E-TEK 60%), PtRu/C (60%, prepared by the microemulsion method, at room T, 220°C, 420°C and 620°C), Pt₈Au@Ru₈/C (60%, prepared by the microemulsion method, at 220°C)
Figure 3.4(a) HRTEM image of PtRu nanoparticles (by microemulsions method, room temperature). FFT image can be seen on the right.

Figure 3.4(b) HRTEM image of PtRu nanoparticles (by microemulsions method, heated at 620°C). FFT image can be seen on the left.
Figure 3.5 Surface coverage of Pt on PtRu/C catalyst (60%, prepared by the microemulsion method) heated at different temperatures.
Figure 3.6 Cyclic voltammograms for glassy carbon electrodes modified by PtRu/C (60%) prepared by the micromulsion method at different temperatures in 0.5M H₂SO₄, Pt loading: 15ug/cm², Sweep rate 50 mV s⁻¹ (room temperature).
Figure 3.7 Cyclic voltammograms for glassy carbon electrodes modified by PtRu/C (60%) prepared by the micremulsion method at different temperatures, in 0.5M H$_2$SO$_4$ +1M methanol, Pt loading: 15ug/cm$^2$, Sweep rate 10 mVs$^{-1}$ (room temperature).
Figure 3.8 Semilogarithmic $\log(i_{t=0})$ vs. electrode potential plots for methanol oxidation on PtRu/C (60%) prepared by the micremulsion method, at different temperature, in 0.5M H$_2$SO$_4$. Methanol concentration was 1M.
Figure 3.9 long term Chronoamperometric study with PtRu/C (60%) prepared by the micremulsion method, at different temperature in 0.5M H₂SO₄ +1M methanol.
Figure 3.10 Cyclic voltammograms for glassy carbon electrodes modified by PtRu/C (E-TEK 60%) and Pt₈Au@Ru₈/C (60%, prepared by the microemulsion method, heated at 220°C under H₂/Ar), in 0.5M H₂SO₄, Pt loading: 15ug/cm², Sweep rate 10 mVs⁻¹. (room temperature)
Figure 3.11 Cyclic voltammograms for glassy carbon electrodes modified by PtRu/C (E-TEK 60%) and Pt\textsubscript{8}Au\textsubscript{8}Ru\textsubscript{8}/C(60%, repared by the microemulsion method, heated at 220\textdegree C under H\textsubscript{2}/Ar), in 0.5M H\textsubscript{2}SO\textsubscript{4} + 1M methanol, Pt loading: 15\mu g/cm\textsuperscript{2}, Sweep rate 10 mVs\textsuperscript{-1} (room temperature).
Figure 3.12 Semilogarithmic $\log(i_{\theta=0})$ vs. electrode potential plots for methanol oxidation on PtRu/C (E-TEK 60%) and PtRu/C and Pt$_8$Au@Ru$_8$/C (60%, prepared by the microemulsion method, heated at 220°C under H$_2$/Ar), in 0.5M H$_2$SO$_4$. Methanol concentration was 1M.
Figure 3.13 24 hours long term CA measurement for methanol oxidation on PtRu/C (E-TEK, 60%) and PtRu/C (E-TEK 60%) and Pt@Au@Ru/C (60%, prepared by the microemulsion method, at 220°C under H2/Ar), in 0.5M H2SO4. Methanol concentration was 1M.
Figure 3.14 Comparison of oxide coverage on both PtRu/C (E-TEK, 60%) and Pt₈Au@Ru₈/C (prepared by the microemulsion method, 60%, 220°C) as a function of electrode potential as determined by the Δµ-XANES method.
### Table 3.1 Composition of PtRu/C and PtAu@Ru/C catalysts prepared using microemulsions method

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nominal composition</th>
<th>Composition from ICP analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt Wt%</td>
<td>Pt:M (atomic)</td>
</tr>
<tr>
<td>PtRu/C (E-TEK 60%)</td>
<td>39.5</td>
<td>1:1</td>
</tr>
<tr>
<td>PtRu/C (60%, microemulsions)</td>
<td>39.5</td>
<td>1:1</td>
</tr>
<tr>
<td>PtAu @Ru/C (60%, microemulsions)</td>
<td>36.5</td>
<td>8 : 8 : 1</td>
</tr>
</tbody>
</table>

( Pt: Ru : Au )
Table 3.2 XRD data of PtRu/C catalysts by microemulsions method

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lattice types</th>
<th>Pt (111) @2θ</th>
<th>Crystallite Size/ nm</th>
<th>Lattice parameter /Å</th>
<th>Pt-Pt bond distance / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtRu/C (E-TEK 60%)</td>
<td>fcc</td>
<td>40.27</td>
<td>4.0</td>
<td>3.88</td>
<td>2.74</td>
</tr>
<tr>
<td>PtRu/C (microemulsions, room T)</td>
<td>fcc</td>
<td>40.33</td>
<td>3.5</td>
<td>3.87</td>
<td>2.74</td>
</tr>
<tr>
<td>PtRu/C (microemulsions, 220 ºC)</td>
<td>fcc</td>
<td>40.34</td>
<td>3.8</td>
<td>3.87</td>
<td>2.74</td>
</tr>
<tr>
<td>PtRu/C (microemulsions, 420 ºC)</td>
<td>fcc</td>
<td>40.39</td>
<td>5.6</td>
<td>3.86</td>
<td>2.73</td>
</tr>
<tr>
<td>PtRu/C (microemulsions, 620 ºC)</td>
<td>fcc</td>
<td>40.49</td>
<td>11.6</td>
<td>3.85</td>
<td>2.72</td>
</tr>
<tr>
<td>Ru₈@Pt₈Au/C (microemulsions, 220 ºC)</td>
<td>fcc</td>
<td>39.85</td>
<td>9.0</td>
<td>3.92</td>
<td>2.77</td>
</tr>
</tbody>
</table>

The average crystallite size for PtRu/C catalysts was calculated using the Debye-Scherrer equation \( Z = \frac{\lambda}{B \cos \theta} \).
Table 3.3 Kinetics from Tafel plots

<table>
<thead>
<tr>
<th>Tafel slope (mv/dec)</th>
<th>$i_{E=0.55V}$ mA cm$^{-2}$</th>
<th>$i_0$ (mA cm$^{-2}$) extrapolate to 0.02V</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtRu/C (60%, microemulsions, room T)</td>
<td>100</td>
<td>18.0</td>
</tr>
<tr>
<td>PtRu/C (60%, microemulsions, 220 °C)</td>
<td>125</td>
<td>25.3</td>
</tr>
<tr>
<td>PtRu/C (60%, microemulsions, 420 °C)</td>
<td>107</td>
<td>15.5</td>
</tr>
<tr>
<td>PtRu/C (60%, microemulsions, 620 °C)</td>
<td>109</td>
<td>13.2</td>
</tr>
</tbody>
</table>

- the calculated equilibrium potential of methanol oxidation is $0.02V^{29}$
Table 3.4 surface information of PtRu/C samples before and after long term chronoamperometry test

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Pt coverage (%)</th>
<th>Surface area (m²/g metal)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before test</td>
<td>after test</td>
</tr>
<tr>
<td>PtRu/C (60%, microemulsions, room T)</td>
<td>60.3</td>
<td>80.8</td>
</tr>
<tr>
<td>PtRu/C (60%, microemulsions, 220 °C)</td>
<td>80.2</td>
<td>76.9</td>
</tr>
<tr>
<td>PtRu/C (60%, microemulsions, 420 °C)</td>
<td>89.0</td>
<td>90.2</td>
</tr>
<tr>
<td>PtRu/C (60%, microemulsions, 620 °C)</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 3.5 Surface information of PtRu/C (E-TEK, 60%) and Ru8@Pt8Au/C(60%, by microemulsions method, heated at 220 °C under H2/Ar), before and after long term chronoamperometry test

<table>
<thead>
<tr>
<th></th>
<th>Pt coverage (%)</th>
<th>Surface area remained (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before test</td>
<td>after test</td>
</tr>
<tr>
<td>PtRu/C (60%, E-TEK), room T, 24 hours</td>
<td>69.4</td>
<td>72.3</td>
</tr>
<tr>
<td>PtRu/C (60%, E-TEK), at 50 °C, 4 hours</td>
<td>69.4</td>
<td>76.7</td>
</tr>
<tr>
<td>Ru@PtAu/C (60% 220 °C), room T, 24 hours</td>
<td>74.4</td>
<td>76.9</td>
</tr>
<tr>
<td>Ru@PtAu/C (60% 220 °C), at 50 °C, 4 hours</td>
<td>74.4</td>
<td>76.1</td>
</tr>
</tbody>
</table>
**Chapter 4**

**Development of novel electrocatalysts and techniques for direct oxidation of ethanol in high pH environments**

### 4.1 Introduction

Attention has been focused on Proton Exchange Membrane Fuel Cells (PEMFCs) for a long time. However, there still remain some problems for applying PEMFCs in practice, such as safe hydrogen storage (hydrogen anode feed), sluggish oxygen reduction kinetics in acidic environments, poor electro-oxidation kinetics of methanol, methanol crossover (methanol anode feed), carbon monoxide poisoning, and intrinsically high component expenses. Recently, Anion Exchange Membrane Fuel Cells (AEMFC) have presented the possibility for a revitalization of alkaline fuel cell technology. AEMFCs replace conventional liquid electrolyte with an alkaline anion exchange membrane to prevent precipitation of carbonate (CO$_3^{2-}$/HCO$_3^-$).\(^1\)\(^-\)\(^2\) It has the following intrinsic potential advantages over its acidic counterpart: more facile electrocatalysis; the possibility of using inexpensive non-noble electrocatalysts; wider choices of fuel feed; better water management; and avoiding expensive fluorinated polymers.

As fuel for AEMFCs, methanol has been considered a strong contender as the fuel for portable electronic devices. However, methanol is relatively toxic and can be a serious pollutant. As a potential alternative, ethanol is environmentally friendly and offers higher energy density than methanol.\(^3\) In addition, ethanol can be produced through a fermentation process which makes it less dependent on fossil fuels.

Much greater choice of catalyst is available for electro-oxidation of ethanol in
alkaline medium. Nevertheless, Pt based catalysts are still extensively investigated anode materials. Some oxide promoted Pt catalysts, such as Pt-MgO/C\textsuperscript{3}, Pt-CeO\textsubscript{2}/C\textsuperscript{4} and Pt-ZrO\textsubscript{2}/C\textsuperscript{5}, have been reported to show better performance in comparison to Pt/C. It is presumed that these oxides act as anchors for oxygen-containing species at lower potential, thus enabling the transformation of CO-like poisoning species formed on Pt to CO\textsubscript{2}.\textsuperscript{6} In addition, Pd and Ru are generally used as electrocatalysts for electro-oxidation of ethanol in alkaline environment. One group of Pt-free catalysts consists of the Ru-Ni catalysts. Tarasevich et al\textsuperscript{7, 8} synthesized dispersed metallic ruthenium decorated by nickel oxides and optimized composition of RuNi in the ratio of 68:32. This material shows the highest exchange current density for electro-oxidation of ethanol in comparison with other low-molecular-weight alcohols. Pd-based catalysts were investigated as a replacement for Pt-based catalysts.\textsuperscript{6, 9-12} These materials have shown marked superiority to Pt in terms of activity and poison tolerance. A wealth of prior literature has been devoted towards modifying Pd to improve the performance for electrooxidation of ethanol. Wang et al\textsuperscript{11} and Xu et al\textsuperscript{13} prepared Pd nanowire arrays (NWAs) by a template-electrodeposition method and claimed that the Pd NWA showed almost double the peak current in CVs and slower decay in chronoamperometric curves than commercial PtRu/C. Some studies have also been devoted to studying the influence of the support on the activity of Pd for ethanol oxidation.\textsuperscript{10, 14-16} The anodic transfer coefficient, the diffusion coefficient and overall rate equation were measured by Liu in the study of ethanol electrooxidation kinetics on Ti supported Pd.\textsuperscript{16} Intriguingly, carbon microspheres (CMS) were also
used as a support to make Pd electrocatalyst. Better performance was found on these CMS supported Pd catalyst than on carbon black due to a synergistic interaction between Pd and CMS. Xu, Hu and Shen investigated the activities of oxide-promoted Pd/C electrocatalysts for ethanol electrooxidation in alkaline media by cyclic voltammograms and chronopotentiometry. Such electrocatalysts showed orders of magnitude enhancement in activity and good steady-state behavior for ethanol oxidation. The authors proposed an analogy between the function of oxide in Pd/C catalysts with the effect of Ru in PtRu catalysts and SnO in PtSnO catalysts. It is possible that these oxides play the role of donor of the oxygen-containing species at lower potential to transform CO-like poisoning species on the surface of Pd to CO$_2$. The other postulation is that the oxides have sufficient electron affinity to help break C-C bonds, as SnO does in PtSnO and PtSnInO catalysts.

However, it is well recognized that the majority of the oxidation products of electro-oxidation of ethanol are still species containing C-C bond, even though some binary or ternary Pt-based catalysts show improved performance. It is crucial and necessary to develop novel catalysts or techniques to enable higher specific activity of dehydrogenation, C-O and C-C bond cleavage during the ethanol oxidation process. Slight improvement of C-C bond dissociation has been found on some novel materials such as PtRh and Pt/SnO$_x$/C. Another approach to achieve this goal is to deliberately introduce species to the electrochemical reaction environment which may not only initiate C-C bond cleavage to enhance the activity of the catalysts, but also
weaken CO or other organic species poisoning.

In this chapter, some Pd based Au and Sn alloy catalysts were synthesized in house using components that may possess novel functions. The catalysts were characterized with X-ray diffraction (XRD) and TEM to establish a thorough structure property relationship. An array of electrochemical investigations (cyclic voltammetry (CV), Tafel plot, chronoamperometry and electrochemical impedance spectroscopy (EIS) were performed to understand the mechanism of ethanol oxidation on as-synthesized catalysts. Inspired by the work of Pierre et al\textsuperscript{28} who found that breaking of the C-C bond of glyoxal and ethylene glycol on a platinum anode is favored with addition of metal salts (Ag, Sn, Pb, Tl). A new concept was developed using the Pb(IV)/Pb(II) redox couple for C-C bond cleavage, which produced a novel method to improve efficiency of electrooxidation of ethanol in high pH environments with addition of the Pb(IV) ion. This heterogeneous redox process coupled to a homogeneous reaction is interesting fundamentally and has promising applications.

4.2 Experiment

4.2.1 Chemicals

Unless otherwise stated, all chemicals were ACS reagent grade and used as received. Palladium chloride (PdCl\textsubscript{2}), gold chloride (AuCl\textsubscript{3}), tin acetate (SnAc\textsubscript{2}), citrate acid, lead acetate (PbAc\textsubscript{4}) and sodium borohydride (NaBH\textsubscript{4}) were obtained from Sigma-Aldrich. Dihydrogen hexachloroplatinate(IV) hydrate(H\textsubscript{2}PtCl\textsubscript{6}·xH\textsubscript{2}O) was from Sigma-Aldrich. The Vulcan carbon was dried at 100\textdegree°C in a high vacuum
oven prior to use. Commercially available catalysts of 30wt% platinum and 40wt% platinum ruthenium supported on Vulcan XC72 were obtained from E-TEK.

4.2.2 Synthesis of catalysts

To make PdAu/C nanoparticles, 200 mg of carbon was dispersed by sonication for 30 min in a 0.2 mol/L citrate acid solution. A calculated amount of a mixture of 0.1 mol/L PdCl₂ and AuCl₃ was added into the above solution under magnetic stirring. The atomic ratio of Pd to Au was kept constant at 4:1 and the combined metal loading on carbon was 30%. In the case of PdSn/C catalysts, the atomic ratio of Pt to Sn was kept constant at 3:1 and the metal loading was 30%. After the temperature of the slurry was increased to 60°C, NaBH₄ was added slowly and the solution was stirred for another 4 hours. The resulting precipitate was washed with a copious amount of water and dried at 80°C overnight. The compositions of the catalysts were then analyzed by VG Elemental Plasmaquad-2 (PQ2) ICP-MS. The results are summarized in Table 4.1, where the resulting particles exhibited a composition of Pd₄Au/C and Pd₂.5Sn/C respectively, close to the initial feed ratio in the nanoparticle preparation.

4.2.3 Characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were taken on a Rigaku X-ray Diffractometer with CuKα radiation. An incident beam of X-rays of wavelength 1.5418 Å (CuKα) filtered by a nickel filter was used. The particle size of the dispersed metal crystallites is estimated from the broadening of diffraction peaks using the Scherrer formula.

The morphology and particle size distribution of Pd based alloy catalysts were
examined by a JEOL 2010 Advanced High Performance transmission electron microscope (TEM). The facility is capable of an ultimate point-to-point resolution of 0.19 nm.

4.2.4 Electrochemical measurements

The electrochemical measurements were conducted in a standard three-compartment electrochemical cell at room temperature using a rotating disk electrode (RDE) setup from Pine Instruments connected to an Autolab (Ecochemie Inc. Model-PGSTAT 30). A glassy carbon disk with 5mm diameter was used as the substrate for deposition of catalyst films. Before deposition of catalyst films, the RDE was first polished with 0.05 micron alumina slurry (Buehler, Lake Bluff, IL) and then cleaned with distilled water under sonication. All electrochemical experiments were carried out at room temperature (25ºC).

The catalyst inks were prepared by dispersion of certain amounts of catalyst powders into 20 ml of isopropanol and then sonicated for at least 30 minutes to reach a uniform suspension. The catalyst film was prepared by dispersing 8 µL of the catalyst ink on the glassy carbon (GC) substrate and dried at room temperature to reach a total catalyst loading of 75 µg cm⁻². CVs and CAs were taken in 1.0 mol L⁻¹ KOH vs. a Hg/HgO (KOH 1.0 mol L⁻¹) reference electrode.

Also, instantaneous current (t=0) during ethanol oxidation on Pd₄Au/C and Pd₂₅Sn/C was measured by potential step techniques or short term chronoamperometry to evaluate the kinetic parameters.²⁹,³⁰ Specifically, the electrode potential was oscillated between lower and upper potential biases for two cycles.
The lower potential was set at 0 V, corresponding to the hydrogen UPD region. The upper potential was set at 1.05 V to remove residues of adsorbed species on the electrode. Then the potential was programmed to a desired value for current transient measurements. Electrochemical impedance spectroscopy (EIS) measurements were carried out using an EG&G PARC Potentiostat/Galvanostat model 283 and Frequency Response Detector (model 1025). The impedance spectra were recorded between 100 kHz and 10 mHz with a 10 mV (rms value) ac signal amplitude.

All experiments on the Pb(IV) effect on C-C bond breakage during electrooxidation of ethanol were performed on a glassy carbon working electrode modified with 15ug/cm² Pt/C (E-TEK, 30%) in 0.25M KOH.

4.3 Results and Discussion

4.3.1 Au and Sn alloy Pd/C electrocatalysts for electrooxidation in high pH environments

The structures of the Pd₄Au/C and Pd₂.₅Sn/C nanoparticle catalysts were first characterized by XRD and TEM studies. From the XRD patterns depicted in Figure 4.1, it can be seen that the diffraction peaks for Pd(111), (200) and (220) are very well-defined in both samples, along with C(002) of the supporting matrix. For the Pd₄Au/C sample (dashed curve), a series of diffraction peaks can be indexed to gold crystalline planes such as Au(111), (200), and (220); and the XRD pattern of Pd₂.₅Sn/C (solid curve) is very similar to that of Pd₃Sn/C in reference to JCPDS files (41-1409, JCPDS–ICDD ©1997), with rather intense peaks for Sn(311) and (221).
These results suggest that the catalysts obtained were highly crystalline. In addition, based on the crystal lattice unit cells (Table 4.2), the Pd₄Au/C sample may be ascribed to the cubic crystal system and Fm3m space group with a lattice constant of $a = b = c = 3.91$ Å. In contrast, Pd₂.₅Sn/C appears to be consistent with an orthorhombic crystal system and Pnma space group, with lattice constants of $a = 5.65$ Å, $b = 4.31$ Å, and $c = 8.12$ Å.

Furthermore, based on the width of the Pd(111) peak, the size of the nanocrystallites was estimated using the Debye-Scherrer equation\textsuperscript{31}, which gave 6.5 nm and 7.4 nm, respectively, for the Pd₄Au/C and Pd₂.₅Sn/C samples. These values are in good agreement with results from the TEM measurements. Figure 4.2 shows the representative TEM micrographs of the Pd₄Au/C and Pd₂.₅Sn/C samples. It can be seen that in both samples, the nanoparticles were very well dispersed on the carbon supports. The average particle size of Pd₄Au/C and Pd₂.₅Sn/C was found to be 6.8 nm and 8.4 nm, respectively. These samples were then subject to electrochemical assessment of their electrocatalytic activity in ethanol oxidation.

Figure 4.3 (A) shows the cyclic voltammograms of the Pd₄Au/C and Pd₂.₅Sn/C particles as well as commercial Pt/C catalysts in 0.25 M KOH, all at a loading of 15 g/cm² of noble metal. The geometric area of the electrode (0.196 cm²) was used in calculating the current density. It can be seen that all catalysts exhibited similar responses in the double-layer charging region from 0.5 V to 0.7 V. However, hydrogen evolution occurred at somewhat more positive potentials on the PdAu/C and PdSn/C electrodes than on the Pt/C electrode, suggesting that hydrogen adsorption
might be better facilitated at the Pd based catalyst surface. The corresponding electrochemical active surface area (EAS) of the catalysts was then evaluated by the Coulombic charge associated with hydrogen desorption ($Q_{H}$),\textsuperscript{11, 13} which was reflected by the broad peaks between +0.2 and +0.5 V in the anodic scan.\textsuperscript{18} $Q_{H}$ for Pt/C (0.67 C) was somewhat higher than those for Pd\textsubscript{4}Au/C (0.244 C) and Pd\textsubscript{2.5}Sn/C (0.242 C).

The voltammetric responses of the catalysts in ethanol oxidation are shown in Figure 4.3 (B). It can be seen that the anodic onset potential (Pt @ 0.47 V, Pt\textsubscript{4}Au/C @ 0.5 V, Pd\textsubscript{2.5}Sn/C @ 0.53 V) and peak potential (Pt @ 0.8 V, Pd\textsubscript{4}Au/C @ 0.9 V, Pd\textsubscript{2.5}Sn/C @ 0.87 V) appear to be more negative on Pt/C than on the Pd\textsubscript{4}Au/C and Pd\textsubscript{2.5}Sn/C catalysts. However, the current density of the Pd based catalysts was substantially greater (12 mA/cm\textsuperscript{2} for Pt/C, 20 mA/cm\textsuperscript{2} for Pd\textsubscript{4}Au/C and Pd\textsubscript{2.5}Sn/C). In the reaction mechanism of Pt-catalyzed ethanol oxidation that was proposed by Li et al.,\textsuperscript{32} the adsorption intermediates were CH\textsubscript{3}CHOH\textsubscript{ads} and CH\textsubscript{3}COOH\textsubscript{ads} in the low and high potential regions, respectively. Yet, our previous studies have shown that acetic acid is fairly resistant to electrooxidation in basic media.\textsuperscript{33} Therefore, the anodic currents observed in Figure 4.3 (B) are most likely due to the oxidation of acetaldehyde-based intermediates as the electrode potential sweeps anodically, and reach a peak that corresponds to the oxidation of freshly chemisorbed species of ethanol.\textsuperscript{14} At more positive electrode potentials, the oxidation current drops because of Pd oxidation and hence loss of catalytically active sites. In the return scan, Pd active sites are recovered by electroreduction of the Pd oxide species and the adsorbed intermediates may be converted to acetaldehyde from acetic acid. Consequently, the
positive current peak in the cathodic scan is primarily associated with the oxidative removal of carbonaceous species that were not completely oxidized in the forward scan, in addition to newly adsorbed species from bulk ethanol.

The results observed in Figure 4.3 (B) are in line with kinetic studies that are shown in the Tafel plots of Figure 4.4. Tafel plots for electrooxidation of methanol or ethanol have been converted directly from cyclic voltammograms in several prior literature reports.\textsuperscript{12, 16, 34, 35} However, the voltammetric current in ethanol oxidation may not fully reflect the kinetic current on certain catalysts, as it is inevitably affected by surface poisoning ethanolic species, including the original ethanol fuel,, surface poisoning species (e.g., linearly adsorbed CO\textsubscript{L} and CO\textsubscript{2}, CH\textsubscript{x,ad} species),\textsuperscript{24, 36-38} and final products (CO\textsubscript{2}, acetaldehyde and acetic acid).\textsuperscript{24} Therefore, fast chronoamperometric techniques have been employed to assess kinetic current density of the elementary processes involved in ethanol decomposition and obtain instantaneous ethanol oxidation current within the context of platinum or palladium surface structure and composition of supporting electrolyte with respect to the anions.\textsuperscript{30} Figure 4.4 shows the Tafel plots (kinetics current as a function of potential) of the ethanol oxidation on the three catalysts, where an appreciable difference of the Tafel slope can be seen, suggesting that the mechanism of ethanol oxidation varies on the Pt and Pd based catalysts. Furthermore, the instantaneous current appears to decrease in the order of Pt/C $\gg$ PdAu/C $>$ PdSn/C, in particular at low electrode potentials, whereas at potentials more positive than $+0.8 \, V$, the changing trend reverses, Pt/C $<$ PdAu/C $<$ PdSn/C. The observed discrepancy of the oxidation current
may be explained by higher activity for Pd to form metal-oxide surface species. Consequently, more Pt active sites are exposed to ethanol at low potentials due to less coverage of oxide containing species. In addition, the activation energy change which is inherently determined by the surface-state energy levels occupied by ethanol relative to the Fermi level of the solid (Pt, Pd), is an important determinant for interpreting the better kinetic performance of the Pt catalyst. Previous studies have suggested that formation of metal oxides on the Pd surface alters the Fermi level, leading to a larger overpotential for ethanol adsorption, higher activation energy, and consequent slower kinetics of ethanol oxidation. However, the mechanism of ethanol electrooxidation is still controversial and debatable. A general consensus is that the first step is dissociative adsorption of ethanol on catalyst surface.

\[
P_t + CH_3-CH_2OH \rightarrow Pt\text{-adsorbate} + e^- \quad (4.1)
\]

Of interest is the observation that peak current density on both Pd4Au/C and Pd2.5Sn/C is higher than that on Pt/C as depicted in the cyclic voltammetric measurements in Figure 4.3 (B). This suggests that the Pd-based catalysts are less likely to be poisoned and have better stability, which was confirmed by the chronoamperometric test in Figure 4.5. From the long-term current-time curves, the current decays more rapidly on Pt/C than on Pd4Au/C or Pd2.5Sn/C although the initial current on Pt/C is the highest. From the point of view of real application in the direct ethanol fuel cell, as-synthesized Pd4Au/C and Pd2.5Sn/C, with their better efficiencies, are more suitable than commercial Pt/C catalyst.

Electrochemical impedance spectroscopy (EIS) has been proved to be a sensitive
electrochemical technique in the studies of the electro-oxidation kinetics of small organic molecules in fuel cells. Here, the kinetics of ethanol oxidation on the three kinds of electrodes was investigated with EIS. Figure 4.6 A, B and C display the Nyquist complex-plane impedance spectra of the ethanol oxidation on Pt/C, Pd₄Au/C and Pd₂.₅Sn/C electrodes respectively in 0.25 M KOH + 1 M ethanol and with electrode potentials varied from 0.35 to 0.90 V (shown in the figure legends). For ethanol oxidation on the Pt/C electrode (Figure 4.6A), it can be seen that at potentials below +0.55 V, the impedance arcs appear in the second quadrant instead of the conventional first one. Negative impedance behaviors were also observed during electro-oxidation of methanol and formic acid on Pt and other Pt-based alloy electrodes in the previous studies, and were usually ascribed to the adsorption of reaction intermediates on the catalyst surface. It is well-known that for fuel oxidation on Pt materials, there is heavy CO adsorption (poison) on the Pt surface. So here, the negative impedance can be attributed to the oxidative removal of the CO intermediate because of the formation of chemisorbed hydroxyl species in this potential range. With a further increase of the electrode potential above 0.60 V, the impedance changes from negative to normal positive, and the diameter of the arcs decreases, indicating faster electron-transfer kinetics at higher potentials. This result indicates that CO adsorbed on Pt surface was completely removed and the surface reaction sites occupied by CO were recovered, leading to the diminishment of charge-transfer resistance.

For ethanol oxidation on Pd₄Au/C and Pd₂.₅Sn/C electrodes, one can see that the
impedance profiles (Figure 4.6 B, C) are different from that on Pt/C. All the impedance spectra obtained on both PdAu/GC and PdSn/GC electrodes are located within the first quadrant and the diameter of the arcs decreases with increasing potential. As we know, Pd and Pd alloys have a much better tolerance to CO poisoning. So the absence of negative impedance for PdAu/C and PdSn/C electrodes strongly suggest that the PdAu and PdSn have excellent CO-tolerance properties. It also should be noted that the impedance of Pt/C shows arcs with the diameter smaller than those on Pd4Au/C and Pd2.5Sn/C electrodes, showing the faster reaction rate of ethanol oxidation on Pt particles than that on the present two kinds of Pd alloy particles. The impedance results agree well with the voltammetric results presented earlier.

Figure 4.7 depicts the corresponding Bode plots of ethanol oxidation on the Pt/C, Pd4Au/C and Pd2.5Sn/C electrodes. It can be seen that there is a maximum phase angle at a characteristic frequency \( f \) for all the electrodes. Clearly, the characteristic frequency increases with increasing potential, suggesting the corresponding electrochemical reaction rate increases with potential, as \( f \) usually represents the time constant of the electrochemical reaction.\(^{54, 58}\) It should be noted that on Pt/C, at potentials lower than +0.60 V, there is an abrupt jump between the positive and negative phase angles, corresponding to the negative faradic impedance in the Nyquist plots shown in Figure 4.6 A. This phenomenon can be ascribed to the oxidation of adsorbed CO and the resulting inductive component of the Pt/C electrode. Again, for Pd4Au/C and Pd2.5Sn/C electrodes, no such behavior was observed due to the greatly
based CO poisoning.

Based on the voltammetric and impedance results, the equivalent circuit shown in Figure 4.8 was used to fit the EIS data. Figure 4.8 (A) depicts the equivalent circuit for the electrodes that exhibit normal impedance behaviors, where $R_s$ represents the solution resistance, and CPE (constant-phase element) and $R_{CT}$ are the double layer capacitance and charge transfer resistance, respectively. For the negative impedance observed on Pt/C electrode, the equivalent circuit is shown in Figure 4.8 (B), where $C_0$ and $R_0$ represent the capacitance and resistance of the electro-oxidation of adsorbed CO intermediates. The representative fits (solid lines) for the three electrodes are shown in each of the Nyquist plots in Figure 4.6. From the fitting, the variation of the charge transfer resistance ($R_{CT}$) with the potentials on the three electrodes is shown in Figure 4.9. Firstly, negative $R_{CT}$ was obtained on Pt/C electrode at potentials lower than 0.55 V due to the electro-oxidation of surface-adsorbed CO species. Secondly, $R_{CT}$ on all the electrodes decreases with increasing electrode potential, indicating enhanced ethanol oxidation at high potentials. Thirdly, the $R_{CT}$ for ethanol oxidation on the Pd$_{2.5}$Sn/C electrode is much larger than that on the Pt/C and Pd$_4$Au/C electrodes, suggesting that the Pd$_{2.5}$Sn/C electrode has poorer kinetics for ethanol oxidation. Overall, from the impedance results, it can be seen that Pt/C exhibits heavy CO poisoning and Pd$_{2.5}$Sn/C shows low electrocatalytic activity for ethanol oxidation. The Pd$_4$Au/C electrode displays the best catalytic activity for ethanol oxidation among the three kinds of particles since it has an excellent CO-tolerance and high reaction kinetics.
The promoting mechanism whereby Au and Sn render the Pd/C catalyst more tolerant to poisoning than Pt/C during electro-oxidation is unclear at this stage. A reasonable hypothesis is that Au or Sn still behave as bi-functional elements, by analogy with what Ru does to Pt/C during methanol oxidation. The gold itself is a good catalyst for CO oxidation and methanol oxidation. In the case of Sn, an oxide layer may be formed in the high pH environment. Thus it may be necessary to achieve a good compromise between the effect of tin oxide and available Pt catalytic sites by optimizing the Sn content.32

4.3.2 The enhancement effect of the Pb(IV)/Pb(II) couple: a heterogeneous redox process coupled to a homogeneous reaction in electro-oxidation of ethanol

Result shown in Figure 4.10 and Figure 4.11 have tremendous implications on enhanced activity of catalysts for direct alcohol oxidation. From Figure 4.10, the onset potential for ethanol oxidation shifts negatively by 200mV in the presence of Pb(IV), which means the ethanol oxidation kinetics has been improved due to some promotional effect of Pb(IV). On the cathodic scans, Pt has a cleaner surface in the absence of Pb(IV) in the potential window between 0.3V to 0.5V, which is probably due to some dynamic state of the system rather than steady state. Aside from the single cell test, CA is one of the most direct and reliable ways to compare properties of different catalysts for alcohol oxidation, especially in the context of sustained activity. The instantaneous current is doubled in the presence of Pb(IV) indicating that the Pb(IV)/Pb(II) redox couple plays a key role in enhancing initial activity. Of interest is the observation that 40% and 56.2% “life-time” still remained for the
systems containing 3mM and 1mM Pb(IV) after 1 hour, which reflects less poisoning on the Pt electrode. A lower number of Pt active sites are available for adsorption of ethanol due to higher coverage of Pb, which accounts for the shorter “life-time” and lower activity in the presence 3mM Pb(IV) compared to that of 1mM Pb(IV).

In order to understand the promoting mechanism of Pb, CVs were carried out in 0.25M KOH with different concentrations of Pb(IV) under inert conditions (Ar purged). As can be seen in Figure 4.12, Pt features corresponding to the lower potential hydride formation (anodic) and its removal (cathodic) decay appear in direct proportion to the concentration of Pb acetate (Pb(Ac)_4) in the system. We are inclined to believe that progressive formation of underpotentially deposited (UPD) Pb as a function of concentration results in progressively fewer Pt sites for hydride formation. Curiously the oxide formation and concomitant reduction are minimally affected beyond the initial concentration of 1 mM. Further, the initial addition of 1mM Pb (IV) significantly enhances the specific adsorption of oxides on the Pt surface and their concomitant reduction. Such features exhibited in the observed CV (Figure 4.12) resemble those reported earlier with PtPb alloys and also as UPD ad-metals on the Pt surface.

The promoting mechanism of Pb(IV) towards electro-oxidation of ethanol is not clear at this stage. One hypothesis is that Pb(IV)/Pb(II) acts as heterogeneous redox couple and goes through reaction (4.5) at the electrode surface,

\[ Pb(II) - 2e^- \rightarrow Pb(IV) \quad (4.5) \]

while C-C bond cleavage is assisted in KOH solution by the Pb(IV)/Pb(II) couple
through the homogeneous process of reaction (4.6).

\[ \text{Pb}(IV) + H_2C - CH_3OH \rightarrow \text{Pb}(II) + CH_4 + CH_3O, \quad (4.6) \]

\( \text{Pb}(II) \) in reaction (4.6) is most likely a coordination complex of \( \text{Pb}(II) \) with organic compounds (\( CH_2OH \) in this case) instead of the free ion. This is due to the high tendency of \( \text{Pb}(II) \) to form complexes with organic ligands.\(^{66, 67}\) As a result, the activation energy barrier is decreased and the reaction is accelerated by facilitating electron transfer.

There still remains a question as to whether only a heterogeneously catalytic ethanol oxidation reaction happens at the electrode/electrolyte interface after deposition of \( \text{Pb} \) onto the Pt electrode. “Intermetallic PtPb Nanoparticles”\(^{68-70}\), “PbO\(_x\)-containing Pt electrode”\(^{71}\) and “Pt electrode modified with foreign Pb adatom”\(^{72-75}\) have been reported to exhibit significantly enhanced catalytic activity for small organic molecule oxidation. In order to answer this question, electro-oxidation of ethanol was carried out on Pt/C electrode with deposition of Pb in 0.25M KOH +1M ethanol in the absence of Pb(IV) ion in solution. This experiment can be described as follows:

(1) An electrode modified with Pt/C (E-TEK, 30%) was cycled in 0.25M KOH +1mM Pb(Ac)\(_4\) between potential limits of 1.2V and 0.06V and the scan ended at 0.06V;

(2) The electrode was taken out and transferred into 0.25M KOH +1M ethanol after washing;

(3) CV between potential limits of 0.2V and 1.1V and 1 hour CA at 0.55V were
performed thereafter

As can be seen from Figure 4.13, CVs on Pt/C with deposition of Pb in 0.25M KOH +1M ethanol is almost identical to that of Pt/C in 0.25M KOH +1M ethanol +1mM Pb(IV), suggesting the same electrode properties in the two cases. Both show a negative potential shift by as much as 200mV relative to that of Pt/C in 0.25M KOH containing ethanol only, which indicates that Pb adatom leads to appreciable enhancement of the Pt electrode activity towards ethanol oxidation.

Even though an intial instantaneous current density in 0.25M KOH+1M ethanol was observed on the Pt/C electrode with UPD Pb for ethanol oxidation as shown in Figure 4.14, this electrode has limited ability to sustain activity and can still be poisoned badly by CO, CₓHᵧOz or other species produced by ethanol during the oxidation process. The good maintenance of current density on Pt/C in a solution of 0.25M KOH+1M ethanol in the presence of 1mM Pb(IV) in solution is in line with our expectation that Pb(IV) ion helps to break C-C bond of ethanol through a homogeneous catalysis process and produces fewer poisoning species containing two carbon atoms. This expectation is based on our finding that the efficiency of electrooxidation of methanol (C₁ molecule) is 10 times higher than that of electrooxidation of ethanol (C₂ molecule) on Pt/C (E-TEK, 30%) in 0.25M KOH.

For comparison, the same test was also performed on PtₓPb/C and PtRuPbₐ₃/C synthesized from Pt/C (30%, E-TEK) and PtRu/C (40%, E-TEK) by Li’s method.⁷⁶ The obtained CVs on Pt/C with Pb adatom and PtₓPb/C are identical to that on Pt/C for ethanol oxidation in 0.25M KOH +1M ethanol+1mM Pb(IV), showing a negative
shift of onset potential by as much as 200mV (Figure 4.13). However, the CAs obtained at 0.55V show lower efficiency than that in the system containing 1mM Pb(IV) (Figure 4.14). The experiments elucidate that the enhancement of the catalytic activity of noble metals for the electro-oxidation of ethanol with embodiment of onset potential and instantaneous current is because of the UPD of Pb adatoms (formation of an under potential deposit of Pb species on the electrode). Meanwhile, the efficiency of sustained ethanol oxidation over a significant system life time during CA measurement can be further improved by the Pb(IV)/Pb(II) couple in solution, which may help catalytic C-C bond cleavage homogeneously in solution.

One may however consider possible contamination concerns regarding the poisoning issue of Pb ions at the cathode where the oxygen reduction reaction (ORR) occurs. The ORR was measured as a function of Pb(IV) concentration in 0.25M KOH. No negative effects were observed on ORR activity, which still undergoes 4 electron reduction pathway and kinetics. The mass transport limited performance was slightly enhanced in the system containing Pb(IV) as evidenced in the limiting current. This is evident in Figure 4.15 which shows ORR polarization curves for Pt/C (E-TEK, 30%) catalysts at 900rpm in 0.25M KOH as a function of different concentration of Pb(Ac)₄. Kotecky-Levich plots along with the theoretical lines for 2 and 4 electron process of ORR are shown in Figure 4.16. The slopes found on Pt/C in 0.25M KOH in the presence and absence of Pb(IV) are similar to the theoretical line for $n=4$ indicating the 4 charge-transfer pathway of ORR process in both cases.

While a slight improvement in mass transport for ORR is observed for Pt/C
containing Pb ad-atoms, the exact reasons for such behavior is unclear. Prior work has alluded to a possible enhancement of ORR activity resulting from a decrease of the work function of the electrode surface, an increase in the surface concentration of the negatively charged species and a substantial increase of the rate of electron transfer to O$_2$ in the first reduction step.

In addition to ethanol, other fuels including methanol, acetic acid, formic acid and acetaldehyde were also tested for the Pb(IV) promoting effect. From the results shown in Figure 4.18-21, some conclusions can be drawn. First of all, aside from ethanol, only methanol activity enhancement is observed, as is evident from both the CV and the chronoamperometric profiles (Figure 4.18 and 4.20). It is also interesting to note that the activity for methanol oxidation is significantly higher than that of ethanol even in the absence of the co-catalyst containing Pb. This is clearly evident from the chronoamperometric profile in figure 4.19.

### 4.4 Conclusions

This chapter demonstrates the feasibility of replacing Pt/C with Pd$_4$Au/C and Pd$_{2.5}$Sn/C synthesized in house as electrocatalysts for electro-oxidation of ethanol in a high pH environment. XRD results show that Pd$_4$Au/C and Pd$_{2.5}$Sn/C belong to different space groups and have appreciable differences in their crystal structure. The average particle size of as-synthesized Pd$_4$Au/C and Pd$_{2.5}$Sn/C catalysts are 6.8 nm and 8.4 nm, respectively, combining XRD data and TEM measurements. Although Pt/C shows better kinetics for ethanol oxidation with the embodiment of more
negative onset potential and larger instantaneous current density, it turns out that 
Pd_{4}Au/C and Pd_{2.5}Sn/C are more tolerant to poisoning as shown in 
chronoamperometry tests. From the impedance results, Pt/C exhibits heavy CO 
poisoning and Pd_{2.5}Sn/C shows low electrocatalytic activity for ethanol oxidation. 
Pd_{4}Au/C displays the best catalytic activity for ethanol oxidation in alkaline media. In 
addition, we have described a novel method to improve the efficiency of ethanol 
electro-oxidation in high pH environment through the addition of Pb(IV) ion in 
solution. The heterogeneous redox process coupled to a homogeneous reaction is 
interesting fundamentally and has promising applications. UV-vis, in-situ XANES, 
mass spectroscopy, single cell tests and other techniques are still needed for further 
understanding the mechanism of the enhancement effect of Pb(IV) on 
electro-oxidation of ethanol and methanol in both alkaline and acid media.
4. 5 Chapter 4 References:


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4.6 Chapter 4 Figures:

Figure 4.1 XRD patterns of Pd₄Au/C (---) and Pd₂.₅Sn/C (—).
Figure 4.2 TEM micrographs of (A) Pd$_4$Au/C and (B) Pd$_{2.5}$Sn/C. Scale bars are 100 nm
Figure 4.3 Cyclic voltammograms of glassy carbon electrodes modified with Pt/C (E-TEK, 30%, …), Pd₃Au/C (—) and Pd₂₅Sn/C (---) in (A) 0.25 M KOH and (B) 0.25 M KOH + 1M ethanol at room temperature. The Pt and Pd loadings were 15 µg/cm², and the potential sweep rate was 10 mV s⁻¹.
Figure 4.4 Semi-logarithmic log($j_\text{o}$) vs. electrode potential plots for ethanol oxidation on Pt/C (E-TEK 30%), Pd$_{2.5}$Sn/C and Pd$_4$Au/C in 0.25M KOH. Ethanol concentration was 1 M and Pt and Pd loadings were 15 $\mu$g/cm$^2$. 
Figure 4.5 Chronoamperometric tests of Pt/C (E-TEK, 30%), Pd$_{2.5}$Sn/C and Pd$_4$Au/C at +0.55 V in 0.25 M KOH + 1M ethanol. Pt and Pd loadings were all 15 µg/cm$^2$. 
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Figure 4.20 Chronoamperometry test of Pt/C (E-TEK, 30%), at 0.55V in 0.25M KOH +1M methanol with 0mM and 1mM Pb (IV), Pt loading: 15ug/cm²
### Table 4.1 Composition of Pd₄Au/C and Pd₂₅Sn/C catalysts prepared in house

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nominal composition</th>
<th>Composition from ICP analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd Wt%</td>
<td>Pd:M (atomic)</td>
</tr>
<tr>
<td>Pd₄Au/C</td>
<td>28.7</td>
<td>4:1</td>
</tr>
<tr>
<td>Pd₂₅Sn/C</td>
<td>29.3</td>
<td>3:1</td>
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</table>
Table 4.2 XRD data of Pd$_4$Au/C and Pd$_{2.5}$Sn/C catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lattice types</th>
<th>Pt (111) @2θ</th>
<th>Crystallite Size / nm</th>
<th>Lattice parameter /Å</th>
<th>Pd-Pd bond distance / Å</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_4$Au/C</td>
<td>Face centered cubic</td>
<td>39.89</td>
<td>6.5</td>
<td>a = b = c = 3.91</td>
<td>2.77</td>
<td>Fm3m</td>
</tr>
<tr>
<td>Pd$_{2.5}$Sn/C</td>
<td>Cubic</td>
<td>40.15</td>
<td>7.4</td>
<td>b = 4.31, c = 8.12</td>
<td>2.46</td>
<td>Pnma</td>
</tr>
</tbody>
</table>

† The average crystallite size was calculated using the Debye-Scherrer equation \( Z = \frac{C}{\lambda B \cos \theta} \)\(^7\)
Chapter 5

Study of Oxygen Reduction Reaction in Phosphoric Acid Fuel Cell

5.1 Introduction

Phosphoric acid fuel cells (PAFC) have been commercialized successfully and used for stationary applications with a combined heat and power efficiency of about 80%. However, there is still a lot of room for improvements in this technology through further research and development. Continual improvements are still imperative if PAFCs are to hold their position in the market or penetrate into other markets with more stringent cost and efficiency targets. The most favored material for PAFC cathode catalysts is still Pt in high-surface-area form supported on carbon. Over the years, extensive studies have been devoted to identifying suitable ways to make the smallest possible Pt particles to yield the highest active surface area. Technologies have been improved to achieve equal accessibility to the electrolyte and gaseous phases for all catalyst-containing parts and a three-phase contact between the electrolyte film, gaseous reactant, and the electronically conducting catalyst support. However, one major factor limiting the performance of PAFCs is the sluggish ORR kinetics in H₃PO₄, which is attributed chiefly to the impeding effect of phosphate anion adsorption on ORR activity. The fact that ORR performance is highly sensitive to the structure of the catalyst stems originally from the structure-sensitive adsorption of anions. The adsorption can be reversible (e.g. adsorption of hydroxyl species from water activation) or partially reversible (e.g. adsorption of sulfate, phosphate,
halogen). Although the adsorption does not affect the pathway of oxygen reduction reaction, it certainly inhibits the reduction of molecular \( \text{O}_2 \) by blocking the initial adsorption of \( \text{O}_2 \).

The adsorption of anions ((bi)sulfate \(^{6-11}\), chloride \(^{5,12,13}\), hydroxyl \(^{14,15}\)) on Pt single crystals and Pt nanoparticles in electrochemical environments has been extensively studied. However, there are only a few reports about phosphate anion adsorption on Pt due to the polyprotic nature \(^{16}\) of phosphoric acid, which makes the study complicated. Weber et al\(^{17}\) claimed that the adsorption of phosphate species is insensitive to the Pt surface geometry with mainly \( \text{H}_2\text{PO}_4^- \) adsorbed in the low potential region and a mix of \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) adsorbed in the high potential region. In contrast, Tanaka et al.\(^{18}\) showed that phosphate anion adsorption is structurally dependent, based on evidence that the oxygen reduction reaction in \( \text{H}_3\text{PO}_4 \) solutions is structure-sensitive.

There also remains debate on the nature and mode of phosphate adsorption on the Pt surface. It was found that both \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) can be adsorbed on both the Pt(111) and the Pt(100) surface. The stretching vibrations of the two oxygen atoms with \( \text{C}_{2v} \) symmetry in \( \text{H}_2\text{PO}_4^- \) ions, and the stretching vibration of the three equivalent oxygen atoms with \( \text{C}_{3v} \) symmetry in \( \text{HPO}_4^{2-} \) ions were observed in the \textit{in situ} FTIR spectra.\(^{17}\) Nevertheless, it was proposed by Tanaka et al that the adsorption of phosphate anions involves three oxygen atoms on the Pt(111) surface which features mostly three fold sites, whereas only one or two oxygen atoms are involved in phosphate adsorption on Pt(100) and Pt(110) surfaces.\(^{18}\)

The first part of this chapter aims to obtain information on the oxygen reduction
reaction on different crystallographic structures of the Pt basal plane in 0.1M HClO₄ as a function of varying concentration of H₃PO₄. A hanging meniscus rotating disk (HMRD) method was used to determine quantitatively the kinetic parameters of the ORR on three low index Pt single crystals as well as a surface modified single crystal. Electrochemical impedance spectroscopy (EIS) was used to characterize the ORR mechanism.

As one of the approaches to overcome the phosphate anion poisoning problem, Pt transition metal alloys have shown the tendency to mitigate the anion species adsorption on the Pt surface in acid media and expose more active sites to facilitate the coverage of O₂ molecules and increase the likelihood of its dissociation.¹⁹ Subsequent to the ORR study on Pt single crystals, an exploration of how phosphate anion poisoning of the cathodic Pt/C catalyst may be mediated by alloying Pt with Ni in Phosphoric Acid Fuel Cell will be introduced. An array of electrochemical investigations (cyclic voltammetry, CV, and Tafel plots for different concentration of H₃PO₄) were performed to understand the mechanism of phosphate anion adsorption on as-synthesized catalysts. The activity and durability of catalysts were also tested in a home designed high temperature half cell operated at 150°C to mimic the real conditions of a PAFC. An X-ray absorption spectroscopy study gave strong proof that phosphate anion adsorption on the PtNi/C catalysts was limited to a extremely low level.

5.2 Experiment
5.2.1 Single crystal measurement

5.2.1.1 Pretreatment of single crystals

The preparation of cleaning crystals was performed in a stainless steel ultra-high vacuum (UHV) chamber with a base pressure $1.0 \times 10^{-10}$ torr. This system is equipped with low energy ion scattering (LEIS), high-resolution x-ray photoelectron spectroscopy (XPS) and low energy electron deflection (LEED). The crystals were cleaned by cycles of Ar$^+$ sputtering ($2.0 \times 10^{-5}$ torr, 500 ev) and annealing at 900K by $5.0 \times 10^{-8}$ torr oxygen. Flushing to 1100K was required to remove residual oxygen and sharp LEED patterns were obtained to ensure the good quality of the single crystal surfaces. A tin doser was also installed to evaporate Sn on the Pt(111) surface to generate Sn/Pt(111) alloy surfaces. Two kinds of Sn/Pt(111) alloy surfaces, $(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3}) R30^\circ$, were prepared by dosing Sn onto a clean Pt(111) surface, followed by annealing to different temperatures. LEIS and XPS also were performed to ensure that there is no detection-limit level of impurity on any the surfaces. After the crystals were cleaned, they were transferred from the UHV to an argon gas-filled box which provides a clean and inert working environment. In this box, a hanging meniscus disc was made by mounting the crystal on top of the rotating electrode disc using a spot-welding method. In detail, a small metal wire was welded on the low edge of the crystal and side of the rotating electrode disc. This epoxy free hanging meniscus disc turned out to be very stable during rotation.

5.2.1.2 Electrochemical measurement

The electrochemical measurements were conducted in a standard
three-compartment electrochemical cell at room temperature using a rotating disk electrode (RDE) setup from Pine Instruments connected to an Autolab (Ecochemie Inc. Model-PGSTAT 30). All potentials were measured with respect to a sealed hydrogen reference electrode (RHE) made from the same electrolyte as used in the ORR experiments. A platinum wire was used as the counter electrode. The electrolytes were prepared with HClO$_4$ (GFS Chemicals) and purified H$_3$PO$_4$ (Sigma-Aldrich) with standard procedure described in detail elsewhere$^{20}$. CVs were taken on Pt(111), Pt(110), Pt(100) and PtSn(111) electrodes in deoxygenated 0.1M HClO$_4$ with doping of different concentration of H$_3$PO$_4$. After retreatment of the single crystals in the UHV chamber, ORR measurements were carried out on above electrodes in oxygen saturated 0.1M HClO$_4$ with different concentrations of H$_3$PO$_4$. Finally, EIS measurements were conducted on the same Autolab potentiostat and the impedance spectra were recorded between 100 kHz and 10mHz with an ac signal amplitude of 5 mV. In addition, EIS measurements were performed at 0.85V (Vs. RHE) with a rotation rate of 400rpm.

5.2.2 Physical & Electrochemical characterization for PtNi/C: a special catalyst towards mediation of phosphate anions adsorption

5.2.2.1 Average (bulk) structural and chemical compositional characterization

5.2.2.1.1 Quantitative elemental analysis by using EDS (EDAX)

Energy-Dispersive X-ray Spectroscopy (EDS) was used to explore any impurities present in the E-TEK Pt/C and BASF PtNi/C electrocatalysts as well as to
determine the average composition of the PtNi alloys. The results and sample information provided by BASF can be seen in Table 5.1.

5.2.2.1.2 XRD

Powder X-ray diffraction (XRD) patterns of the catalysts were taken on a Rigaku X-ray Diffractometer (D-Max 2000) with CuKα radiation. The particle size of the dispersed metal crystallites is estimated from the broadening of diffraction peaks using the Scherrer formula.

5.2.2.2. Surface-sensitive studies: SEM imaging

SEM images were taken on a Hitachi 4800 lower resolution (magnification is 150,000) scanning electron microscope.

5.2.2.3 Method (example) to measure ratio of alloy on the surface of catalysts

(a) Cu UPD method

Details were given in Chapter.3

(b) CO stripping method

Step.1 Obtain the surface areas of both Pt and Ni using CO stripping method

All CO stripping experiments were carried out in 0.1M HClO₄ solution. First of all, the electrode modified with 15μg/cm² of catalyst was cycled (from 0.05V to 1.1V or 1.2V) at 10mv/s. Then potential of the working electrode was held at 0.05V while CO was bubbled through the solution. This was followed by bubbling Ar for 15 minutes to remove CO from the bulk solution. Two cycles of CV were recorded at 10mv/s. As can be seen from Figure 5.1 CO can be adsorbed on the Ni surface. Therefore, the
total electrochemical surface area of Pt and Ni can be obtained from integration of the peak shown in Figure 5.2 using a charge density associated with monolayer adsorption of CO of 420 μC cm$^{-2}$. The charge involved after background subtraction was named $Q_{Pt+Ni(CO)}$.

Step.2: Obtain the surface area of Ni using Pt$_{H(UPD)}$ and CO stripping data

We may easily get the Pt surface area of PtNi/C catalyst from H$_{upd}$ region of the CV in 0.1M HClO$_4$. (The charge involved was named $Q_{Pt}$). As a result, the Pt ratio on the surface of catalyst can be calculated using formula (5.1)

$$Pt\% \text{ (on the surface)} = \frac{Q_{Pt}}{Q_{Pt+Ni(CO)}} \times 100\% \quad (5.1)$$

5.2.2.4 RDE measurement

5.2.2.4.1 Cyclic voltammetry and rotating disk electrode studies of catalysts in perchloric acid (HClO$_4$) as a function of phosphoric acid (H$_3$PO$_4$) concentration

Cyclic voltammetry (CV) and rotating disk electrode (RDE) methods were used to study various samples including a bulk Pt disk electrode, BASF Pt/C (ES365 2201), and Pt-Ni/C (ES391). Every sample was first measured in 0.1M HClO$_4$ solution. H$_3$PO$_4$ was then gradually added into the solution with increasing concentration up to 0.1M to observe its impact to the CV and RDE results. All experiments in this section were carried out at room temperature.

Next electrodes were prepared with Pt and Pt-Ni nanoparticles supported on carbon from BASF. The catalyst materials were bound to the gold electrode with Nafion® binder. The gold electrode diameter was 5 mm. Both Pt and Pt-Ni were
tested first in 0.1M perchloric acid and then with additional 0.1M phosphoric acid. For this experiment the Pt loading was relatively small, about 5 µg(Pt)/cm² (for Pt-Ni the loading is defined for Pt only and does not include the weight of Ni).

Before performing any electrochemistry, each sample was exposed to at least 20 potential cycles between the onset of hydrogen evolution and the theoretical onset of oxygen reduction in order to remove surface impurities and obtain well-defined surface conditions. After activation, the voltammetric responses did not noticeably change during further potential cycling. The fairly stable character of the electrocatalysts was also confirmed by recording identical voltammograms taken before and after the experiments.

5.2.2.4.2 RDE measurement of Pt/C (ES365 2201) and Pt-Ni/C (ES391)

Along the CV investigation, the ORR current was measured with the RDE technique. The CV and RDE experiments were performed on the same experimental setup by alternating the gas bubbling through the solution (Ar for CV and O₂ for ORR). Again, the solution is 0.1M perchloric acid with and without the additional 0.1M phosphoric acid.

5.2.2.5 ORR studies of catalysts in concentrated phosphoric acid (H₃PO₄)

5.2.2.5.1 Developing a High Temperature RDE Setup

The RDE technique has been extensively used to measure the ORR activity of cathode materials for low temperature PEM fuel cell applications. Usually the measurements are performed at room temperature in a 0.1M perchloric acid solution.
Conventional RDE tips in which the electrodes are press-fitted into the Teflon material or other techniques such as molding the electrode into the insulating material can leak and cause contamination at elevated temperatures\textsuperscript{21}.

This is due to the fact that the plastic and the electrode material (glassy carbon or gold) have very different thermal expansion coefficients. Therefore a cylindrical electrode was used without an isolating mantle (to be referred to as "Sleeveless RDE" in this report), which is lowered into the glass cell until it just touches the electrolyte surface.\textsuperscript{22} Figure 5.3 shows a photo and a schematic drawing of the sleeveless RDE.

5.2.2.5.2 Sleeveless RDE measurements of catalysts in concentrated phosphoric acid at elevated temperature

The Sleeveless rotating disk electrode is employed to study the ORR kinetics of the BASF samples Pt/C (ES365 2201) and Pt-Ni /C (ES391) in concentrated phosphoric acid at an elevated temperature of 50°C. A dynamic hydrogen electrode (DHE) was used as the reference electrode. The kinetic currents were derived from the disk current (cathodic scans) at a rotation speed of 900 rpm corrected by the mass transport limited disk current at a potential of 0.45V vs. DHE. The potential was swept with a scan rate of 10mV/s. As already mentioned for the room temperature measurements, the upper limit of the potential scan range was maintained at 1.0 V (vs. DHE) to prevent Pt dissolution and Ni leaching. This is even more relevant for measurements at higher temperatures. A gold electrode with a diameter of 5 mm was used as the substrate for the catalysts in this study. The catalysts had a Pt loading of about 13 µg (Pt)/cm\textsuperscript{2} and were bound with Nafion onto the gold electrode surface.
5.2.2.6 X-ray absorption spectroscopy study

In-situ X-ray absorption spectroscopy data were collected on the Pt-Ni/C (BASF) catalysts as well as Pt/C (E-TEK) as a function of potential (0.01V, 0.24V, 0.54V, 0.84V and 1.04V) at various phosphoric acid concentrations (0, 1mM, 10mM, 100mM and concentrated phosphoric acid) in 0.1 N HClO₄. All data were processed with standard procedures using the IFEFFIT suite (v.1.2.9). Briefly, the reference foils corresponding to each scan were calibrated to the standard Pt L₃ edge energy and then carefully aligned to a selected standard (0.54V). The energy shifts were then automatically applied to all the subsequent sample scans. The difference spectra were generated using the relation

\[ \Delta \mu(V) = \mu(V) - \mu(0.54V, 0.1M HClO_4) \]  \hspace{1cm} (5.2)

In all previous work using the \( \Delta \mu \)-XANES technique on Pt catalysts in acid media, the catalyst surface was found to be the 'cleanest' and relatively free from any adsorbates at around 0.5V and therefore the spectrum at 0.54V in 0.1M HClO₄ was used as the reference to generate all difference spectra in the present study.

5.3 Results and Discussion

5.3.1 Single crystals study

5.3.1.1 Cyclic voltammetry curves on Pt(111), Pt(110), Pt(100) and PtSn(111) as a function of concentration of H₃PO₄

Figure 5.4 – Figure 5.6 show the cyclic voltammograms on Pt(100), Pt(110) and Pt (111) planes in 0.1M HClO₄ with progressive addition of different amounts of
H$_3$PO$_4$. LEED patterns and two dimensional crystallographic models are also shown. In Figure 5.4 and Figure 5.5 symmetric peaks in H$_\text{upd}$ region can be seen on both Pt(100) and Pt(110) in 0.1M HClO$_4$. The double layer region current is much higher on Pt(100) than that on Pt (110). The shape of the CVs on Pt(100) and Pt(110) is in line with those$^{27, 28}$ reported earlier and indicates well-defined Pt(100) and Pt(110) surfaces. After addition of H$_3$PO$_4$ the double layer current diminishes; this effect is more pronounced on Pt(100). Of interest is the observation in Figure 5.6, where di-hydrogen phosphate anion adsorption/desorption peaks are prominent and evolve as well as shift towards negative potential as more H$_3$PO$_4$ is doped into the solution. The main points which emerge from the CVs are as follows: [i] As reported earlier by Weber et al$^{17}$, the onset potential for phosphate anion adsorption on the Pt(100) surface occurs approximately at 0.3V (Vs. RHE). The peaks seen in the H$_\text{upd}$ region are typical of those observed on Pt (100) sites in the absence of phosphate anion; [ii] The emergence of new peaks in the H$_\text{upd}$ region upon addition of phosphoric acid are ascribed to adsorption of phosphate anion accompanied by a surface reconstruction. Such anion induced surface reconstruction has been reported with Au(100)$^{29, 30}$ These prior reports also mention that such reconstruction causes extra positive surface charge due to change in the potential of zero charge (pzc). The emergence of the new peaks upon addition of phosphoric acid is therefore explained in terms of compensation of charges and ordering of the adsorbed anions.$^{18, 31}$ If the hypothesis of surface reconstruction and the concomitant changes in the surface free energy is correct, we should see the same sharp peaks in the H$_\text{upd}$ region after washing the
H$_3$PO$_4$ off the electrode surface and transferring the electrode into a fresh 0.1M HClO$_4$ solution. However, the sharp peaks nearly disappear as can be seen in Figure 5.7 and Figure 5.8. Therefore surface reconstruction is not considered to be the main reason for the observed peaks; this is also true using analogous reasoning for the Pt (110) surface as shown in Figure 5.8. Actually, the surface reconstruction is highly dependent on the crystallographic orientation on the terrace and the nature of the anions. The effect observed here clearly indicates no irreversible surface realignment as a result of phosphate anion adsorption. More techniques such as in-situ STM, in-situ FTIR, and radiotracer analysis need to be utilized to confirm the hypothesis. In the case of Pt(111) significant change in the H$_\text{upd}$ region is observed after adsorption of H$_3$PO$_4$, the anomalous state or butterfly envelope moves toward lower potentials with increasing concentrations of H$_3$PO$_4$. A similar finding can also be seen in Nikolic’s work to determine the valence of phosphate anions adsorbed on Pt(111). The gradual evolution of peaks in the potential window of 0.4V-0.75V is caused by specific adsorption/desorption processes of phosphate anions. Appreciable change can be seen after addition of 1mM H$_3$PO$_4$ into the blank solution. Further addition of H$_3$PO$_4$ produces slight changes of the CV curves, and adsorption equilibrium is reached after addition of 50mM H$_3$PO$_4$. The adsorption of phosphate anions happens directly after desorption of H and ceases at the onset potential of OH species adsorption. In support of this conclusion is the observation that the CV recovers after washing off H$_3$PO$_4$ on the Pt (111) electrode as shown in Figure 5.9, consistent with in-situ FTIR experiments reported previously. Further, the
inhibition to water activation$^{32}$ and Pt oxide formation$^{27, 29}$ (onset potential shifts positively) on Pt(111) due to adsorption of phosphate anions is more serious than that on Pt(100) and Pt(110); this is discussed in more detail in next section about ORR experiments. As an FCC crystal, Pt exposes a closed packed hexagon in the (111) face. Sites on Pt(111) for adsorption can be atop, bridge, or hollow sites. Atoms on the (110) face only allows atop hollow sites with an up and down arrangement. The ideal (110) face is not energetically favorable, and it is reconstructed to form a (2×1) structure with missing rows in the (110) direction. This reconstructed surface actually exposes two kinds of (111) planes. They are perpendicular to each other with only two rows of atoms exposed on the (111) surface. However, the space hindering effect prevents PA adsorption on these two (111) planes simultaneously. Atoms in the (100) surface have a square arrangement. It is also not energetically unfavorable. Surface reconstruction of ideal (100) forms a quasi- hexagonal packed structure. But, adsorption of small molecules (NO, CO, etc.) on Pt(100) is able to remove this reconstruction.

In order to investigate phosphate anion adsorption on Pt single crystals with steps and defects on the surface, we prepared a PtSn(111, 2x2) single crystal and generated steps and defects by removing Sn in an acid wash step. As shown in Figure 5.10 all typical Pt(111) peaks show up after 60 continuous scans in 0.1M HClO$_4$, which means all Sn on the surface was removed. Figure 5.11 shows CVs on PtSn(111) in 0.1M HClO$_4$ and 0.1M HClO$_4$ + 100mM H$_3$PO$_4$. No marked difference of the shape of curves can be seen as compared with those in Figure 5.6(a). The similarity of CV peaks between the Pt(111) surface before and after addition of Sn and its subsequent
removal shows that, as far as phosphate anion adsorption is concerned, the presence of additional steps and defects on the surface does not significantly alter the nature of adsorption of phosphate anions. The principal sites responsible for the butterfly peaks unique to the Pt (111) surface result from the presence of three fold bulk sites common to both surfaces.

5.3.1.2 ORR study on Pt(111), Pt(110), Pt(100) and PtSn(111) as a function of concentration of H₃PO₄

As the polyprotic nature of H₃PO₄ causes the study to be complicated, we chose the progressive doping method by varying the concentration of H₃PO₄ from 1 to 100 mM in 0.1 N HClO₄ in order to maintain pH as well as the permeability of O₂ constant. Figures 5.12 –Figure 5.15 show the ORR curves on Pt(110), Pt(100), Pt(111) and PtSn(111) single crystals in 0.1M HClO₄ at different rotation rates. The shape of the current-potential curves on Pt(111) and PtSn(111) are very similar to that on Pt nanoparticles and can be considered from the perspective of three regions, namely, the kinetic control region (>0.9V), the mixed diffusion-kinetic limitation region (0.7V to 0.9V) and a diffusion-controlled region (<0.7V). However, the limiting current region on Pt(100) and Pt(110) is not well defined, especially at high rotation rates. Possible reasons for this include: (i) Surface tension at Pt(100) with the largest geometric area may hinder O₂ transport from solution to the electrode through the thin film of electrolyte, and (ii) Traces of Cl⁻ and NO₃⁻ in the solution are prone to be adsorbed on Pt(100) and affect the oxygen reduction reaction. In addition, the small decrease of the limiting current shown in polarization curves of
Pt(100) and Pt(111) is associated with the change of numbers of electron transfer for ORR due to H adsorption at low potentials. Some rotating ring disk experiments have confirmed that H2O2 is generated in this region which means that the ORR mechanism has varied from a 4-electron pathway to a 2-electron pathway.6, 35 Such a decrease does not happen on Pt(110), which was also observed in H2SO4 and H3PO4. Tanaka et al18 has pointed out that hydrogen is mainly adsorbed on the layers below the surface of Pt(110). Kuzume et al36 also speculated that the hydrogen is only adsorbed in the valley of Pt(110), leaving the atop sites available for oxygen.

The ORR current density j can be expressed by the Koutecky-Levich equation37

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}$$  (5.3)

Due to the hydrodynamic behavior of the hanging meniscus rotating disk system11, 36, 38, the diffusion limiting current density has to be described using a modified Levich equation:

$$j_d = 0.620nFD^{2/3}C_0\nu^{-1/6}\omega^{1/2}[1 - 2KR_0^{-1}(\nu/\omega)^{1/2}]$$  (5.4)

All of the parameters have the same meaning and values reported in the literature:11, 27 $j_k$ is the kinetic current density, $j_d$ is the diffusion limiting current density, $n$ is the number of exchanged electron; $\omega$ is the rotation rate, $F$ is the Faraday constant (96485 C mol⁻¹), $D$ is the diffusion coefficient of the molecular O₂ in 0.1 M HClO₄ solution, $\nu$ is the kinematic viscosity, $C_0$ is the concentration of molecular oxygen. $R_0$ is the geometric radius of the electrode, and $K$ is a constant related to the meniscus height.
The plots of $j_L$ vs. $w^{1/2}$ were made based on data in Figures 5.12 –5.15. In each case, a linear plot with negative intercept is observed as shown in the representative plot for Pt(100) in 0.1 N HClO$_4$, shown in Figure 5.16. The slopes are identical to those expected for a theoretical 4 electron reduction, indicating that to be the predominant process on all of the above Pt single crystals in the potential range studied. In addition, the negative intercepts indicate that lateral wetting effect has been successfully avoided.$^{11}$

According to equation (5.3) and equation (5.4), the plot of $j^{-1}$ vs. $\omega^{-1/2}$ is no longer linear when the HMRD technique is used in the experiment. Instead, plots of $j^{-1}$ vs. $j_d^{-1}$ were made and can be seen in Figure 5.17. The parallel curves for different potentials demonstrate that the ORR on the three low index Pt single crystals as well as PtSn(111) has first order kinetics with respect to the diffusing reactant (O$_2$).$^{27}$ The intercept of each plot equals to the value of $j_k$ at the given potential. The $j_k$ value has been correlated with the reaction rate constant by equation (5.5)$^{11, 27, 39}$:

$$j_k = nFk(E)(C_0^*)$$  \hspace{1cm} (5.5)

All values of rate constants for ORR on the above single crystals in different acid systems are tabulated in Table 5.2.

As an example, the mass transport corrected Tafel curves obtained from the plot of $j/(j_d f)$ vs. $E$ are shown in Figure 5.18. The Tafel slopes for the ORR on all Pt single crystals in 0.1M HClO$_4$ with addition of different concentration of H$_3$PO$_4$ can be found in Table 5.2. Two Tafel regions are observed. At low current densities the slopes are close to 120 mv/decade. At high current densities, the slopes change to 60
mv/decade. The mechanisms for change of Tafel slopes for the ORR on Pt single crystals and polycrystalline Pt have been well documented in the literature.\textsuperscript{18, 27, 40} It can be noticed that the order of electrocatalytic activity of these single crystals towards the ORR is PtSn(111)>Pt(111)>Pt(110)>Pt(100) in 0.1M HClO\textsubscript{4}, which is slightly inconsistent with the reports of other researcher.\textsuperscript{7, 11, 27, 41} We are inclined to believe that the difference of pretreatment for the single crystals is the main reason accounting for the variation. In our case, high temperature treatment was performed under ultra high vacuum, which is different from the hydrogen flame method used previously. Cleaner and flatter surfaces are made in UHV rather than hydrogen flame because hydrogen flame annealing cannot remove nonvolatile impurities. The discussion is out of the scope of this work, since our focus resides primarily in critically examining the inhibition effect of phosphate anion adsorption on the ORR carried out on Pt single crystals with different surface orientation and morphology.

The observation that the overpotential is getting larger in the presence of H\textsubscript{3}PO\textsubscript{4} dictates clearly the severe impediment of phosphate anion adsorption to ORR activity, which can be found on all Pt single crystals studied in this paper. However, the inhibition extent is different on the various single crystals. The half wave potentials\textsuperscript{27} (E\textsubscript{1/2}) as representative of activity of ORR performance is shown in Figure 5.19 (a-d). The decrease of E\textsubscript{1/2} after addition of 100mM H\textsubscript{3}PO\textsubscript{4} in the case of Pt(111) is much more than the other three crystals. This is also evident from the comparison of the corresponding Tafel plots with and without phosphate anion in 0.1 N HClO\textsubscript{4} (Figures 5.19a and 5.20). Furthermore, Figure 5.21 shows that the kinetics current density at
0.85V decreased by 89.4% of the original on Pt(111) after addition of 100mM H$_3$PO$_4$.

In contrast, the decrease of current density is much less in the case of Pt(100) or Pt(110). Other than kinetic current density, more information can be obtained from the slopes of the Tafel plots shown in Figure 5.18, Figure 5.20 and Table 5.2. If we assign the different Tafel slopes at high and low current density in 0.1M HClO$_4$ and 0.1M HClO$_4$ +100mM H$_3$PO$_4$ as $\Delta_0$ and $\Delta_{100}$, we may achieve a value of $\eta$ according to equation (5.6):

$$\eta = \Delta_{100} / \Delta_0$$ (5.6)

The order of the value $\eta$ for Pt(100), Pt(110), Pt(111) and PtSn(111) is Pt(100)$>$Pt(110)$>$PtSn(111)$>$Pt(111). This sequence matches the result shown in Figure 5.21. In contrast to the conclusion in the study of Tanaka et al.$^{18}$ that phosphate anion adsorption does not affect the reaction pathway for ORR on Pt single crystals, we find that the phosphate anions do hinder or block the oxide species formation or even O$_2$ molecule adsorption on Pt as evidenced by the slope change on the Tafel plots.$^{18, 27, 40, 42}$ In general, it can be confirmed that the phosphate anion adsorption seems to be very orientation and structure-sensitive. The variation of of phosphate anion affinity for the Pt surface is directly related to the corresponding ORR performance; in other words, the more facile the phosphate anion adsorption on Pt surface, the greater is the effect on ORR catalytic activity. The interaction of phosphate anions with platinum is strongest on Pt(111), which agrees with prior reports from Tanaka$^{18}$ and Kadiri et al.$^7$. The general consensus in literature regarding why PA is adsorbed on these three surfaces differently indicates the following:
1. Different adsorption energy. It is well known that hydrogen and oxygen adsorbs on the (111), (110) and (100) faces with different adsorption energy. Those differences hold when PA adsorbs on these surfaces.

2. Corrosive adsorption, or adsorption-induced surface reconstruction. This most likely happens on the Pt(100) surface, since the experiment for this surface showed that adsorbed PA was not completely recovered by washing the surface with clean water.

3. Dissociative adsorption. The dominant species in 0.1M HClO\textsubscript{4} solution with an initial H\textsubscript{3}PO\textsubscript{4} concentration of 100mM (or less) is H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}.\textsuperscript{31} On the surface, it is quite complicated. Dissociation of H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} on the surface might take place. In most cases, a H-O or P-O bond can be broken causing hydrogen or a hydroxyl group to leave H\textsubscript{2}PO\textsubscript{4}. Then the surface species can be H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}, HPO\textsubscript{4}\textsuperscript{2−}, PO\textsubscript{4}\textsuperscript{3−}, HPO\textsubscript{3}, etc. On different surfaces, the surface species can be different due to the different reactivities of each surface.

4. Different saturated coverage due to specific adsorption. Saturated coverage of PA can be very different on these surfaces because of the different geometrical arrangement of the surface atoms. However, the most salient difference between Pt(111) and Pt(110) and Pt(100) is that the surface of Pt(111) is full of 3-fold hollow sites. Since phosphate anions tend to be adsorbed on 3-fold hollow sites the Pt(111) system should have the lowest adsorption energy. An \textit{in-situ} XAS measurement has strongly supported this presumption and the details will be illustrated in following section.
Another interesting phenomenon is that the drop in kinetic current density on PtSn(111) with steps and defects is less than that on Pt(111). The exact reason for the improvement is unknown. However, a reasonable analogy can be made with the study of Kuzume et al. related to oxygen reduction on stepped Pt surfaces.\textsuperscript{36} From their experimental results, the $E_{1/2}$ value for the ORR on Pt[$n$(111)$x$(111)] surfaces decreases as the step density decreases in sulfuric acid solution. The Pt[$n$(111)$x$(111)] (i.e Pt[$(n-1)$(111)$x$(110)]) surfaces imply (111) terraces separated by monatomic (110) steps. With increasing number of (110) steps, the adsorption of (bi)sulfate anions on (111) terraces is hindered. This is because the adsorption of (bi)sulfate anions on stepped surfaces gives rise to disordered adlayers, which is less stable than the bi-dimensionally ordered adlayers formed by adsorption of (bi)sulfate anions on (111) terraces.\textsuperscript{7,36} The fact that H$_2$PO$_4^-$ and HPO$_4^{2-}$ anions have the same numbers of free O atoms to interact with Pt as HSO$_4^-$ and SO$_4^{2-}$ provides further confirmation to this argument.

5.3.1.3 EIS study on Pt(111), Pt(110), Pt(100) and PtSn(111) as a function of concentration of H$_3$PO$_4$

Electrochemical impedance spectroscopy (EIS) is a sensitive and powerful technique in the study of the kinetics of electro-transfer processes. In recent years, EIS has been widely used in fuel cells to study the kinetics of electrode reactions on both anode\textsuperscript{43-45} and cathode\textsuperscript{46-48}. Here, the kinetic of the ORR on the four platinum single crystals as a function of H$_3$PO$_4$ concentration is examined by EIS. Figure 5.22 shows the Nyquist complex-plane impedance spectra of ORR with four different
electrodes in an O\textsubscript{2} saturated 0.1 M HClO\textsubscript{4} at different concentrations of H\textsubscript{3}PO\textsubscript{4} (shown in the figure legends). It can be seen that on all Pt single crystal surfaces the EIS spectra exhibit a well-defined semicircle. Usually for the ORR on electrocatalyst surfaces with high roughness (such as those modified with Nafion films, metal nanostructured surfaces, etc), there are two pronounced arcs corresponding to the charge transfer at high frequencies and mass transfer process at low frequencies.\textsuperscript{49-51} In the present study, the appearance of a single impedance arc suggests that the electrode process under the experimental conditions is dominated by the interfacial kinetics of the ORR process.

It should be noted that the intercept of the impedance arc on the $x$-axis represents the total ohmic resistance of the system and the diameter of the kinetic arc represents the charge transfer resistance of ORR on the electrode surface. It can be seen clearly that for each electrode in Figure 5.22, the diameter of the arcs increases with the increase of H\textsubscript{3}PO\textsubscript{4} concentration in the electrolyte. This result suggests that the electrocatalytic activity for oxygen reduction might be decreased by phosphate adsorption on Pt single crystal surface. Specifically, phosphate ions act as poisonous species by occupying the active sites on the Pt surface and hence impeding the adsorption of O\textsubscript{2} molecules. One can see that the effect of H\textsubscript{3}PO\textsubscript{4} concentration on the electrocatalytic activity for ORR is strongly dependent on the Pt single crystal surface structures. For example, in the O\textsubscript{2} saturated 0.1M HClO\textsubscript{4} without H\textsubscript{3}PO\textsubscript{4}, the diameter of the arc for Pt(111) is much smaller than that for Pt(100) and Pt(110).

More insights about the electron-transfer dynamics can be obtained from
quantitative analysis of the Nyquist impedance spectra, where the same equivalent circuit shown in Figure 5.23A was used to fit the impedance data obtained above. Here, $R_S$ represents the solution (uncompensated) resistance, $C_{DL}$ and $R_{CT}$ are the double layer capacitance and charge transfer resistance, respectively. The representative fits (solid lines) for the four electrodes are shown in each of the Nyquist plots in Figure 5.22. It can be seen that all the fits are excellent. From the fitting, the variation of the charge transfer resistance ($R_{CT}$) with concentration of $\text{H}_3\text{PO}_4$ is shown in Figure 5.23B for each electrode. First, on the all electrodes $R_{CT}$ increases very quickly with increasing $\text{H}_3\text{PO}_4$ concentration and at concentrations above ca. 50 mM the $R_{CT}$ remains virtually invariant. This variation of $R_{CT}$ with $\text{H}_3\text{PO}_4$ concentration suggests that the adsorption of phosphate on the four single crystal surfaces is saturated when the phosphate concentration is above 50 mM $\text{H}_3\text{PO}_4$. However, the phosphate poisoning effect for ORR on the four Pt electrode surface is drastically different. In the electrolyte without $\text{H}_3\text{PO}_4$ (0 mM), $R_{CT}$ on Pt(111), PtSn(111), Pt(110) and Pt(100) is 81.27, 204.57, 292.53 and 493.68 $\Omega$, respectively, suggesting that in the absence of phosphate ions, the electrocatalytic activity towards the ORR decreases in the order of Pt(111)(and PtSn(111)) > Pt(110) > Pt(100). The result is consistent with those obtained from RDE measurements and Tafel plots. With the introduction of $\text{H}_3\text{PO}_4$ into the electrolyte solution and at a concentration of 100 mM, $R_{CT}$ for ORR increases to 1677.4 $\Omega$ (Pt(111)), 1233.9 $\Omega$ (PtSn(111)), 963.3 $\Omega$ (Pt(110)), and 1545.7 $\Omega$ (Pt(100)). Therefore, the degree of $\text{H}_3\text{PO}_4$ poisoning, reflected by the increase of $R_{CT}$, decreases in the order of Pt(111) > PtSn(111) >
Pt(100) > Pt(110). This kinetic result agrees well with the results shown in Figure 5.21, where the catalytic activity of Pt(111) for the ORR exhibits the most sensitive variation with H₃PO₄ in electrolyte. In contrast, Pt(110) displays the best tolerance to H₃PO₄ adsorption toward ORR among the four single crystal surfaces. Additionally, modification of the Pt(111) surface with Sn appears to improve the tolerance to H₃PO₄ poisoning, suggesting that interfacial engineering may be an effective route toward the further optimization of the electrocatalytic performance. From the above impedance results, it can be concluded that within the present experimental context, Pt(110) appears to be the optimal catalytic surface for ORR in phosphoric acid fuel cells if the H₃PO₄ concentration in the electrolyte is larger than 1 mM, as the R_Cf at Pt(110) is the smallest among the four Pt single crystal surfaces with the H₃PO₄ concentration larger than 1 mM.

5.3.1.4 In-situ XAS results

Shown in Figure 5.24 are the Δμ curves for the Pt/C (E-TEK) catalyst samples as a function of H₃PO₄ concentration. The signatures at 0.01V and 0.24V correspond very well to H/Pt adsorbed at 3-fold sites. As expected, the magnitude of the signature of H/Pt decreases as the potential is increased. For the data in pure 0.1M HClO₄, there is no signature for 0.54V, so it was used as the reference spectrum. In 0.1M HClO₄ + 100mM H₃PO₄, the lineshape at 0.54V has a small negative feature at ca. 0 eV followed by a small, broad positive feature of roughly the same magnitude at ca. 5 eV. Given that oxygen does not bond to the Pt surface at such low potentials, and that the magnitude of the positive feature is much smaller than for a strongly bonded
3-fold O/Pt, we believe that this is due to the more weakly bonded H$_2$PO$_4$/Pt with the oxygens occupying the 3-fold hollow sites on the Pt surface. This is very similar to the lineshape found previously for 3-fold Cl/Pt.\textsuperscript{13} As the potential is increased to 0.84V and 1.04V, the lineshape approaches the theoretical 3-fold mode in Figure 5.25, along with a negative peak close to 0 eV.

5.3.2 Study on PtNi/C catalysts designed aid in mediation of phosphate anions adsorption and better ORR catalytic performance

5.3.2.1 XRD

The XRD spectra are plotted in Figure 5.26. Both the pure Pt and the PtNi alloy nanoparticles have fcc crystal structure. The positions of the alloy diffraction peaks are shifted to higher diffraction angle compared to platinum, indicating contraction of the crystal lattice due to alloying. The important crystallographic parameters are summarized in Table 5.3.

5.3.2.2 Surface-sensitive studies: SEM imaging

The comparison of lower resolution (magnification 150,000) scanning electron microscopy (SEM) images is shown in Figure 5.27(a). Pt/C (E-TEK, 30%) has a particle size distribution (ca. 4nm). In contrast, Figure 5.27(b) manifests that the metal crystallites are located mainly, if not exclusively, on the edges of the carbon particles for the PtNi/C (BASF, ES391) catalyst. Also, there are domains where a large variation in nanoparticle size can be found.

5.3.2.3 CVs and RDE results with doping method
As shown in Figure 5.28 the upper limit of the potential sweep range was lowered slightly to 1.0 V (vs. RHE) to avoid possible catalyst degradation associated with Ni leaching. Despite the reduced voltage sweep range, the result for Pt was similar to that for the Pt disk electrode. The oxidation and reduction peaks around 0.8 - 0.9 V vs. RHE were clearly suppressed after the addition of 0.1M of H₃PO₄. On the other hand, with Pt-Ni (ES391), the impact of H₃PO₄ on the CV current was much smaller. However, the absence of oxidation and reduction peaks around 0.8 - 0.9 V (vs. RHE) does not necessarily mean that there are no OH groups adsorbed on the catalyst surface. Strong oxidation and reduction peaks are only indications of rapid increase and decrease of surface density of adsorbed OH groups. It is likely that a limited amount of adsorbed OH groups are still present on these catalyst surfaces over a rather broad potential range. This is the most plausible explanation for the observed hysteresis in the anodic and cathodic scans in the RDE measurement, which will be presented later for Pt and Pt-Ni nanoparticles. The added H₃PO₄ is likely to block active sites on Pt and Pt-Ni and slow down the ORR in a similar way. The effect appears to be large enough to impede the rapid adsorption of OH groups on both Pt and Pt-Ni. As a result, no distinct OH adsorption and desorption peaks can be easily recognized in the CV curves of either Pt or Pt-Ni after the addition of H₃PO₄.

We have used the hydrogen adsorption and desorption peaks in the lower potential range to determine the catalyst's electrochemically active surface area. Figure 5.29 illustrates how the total charge under these peaks (above the double-layer charging background) was calculated to obtain the total charge associated with
hydrogen adsorption and desorption. For better accuracy, both adsorption and desorption charges were calculated and the average value is used. For the Pt sample, the average charge calculated from two the hydrogen peaks is 130 C. Divided by the charge density of 210 C/cm² for atomically flat Pt surface, this yields a total Pt surface area of 0.62 cm². The geometric disk area is \( \pi (0.5/2)^2 = 0.196 \text{ cm}^2 \), and the total Pt mass in this sample is \( 5 \text{ g/cm}^2 \times 0.196 \text{ cm}^2 = 1.0 \text{ g} \). So the catalyst surface area normalized to the Pt loading is \( 0.62 \text{ cm}^2 / 1.0 \text{ g} \approx 62 \text{ m}^2/\text{g}(\text{Pt}) \). For the Pt-Ni sample (ES391), the average charge calculated from the two hydrogen peaks is 100 C, and the corresponding surface area of Pt is 0.48 cm². Note this area does not include the area occupied by Ni because hydrogen does not adsorb to Ni. Assuming 80% of the surface area is occupied by Pt and 20% of the area is occupied by Ni (this ratio was also measured with Cu under-potential deposition and CO stripping), we estimate that the total catalyst surface area including Ni is \( 0.48 \text{ cm}^2 / 0.8 = 0.60 \text{ cm}^2 \). Thus, the two samples under investigation had about the same total surface area.

Figure 5.30 shows the kinetic current on the logarithmic scale versus the potential. The kinetic current \( I_K \) is derived as follows:

\[
I_K = \frac{I_{\text{Diffusion}} I_{\text{Disk}}}{I_{\text{Diffusion}} - I_{\text{Disk}}} \tag{5.7}
\]

where \( I_{\text{Disk}} \) refers to the measured disk current, and \( I_{\text{Diffusion}} \) refers to the diffusion limit current (the saturation disk current at the potential of 0.35V vs. RHE will be used as the diffusion limit current). The CV contribution has been subtracted from the disk current for the calculation of kinetic current.
In this experiment, Pt-Ni exhibited superior catalytic performance to Pt, which has been also observed by others.\textsuperscript{53} The addition of 0.1M of H\textsubscript{3}PO\textsubscript{4} resulted in a drastic decrease of the kinetic current of both Pt and Pt-Ni. Nevertheless, in the presence of 0.1M of H\textsubscript{3}PO\textsubscript{4}, Pt-Ni still demonstrated higher kinetic current than Pt by approximately a factor of 2. Hysteresis between the anodic and cathodic scans was observed in all cases, suggesting the presence of adsorbed OH groups on the catalyst surfaces over a broad potential range for both Pt and Pt-Ni. The typical shift of potential between the anodic and cathodic scans at the same \( I_k \) value was less than 20 mV. This is much smaller than the potential shift (from 40 to 60 mV) observed earlier with the bulk Pt disk, mainly because of the different sweep range. In the experiment with the Pt disk, the upper limit of the sweep range was 1.2 V vs. RHE, which resulted in stronger hysteresis in the ORR current.

In the small-current regime, the relation between the ORR kinetic current and the potential \( E \) can be expressed as

\[
E = E_0 + b \log \left( \frac{I_k}{i_0 A} \right)
\]  
(5.8)

where \( E_0 \) stands for the equilibrium open-circuit potential (\( E_0 = 1.229 \) V vs. RHE under standard conditions), \( b \) is the Tafel slope, \( A \) is the catalyst's surface area, and \( i_0 \) is the exchange current. From curve fitting shown in Figure 5.31 (anodic scan only), we find that the Tafel slope remains about the same in all cases, and the value is \(-75 \pm 5\) mV/dec (derived from curve fitting in the potential range from 0.92 to 0.99 V vs. RHE). Some fluctuations of the Tafel slope from individual scans were within the
experimental error range. The same curve fitting procedure also yields the exchange current \( i_0 \), which is a good quantitative assessment of the catalytic performance. The surface area \( A \) had previously derived from the hydrogen adsorption and desorption peaks in CV (0.62 cm\(^2\) and 0.60 cm\(^2\) for the Pt and Pt-Ni samples, respectively). Another useful parameter to assess the catalytic activity is the kinetic current \( I_K \) normalized to the Pt loading at the potential of 0.9 V vs. RHE. This will be denoted \( i_{900\text{mV}} \). These results are shown in Table 5.4.

5.3.2.4 ORR studies of catalysts in concentrated phosphoric acid (H\(_3\)PO\(_4\))

As seen in Figure 5.32, experiments using a flat Pt electrode disk demonstrate the capability of sleeveless RDE to measure disk currents \( (I_D) \) at various rotation rates at elevated temperature (50ºC) in concentrated phosphoric acid (91%). Based on the hydrodynamics of a rotating disk there are two possibilities to obtain the kinetic parameters of the ORR from the measured disk current. As already mentioned in the previous section, one option is to correct the disk current with the diffusion limited current \( I_{\text{Diffusion}} \).

\[
\frac{1}{I_D} = \frac{1}{I_K} + \frac{C}{\omega^{0.5}} \quad (5.9)
\]

Another way is, based on the Koutecky-Levich equation, to plot the inverse disk current versus the inverse square root of the rotation rate \( (\omega^{-0.5}) \). A linear fit for a certain potential intercepts the vertical axis and yields the kinetic current \( I_K \) at that potential. The Koutecky-Levich plot of the data shown in Figure 5.32 is presented in Figure 5.33. From the semi-log plot of the potential versus the kinetic current shown
in Figure 5.34, we derived a Tafel slope of 122mV/decade. Similar values had been reported in the literature\textsuperscript{54, 55}. At the potential of 900 mV vs. DHE we obtained a kinetic current of 15\(\mu\)A.

As shown in Figure 5.33, the Koutecky-Levich analysis agrees well with the disk currents that were corrected with the diffusion limit in the small-current regime. Therefore, we conclude that the hydrodynamic laws used for the traditional RDE are also valid for Sleeveless RDE. The result of sleeveless RDE measurements of catalysts in concentrated phosphoric acid for 50°C is presented in Figure 5.35. Consistent with the RDE room temperature measurements in 0.1M perchloric acid with small amount of added phosphoric acid (see Figure 5.30), Pt-Ni/C (ES391) exhibits a higher catalytic activity for the oxygen reduction reaction than Pt/C. At a cell potential of 900mV (vs. DHE) the kinetic current for Pt-Ni/C (ES391) is larger than that of Pt/C by a factor of 1.7. The fitted Tafel slopes as well as the calculated normalized kinetic currents \(I_K\) at 900 and 800mV (vs. DHE) are shown in Table 5.5.

5.3.2.5 \(\Delta\mu\)-XANES results

Figures 5.36 and 5.37 contain the \(\Delta\mu\) curves for Pt-Ni/C (BASF) in pure 0.1M HClO\(_4\) without and with100mM H\(_3\)PO\(_4\) respectively. It is remarkable that there is little difference, if any, between the two sets of data. The main difference seems to be in the amount of the H/Pt adsorbed onto 3-fold sites at 0.01 and 0.24V. This is reduced in intensity by ca. 25%, most probably due to adsorbed PO\(_4^{3-}\)/Pt at these low potentials. However, it appears that at higher potentials, the ligand effect exerted by nickel on platinum increases and reduces dramatically the amount of adsorbed PO\(_4^{3-}\)/Pt. It was
found earlier that the ligand effect exerted by Ni and other transition metals on Pt keeps O(H) off the surface until higher potentials\textsuperscript{26}, but this is the first instance where we have evidence that it is also effective in keeping PO\textsubscript{4}\textsuperscript{3-} ions away from the surface.

Finally, as the potential is increased from 0.54V to 1.04V, the classic transition in lineshape\textsuperscript{24} from atop O(H)/Pt to strongly adsorbed 3-fold O/Pt is seen. To make this more apparent, the spectral lineshapes at 0.54V for the two catalysts are compared (see Figure 5.38). The lineshape for the adsorption of PO\textsubscript{4}\textsuperscript{3-}/Pt as described above is clearly seen for Pt/C whereas it is completely different in the case of the Pt-Ni/C. In fact, it resembles very strongly the lineshape found previously for atop O(H)/Pt\textsuperscript{24} suggesting that the processes occurring on the surface of Pt-Ni/C even in the presence of phosphate anions are very similar to those occurring in pure 0.1M HClO\textsubscript{4}.

An alternate, more revealing representation of the above data is presented by plotting the intensities of the lineshapes as a function of potential (Figure 5.39 and Figure 5.40). The effect of concentration on phosphate anion adsorption on platinum is highlighted in Figure 5.39 while the difference in activities between the Pt/C (E-TEK) and the Pt-Ni/C (BASF) are seen in Figure 5.40. While the changes in intensity in $\Delta\mu$-XANES curves do not quantitatively mirror the coverage of adsorbed species, it does furnish a good qualitative estimate. Because the features at 0.84V and 1.04V can be unambiguously be assigned chiefly to O(H)/Pt and O/Pt, only these two intensities are plotted as a function of potential and H\textsubscript{3}PO\textsubscript{4} concentration. As there is still adsorbed 3-fold H/Pt at 0.01V and 0.24V, the O coverage (and hence, intensity) is assumed to be 0 at these potentials. Figure 5.40 shows the effect of concentration on
the coverage of O(H) and O on Pt as a function of H$_3$PO$_4$ concentration. Except for one data point (1mM H$_3$PO$_4$ at 0.84V), it is immediately seen that at higher potentials, the amount of oxygen on the surface is the same within the entire concentration range of H$_3$PO$_4$ used for the experiments. This suggests either that the amount of PO$_4^{3-}$ ions on the Pt surface is insensitive to any increase in concentration exceeding 1mM H$_3$PO$_4$ or that O(H) and O species can only displace a certain fraction of adsorbed PO$_4^{3-}$/Pt regardless of the actual number of phosphate ions on the surface of the catalyst. Figure 5.40 highlights the difference in activity between the Pt/C (E-TEK) and the Pt-Ni (BASF) catalyst samples. Note the difference between the two catalysts in pure 0.1M HClO$_4$ and in the presence of 100mM H$_3$PO$_4$. While the difference is obvious for Pt/C, indicating the susceptibility to poisoning due to adsorbed PO$_4^{3-}$/Pt, the curves are virtually similar in the case of the Pt-Ni sample. As mentioned earlier, this is attributed to the ligand effect exerted by nickel on platinum which allows it to keep off PO$_4^{3-}$ from the Pt surface, and thus we see the same amount of O(H) and O/Pt even in the presence of a significant amount of phosphate ions (100mM).

5.4 Conclusions

The kinetics of the oxygen reduction reaction on Pt single crystal electrodes with different orientation surfaces is affected variously by adsorption of phosphate anions. The ORR still maintains first order kinetics with respect to the diffusion limited reactant (O$_2$) and proceeds in a 4-electron pathway to water as the main product on all Pt single crystals at the potentials studied. However, the Pt(111) surface, comprised
mostly of 3-fold sites, presents the greatest decline in kinetics and smallest deviation of Tafel slopes as determined using a hanging meniscus RDE measurement after addition of varying amounts of H$_3$PO$_4$ into the 0.1M HClO$_4$ solution. Adsorption induced surface reconstruction was found only on Pt(100) with the evidence that the surface cannot be recovered by washing the surface with clean water. PtSn(111) shows better ability for inhibition of phosphate anions adsorption by means of introducing steps and defects. The kinetics of ORR on the different Pt single crystal surfaces with and without H$_3$PO$_4$ in electrolyte were studied with electrochemical impedance spectroscopy (EIS). The results showed that the poisoning of H$_2$PO$_4$ for ORR strongly depends on the Pt single crystal surface structures, and the smallest charge transfer resistance($R_{CT}$) was obtained with Pt(110) surface, suggesting the optimal catalytic surface for ORR among the low-index platinum single crystal surfaces. The effect of H$_2$PO$_4$ ion poisoning on Pt/C (E-TEK) was also studied using in situ X-ray absorption spectroscopy $\Delta \mu$ -XANES results strongly suggest that adsorption of phosphate anions occurs mainly on 3-fold hollow sites on Pt surface.

SEM images indicate that the Pt-Ni/C (BASF) catalysts are smaller in size when compared with the Pt/C (E-TEK) samples. This is consistent with the Scherer analysis from XRD data which reveals that the sizes for the two catalysts are 3.3 and 4.1 nm for the BASF and E-TEK samples respectively. This is very interesting as it suggests that even smaller Pt-Ni/C particles, which should be more reactive than the larger Pt/C (E-TEK) samples, are less susceptible to PO$_4^{3-}$ anion adsorption. This obviously advantageous effect should be magnified if catalysts of the same size were to be
compared for performance.

The effect of PO$_4^{3-}$ ion poisoning on two catalysts, Pt/C (E-TEK) and Pt-Ni/C (BASF), was studied using RDE, high temperature half cell and in situ X-ray absorption spectroscopy. It has been demonstrated that PtNi/C shows better kinetics and stability performance than Pt/C towards the ORR in concentrated H$_3$PO$_4$ solution at room temperature and at elevated temperature. Cu UPD and CO stripping methods have been used to indentify surface elemental ratio in the electrochemical environment. It has been found that a quarter of the surface sites were occupied by Ni, which results in lower availability of 3-fold Pt sites on the surface. The $\Delta \mu$ XANES data revealed that the oxygen coverage on the Pt/C catalysts was the same over the entire range of concentration of H$_3$PO$_4$ investigated. It also suggests that O(H) and O species are able to displace a only a finite fraction of the adsorbed PO$_4^{3-}$/Pt at any concentration above 1mM H$_3$PO$_4$. Further, it was found that despite being smaller than the Pt/C (E-TEK) catalysts, the Pt-Ni/C (BASF) catalysts are less susceptible to PO$_4^{3-}$ anion adsorption/poisoning. The data suggest that this effect is more apparent at higher potentials. It also appears that PO$_4^{3-}$ is able to adsorb at lower potentials and therefore, more readily than HSO$_4^-$. This is consistent with previous findings where it was shown that HSO$_4$/Pt is only ‘seen’ on the surface after some O(H) adsorption (>0.70V), thereby allowing the ions to orient and ‘lock’ onto the surface more easily. It is also confirmed that the strength of adsorption of ions on the Pt surface decreases in the order PO$_4^{3-}$ > HSO$_4^- >$ ClO$_4^-$. To conclude, owing to lower susceptibility to poisoning by PO$_4^{3-}$ ions, the Pt-Ni (BASF) catalysts can be expected to perform better
than the Pt/C (E-TEK) catalysts in a PAFC.
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5.6 Chapter 5 Figures:

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### 5.6 Chapter 5 Tables:

#### Table 5.1 Surface and bulk information of Pt/C and PtNi/C samples

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<th>Sample provided</th>
<th>Pt% (atomic percentage, total metal based) in bulk (from EDS)</th>
<th>Pt% coverage on surface (atomic percentage, total metal based) (from CO stripping)</th>
<th>Pt% coverage on surface (atomic percentage, total metal based) (from Cu UPD)</th>
<th>Real surface area of Pt (m²/g)</th>
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<td>76.9</td>
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Table 5.2 Kinetic parameters for ORR on Pt(100), Pt(110), Pt(111) and PtSn(111) single crystals electrodes in 0.1M HClO₄ with addition of different amounts of H₃PO₄

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<th>E₁/₂ (V)</th>
<th>Slope of tafel plots, 900rpm (mV decade⁻¹)</th>
<th>Rate constant k (cm s⁻¹) @0.7V</th>
<th>Kinetics current <a href="mailto:density@0.85V">density@0.85V</a>, 900rpm (mA cm⁻²)</th>
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Table 5.3 Crystal structure and lattice parameters for Pt/C (E-TEK, 30%) and PtNi/C (BASF, ES391)

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<th>Lattice parameter /Å</th>
<th>Pt-Pt bond distance / Å</th>
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Table 5.4 Kinetics parameters obtained from ORR experiments at room temperature

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<th>$I_{a990mV}$ (A/g-Pt)</th>
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<td>0.1M HClO$_4$</td>
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<td>Pt/C</td>
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<td>Pt-Ni (ES391)</td>
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Table 5.5 Parameters obtained from ORR experiments at 50 °C

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Chapter 6
Summary and Suggested Future Work

6.1 Summary

A tremendous acceleration in research dedicated to development of catalytic materials used in low and moderate temperature fuel cells has been witnessed in the last decade. Novel synthesis strategy and fundamental characterizations are essential in making groundbreaking progress of these new materials for fuel cell application. In this dissertation, a detailed study on the micro-emulsion method for synthesis of nano alloy with particle size, surface structure and morphology designed was undertaken. A specially designed PtAu@Ru/C core-shell electrocatalyst was prepared for the purpose of enhancing the stability of Ru at DMFC running conditions. The material showed not only outstanding stability but also unexpected better intrinsic catalytic activity than commercial PtRu/C towards electrooxidation of methanol in acid media. Furthermore, in order to fulfill the goal of breakage of the bonds between ethanol's carbon atoms during ethanol electrooxidation, which is believed to be the one of the main challenges of successful application of direct ethanol fuel cells, a novel mediated catalyst of Pb(IV) based redox couple was developed. The concept of a heterogeneous redox process coupled to a homogeneous reaction was proved to be very successful to improve the C-C bond breaking efficacy. Most surprisingly, this enhancement effect is durable as long as there is presence of Pb(IV) mediator in the electrolyte. Lastly, the work was extended to exploration and study on cathode materials which need to sustain severe anion poisoning,
low pH and relatively high temperature in phosphoric acid fuel cells. The following sections outline the main results obtained from the research for this dissertation.

### 6.1.1 Studies of kinetics and parallel pathways for oxygen reduction reactions on carbon supported Pt and PtCo catalysts prepared by micro-emulsion method

The power density and efficiency of PEMFCs depend to a large extent on the inherent electrocatalytic properties of the catalysts. Various Pt based alloy catalysts\(^1\)-\(^7\) have been developed and show enhanced catalytic activity compared to Pt/C towards oxygen reduction reaction in PEMFC. The first reported systematic study of the ORR on Pt alloys was conducted by Mukerjee et al.\(^8\),\(^9\). Five binary alloys of Pt with first row transition elements ranging from Cr to Ni were investigated. All the alloy electrocatalysts were found to enhance ORR activity albeit to different extents. The role of alloying element in engendering enhancement of ORR catalytic activity in Pt based alloy catalysts has been ascribed to a decrease of the desorption free energy (\(\Delta G_{\text{ads}}\)) of oxide species on Pt, particularly OH. The fact can be associated to the following effects: (i) electronic factors\(^10\) (higher Pt 5d band vacancy for the alloys in the oxidized state); (ii) geometric effects\(^4\) (shorter Pt-Pt bond distance and coordination number) and metal particle size effects\(^11\); (iii) other effects (ensemble effects\(^12\), surface segregation effects\(^7\), lower activity of water effect\(^13\), etc). However, not sufficient work has been done on understanding the parallel pathways leading to peroxide yield which is believed to be the most important element for membrane degradation.\(^14\),\(^15\) Consequently, a primary motivation of this work is to understand how crystal structure and surface composition of Pt based catalysts affect ORR kinetics and concomitant peroxide yield. Among the methods to prepare carbon supported Pt alloy catalysts, micro-emulsion is one desirable
and convenient way to provide the twin advantage of size control and phase purity of the alloy formed. Another advantage of this method is that nano alloy can be formed at room temperature so that sintering and agglomeration of nanoparticles can be avoided during high temperature treatment required for other conventional methods. The following conclusions can be drawn from these studies:

(i) The formation of Pt and PtCo nanoparticles in micro-emulsion systems was confirmed clearly by UV-vis. Pt or PtCo particles of as-synthesized catalysts were nano-scale, irregular polyhedron and uniformly distributed on the support. However, the Pt particle size is dependent on both crystal formation rate and $\omega_0$ (molar ratio of water to the surfactant). A minimum average particle size of 5.6nm was presented when $\omega_0$ reached 8. A modified sequential procedure was used to synthesize PtCo/C and achieved lower Co/Pt ratio and smaller particle size than its counterpart by simultaneous procedure.

(ii) Pt/C catalysts prepared with different $\omega_0$ in micro-emulsion systems showed almost the same crystalline parameters. However, the ECA-specific activity of as-synthesized Pt/C catalysts for ORR decreases as particle size of Pt decreases. Better kinetics performance towards ORR was shown for PtCo/C synthesized by micro-emulsion system comparing with the commercial Pt/C catalyst. PtCo/C-SB synthesized in alkaline media with simultaneous procedure shows the highest mass activity and specific activity. Some general trends have been summarized: PtCo/C-SB > PtCo/C–S > PtCo/C-T ~ PtCo/C-TB ~ PtCo/C-TH > Pt/C (E-TEK) > PtCo/C-SH (Mass Activity); PtCo/C-SB > PtCo/C-TB > PtCo/C-TH ~ PtCo/C–S > PtCo/C-T ~ PtCo/C-SH > Pt/C (E-TEK) (Specific Activity).
(iii) Peroxide yield detected by RRDE technique was found to be dependent on Pt particle size. As it can be seen in Table 6.1 the sequence of $\text{H}_2\text{O}_2$ yield during the ORR on Pt/C ($\omega_0=5$, $\omega_0=8$, $\omega_0=11$) has been correlated with the particle size of the catalysts very well. Insignificant peroxide yield was found for ORR on as-synthesized PtCo/C catalysts, which suggests that overwhelming ORR was undergoing a 4 electrons pathway. R values representing a measure of Co surface composition were obtained from ratio of integration of oxidized peak related to Co and $\text{H}_{\text{upd}}$ region of Pt. The results show good correlation with S.A. of different PtCo/C catalysts and $\text{H}_2\text{O}_2$ yield. The catalyst of PtCo/C-SB gives the highest peroxide yield along with the best performance towards ORR and highest presence of surface cobalt. A sacrificial Co oxidized effect on inhibition of adsorption of OH may be an explanation to higher catalytic properties and higher $\text{H}_2\text{O}_2$ yield of Pt based alloy catalysts.

6.1.2 Durability Studies for PtAu@Ru/C core-shell catalysts for methanol electrooxidation

The PtRu alloy is still the state-of-the-art anodic catalyst for electrooxidation in DMFCs due to its effective CO tolerance. Nevertheless, a large obstacle to the successful application and widespread use of PtRu bimetallic catalysts is the eventual dissolution of the metallic components of the catalyst. Previous Studies in our group have shown that Ru may migrate through the membrane and migrate to cathode of DMFC leading to Ru crossover losses where ORR kinetics is severely affected with the presence of even micro molar concentration of Ru as shown in Figure 6.1. To enhance the stability of PtRu catalysts that results from either chemical or morphological alteration in the materials during the course of fuel cell operation are of superior importance for
commercial acceptance. Eventually, a successful example\(^{18}\) of stabilization of Pt with gold cluster inspired us to explore the possibility of enhancing the stability of PtRu alloy catalysts through the synthesis of a ternary PtRuAu alloy. In this work, sequential reduction associated with the micro-emulsion method was used to synthesize PtAu core with Ru shell (PtAu@Ru/C) catalysts followed by heat treatment at 220 \(^{\circ}\)C. The excellent catalytic activity towards methanol oxidation and high stability of Ru in acid media of the PtAu@Ru/C electrocatalyst were investigated through electrochemical characterization, Cu UPD measurements and in-situ XAS measurements. Some preliminary results can be found as follows:

(i) PtRu supported on carbon catalysts were synthesized in AOT/cyclohexane micro-emulsions and heated at different temperature. Good alloy of PtRu can be formed even at room temperature. Surface segregation happens when temperature of heat treatment increases. It has been found that PtRu/C catalyst heated at 220 \(^{\circ}\)C shows the highest activity and stability towards methanol oxidation in 0.5M H\(_2\)SO\(_4\). PtAu core-Ru shell could be synthesized under the same reaction conditions. The PtAu@Ru/C catalyst was found to be remarkably resistant to Ru dissolution with marginal change on the surface area from Cu UPD measurement and therefore, quite stable during long term chronoamperometric measurements, a result which we hope will fuel further efforts to correctly understand aging mechanisms in catalytic studies and thus, help us to successfully address the problem of Ru dissolution in the application of PtRu catalysts towards the widespread use of direct methanol fuel cells.

(ii) This enhanced stability is attributed to both, a size-effect and the composition, more specifically, due to the alloying with Au which stabilizes the surface
composition of the nanoparticles. As a direct proof, in-situ XAS results have shown that the oxide growth on Au stabilized PtRu is slower compared to the corresponding E-TEK PtRu catalyst suggesting a clear increase in Ru oxidation potential in the presence of Au. The Ru-Ru bond distance does not change notably regardless of ascending potentials.

6.1.3 Comments on development of novel electrocatalysts for electrooxidation of ethanol in alkaline fuel cell

With the advent of anion exchange membranes preferred to the liquid electrolyte, the problem of carbonate formation can be surmounted making thereby the application of small organic molecules (alcohol) as fuels feasible. Considering the fuel for AEMFC, ethanol is environmental friendly and offers higher energy density against methanol. However, the oxidation of ethanol presents additional complication in the sense that a C-C bond must also be cleaved in order to accomplish full oxidation to CO$_2$. The successful application of DEFC has been impeded by inefficient oxidation of ethanol, poisoning of electrodes by strongly adsorbed species and low Faradaic efficiency. Given the fact that the majority of the oxidation products of electro-oxidation of ethanol on the state-of-the-art Pt based alloy catalysts are still the species containing C-C bond, introduction of species to the electrochemical reaction environment which may not only initiate the C-C bond cleavage to enhance the activity of the catalysts but also weaken CO or other organic species poisoning is thought to be one of the most attractive routes to improve the C-C bond breaking efficiency.

Ethanol electro-oxidation on Pt/C was studied in the presence of millimolar quantity of a polyvalent metal ion complex using chronoamperometry. Significant increase in steady state currents was achieved in the presence of the polyvalent metal ion
complex, which stands for excellent sustainability of working electrode and high efficiency of electrooxidation of ethanol. The promoting mechanism of Pb(IV) towards electro-oxidation of ethanol is not clear at this stage. One hypothesis that Pb(IV)/Pb(II) acts as heterogeneous redox couple has been proposed and can be seen in Figure 6.2, where we can clearly see how the mediated system distinguish from the previous direct electron transfer system and how it take effect on cleavage of C-C bond in ethanol.

6.1.4 Towards mediation of corrosion and phosphate anion poisoning to cathodic Pt/C catalysts in phosphoric acid fuel cell

One major factor that limits the performance of PAFCs is the sluggish kinetics for oxygen reduction reactions (ORR) in H₃PO₄, and this is attributed primarily to the poisoning effects of phosphate ion adsorption (H₂PO₄⁻) on ORR activity. In this work, the results from the hanging meniscus rotating disk electrode measurement have demonstrated that the kinetic current for ORR decreased dramatically on Pt(100), Pt(110), Pt(111), and PtSn(111) single crystals even with the addition of a small amount (1 mM) of H₃PO₄ into the perchloric acid solution, most probably due to the adsorption of phosphate anions onto the Pt active sites that impeded the electroreduction of O₂. As one of the approaches to overcome this problem, Pt transition metal alloys have shown the tendency to mitigate the anion species adsorption on Pt surface in acid media and expose more active sites to facilitate the coverage of O₂ molecules and increase the likelihood of its dissociation. In this study, a Pt based Ni alloy catalyst was synthesized in house using components that may possess novel functions. The catalysts developed and other standard catalysts were characterized with XRD, XPS and SEM for a thorough structure property relationship. An array of electrochemical investigations in various
concentrations of H$_3$PO$_4$ was performed to understand the mechanism of phosphate anions adsorption on as-synthesized catalysts. Detailed electrochemical and X-ray absorption spectroscopy (XAS) investigations have been carried out on our electrocatalysts under *in-situ* conditions. Using the $\Delta \mu$-XANES analysis, it was found that despite being smaller than the Pt/C (E-TEK) catalysts, the Pt-Ni/C catalysts are less susceptible to PO$_4^{3-}$ anion adsorption/poisoning. The data suggests that this effect is more apparent at higher potentials. It also appears that PO$_4^{3-}$ ions are able to adsorb at lower potentials and therefore, more readily than HSO$_4^-$ ions. This is consistent with previous findings where it was shown that HSO$_4^-$/Pt is only ‘seen’ on the surface after some O(H) adsorption (>0.70V), thereby allowing the ions to orient and ‘lock’ onto the surface more easily. It is also confirmed that the strength of adsorption of ions on the Pt surface decreases in the order PO$_4^{3-}$ > HSO$_4^-$ > ClO$_4^-$ . To conclude, owing to lower susceptibility to poisoning by PO$_4^{3-}$ ions, the Pt-Ni catalysts can be expected to perform better than the Pt/C (E-TEK) catalysts in a PAFC.

Besides, there remains another major problem of electrode materials degradation in low pH and high temperature environment. As far as Pt and Pt based alloys are concerned, sintering/agglomeration, dissolution of metals into electrolyte and some other deteriorative issues usually happen during long term operation of fuel cells. In order to improve the stability of Pt catalysts for use in PAFCs, we prepared Pt/C and PtMO$_2$/C (M=Ce, Zr or Ce$_{0.9}$Zr$_{0.1}$) samples and characterized their physical and electrochemical properties. It is very interesting to find that a higher dispersion of Pt is maintained during durability tests when metal oxides are used in conjunction with Pt even though the metal oxide dissolves to some extent. During the 24 hours chronoamperometric tests at 0.88V
in hot concentrated $\text{H}_3\text{PO}_4$, the performance of PtCeO$_2$/C was similar with Pt/C facing serious reduction of power density. By means of incorporation of Zr with lower value of point of zero charge, PtZrO$_2$/C manifested better ECA retention than PtCeO$_2$/C and Pt/C after the CA tests due to an “anchor effect”. Interestingly, PtCeZrO$_2$/C gave the highest steady state current during the CA test as well as excellent sintering and corrosion resistance with the evidences of small reduction of ECA and power density. The structure modification or mixed oxides passivation are believed to take effect on preventing the catalyst nanoparticles from sintering in rather critical environment.

6.2 Suggestions for Future work

6.2.1 Optimization of reaction conditions for micro-emulsion synthesis method

At present only small amount of catalysts can be synthesized in house using the micro-emulsion synthesis procedure. For example, it requires more than 1 liter of organic solvent to prepare 200 mg of Pt nanoparticles in one batch. It is because that the concentration of the oil phase with the surfactant of AOT dissolved in cyclohexene cannot reach more than 0.2 M in order to avoid difficulty to form stable reverse micelles after the introduction of the water phase. In addition, plenty of acetone has to be used to wash the surfactant off the products. As such, it is necessary to find alternatives for AOT/cyclohexene system for lowering the consumption of organic solvent.

6.2.2 Exploring the mechanism for unexpected enhancement of catalytic activity of Au stabilized PtRu catalysts for methanol oxidation along with significantly improved stability
Further work is underway to systematically investigate whether the Au is really aiding the catalysis at all and if so, to what extent and also to determine the nature of the effect of surface Au on the methanol oxidation properties of PtRu catalysts in acid medium. Surface characterization techniques such as HR-TEM and XPS for gaining insight into the structure of matter on the atomic level are needed for further detailed study.

### 6.2.3 Real application of Pb(IV)/Pb(II) mediated system in direct ethanol alkaline fuel cells

Although it is a tremendous breakthrough to break C-C bond of ethanol during the electrooxidation at room temperature by means of adding mill molar amount of Pb(IV) salts into the alkaline solution, the success has been limited in high pH environment. For instance, the current did not change during CA test on Pt/C electrode in 1M HClO₄ + 1M ethanol after putting 1mM of lead acetate in. Accordingly, the Pb(IV) mediator can only take effect in alkaline solution due to poor solubility in water or acid media.

Obviously it is not practical to pump KOH solution through the next generation anion exchange membrane fuel cells. One feasible strategy to overcome this problem is to immobilize Pb on sites close to the hydroxyl groups on the anion exchange membrane with structure shown in Figure 6.3. It is indispensable to improve technologies aimed at achieving equal accessibility to electrolyte and liquid phases for all catalyst-containing parts and a tight contact between the Pt/C catalysts, ethanol reactant, and the Pb(IV) mediators embedded in the membrane.

### 6.2.4 Durability investigations on metal oxides promoted Pt/C cathodic catalysts used in phosphoric acid fuel cells
Since the basic concept of inhibiting Pt particle growth with metal oxides is established, and some of these materials were already screened for durability in phosphoric acid, advancement in the understanding of this phenomenon and exploration of new materials with significantly improved durability properties are needed. More rigorous durability testing (cycling, etc.) or validation in fuel cells would demonstrate a practical advance, or at least a path forward to a practical advance. It is very interesting to use more chemically sensitive techniques than TEM or XRD to show the Pt durability persists long after the disappearance of the metal oxides.
6.3 Chapter 6 References:


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22. N. M. Markovic; H. A. Gasteiger; P. N. Ross; X. Jiang; I. Villegas; M. J. Weaver, Electro-oxidation mechanisms of methanol and formic acid on Pt-Ru alloy surfaces _Electrochim Acta_ **1995**, *40*, 91-98.
Figure 6.1 Mass transport-corrected Tafel plots for oxygen reduction on a thin film 30 wt. % Pt/C, 0.28 cm², 15 µgPt cm⁻² GC and PtRu black electrode in O₂-saturated 0.5 mol dm⁻³ H₂SO₄ solution containing dissolved Ru species in various concentrations. The inset shows the corresponding changes to the mass-specific kinetic current densities of oxygen reduction on Pt as a function of Ru concentration of the electrolyte at three electrode potentials.
Figure 6.2 Tunable redox mediator-Catalyzed Electron Transfer

Direct Electron Transfer

Mediated Electron Transfer

Strong adsorption

Weak C-C bond

OH⁻

CH₃CHO

CH₃COOH

OH⁻

CO₂ + H₂O

M(ox⁺)

M(red⁺)

ne⁻
n’e⁻
Figure 6.3 OH\textsuperscript{−} form of alkaline anion exchange poly ether sulfone
6.5 Chapter 6 Tables:

Table 6.1 Particle size and peroxide yield for Pt/C catalysts by micro-emulsion method with different $\omega_0$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystallite Size/ nm</th>
<th>$\text{H}_2\text{O}_2% @0.4\text{V (vs. RHE)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C ($\omega_0$=5)</td>
<td>6.9</td>
<td>4.6</td>
</tr>
<tr>
<td>Pt/C ($\omega_0$=8)</td>
<td>4.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Pt/C ($\omega_0$=11)</td>
<td>6.1</td>
<td>4.1</td>
</tr>
</tbody>
</table>
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