STUDY OF PLATINUM-FAMILY CATALYSTS IN DIRECT METHANOL FUEL CELL AND PARAHYDROGEN-INDUCED HYPERPOLARIZATION APPLICATIONS

By

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To my loving father, mother, family, and friends for their love, sacrifice, and full support
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<td>ACL</td>
<td>Anode catalyst layer</td>
</tr>
<tr>
<td>AFC</td>
<td>Alkaline fuel cell</td>
</tr>
<tr>
<td>AGDL</td>
<td>Anode gas diffusion layer</td>
</tr>
<tr>
<td>ALTADENA</td>
<td>adiabatic longitudinal transport after dissociation engenders net alignment</td>
</tr>
<tr>
<td>CCL</td>
<td>Cathode catalyst layer</td>
</tr>
<tr>
<td>CFC</td>
<td>Cathode flow channel</td>
</tr>
<tr>
<td>CGDL</td>
<td>Cathode gas diffusion layer</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DEMS</td>
<td>Differential electrochemical mass spectrometric</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct methanol fuel cell</td>
</tr>
<tr>
<td>EASA</td>
<td>Electrochemical active surface area</td>
</tr>
<tr>
<td>HFC</td>
<td>Hydrogen fuel cell</td>
</tr>
<tr>
<td>H_{upd}</td>
<td>Hydrogen underpotential deposition</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>LBL</td>
<td>Liquid barrier layer</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>LVADT</td>
<td>Low voltage accelerated durability test</td>
</tr>
<tr>
<td>MCFC</td>
<td>Carbonate fuel cell</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrolyte assembly</td>
</tr>
<tr>
<td>MEK</td>
<td>Methyl ethyl ketone</td>
</tr>
<tr>
<td>MEM</td>
<td>membrane</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
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<td>PAFC</td>
<td>Phosphoric acid fuel cell</td>
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<td>PASADENA</td>
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<td>PEMFC</td>
<td>Polymer electrolyte membrane fuel cell</td>
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<tr>
<td>PHIP</td>
<td>Parahydrogen-induced polarization</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disk electrode</td>
</tr>
<tr>
<td>rEASA</td>
<td>Relative electrochemical active surface area</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>SLPM</td>
<td>Standard liter per minute</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TOF</td>
<td>Turnover frequency</td>
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<tr>
<td>TPR</td>
<td>Temperature programmed reduction</td>
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Platinum is an important and widely used metal, which finds many applications in various catalytic processes. In this study, platinum and iridium catalysts were investigated in two different applications: as electrocatalysts in a direct methanol fuel cell and as hydrogenation catalysts in parahydrogen-induced polarization (PHIP), an important NMR signal enhancement technology.

The success of direct methanol fuel cell (DMFC) technology depends largely on the platinum electro-catalyst. A low-voltage accelerated durability test method, together with various other electrochemical measurements, was employed to study the anode/cathode degradation in four commercial anode catalysts. It was found that two anode catalysts from Johnson Matthey Co. demonstrated higher anode activity than the two anode catalysts from Tenaka Co. and Cabot Co. Between the two Johnson Matthey catalysts, the stabilized DMFC anode catalyst, ELE170, demonstrated the best degradation resistance properties among the four anode catalysts investigated. Efforts have also been devoted to determining the effects of contaminants, such as methyl ethyl ketone (MEK), on the oxygen reduction reaction (ORR) in the direct methanol fuel
cell cathode reaction. In this study, MEK was proved to negatively affect the ORR at the DMFC cathode. The rotating disk electrode data showed that the rate of oxygen reduction reaction can decrease by ~15-40% in terms of kinetic current density (corrected for transport limitation). This can translate into a ~15-30 mV overpotential penalty, upon introduction of 1 µM-1 mM MEK into an acidic electrolyte. This is the first report on the effects of MEK contamination on the ORR kinetics in the DMFC cathode.

Parahydrogen-induced polarization has been employed in homogenous processes, as an important technology to enhance NMR signals. PHIP requires pairwise hydrogen addition, where the two hydrogen atoms come from a single parahydrogen (nuclear spin isomer of hydrogen) molecule. When the two hydrogen atoms from parahydrogen are added pairwise and retain their spin correlation, the NMR signal is enhanced up to several orders of magnitude. PHIP provides a unique spectroscopic tool to study pairwise hydrogen addition kinetics. In this research, PHIP was used to study propylene hydrogenation over both platinum and iridium nanoparticles supported on TiO$_2$, and the PHIP effect was observed for the first time on iridium supported on TiO$_2$ catalyst. Pairwise hydrogen addition reaction selectivity was found to be temperature dependent for both catalysts.
CHAPTER 1
INTRODUCTION

1.1 Overview of Platinum Catalysts

Platinum, the most expensive of the widely traded precious metals, is of vital importance and interest to the modern evolving chemical industry for catalysis purposes [1, 2]. Because it was first discovered as a contaminant in South American gold mines in 1557, the metal was named after the Spanish term *platina*, which is literally translated into "little silver" [3]. Platinum is very resistant to corrosion, high temperature, tarnish and wear, which make it ideal for fine jewelry. Although it was primarily used to adulterate gold in the 16th to 17th centuries, platinum gained its own status and name as a desirable and decorative metal during the early 18th century in France [4]. From then on platinum became an important precious metal in the jewelry industry, as well as in the storage of wealth. Bearing so many similarities with gold, platinum earned another name ‘white gold’, which addresses the importance of the status of platinum as a precious metal commodity.

However, the decorative use of platinum metal has not been the driving force in the huge demand for this metal. With so many extraordinary characteristics of its own, such as low reactivity, remarkable resistance to corrosion even at high temperatures, stable electrical properties [5, 6], platinum is now widely utilized for industrial purposes.

After the Second World War, the price and demand for platinum escalated due to its important industrial application in catalysts. Since the 1970s, the automotive industry has become the largest demand for platinum. To accommodate the regulations on air quality, catalytic converters on automobile were introduced to reduce the polluting gas in automobile exhaust. Platinum is one of the most widely used catalysts in converters,
allowing complete oxidation of low concentrations of unburned hydrocarbons [7]. Platinum catalysts are also used in nuclear reactions, in crude oil refining process, and in many other petrochemical processes [8]. PtO₂, known as Adams’ catalyst, is used as a hydrogenation catalyst, specifically for vegetable oils [9]. Also, platinum is used extensively in many other applications, including laboratory equipment [10], electrical contacts [11] and electrodes [12].

In this study, two applications for platinum based catalysts were investigated: 1) Pt-based catalysts in direct methanol fuel cell research; 2) Pt-based catalysts for the parahydrogen-induced polarization reaction.

1.2 Pt-based Catalysts in Direct Methanol Fuel Cell Applications

As early as 1838, platinum was used by William Robert Grove (1811 -1896) in his development of an improved crude fuel cell battery [13]. Fuel cells are devices for generating electric power directly from chemical fuels. They share many properties of batteries - silent operation, eliminating moving parts, and use of an electrochemical reaction to generate power. However, unlike batteries, fuel cells requires no recharging and will run endlessly as long as they are supplied with fuel and have functional components. Of the various kinds of fuel cells, the proton exchange membrane fuel cell (PEMFC), which typically employs platinum catalysts, has attracted the most research interest. PEMFC fuel cells can run on hydrogen or methanols, which are the two most commonly used fuels. Because of their potential to replace the internal combustion engine in vehicles, hydrogen fuel cells are being studied in effort to reduce transportation related air pollution. Direct methanol fuel cells (DMFC) are especially suitable for applications as portable power sources, because they operate at low
temperature (typically 50-60°C) and because methanol is a liquid fuel which is easy to store, transport and handle in small fuel cell devices.

It has been acknowledged that the success of DMFC largely depends on two key components: the membrane and the electro-catalyst. Pt-based catalysts are the most used for both anode and cathode reactions in DMFC designs. Due to their desirable catalytic and electrical characteristics [14-16].

1.2.1 Pt-based Catalysts in DMFC Anode Application

There has been steady progress has been made in various aspects of fuel cell research, including catalysts, electrolytes, electrode structure, gas diffusion layer design and engineering efforts in manufacturing. However, the DMFC has been considered the most difficult fuel cell technology due to methanol crossover (methanol fuel from the anode side through the proton exchange membrane to the cathode catalyst) and slow anode kinetics for methanol oxidation [16]. The latter issue can be overcome only by employing better anode catalysts.

The two main goals for DMFC anode catalyst research are improved activity and increased durability. To improve anode activity, decades of extensive research efforts have been devoted to finding better materials for DMFC anodes. Unfortunately, it seems that very few electrode materials are suitable for direct methanol oxidation electro-catalysis, especially in the acidic DMFC environment and at electrode/membrane interface. Traditionally, the active component in DMFC anode catalysts is platinum. However, employing pure platinum in DMFC would trigger the problem of CO poisoning. Adsorbed CO, an intermediate in methanol oxidation, occupies the active Pt catalyst surface sites and causes low activity. When ruthenium metal is incorporated with platinum, the methanol oxidation kinetics are improved considerably to a practical level,
since the ruthenium helps in the oxidation of CO species in a region of low potential [17]. Other binary Pt-based catalysts have been investigated to improve DMFC anode activity, such as PtRu, PtOs, PtSn, PtW and PtMo, but platinum/ruthenium alloys showed the best activities and durability in methanol oxidation, and are thus the most practical anode catalysts for the DMFC. At the current stage of development, non-noble metal DMFC anode catalysts are not yet feasible [18].

To improve the durability of Pt-based anode catalyst in DMFC, considerable research effort has been devoted to understanding the underlying mechanism causing the performance degradation, and a number of deactivation pathways have been identified leading to PtRu anode catalyst degradation. The deterioration of anode catalysts can be due to a decrease in the number of catalytically active sites or to the alternating electronic properties caused by metal particle agglomeration [19, 20], poisoning, or oxidation [21]. In addition, ruthenium crossover has been found to contribute to anode performance degradation, as well as to contamination of the cathode catalyst in DMFCs [22]. Ruthenium contamination of the cathode catalyst decreases the number of available active Pt sites for the oxygen reduction half-reaction, and it decreases the cathode’s ability to handle methanol crossover [22]. Platinum in the PtRu anode catalyst can also be driven to the cathode compartment by the electrical field gradient, which damages the structure and integrity of anode catalyst [23]. Mitigation of the anode component crossover contamination could be achieved by developing stable PtRu anode catalysts, novel fuel cell designs, or more Ru-tolerant cathode catalysts.
1.2.2 Pt-based Catalysts in DMFC Cathode Application

As proven by decades of research efforts in search of an ideal cathode catalyst for DMFC purposes, platinum has the highest catalytic activity for oxygen reduction of any of the pure metals [24]. Platinum supported on conductive carbon serves as the state-of-art cathode catalyst in low temperature DMFCs.

Although platinum catalysts are the best and most commonly employed DMFC cathode catalysts, they still face many challenges. One of the significant problems hindering the large scale application of DMFC technology is cathode catalyst performance loss during extended operation. Cathode degradation is predominantly sintering and dissolution of platinum-based cathode catalysts under high dynamic operation environment [25] and ruthenium crossover from the anode catalyst [22]. Also, oxidation of the cathode catalyst support (the conductive carbon) [26], and defect formation in proton exchange membranes [27] are other DMFC cathode performance degradation pathways.

Another problem with Pt cathode catalysts is methanol crossover. Methanol adsorbed on active Pt sites on the cathode catalyst could react directly with oxygen, thereby wasting fuel and resulting in reduced cathode potential, production of additional water, and increased oxygen consumption. Moreover, as mentioned above, the Pt active surface would be poisoned by carbon monoxide, which is an intermediate product of methanol electro-oxidation. The methanol crossover problem can be mitigated by using electrolytes allowing lower methanol permeability, or by employing new cathode catalysts with higher methanol tolerance without sacrifice of oxygen reduction activity [24, 28].
In addition, many compounds have been identified as poisons to cathode catalysts, including CO, CO$_2$, NH$_3$, H$_2$S, NO$_x$, SO$_x$, other sulfur compounds and chloride ions [24, 29], which are either normally present in air or can be introduced by manufacturing processes of various fuel cell components. These contaminants should be removed before entering the fuel cell.

1.3 Pt-based Catalysts in Parahydrogen Induced Polarization Applications

In nuclear magnetic resonance (NMR) nuclei with nonzero spin absorb and emit electromagnetic radiation, when placed in a magnetic field. The frequency of the resonant radiation depends on the magnetic field and the electronic environment surrounding the nuclei. Since first described and measured in molecular beams by Isidor Rabi in 1938 [30], NMR has found numerous applications in modern science, including molecular structure elucidation, investigating solids [31], and advanced medical imaging [32]. However, NMR suffers from inherently low sensitivity, due to low population difference between the probed nuclear spin states in a magnetic field. This issue has hindered application of NMR in probing low concentration species.

A range of techniques have been developed to increase the NMR signal, including dynamic nuclear polarization [33], optical pumping [34], and parahydrogen induced polarization (PHIP) [35], with the latter being directly related to catalysis. In PHIP, parahydrogen, a spin isomer of H$_2$ with antiparallel spins, is chemically introduced into targeted substrate molecule, loading to a dramatic NMR signal enhancement by a factor of $10^4$ to $10^5$ [36].

The nature of PHIP reaction requires addition of two hydrogen atoms from one parahydrogen molecule to a nonsymmetrical substrate molecule [37], in order to achieve a hyperpolarized NMR signal. Originally, the PHIP reaction was achieved by
employing homogeneous hydrogenation reactions, such as those involving the famous Wilkinson’s catalyst (RhCl(PPh₃)₃) [38] and Vaska’s complex (Ir(CO)Cl(PPh₃)₂) [39]. Homogenous reactions can preserve the correlation between the two proton nuclei of a parahydrogen molecule. However, the homogeneous catalysts used in the reaction mixture cause separation problems, precluding further application of the reaction product in novel NMR techniques.

Supported heterogeneous metal catalysts, predominantly used in industrial hydrogenation processes, are not expected to produce PHIP effects, as the reaction is likely to destroy the original correlation of the two nuclear spins. More specifically, molecular hydrogen would easily dissociate on the catalyst surface upon chemisorption, and the adsorbed hydrogen atoms would diffuse over the metal surface, or dissolve into the bulk of the metal, and thus losing correlation. However, recently Koptyug et al. [40] showed that Wilkinson’s catalyst (RhCl(PPh₃)₃) supported on either modified silica gel or polymer could hydrogenate styrene into ethylbenzene to enhance the observed NMR signal. Kovtunov et al.[41] demonstrated that platinum supported on alumina or titanium oxide catalysts the PHIP reaction.

The use of heterogeneous catalysts in PHIP reaction is a novel field which has emerged over the last decade, with platinum supported on metal oxide catalysts as the most studied heterogeneous catalyst up to now. The structure sensitivity and the catalyst support effects on the hydrogenation of propylene over Pt catalysts supported on a range of commonly used metal oxide supports have been investigated using the PHIP technique [42]. The study indicated that different types of active Pt catalyst
surface sites are responsible for pairwise and non-pairwise hydrogen addition to C=C double bonds during propylene hydrogenation.

The successful use and the advantages of pt-based heterogeneous catalysts for dramatically NMR signal enhancement has a number of important potential applications, for example in NMR imaging [43, 44]. And another important application is a method for a unique type of reaction product labeling, as only product generated from pairwise addition of parahydrogen can be detected with enhanced NMR signal. This kind of labeling technique could be useful in studying the mechanisms of hydrogenation reactions.

1.4 Ir-based Catalysts in Parahydrogen Induced Polarization Applications

Recent research has shown that transition metal catalysts other than platinum can also trigger PHIP reactions. Koptyug’s also demonstrated the PHIP effect using a Au(III) Schiff base complex catalyst immobilized within a metal organic framework material IRMOF-3 [45], and using Pd(0) nanoparticles embedded in an ionic liquid phase supported on activated carbon fibers [46].

Iridium containing compounds are also commonly used as homogenous catalysts for PHIP reactions. For example, Vaska’s complex (Ir(CO)Cl(PPh₃)₂) [39], Ir(CO)(dppe)Br, and Ir(CO)(dppe)(CN) [47] have been used in PHIP reactions as homogenous catalysts. In addition, small clusters of iridium (Ir₄ and Ir₆) (as well as of larger aggregates of these metals) on oxide supports (gamma-Al₂O₃, MgO, and La₂O₃) [48] have shown catalytically activity in the hydrogenation reactions of propylene. However, to the best of our knowledge, there is no reported study on PHIP reactions involving heterogeneous Iridium catalysts.
1.5 Objective and Motivations

In the present study, different Pt-based catalysts were investigated for use in two applications: 1) as anode and cathode catalysts in direct methanol fuel cell applications; and 2) as supported metal particle catalysts in parahydrogen induced hyperpolarization applications. In addition, one other transition metal in platinum family, iridium, was investigated as a supported catalyst on titanium oxide in PHIP applications.

1.5.1 Commercial Anode Catalyst Screen Study for An Open-Cathode Design DMFC

The first part of this study focused on evaluating the performance and degradation of four commercial anode catalysts in an open-cathode design DMFC single stack. Technical considerations for anode catalyst choice for the open-cathode design DMFC were proposed based on the research result.

1.5.2 Investigation of Contamination Effects of Methyl Ethyl Ketone on A Platinum /Carbon Electro catalyst for Oxygen-Reduction Activity

The second focus in this work is understanding to what extent the presence of one type of wetting agent, methyl ethyl ketone, would influence the oxygen reduction reaction and thus the performance of a typical Pt/Carbon DMFC cathode catalyst. The thin-film rotating disk electrode (RDE) method was employed to study the ORR kinetics of a DMFC cathode Pt/Carbon catalyst upon MEK contamination. The results from this study provide important knowledge of the effects of trace MEK contamination on DMFC cathodes, leading to suggestion to mitigate performance losses and degradation phenomena.
1.5.3 Platinum- and Iridium-based Catalysts in Parahydrogen Introduced Hyperpolarization Applications

Platinum and iridium supported on titanium (IV) oxide were used as model heterogeneous catalysts to study the kinetics of heterogeneous propylene hydrogenation with parahydrogen. The temperature dependence of NMR signal enhancement and the pairwise hydrogen addition reactions were investigated over the Pt/TiO₂ and Ir/TiO₂ catalysts.
CHAPTER 2
COMPARATIVE STUDY OF COMMERCIAL ANODE CATALYSTS IN AN OPEN-CATHODE DIRECT METHANOL FUEL CELL

2.1 Background

Since the Welsh Physicist William Grove developed the first crude fuel cells in 1839 [13], fuel cells have attracted substantial attention from academia and industry all across the world for their great potential as an economic, efficient, and environmentally-friendly means to convert chemical energy into electric energy.

Fuel cells can efficiently harvest energy that is preserved in chemical bonds and convert it into electrical energy. Conventional power plants or other heat engine-based technologies introduce several steps to convert chemical energy to electricity and comes with the efficiency limitation established by Carnot. In contrast, fuel cells do the conversion in one step, giving a higher energy conversion efficiency than any other known device. For the same power output, fuel cells using propane or methanol emit less carbon dioxide compare to traditional heat engines using fossil fuels, and no greenhouse gases are emitted when hydrogen is used [49]. In addition, a fuel cell’s high efficiency is independent of unit size, and can be scaled down from very large to very small units without efficiency loss.

2.1.1 Types of Fuel Cell

Fuel cells can be classified into many different types according to catalyst, material separating anode and cathode, and type of fuel utilized. There are five types of fuel cells most commonly studied: alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC), and polymer electrolyte membrane fuel cell (PEMFC) [50].
The alkaline fuel cell (AFC), which has been used in NASA’s space missions, can achieve efficiencies as high as 70%. AFC, use the aqueous potassium hydroxide as electrolyte, to accelerate cathode reaction kinetics, and platinum or non-precious metals, such as nickel, as catalysts, for a power outputs of 300 W - 5 kW. Two noticeable limitations of AFCs are that high purity hydrogen and oxygen are needed as feeds, and the tolerance for atmospheric carbon dioxide is poor, as CO₂ would react with the KOH electrolyte. Due to these limitations, the applications of AFCs are very restricted [51-54].

The phosphoric acid fuel cell (PAFC) uses phosphoric acid as electrolyte, typically operating at temperatures ranging from 180-210°C, with power outputs between 50 and 200 kW. The efficiency for PAFC itself can reach about 40%, and can be increased to about 60-70% if used in a combined heat and power system. Due to the acid nature of the electrolyte, PAFCs overcome the CO₂ tolerance problem in AFCs, thereby broadening its fuel feed selections. However, the carbon monoxide concentration must be maintained below 0.5% in the fuel feed, to avoid catalyst poisoning. The acid electrolyte also causes corrosion problems for fuel cell components. Because pt-based catalysts must be employed in PAFCs, large-scale applications are limited due to the high cost of platinum usage [51-54].

Molten carbonate fuel cells use lithium carbonate, sodium carbonate or/and potassium carbonate solution as the electrolyte, and can achieve an efficiency as high as 60-85%, while operating at 620-660°C. High operation temperature gives the advantage of higher energy efficiency and more choice of fuel/catalyst options. MCFCs can use hydrogen, carbon monoxide, natural gas, propane or diesel as fuels, reaching a
power output range of 10 kW-2 MW. MCFCs are mainly used as stationary power generators. One disadvantage of MCFCs is severe corrosion to fuel cell components due to the high temperature [51-54].

The solid oxide fuel cell (SOFC) is promising in large stationary power generator applications, with outputs up to 2 MW. SOFCs use a solid oxide as electrolyte, and operate at very high temperatures (500-1000 °C) with high efficiency (60-85%). SOFCs use non-precious metal catalysts, including a Co-, or Ni-based anode catalyst, and a Sr-promoted LaMnO₃ cathode catalyst. High operation temperature enables SOFC to use a large range of different fuels, including light hydrocarbons, such as methane, propane and butane. However, high operation temperature, which causes corrosion and mechanical problems for various SOFC components, is one of the major disadvantages of this type of fuel cell [51-54].

Polymer electrolyte membrane fuel cells are characterized by use of a proton conducting polymer based membrane as electrolyte. Depending on fuel types, PEMFCs can be further classified into hydrogen fuel cells and direct methanol fuel cells.

For the hydrogen fuel cell, the anode and cathode reactions are

\[
\text{Anode reaction: } \quad \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \\
\text{Cathode reaction: } \quad \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}
\]  

(2-1)

In the hydrogen fuel cell (HFC), hydrogen and oxygen flow through the gas channels on bipolar plates, and reach the anode/cathode sites, respectively. The anode catalyst breaks down hydrogen molecules into protons and electrons. The protons exist in the form of hydrates and are transported into the cathode side through the proton exchange membrane. To fulfill the proton conduction process, at the same time, the
electrons from hydrogen pass through the external circuit and reach the cathode side, where they reduce oxygen to oxide. The proton and reduced oxygen react at the cathode catalyst surface, and produce water at the same time. The HFC typically operates at temperatures of 60-80°C, making them convenient in vehicle and portable power device applications, due to simplification of heat management. The theoretical efficiency of the combined heat and power system for an HFC can reach approximately 90%. However, due to the limitations of all types of polarization processes, the typical realistic efficiency for HFC is about 60% in transportation applications, and around 35% in portable power supply application. The typical power output for HFC ranges from a few watts to 100 kW. The HFC demonstrates the highest power density (300-1000 mW cm⁻²) among all types of fuel cells and can be turned on/off rapidly, making it very suitable for portable power supply and transportation applications. However, the HFC relies on expensive noble metal catalysts, requires an accessory system for hydrogen storage and water management, and has limited tolerance to carbon monoxide and sulfur contamination. In particular, the necessary accessories for hydrogen storage and water management make it very difficult to minimize HFC size to adapt to the requirement for portable power supply applications [51-54].

The direct methanol fuel cell (DMFC) is another type of PEMFC that uses methanol as liquid fuel, and it especially suitable for developing portable power source devices. Unlike hydrogen, methanol can be stored as a liquid, which is reasonably safe and convenient for storage, transporting, and filling into fuel cell devices. In the DMFC, methanol is supplied to the anode side, where it is catalytically broken down into protons, electrons and carbon dioxide. As discussed above for the HFC, proton and
electrons travel to the cathode where they with oxygen and form water. The reactions at anode and cathode are:

Anode reaction: \[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \]

Cathode reaction: \[ \frac{3}{2} \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \] (2-2)

Another advantage is that methanol is a mature chemical product, which can be easily produced from coal, gasoline, or biomass. Moreover, methanol has four times the volume energy density compared to hydrogen gas at a pressure of approximately 69 MPa in a state-of-the-art containment system under development [55].

The shortcomings associated with DMFC are methanol oxidation intermediate species, which can possibly poison the electrode [56], slow methanol oxidation reaction kinetics on the anode catalyst [57], and methanol crossover problem [28]. The methanol crossover costs significant power loss and fuel efficiency losses. Another disadvantage of DMFC is water management. In most conventional designs, the water produced in the cathode reaction is condensed and recycled by a dedicated water recycle system downstream from the cathode, and the recycled water is returned to the anode feed. The conventional design of water management system requires a bulky accessory water cycle system and the associated extra power consumption. Also, if the water recycling system is not functioning well, water overflow on the cathode side can occurs, flooding the cathode catalyst layer pores, and inhibiting oxygen transport from the cathode gas diffusion layer to the cathode catalyst layer. Poor water management not only decreases the net power output and energy density of DMFC, but also possibly shuts down the cathode reaction by water flooding.
Despite the disadvantages, DMFC is a very promising candidate for overcoming the difficulty of hydrogen storage and transportation in PEMFC large scale applications, especially for portable power supply purposes.

2.1.2 Anode Catalyst in DMFC

Platinum-ruthenium based catalysts are the most feasible and prevalent anode catalysts currently used in DMFC systems, due to their high activity in the methanol oxidation reaction and their high carbon monoxide tolerance [16, 18]. The ruthenium in the alloy catalyst has two functions: 1) interaction with the d-orbital electrons of platinum to help prevent Pt poisoning by CO; and 2) formatting active oxygen species on the ruthenium surface, thereby facilitating oxidation of intermediates formed during methanol oxidation, further improving methanol oxidation activity and catalyst poison tolerance. An atomic ratio of Pt to Ru of 1:1 has been considered to be the best composition for the most CO-tolerant DMFC anode catalyst [58]. For better utilization of platinum, the optimum size of the PtRu catalyst particles in a DMFC is on the order of nanometers, in the range of 2-6 nm [16, 59]. Due to the slow anode reaction kinetics, the catalyst loading typically ranges between 2 to 8 mg cm$^{-2}$, in order to maintain the desired performance and life span.

Improvements in anode DMFC catalysts is mainly directed into two pathways: improved performance and decreased cost. Improvement of DMFC performance can be further specified as improved activity, reliability and/or durability. One known pathway for anode catalyst degradation is particle sintering. For nano-particle anode catalysts, the specific surface energy increases as the particle size decreases [60], thus, the smaller particles are intrinsically more easily to agglomerated/sintered [61]. Once the anode catalyst particles sinter into a larger size, the electrochemical of active surface
area (EASA) decreases accordingly, and the performance of the DMFC also degrades as a result. To overcome the sintering effect, improvement in the support for stabilizing nano-particle catalysts is one promising research direction. To decrease the anode catalyst cost, development of non-noble metal anode catalysts could be the most promising route. Unfortunately, PtRu-based anode catalysts are currently the only feasible options in practice. In order to lower anode catalyst cost, better PtRu formulation and support design are other methods to improve precious metal utilization.

2.1.2 Objectives

DMFC is a very promising technology for portable power supplies. However, there are many problems that need to be tackled before its commercialization. Currently, the main problem with DMFCs, is the need to increase anode catalyst activity/durability, decrease methanol crossover and improve water management.

Figures 2-1 and 2-2 show closed-cathode and open-cathode DMFC stack designs, respectively. For the closed-cathode design, the water condenser, water storage device, and water pump are used to recycle the water to the anode feed. This bulky water recycle system increases the overall DMFC weight and volume, and decreases the net power output by consuming energy in the water recycling effort. However, an open-cathode design removes bulky water recycle system. The open-cathode design of DMFC stacks is achieved by adding a hydrophobic liquid barrier layer (LBL) in the membrane electrolyte assembly (MEA) between the cathode catalyst layer (CCL) and the cathode gas diffusion layer (CGDL). The LBL allows passive recovery of the water produced in cathode reaction back to the anode side through the membrane.

The present research focus on: 1) testing the performance and degradation of four commercial anode catalysts in the open-cathode design DMFC single stack; 2)
investigating the effect of anode choice on cathode performance and degradation in the open-cathode design DMFC single stack; 3) making technical suggestions for anode catalyst choice for the open-cathode design DMFC based on research data.

2.2 Experimental Methods

2.2.1 Membrane Exchange Assembly Configuration

DMFC single cell membrane exchange assembly used in this work has an active cell area of 15.5 \( \text{cm}^2 \). The membrane electrolyte assemblies (MEAs) were manufactured by our collaborating research group at the University of North Florida. Figure 2-3 shows the configuration of the DMFC MEA design. The MEA consists of nine different functional layers, which incorporate the unique DMFC open-cathode design allowing advanced water management. Each layer in the MEA is responsible for its dedicated task.

The backing plate, anode flow channel (AFC) would provide necessary mechanical support from the anode side. It also creates an optimized anode flow channel to ensure an adequate and stable anode fuel supply throughout the adjacent anode catalyst layer in a gas-liquid two phase flow condition. The anode gas diffusion layer (AGDL) is designed to allow the carbon dioxide generated in anode reaction to diffuse back to the AFC and flow out of the DMFC system. Anode catalysts are evenly deposited onto the anode catalyst layer (ACL) is to catalytically facilitate the anode reaction. Membrane (MEM) is responsible for conducting proton flow from the anode side to the cathode side and inhibiting electron transfer through the membrane. The cathode catalyst layer (CCL) is next to the membrane, and is evenly embedded with cathode catalyst particles, where the cathode reduction reaction takes place. The liquid barrier layer (LBL) is a unique functional design dedicated to reduce the water loss from
the cathode reaction to the open atmosphere. The hydrophobic nature of LBL retains most of water molecules generated in the cathode reaction, and forces them to diffuse back to the anode through the small channels in membrane. The cathode gas diffusion layer (CGDL) contains diffusion channels for air from the cathode flow channels getting into the CCL. The bipolar plate is placed between the two MEAs, with one side anode flow channel and one side for the cathode flow channel, thereby enabling the connection of multiple MEAs in series to form a DMFC stack. The cathode flow channel (CFC) is similar in function to the AFC to optimize the air flow and transport from the CFC into the CCL.

In this study, four commercial DMFC anode catalysts were used to manufacture the MEAs. ELE147 (referred to as ELE147), and ELE170 (referred to as ELE170) from the Johnson Matthey Company, a DMFC anode catalyst from the Tanaka Company (referred to as Tanaka), and a DMFC anode catalyst from the Cabot Company (referred to as Cabot). The cathode catalysts in this study were the same for all MEAs: Hispect 11100 from Johnson Matthey Company.

2.2.2 Fuel Cell Testing Experimental Setup

The DMFC single cell test rig consists of a thermocouple, electric current collector plates, a closed container for sealing the cathode inlet, a peristaltic pump for the anode fuel solution supply, and a heating element for achieving desired temperature. The thermocouples were positioned at the anode flow stack outlet, which thermostatically controlled the stack to an accuracy of 0.1°C through a heating patch adhered to the outside of the current collector. A commercial electronic load regulated the output current and voltage of the DMFC single cell test rig, and the mass flow controllers were employed to control gas flow rates through the cathode/anode. The
data were acquired in real time by a customized LabVIEW code and a data acquisition system from National Instruments.

All MEAs were received from the University of North Florida and conditioned at the University of Florida before testing. During MEA single cell assembling, the MEA was held and sealed tightly via two gaskets screwed onto the graphite plates engraved as either anode flow channel or cathode flow channel. Two gold-plated brass plates were pressed in close contact with the outside surface of the graphite plates for collecting the electric current.

2.2.3 Electrochemical Characterization Experimental Setup

Electrochemical characterization of the single DMFC MEA was performed using the commercial electronic load, a Solartron 1260 impedance/gain-phase analyzer (Solartron Electronic Group, UK), and a Solartron 4480 potentiostat analyzer (Solartron Electronic Group, UK).

2.2.3.1 MEA initial performance measurement

Each MEA was subjected to a break-in process for activating and conditioning the MEA into proper stable working condition. The anode channel was first purged with hydrogen to remove any air in the channel; then hydrogen was passed through the anode channel to activate the catalyst surface. Thereafter, nitrogen was again purged through the anode side for removal of any residual hydrogen, before a 0.8 M methanol solution was passed through the anode side for MEA conditioning purposes. At the same time, the cathode was continuously purged with nitrogen to prevent any crossover reaction on the cathode side. Then, the temperature of the MEA was gradually increased to 80°C in order to hydrate the membrane properly, while the anode was provided with 0.8 M methanol solution and the cathode was under nitrogen protection.
After ‘break-in’ treatment, the overall voltage of single cell stack was controlled to drop from 0.8 V to 0.35 V at a rate of 10 mV/min, with the single cell voltage would be held at 0.35 V for 10 minutes. This was followed by a catalyst rejuvenation procedure to reverse degradation effects on the cathode catalyst side. The cell temperature was controlled at 50°C, and anode flow was 2 mL/min with a 0.8 M aqueous solution of methanol, while cathode flow was 1 SLPM air. This ‘potential hold-rejuvenation’ process was cycled for 8 hours. The cell current density at 0.35 V was monitored by a Labview-controlled fuel cell test station during the entire cycling process to measure the continuous performance of the MEA at the beginning of its lifetime.

2.2.3.2 Single cell overall polarization measurement

For the single DMFC MEA polarization curve test, a solution of 0.8 mol/L methanol was prepared and pumped into the anode flow inlet at a constant flow rate of 2 mL/min. Compressed air (Airgas UAS, LLC) at 1 standard liter per minute (SLPM) was purged through the cathode. A polarization curve for the fuel cell can be characterized by three major polarization regions, known as the activation, ohmic, and concentration over potential [62]. In the low current-density region, the activation overpotential of the DMFC dominated the polarization curves. At the medium current-density region, the cell voltage shows a linear loss with the increasing current density, attributed to the ohmic overpotential. The high current-density region concentration overpotential is observed. At a given current density, a higher cell voltage indicates higher cell performance and power output. In this study, polarization curves were measured to understand the cell performance. The current density was controlled at a specified value, from 0 mA/cm² to the maximum 150 mA/cm², which still maintained the MEA voltage above 0.2 V to prevent damage to the MEA.
2.2.3.3 Anode polarization measurement

The anode polarization curve is a plot of current density versus anode potential. It is important to resolve anode polarization from overall polarization in order to assess the performance of the anode individually. It is noteworthy that the potentials obtained in anode polarization experiment are total voltages consisting the anode potential and the resistance loss. An IR (resistance loss)-corrected anode potential is calculated according to the equation 2-3:

\[ E_{\text{total}} + IR(\text{resistance loss}) = V_{\text{corrected}} \]  

(2-3)

in which \( E_{\text{total}} \) is the potential obtained directly, while purging hydrogen through the cathode to set the cathode potential to zero and measuring the potential at various current densities. IR is the resistance loss, which is calculated by multiplying the current by the membrane resistance. \( V_{\text{corrected}} \) is an actual anode polarization potential after resistance-loss compensation.

The anode polarization measurements were performed by a Solartron 1480 MultiStat. Hydrogen was passed through the cathode side of the single cell at the reference electrode, and 0.8M methanol solution was passed through the anode side, where it was connected to the working electrode. The applied voltage on the working electrode was set in a range from 0.01 V to 0.55 V with a scanning rate of 2 mV/s. The limitation of the maximum current was set at 4 A for electrical safety protection.

2.2.3.4 Cathode polarization measurement

The cathode polarization potential \( E_{\text{cathode}} \) can also be obtained by simple calculation as shown in equation 2-4:
The overall cell potential $V_{cell}$ is obtained from overall polarization curve; $IR$ is the resistance loss; and $E_{anode}$ is the anode-corrected voltage as described above.

### 2.2.3.5 Single cell resistance measurement

Impedance spectroscopy was employed to measure the resistance of the single DMFC cell. Impedance spectroscopy imposes a small sinusoidal (AC) voltage or current signal of known amplitude and frequency, and the ratio and phase-relation of the AC voltage and current signal response corresponding to the complex impedance, $Z(w)$. This measurement was performed using a Solartron 1260 impedance/gain-phase analyzer (Solartron Electronic Group, UK), while passing hydrogen through cathode at a rate of 0.3 SLPM for setting a potential baseline, and passing 0.8 M methanol solution at a rate of 2 mL/min through the anode side. The temperature of DMFC was maintained at 50 °C, and the test frequency range from 10 kHz to 0.1 Hz with AC amplitude of 20 mV as the parameter for resistance measurements. A plot of $Z'(w)$ vs $Z''(w)$ was prepared, and the cell resistance was obtained as the $Z'(w)$ (real number part of $Z(w)$), when the phase angle is zero ($Z''(\omega) = \text{Im}(Z)=0$), and therefore the cell behaves in a purely resistive manner.

### 2.2.3.6 Methanol crossover measurement

One intrinsic and almost inevitable problem associated with DMFC is the methanol crossover, in which the methanol solution would diffuse from the anode to the cathode side. Methanol crossover in DMFC operation causes lower power output due to chemical oxidation of methanol at the cathode catalyst, giving rise to several
problems: (1) electrode depolarization; (2) mixed potentials, resulting in a lower open circuit voltage (OCV); (3) cathode catalyst poisoning by CO (an intermediate of methanol oxidation); and (4) water flooding on the cathode, impairing the oxygen transport to the cathode catalyst layer and damaging the cathode reaction. Moreover, the overall fuel utilization efficiency of the fuel cell is lowered when there is excessive methanol crossover [28].

In this study, crossover methanol was assumed to react completely at the cathode side. Nitrogen was used to purge the fuel cell cathode at 1.00 SLPM, while 0.8M methanol solution passed through the fuel cell anode at 2.00 mL/min. A Solartron 4480 potentiostat analyzer (Solartron Electronic Group, UK) controlled by CorrWare software from Scribner Associates, was used to perform a linear sweep voltammetry (LSV) between 0 and 0.8 V. The resulting plot of working electrode current vs working electrode potential was used to derive the methanol crossover flux from Faraday’s Law.

2.2.3.7 Accelerated low-voltage anode durability test

Investigation of the DMFC durability is a time-consuming and potentially inefficient task [63], simply because the targeted design lifetime for our DMFC is more than 3000 hours. Studying the durability of a DMFC anode catalyst under normal operating conditions is very difficult, if not possible, due to experimental time span. Therefore, a more realistic experimental method for probing anode catalyst durability is required to fulfill the task. In this study, a low voltage cycling technique was developed to purposely create a harsh environment for the anode catalyst and induce an accelerated degradation, a so-called low voltage accelerated durability test (LVADT).

The degradation resistance ability of DMFC was measured by operating a designed 144 hour-long LVADT. During the single cell operation, methanol solution
(0.3M, 1.25mL/min) was delivered to anode side at room temperature and atmospheric pressure via a peristaltic pump, while purified air was fed to the cathode site at a flow rate of 2 SLPM. During the experiment, the gas flow, cell temperature and load density were carefully controlled by a NI LABVIEW program connected to the Fuel Cell Test Station. The overall voltage of single cell stack was controlled to drop from 0.8 V to 0.05 V at a rate of 20 mV/min. Then the single cell voltage was held at 0.05 V for 10 minutes, followed by a catalyst rejuvenation procedure to reverse degradation effects on the cathode catalyst side. Moreover, the system was checked for gross leaks every time the MEA was changed, followed by break-in cycling to ensure new MEA was operated in normal. Before starting 144-hours LVADT test, 8 hours of normal cycling was performed to observe the initial performance of each MEA, which is very important when evaluating qualities of different kinds of MEA. A series of electrochemical measurements, including impedance measurement, methanol crossover measurement, anode/overall polarization measurement, were obtained at intervals of 8 hours in normal cycling, and after 48 hours, 96 hours, 144 hours of low voltage cycling, in order to obtain performance and degradation information of the single fuel cell.

2.2.3.8 Calculation of electrochemically active surface area calculation

To investigate the change in the EASA of the anode catalysts, the EASA was calculated by a modified Bulter–Volmer equation [64] during the different periods of LVADT. A general starting point for the development of a relationship between an anode polarization and anode catalyst active surface area for a particular current density is the Butler–Volmer equation (Equation 2-5).
\[ I = A \cdot i_0 \left( e^{\frac{aF\eta}{RT}} - e^{-\frac{(1-a)F\eta}{RT}} \right) \]  

(2-5)

where \( I \) is the actual anode reaction current density; \( A \) is the electrode active surface area; \( i_0 \) represents the exchange current density on the catalyst surface, which is an intrinsic parameter for a catalyst, defined as the value of the current density at zero net current where the reaction is at an equilibrium; \( \alpha \) is the symmetry factor, which is a constant parameter for anode electrochemical reaction with a value between 0 and 1; \( \eta \) is the anode overpotential, which can be calculated by subtracting the actual anode potential, \( E \), by theoretical anode equilibrium potential, \( E_0 \); \( F \) stands for the Faraday constant; \( R \) is the idea gas constant, and \( T \) is the operational temperature.

The ‘high-polarization’ approximation to Equation 2-5 was applied, since a current density of 120 mA cm\(^{-2}\) was chosen for catalyst active surface area calculation, where the polarization is considered to be high enough for adapting the ‘high-polarization’ approximation. Since in the ‘high-polarization’ condition, \( \eta \) is large, Equation 2-5 can be simplified to

\[ I = A \cdot i_0 \left( e^{\frac{aF\eta}{RT}} - e^{-\frac{(1-a)F\eta}{RT}} \right) \]  

(2-6)

For the identical MEA before and after LVADT, the current density of 120 mA cm\(^{-2}\) was chosen for calculation, and was substituted into Equation 2-6:

\[ I = A_{\text{fresh}} \cdot i_0 \cdot e^{\frac{aF\eta_{\text{fresh}}}{RT}} = A_{\text{degraded}} \cdot i_0 \cdot e^{\frac{aF\eta_{\text{degraded}}}{RT}} \]  

(2-7)
where the current density, \( I \), is identical for fresh and degraded MEA. Considering the overpotential definition for fresh and degraded anodes:

\[
\eta_{\text{fresh}} = E_{\text{fresh}} - E_0 \quad ; \quad \eta_{\text{degraded}} = E_{\text{degraded}} - E_0
\]

Equation 2-7 can be rewritten as

\[
\frac{A_{\text{fresh}}}{A_{\text{degraded}}} = \frac{A_{\text{fresh}} \cdot i_0}{A_{\text{degraded}} \cdot i_0} = e^{\frac{\alpha F (E_{\text{fresh}} - E_{\text{degraded}})}{RT}} \quad (2-8)
\]

Therefore, Equation 2-8 can be used to calculate relative electrode active surface area regarding fresh and degraded MEAs. In this study, all relative electrode active surface areas of MEAs with different anodes were normalized to the percentage of the beginning life electrode active surface area of ELE147 anode MEA, which were arbitrarily set to 1.

All electrochemical measurements and LVADT described in this section were performed on two MEAs for each type of anode catalysts independently, and same trend during degradation tests were observed. One set of data obtained from one MEA for each type of anode catalysts were presented as result.

2.3 Results and Discussion

2.3.1 Initial Performance of MEAs

Before carrying out accelerated the voltage anode durability test, an 8-hour performance test was used to measure the initial performance of each MEA with different anodes. The MEAs’ initial performances were measured by monitoring the current density of the MEA at 0.35 V. Fig 2-4 shows the initial performance of MEAs with Johnson Matthey ELE147, JM ELE170, Tanaka, Cabot anodes. From Fig 2-4, all MEAs demonstrated higher performance at the very beginning of life, and most of the
performance degradation happened within the first 60 minutes, after which the performance plateaued at a relatively stabilized value. This is observed because at the very beginning life of MEA, various components are not conditioned or stabilized in actual working conditions, and a significant performance loss occurs due to the adaption of the MEA to working conditions. For example, during conditioning potential hold and rejuvenation cycling, any loosely deposited Pt or Ru catalyst from for anode may detach from the catalyst support, and Ru could migrate across the membrane and deposit on the cathode side, thus causing performance degradation [22].

Figure 2-5 (a) shows the initial power densities of the various MEAs and the stabilized power density value observed during the initial 8-hour performance test. The initial power density is defined as the average power density over the first ten minutes of operation right after the ‘break-in’ process, and the stabilized power density is defined as the average power density across the plateau region as shown in Fig 2-4. Initial power density loss in Fig 2-5 (b) corresponds to the loss between initial power density and stabilized power density. Tanaka anode MEA demonstrated the largest initial power density loss: 7.25 mW cm\(^{-2}\). ELE147 and Cabot anode MEAs also showed significant power loss: 5.11 mW cm\(^{-2}\) and 3.07 mW cm\(^{-2}\), respectively. However, ELE170 anode MEA appeared to be the most stable MEA for initial performance loss, with a loss of only 0.34 mW cm\(^{-2}\).

This study indicates that ELE170 is the most stable anode during the first few hours of fuel cell operation and conditioning, which may due to its having the least unstable components in anode catalyst composition. Tanaka and ELE147 all showed significant initial performance degradation during the first hour at the very beginning
operating life, implying that those two anode catalysts contain relatively unstable anode catalysts during the beginning life conditioning process.

2.3.2 Single Cell Polarization and Power Density Curves

Figure 2-6 shows the current density-voltage polarization curves and power density-voltage curves recorded under current control, at various periods of potential cycling. The data demonstrate that the loss in fuel cell performance throughout the polarization curve occurred during the entire time range investigated in LVADT. From Table 3-1, the ELE147 DMFC started with the best fresh DMFC performance, with a power density of 49.16 mW·cm$^{-2}$ at a current density of 120 mA·cm$^{-2}$, which is about 10% higher than performance of other three DMFCs. ELE170, Cabot and Tanaka started with almost the same initial performance, a power density around 40 mW·cm$^{-2}$. However, at the end of 144 hours LVADT, and ELE 147 showed almost the same, or slightly worse, performance compared to ELE170, both around 40 mW·cm$^{-2}$. Tanaka DMFC and Cabot DMFC showed a power density of 38.36 mW·cm$^{-2}$ and 35.97 mW·cm$^{-2}$, respectively, which was much lower than the ELE147 and ELE170 end of life performance.

ELE147 demonstrated the most rapid performance loss during entire course of 144 hours LVADT (Table 3-2), which is 66.32 μW cm$^{-2}$·h$^{-1}$. The ELE170 experienced the least power loss during LVADT, corresponding to a power density loss rate 24.95 μW cm$^{-2}$·h$^{-1}$ for the entire time range. Cabot and Tanaka anode DMFCs showed moderate performance degradation rates, 49.90 μW cm$^{-2}$·h$^{-1}$ and 41.59 μW cm$^{-2}$·h$^{-1}$, respectively.

From the overall polarization and power density curves, ELE170 DMFC stands out as the candidate with best degradation resistance, and thus the best end-of-life performance among all the DMFCs. ELE147 started with the highest initial of life
performance, but had the most rapid performance degradation rate among all four anodes investigated. Tanaka and Cabot anodes’ DMFCs both started with a moderate initial life performance, but with a significant performance degradation rate of 40-50 µW cm⁻²·h⁻¹, they ended up with the worst performance at the end of the LVADT.

2.3.3 Anode Polarization

The anode polarization curves of the DMFCs with four anodes after different LVADT times are shown in Fig. 2-7. With durability test time increasing, the anode potential at the same current density increased to a larger positive value, indicating that the activity of the anode catalysts had degraded for all four DMFCs. Table 2-3 shows the anode potential evolution during the durability test time frame at a current density of 120 mA·cm⁻². Tanaka and ELE170 anode demonstrated very similar degradation patterns, with 0.138 mV·h⁻¹ and 0.132 mV·h⁻¹ degradation rates across entire 144 hours durability test, while ELE147 anode showed the largest degradation rate of 0.146 mV·h⁻¹, and Cabot anode showed the least degradation rate of 0.118 mV·h⁻¹.

2.3.4 Relative Electrochemical Active Surface Area

In order to better access the anode catalyst degradation, relative electrochemical active surface areas (rEASA) were calculated for anode activity across the LVADT. Fig 2-8 shows rEASAs, normalized to the fresh ELE147 anode EASA, all of anodes during durability test. The rEASA of all anodes decreased during the durability test, until ELE147 anode showing the largest rESAS both at fresh conditions and at end-of-durability test conditions. Across the entire durability test, the rEASA value decreased at the order of ELE147>ELE170>Tanaka>Cabot, which again confirmed that ELE147 has the best anode active surface area, as well as the best anode activity. However, the rEASA degradation percentages decreased in the order of ELE147 > Tanaka = ELE170
> Cabot, showing 33.0%, 29.9%, 29.9% and 18.8% loss of beginning life rEASA for each anode, respectively.

It is generally accepted that the electrochemical active surface area for DMFC anode catalysts is an important parameter for anode performance[65], as larger EASA indicates that more catalyst sites are available for anode reaction. Previous research has shown that the performance degradation of PEMFC is largely due to the EASA loss of the electrode catalysts [66]. Different mechanisms were discovered to contribute to the EASA loss, including the agglomeration of Pt-Ru catalyst particles, dissolution/leaching of ruthenium species from the anode catalyst, detachment of catalyst particles from the carbon support, and etching of the carbon support itself [25, 65]. The degradation mechanism for Pt-based DMFC catalysts was also found to depend on various working conditions, and the dissolution/leaching of ruthenium mechanism may be more prevalent during load cycling. In this study, ELE147 was found to experience the largest rEASA loss, indicating that ELE147 may have the largest ruthenium dissolution/leaching from the anode, and this may also contribute to ELE147’s significant cathode degradation.

2.3.5 Methanol Crossover

Methanol crossover was measured by linear sweep voltammetry. Methanol crossover current densities for all four DMFCs across the entire LVADT are shown in Fig 2-9. It was found that in all time periods sampled during the durability test for all DMFCs, methanol crossover current density always stayed around 50 mA cm\(^2\), indicating that no noticeable degradation in the proton exchange membrane occurred during the course of LVADT. Thus, we can safely assume that methanol crossover effect is same during entire time range of LVADT for all DMFCs.
2.3.6 Cathode Polarization

In order to investigate the cathode performance during LVADT, the relationship between the cathode potential and the current density for all DMFCs were compared. As shown in Fig 2-10, the cathode potential of all DMFCs decreased at the same current density as the LVADT time increased, which is evidence for cathode degradation occurrence. At the current density of 120 mA cm\(^{-2}\), ELE147 and Tanaka DMFC started with higher cathode potentials than ELE170 and Cabot. However, ELE170 DMFC stands out with the best cathode performance at the end of the entire LVADT, while Cabot DMFC showed the lowest end-of-test cathode performance.

Considering the cathode degradation rate, ELE147 DMFC showed the greatest rate at 0.382 mV·h\(^{-1}\), while Cabot and Tanaka DMFC degraded at a moderate rate of 0.292 mV·h\(^{-1}\) and 0.208 mV·h\(^{-1}\), respectively. Again, ELE170 DMFC showed almost no cathode degradation for the entire durability test.

Considering that identical cathodes were utilized in all four DMFCs with different anodes, the difference behavior of cathode degradation most likely was rooted in the interaction with other components in the DMFC, especially the anode. There is some known mechanism for anode-cathode interaction could affect cathode degradation significantly, such as ruthenium crossover. It has been reported that the amount of oxidized Ru species generated by the oxidation of crossed Ru is closely correlated to the performance degradation [23]. The observation of significant cathode degradation for ELE170 may be largely due to ruthenium crossover from the anode to the cathode side.
2.3.7 MEA Resistance

Single MEA resistance of four anodes DMFC was monitored by impedance spectrum test throughout durability test (Fig2-12). At all time periods sampled during the durability test, MEA resistance for ELE147, ELE170 and Cabot DMFC were relatively constant, and stayed around 0.3 $\Omega$ cm$^2$. These values agreed with the methanol crossover measurements, further indicating that no noticeable degradation in the proton exchange membrane occurred during the course of LVADT. Tanaka DMFC showed a relatively larger change in impedance, from 0.3 $\Omega$ cm$^2$ to 0.5 $\Omega$ cm$^2$. The common mechanism for membrane degradation includes mechanical failure, thermal degradation, chemical radical induced degradation and trace metal induced degradation [27]. For Tanaka DMFC, the reason for relatively noticeable change in resistance is still not clear.

2.4 Summary

The anode electrode durability is an important factor determining the performance and degradation of DMFC. In this study, we examined four commercial anode catalysts - Johnson Matthey ELE147, ELE170, Cabot and Tanaka anode DMFC catalyst - in one unique DMFC configuration with an open-cathode design. One low voltage accelerated durability test method, employing a low voltage cycling and rejuvenation technique, was developed to evaluate the durability of DMFC anodes.

For better comparison of before-test and post-test performance of anodes, the DMFC overall power output, cathode and anode potentials are listed in Table 2-5, and degradation rate data for various fuel cell components are summarized in Table 2-6. ELE147 DMFC has the best fresh anode performance, cathode performance and power output (Table 2-5). However, ELE147 also demonstrates the largest output degradation
rate, anode degradation rate and cathode degradation rate. The post-test overall power output of ELE147 DMFC decreased by about 20%, which was slighter lower than post-test power output ELE170 DMFC.

ELE170 DMFC showed excellent durability among all four DMFC anode catalysts, in terms of initial power loss rate, overall power output degradation rate, anode degradation rate and cathode degradation rate for the entire durability test time range (Table 2-6). The excellent degradation resistance indicates that the ELE170 anode is the most stable among the four anode catalysts investigated.

Cabot and Tanaka DMFCs both started with a moderate power output, similar to that of ELE170 DMFC, but they both degraded more rapidly than ELE170 in terms of overall power output, and cathode degradation rate. Cabot and Tanaka both ended with low post-test power output.

An extra-stable anode would not only possess very reliable anode activity/durability, but also demonstrate very positive effects on the durability performance on the other components in the DMFC. For instance, the stability of ELE170 may contribute to the very small cathode degradation rate for ELE170 DMFC, since one of the most known cathode degradation mechanism, ruthenium crossover, would be greatly reduced if the anode is stable.

The above results demonstrate that ELE170 is the best anode candidate among the four anodes investigated for the DMFC configuration with the unique open-cathode design, with a stable anode performance and overall durability when it is incorporated into a DMFC. Based on data obtained from this study, ELE170 was recommended to be
the choice for anode catalyst to be used in the open-cathode design direct methanol fuel cell.
Figure 2-1. Conventional design of a close-cathode DMFC system with its water recycling system (Courtesy of Dr. James Fletcher, University of North Florida).
Figure 2-2. Simplified design of an open-cathode DMFC system with liquid barrier layer. (Courtesy of Dr. James Fletcher, University of North Florida).
Figure 2-3. Schematic of a DMFC stack.
Figure 2-4. Initial durability test of DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes. Operating condition: cell temperature: 50 °C, cell voltage 0.35 V. Anode feed: 0.8 M CH₃OH solution, flow rate 2 mL min⁻¹.
Figure 2-5. Initial life/stabilized power density and initial operational power density loss for DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes. a) Comparison of beginning life and stabilized power densities. b) Comparison of operational power density loss for the first hour of operation. The power density loss was calculated by subtracting stabilized power density of the specific DMFC from the initial power density. Operating condition: cell temperature: 50 °C, cell voltage 0.35 V. Anode feed: 0.8 M CH₃OH solution, flow rate 2 mL min⁻¹.
Figure 2-6. Polarization curves and power densities of DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during a course of 144 hours low voltage accelerated durability test. Polarization test conditions: cell temperature: 50 °C, anode feed: 0.8 M CH₃OH solution, flow rate 2 mL min⁻¹, cathode feed: air, flow rate 2 SLPM.
Figure 2-7. Anode polarization curves and power densities of DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during a course of 144 hours low voltage accelerated durability test. Polarization test conditions: cell temperature: 50 °C, anode feed: 0.8 M CH₃OH solution, flow rate 2 mL min⁻¹, cathode fee: hydrogen, flow rate 0.3 SLPM.
Figure 2-8. Anode relative electrochemical active surface areas of DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during a course of 144 hours low voltage accelerated durability test. Data calculated at 120 mA cm$^{-2}$. Test conditions: cell temperature: 50 °C, anode feed: 0.8 M CH$_3$OH solution, flow rate 2 mL min$^{-1}$, cathode feed: hydrogen, flow rate 0.3 SLPM.
Figure 2-9. Methanol crossover of DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during a course of 144 hours low voltage accelerated durability test. Polarization test condition: cell temperature: 50 °C, anode feed: 0.8 M \( \text{CH}_3\text{OH} \) solution, flow rate 2 mL min\(^{-1}\), cathode feed: nitrogen, flow rate 1 SLPM.
Figure 2-10. Cathode polarization curves of DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during a course of 144 hours low voltage accelerated durability test. Test conditions: cell temperature: 50 °C, anode feed: 0.8 M CH3OH solution, flow rate 2 mL min⁻¹, cathode feed: air, flow rate 2 SLPM.
Figure 2-11. Impedance spectrum of DMFCs with JM ELE147, JM ELE170, Tanaka, Cabot anodes during a course of 144 hours low voltage accelerated durability test. Operating condition: cell temperature: 50 °C, anode feed: 0.8 M CH3OH solution, flow rate 2 mL min⁻¹, cathode feed: hydrogen gas, flow rate 0.3 SLPM, test frequency range: 10 kHz to 0.1 Hz with an AC amplitude of 20 mV.
Figure 2-12. Resistance of DMFCs with JM ELE147, JM ELE170, Tanaka, Cabot anodes during a course of 144 hours low voltage accelerated durability test. Operating condition: cell temperature: 50 °C, anode feed: 0.8 M CH₃OH solution, flow rate 2 mL min⁻¹, cathode feed: hydrogen gas, flow rate 0.3 SLP, test frequency range: 10 kHz to 0.1 Hz with an AC amplitude of 20 mV.
Table 2-1. Power density of DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during 144 hours LVADT at a current density of 120 mA cm\(^{-2}\)

<table>
<thead>
<tr>
<th>LVADT Time (hours)</th>
<th>Power density of DMFCs during the course of LVADT (mW cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ELE147</td>
</tr>
<tr>
<td>Fresh</td>
<td>49.16</td>
</tr>
<tr>
<td>48</td>
<td>44.36</td>
</tr>
<tr>
<td>96</td>
<td>43.16</td>
</tr>
<tr>
<td>144</td>
<td>39.57</td>
</tr>
</tbody>
</table>

Table 2-2. Power density loss rate for DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during 144 hours LVADT at a current density of 120 mA cm\(^{-2}\)

<table>
<thead>
<tr>
<th>LVADT Time Range (hours)</th>
<th>Power density degradation rate for DMFCs (µW cm(^{-2}) h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ELE147</td>
</tr>
<tr>
<td>0-48 hours</td>
<td>99.79</td>
</tr>
<tr>
<td>48-96 hours</td>
<td>25.00</td>
</tr>
<tr>
<td>96-144 hours</td>
<td>74.17</td>
</tr>
<tr>
<td>0-144 hours</td>
<td>66.32</td>
</tr>
</tbody>
</table>

Table 2-3. Anode potential for DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during 144 hours LVADT at a current density of 120 mA cm\(^{-2}\)

<table>
<thead>
<tr>
<th>LVADT Time Range (hours)</th>
<th>Anode Potential for DMFCs (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ELE147</td>
</tr>
<tr>
<td>Fresh</td>
<td>0.383</td>
</tr>
<tr>
<td>48</td>
<td>0.400</td>
</tr>
<tr>
<td>96</td>
<td>0.402</td>
</tr>
<tr>
<td>144</td>
<td>0.404</td>
</tr>
</tbody>
</table>

Table 2-4. Cathode potential for DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during 144 hours LVADT at a current density of 120 mA cm\(^{-2}\)

<table>
<thead>
<tr>
<th>LVADT Time Range (hours)</th>
<th>Cathode Potential for DMFCs (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ELE147</td>
</tr>
<tr>
<td>Fresh</td>
<td>0.829</td>
</tr>
<tr>
<td>48</td>
<td>0.804</td>
</tr>
<tr>
<td>96</td>
<td>0.797</td>
</tr>
<tr>
<td>144</td>
<td>0.774</td>
</tr>
</tbody>
</table>
Table 2-5. Initial and post-test performance for DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during the 144 hours LVADT at current density of 120 mA cm\(^{-2}\)

<table>
<thead>
<tr>
<th></th>
<th>ELE147</th>
<th>ELE170</th>
<th>Cabot</th>
<th>Tanaka</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh overall power output (mW cm(^{-2}))</td>
<td>49.16</td>
<td>44.36</td>
<td>43.16</td>
<td>44.36</td>
</tr>
<tr>
<td>Fresh Anode potential (V)</td>
<td>0.383</td>
<td>0.390</td>
<td>0.40</td>
<td>0.401</td>
</tr>
<tr>
<td>Fresh Cathode potential (V)</td>
<td>0.829</td>
<td>0.789</td>
<td>0.798</td>
<td>0.81</td>
</tr>
<tr>
<td>Post-test overall power output (mW cm(^{-2}))</td>
<td>39.57</td>
<td>40.77</td>
<td>35.97</td>
<td>38.36</td>
</tr>
<tr>
<td>Post-test Anode potential (V)</td>
<td>0.404</td>
<td>0.409</td>
<td>0.417</td>
<td>0.421</td>
</tr>
<tr>
<td>Post-test Cathode potential (V)</td>
<td>0.774</td>
<td>0.790</td>
<td>0.756</td>
<td>0.780</td>
</tr>
</tbody>
</table>

Table 2-6. Degradation in different components for DMFCs with JM ELE147, JM ELE170, Tanaka, and Cabot anodes during the 144 hours LVADT at current density of 120 mA cm\(^{-2}\)

<table>
<thead>
<tr>
<th>Degradation Type</th>
<th>ELE147</th>
<th>ELE170</th>
<th>Cabot</th>
<th>Tanaka</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial power loss rate (mW cm(^{-2}) h(^{-1}))</td>
<td>5.119</td>
<td>0.346</td>
<td>3.071</td>
<td>7.257</td>
</tr>
<tr>
<td>Overall power output degradation rate (µW cm(^{-2}) h(^{-1}))</td>
<td>66.32</td>
<td>24.95</td>
<td>49.90</td>
<td>41.59</td>
</tr>
<tr>
<td>Anode degradation rate (mV h(^{-1}))</td>
<td>0.146</td>
<td>0.132</td>
<td>0.138</td>
<td>0.118</td>
</tr>
<tr>
<td>Cathode degradation rate (mV h(^{-1}))</td>
<td>0.382</td>
<td>0.000</td>
<td>0.292</td>
<td>0.208</td>
</tr>
</tbody>
</table>
CHAPTER 3
THE IMPACT OF METHYL ETHYL KETONE CONTAMINATION OF A PLATINUM/CARBON ELECTROCATALYST ON ITS OXYGEN-REDUCTION ACTIVITY

3.1 Background

For more than several decades fuel cells have been praised for their prospect as efficient, clean means to convert chemical energy into electric energy in many important applications, such as stationary power stations, vehicles [67], and portable power sources [68]. The theoretical efficiency of a fuel cell is higher than the efficiency of a traditional internal combustion engine, electrical power plant at the same power output [69]. Certain type of fuel cell, particularly direct methanol fuel cells, has higher power density than traditional lithium batteries for mobile electronic device applications [70].

However, fuel cell’s great potential has not been achieved. Contaminants in fuel cells, such as CO, CO\textsubscript{2}, NH\textsubscript{3}, H\textsubscript{2}S, NO\textsubscript{x}, SO\textsubscript{x}, sulfur compounds, and carbon – hydrogen compounds, can cause performance damage, or permanent destruction to the anodes, cathodes, membranes, and components [71],[72]. All contaminants listed above could originate from the manufacturing process of fuel cell fuel, such as CO, CO\textsubscript{2}, and CH\textsubscript{4} or from other small organic molecule, produced from hydrogen during reforming process [73]. Contaminants can also come from the air, which is commonly used as the oxidation reactant for fuel cell cathode reactions. For example, NO\textsubscript{x}, SO\textsubscript{x} are commonly present in the atmosphere due to widely existing air pollution [74]. Some undesired ions or organic compounds, such as greases, coming from the system components are also found to be sources of fuel cell contaminantion [75].

Due to the hydrophobic nature of many commercial gas diffusion layer (GDL) materials, GDLs have very low affinity for highly polar solvents, including water. During
the MEA manufacturing process, in order to enable adequate contact between the aqueous platinum catalyst ink and the hydrophobic GDL surface for depositing catalyst ink, wetting agent chemicals are widely used to modify GDL surface properties and improve gas-diffusion electrode performance [76]. Due to the nature of the working environment in the fuel cell, wetting agent chemicals need to be stable and electro-inactive. In other words, the wetting agent is not expected to participate in the electrochemical reactions in the fuel cell, and should not be a poison to the fuel cell catalyst. One commonly used wetting agent is methyl ethyl ketone (MEK) [77].

Despite the large effort made in past decades on electrochemical reactions of adsorbed organic species on platinum electrodes [78-81], many studies have been devoted to analysis of adsorbate configurations in electrocatalytic reactions of simple organic molecules, such as carbon monoxide and methanol. However, knowledge of the oxidation of MEK on Pt-based fuel cell catalysts is very limited due to the nature and complexity of its electrochemical decomposition. The electrochemical response of ketones has not been completely understood on Pt-based catalysts. Zinola et al [82] used differential electrochemical mass spectrometric (DEMS) techniques to elucidate mechanistic details and to monitor product formation of MEK electro-oxidation on Pt surfaces. The oxidation/reduction of MEK adsorbates formed in the potential range of 0.1 to 0.6 V was investigated in their study, and they found that adsorption of MEK takes place in this potential range, reaching a maximum Pt surface coverage by MEK adsorbed species at 0.2 V. The reduction products of MEK were detected to be mainly butane, as well as trace amount of methane, ethane and propane. Carbon dioxide was also detected during the oxidation of the organic residue originating from MEK.
adsorbates not reduced during cycling in the hydrogen region, and 16% of initially adsorbed species from MEK were found to be remaining on the Pt surface after a few cyclic voltammetry cycles. However, to our best knowledge, the effect of the presence of MEK species on ORR activity on DMFC cathodes has not been studied.

The understanding of the kinetic limitations of the oxygen reduction reaction due to the presence of MEK contamination on the fuel cell cathode catalyst is a problem of practical significance. In spite of extensive effort in the past few decades by fuel cell researchers to develop non-Pt-based catalysts for low temperature air cathodes, Pt-based catalysts remain the best known electrocatalysts for the oxygen reduction reaction (ORR) in DMFC applications. The oxygen reduction reaction on different platinum crystal surfaces has been extensively investigated [83-85]. It is well known that the reaction rates of the ORR on Pt surface are very sensitive to surface structure and contamination, due to absorbates [86] such as hydroxyl species and chloride ions [87].

In this study, the main goal is to establish to what extent the presence of the wetting agent methyl ethyl ketone influences the oxygen reduction reaction performance of a typical Pt/Carbon DMFC cathode catalyst. Quantitative kinetic measurements of the ORR of a DMFC Pt/Carbon cathode catalyst upon MEK impurity introduction were performed using the thin-film rotating disk electrode (RDE) method. This technique enables the accurate calculation of kinetic currents of electrochemical reactions on the catalyst without influence from transport limitations. It also allows precise determination of kinetic data, such as Tafel slopes and turnover frequencies. Although this study was conducted in a liquid electrolyte, similar reduced activity can be expected in a DMFC. The result from this study will add to the understanding of the effects of trace amounts
of MEK contamination on DMFC cathode catalyst performance, and will indicate the
necessity of modifying catalyst ink formulations in order to reduce performance losses
and degradation phenomena.

3.2 Experimental Methods

3.2.1 Electro catalyst and Electrolyte

Hispect11100 (70% Pt/C) electrocatalyst (Hispect11100, Johnson Matthey, USA) was chosen as a model cathode catalyst for the investigation of MEK contamination
effects on ORR kinetics. The catalyst was used as received without further treatment. A
0.5 M sulfuric acid solution (Fisher Scientific, USA) was used as electrolyte for the entire
course of study. Ultrahigh-purity nitrogen and oxygen (Airgas, USA) were used for
solution deaeration and oxygen saturation, respectively.

3.2.2 Electrode Preparation

Electrocatalyst suspension ink was prepared by mixing 20 mg of catalyst with
3.84 mL methanol (Acros Organic, USA), 0.08 mL of 5 wt% Nafion (Dupont, USA) and
16 mL DI water. The mixture was agitated continuously in an ultrasonic bath for 15
minutes to achieve a uniform suspension. A glassy carbon rotation disk electrode (Pine
Instruments, 0.196 cm²) was used as the substrate for the supported electrocatalyst.
Before depositing the catalyst ink, the electrode surface was polished to mirror finish
using an Al₂O₃ water suspension, particle size 0.05 μm, and then cleaned ultrasonically
in water for 15 minutes. A 10 μL aliquot of ink suspension (corresponding to 6 μg Pt
metal) was placed on the RDE by micropipette and left overnight to dry completely and
give a constant metal loading of ~30 μg/cm² (geometric). The coating was attached to
the glassy carbon surface.
3.2.3 Electrochemical Measurement

The electrochemical measurements were conducted in a glass cell for rotating electrodes with water jacket. The working electrode was an RDE with a disk made of glassy carbon, the counter electrode was a carbon rod electrode, and the reference electrode was a saturated calomel electrode (SCE), separated from the main glass cell compartment by a reference electrode salt bridge (Pine Instrument, USA) to avoid chloride contamination of the studied solutions. The RDE was screwed onto the Pine Instruments AFSAR-2 electrode rotator for rotating speed control. The cell was thermostated at the desired temperatures by an isotemp cooling/heating recirculating circulator (Fisher Scientific, USA). A Gamry reference 600 potentiostat (Gamry Instruments, Inc., UAS) was connected to the electrochemical reaction cell and used to perform all the measurements.

Cyclic Voltammetry. Special attention was paid to the cleanliness and purity of the electrode surface during cyclic voltammetry measurements. In order to produce a clean surface, the electrode was immersed in deaerated (high-purity nitrogen, Airgas, USA) 0.5M sulfuric acid solution, and cycled between 0 and +1.3 V at 50 mV/s for 10 times until stabilized overlapping curves were obtained. Approximately 150 mL of a 0.5M sulfuric acid electrolyte solution was vigorous bubbled with high-purity nitrogen gas for 1 hour prior to begin the electrochemical test with continuous purging during the experiment. The cyclic voltammetry was obtained between 0 and +1.3 V at 20 mV/s for four cycles. Typically after the first cycle, all successive cycles overlapped with each other, and the last three cycles of CV were averaged. For investigating the contamination effect of different concentrations of MEK on CV, a controlled amount of diluted MEK solution was injected into the sulfuric acid electrolyte using a pipette, to
give a desired concentration of MEK. After changing the MEK concentration in solution, the electrolyte was continuously bubbled with nitrogen for 30 minutes, in order to equilibrate the electrode with the newly introduced impurities and to keep oxygen from dissolving in the solution. The charge due to adsorbed hydrogen was determined from the hydrogen underpotential deposition region [88].

**Oxygen reduction reaction.** The electrode was immersed in sulfuric acid solution previously purged with high purity oxygen (Airgas, USA) for 30 min at 25 °C. The cyclic voltammograms were recorded between 0.05 and 1.2 V at a sweep rate of 20 mV/s for four cycles at each rotation speed, and the last three cathodic scans at each experimental condition were averaged and used for ORR data analysis. The rotation speeds of 400, 625, 900, 1600, and 2500 rounds per minutes were used for the Koutechi-Levich relationship study. For investigating contamination effects of different concentration of MEK on ORR, the desired MEK concentration was introduced into the electrolyte as described in the previous paragraph.

### 3.3 Results and Discussion

#### 3.3.1 Cyclic Voltammetry Studies on the DMFC Cathode Catalyst in the Presence of MEK Contamination

Cyclic voltammetry (CV) was employed as the first approach to probe how the fundamental electrode reactions on a DMFC cathode catalyst are affected in the presence of MEK contamination in an acid electrolyte. Figure 3-1 presents steady-state voltammograms for the Hispect11100 cathode catalyst coated RDE with different concentrations of MEK contamination. After the concentration of MEK was adjusted, the voltammograms typically overlapped with each other after 1-2 cycles, indicating rapid onset of a steady-state at the Pt surface.
The solid blue line represents the base voltammogram with a Pt loading of 60 µg/cm². On the anodic sweep, there are three distinct regions: hydrogen desorption, 0 to 0.4 V, double layer charging, 0.4 to 0.75 V (Note: double layer charging occurs over the entire voltage range applied, but it is the sole process involved over this potential range), and surface oxidation, 0.75 to 1.3V. The features in the hydrogen adsorption region can be rationalized since the carbon-supported Pt particles are normally cubo-octahedral crystallites, mainly consisting of Pt(111) facets with additional Pt(100) facets and low-coordination Pt atoms. The H-adsorption/desorption peak at ~0.12 V are in agreement with data reported for Pt(110) single crystals [89, 90], and may be associated with low-coordination atoms at the edges and corners of Pt particles. The H-adsorption peaks at 0.18 V could also be associated with Pt(110) sites [89, 91]. Furthermore, all the characteristic peaks for H-adsorption/desorption were observed for all voltammograms of MEK contaminated electrolyte at various concentrations.

Progressive changes in the voltammogram profile were observed as a function of increasing MEK concentration. Hydrogen underpotential deposition (H_{upd}) charging current and double-layer charging current were found to decrease with increasing MEK concentration, which suggests that a portion of the Pt catalyst surface is blocked by MEK. The fraction of blocked Pt surface area can be estimated by calculating the area under the hydrogen adsorption/desorption current region between 0.05 and 0.4 V, assuming a hydrogen adsorption stoichiometry of one. In order to minimize influence from the residual oxygen present in solution, the electrochemically active area of Pt, namely SPt, was calculated from an averaged electric charge for the hydrogen desorption/adsorption. Both the positive-going and negative-going potential scans from
0.05 to 0.40 V in cyclic voltammetry at the sweep rate of 20 mV/s at 25 °C were used. The hydrogen adsorption/desorption charge can be determined by \( Q_H = (Q_{\text{Total}} - Q_{\text{DL}}) \), where \( Q_{\text{total}} \) is the total charge transfer in the hydrogen adsorption/desorption region and \( Q_H \) is the capacitive charge from both Pt and carbon-support double-layer charging [92]. The value of \( Q_H \) can be used to calculate the Pt active surface area by assuming that a charge of 0.22 mC cm\(^{-2}\) corresponds to a monolayer of adsorbed hydrogen atoms [93].

The comparisons of \( Q_H \), and Pt active surface areas in various concentration of MEK contamination are shown in Table 3-1. The value of \( Q_H \) of fresh catalyst is 2.42 mC/cm\(^2\), corresponding to a Pt surface concentration of \( 2.51 \times 10^{-8} \text{ mol}_\text{pt} \text{ cm}^{-2} \), assuming a monolayer of adsorbed hydrogen atoms and Faraday constant 96,485 C mol\(^{-1}\). The Pt surface concentration calculated from Pt loading (60 \( \mu \text{g}_\text{pt} \text{ cm}^{-2} \)) and dispersion (13%) is \( 3.69 \times 10^{-8} \text{ mol}_\text{pt} \text{ cm}^{-2} \). Based on Pt surface concentration from hydrogen stripping and dispersion calculation, we can reasonably estimate that roughly 68% of Pt surface atoms are electrochemically active.

The electrochemical active surface area (EAS) for Pt catalyst was decreased by 13%, 21% and 37% in the presence of 10 \( \mu \text{M} \), 100 \( \mu \text{M} \) and 1000 \( \mu \text{M} \) MEK, respectively. Pt catalysts are known for being inefficient in breaking down C-C bonds, but the decrease in Pt EAS with addition of MEK reveal that MEK and/or its electro-oxidation product can block active Pt surface sites and cause catalyst poisoning. This finding agrees with previous work by Zinola et al [82], who found that MEK reached its maximum surface coverage on Pt electrode at 0.2 V, which is within the H\(_{\text{upd}}\) region.

The magnitude of the Pt-oxide formation peak starting from the double-layer region in the positive-going anodic sweep increases with increasing MEK concentration.
This can be explained by the retardation of oxide formation by MEK-related adsorbed species.

The magnitude of the Pt-oxide reduction current peak at around 0.72 V in the cathodic sweep of cyclic voltammetry decreased as a function of MEK concentration, providing additional evidence that absorbent from MEK contamination decreased the number of Pt active surface sites, and the number of available surface Pt atoms for forming Pt-oxide oxidation and reduction current decreased, in agreement with the observation in the Hupd region. The Pt-oxide reduction did not show a shift in peak position, indicating that the reaction potential of the Pt surface may retain the original characteristics after MEK product deposition.

3.3.2 Oxidation Reduction Reaction Kinetics for the DMFC Cathode Catalyst in the Presence of MEK Contamination

3.3.2.1 ORR polarization curves

Fig 3-2 illustrates the RDE polarization curves for the ORR on DMFC cathode catalyst electrode with increasing MEK concentration (0-1000 µM MEK, 1600 rpm, 20 mV s⁻¹, 25 °C, only cathodic sweep shown). From Fig 3-2, the entire polarization curve shifted progressively toward higher overpotential values with increasing concentration of MEK in the electrolyte. However, loss in ORR activity did not seem to be highly sensitive to increasing concentrations of MEK above 10 µM, as demonstrated in the small progressive changes among oxide reduction RDE curves for MEK concentrations between 10-1000 µM.

Fig 3-3 presents the ORR polarization curves (same experimental conditions as in Fig-3-2) for the DMFC Hispect11100 catalyst electrode recorded in oxygen-saturated 0.5 mol L⁻¹ sulfuric acid electrolyte at different rotation rates. The ORR is under mixed
diffusion and kinetic control in the potential range between 0.9 and 0.6 V (cathodic sweep data were used in Fig 3-3), followed by a sole diffusion control region. Apparently, the diffusion controlled limiting current density for ORR was achieved for various rotating rates at cathodic sweeps. As expected, higher rotating rate gave a more robust diffusion of reactant and product species and resulted in a higher ORR current. Another phenomenon which needs to be pointed out is that the ORR was faster during the cathodic sweep than that during the anodic sweep (data not shown). During the cathodic sweep, the Pt-oxide species on surface would be reduced to Pt metal. This phenomenon can be explained by more rapid ORR on reduced compared to than on oxidized Pt surfaces, which is intrinsic characteristic of Pt electrodes.

3.3.2.2 ORR kinetically current density calculation

To quantitatively determine the kinetically limited current density of the electrochemical catalyst, \( j_k \), at different contamination conditions, the measured apparent current density, \( j \), can be described by the following equation [88]:

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} + \frac{1}{j_f}
\]  

(3-1)

where \( j_k \) is the kinetically limited current density of the electrochemical catalyst in the absence of mass-transfer effects, and \( j_d \) is the diffusion-limited current density, and \( j_f \) is the current due to mass transfer through the Nafion polymer/solution interface. It is important to note that equation 3-1 assume a first-order reaction for oxygen [94] reduction in the kinetic current in the mixed activation-diffusion region.

The diffusion-limited current density, \( j_d \), is given by:

\[
j_d = 0.62nFSD^{2/3}C \nu^{-1/6} \omega^{1/2}
\]  

(3-2)
or in short form

\[ j_d = B \omega^{1/2} \] (3-3)

Equation 3-2 is the conventional Levich equation, \( n \) is the number of electrons transferred in the half reaction (mol\(^{-1}\)), \( F \) is the Faraday constant (C mol\(^{-1}\)), \( S \) is the electrode area (cm\(^2\)), \( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( \omega \) is the angular rotation rate of the electrode (rad s\(^{-1}\)), \( \nu \) is the kinematic viscosity (cm\(^2\) s\(^{-1}\)), and \( C \) is the reactant concentration in the solution (mol cm\(^{-3}\)), and \( B \) is the slope of the plot of \( j_d \) vs. \( \omega^{0.5} \). \( j_f \) can be given by the equation

\[ j_f = n_e F D_f C_f / \delta_f \] (3-4)

where \( D_f, C_f \) and \( \delta_f \) are the diffusion coefficient of oxygen, the concentration of oxygen, and the thickness of the Nafion polymer film, respectively. However, the effect of the mass transfer through the polymer/solution interface is significant only when the electrode is covered by a thick Nafion polymer film.

Since the kinetic current density, \( j_k \), is independent of rotation rate, \( \omega \), a linear relationship between \( j_d^{-1} \) and \( \omega^{-0.5} \) can be expected. Fig 3-4 presents the Levich plot for limiting current density, \( j_{\text{lim}}^{-1} \) and \( \omega^{-0.5} \). Clearly, limiting current densities, with or without the MEK presence in electrolyte, were governed by the Koutechi-Levich relationship, as evidenced by the linear relationship in the \( j_{\text{lim}}^{-1} \) vs. \( \omega^{-0.5} \) plot. A least-squares linear fit algorithm was applied to the Koutechi-Levich plots for DMFC catalyst electrode at various MEK concentrations. Therefore the value of \( B \) can be obtained from the slope.
(Table 3-2). Values of B, ranging from 6.64-6.82 mA cm$^{-2}$ rpm$^{0.5}$, are nearly identical with and without presence of different MEK concentrations, indicating that the number of electrons transferred per oxygen molecule in ORR is not changing in the presence of MEK contamination. From Eq 3-1, the diffusion limiting current density can be expressed as:

$$\frac{1}{j_{lim}} = \frac{1}{j_d} + \frac{1}{j_f}$$

(3-5)

If the thickness of the Nafion film $\delta_f$ can be reduced to the extent that $j_f$ becomes much larger than $j_k$ and $j_d$, then the $1/j$ will be a negligible contribution. In this study, the Nafion used in catalyst suspension preparation was in sufficiently small amount, and is not expected to be a significant factor contributing to the limiting current, while only 0.04 $\mu$L of 5% Nafion solution was deposited into a 0.196 cm$^2$ glassy carbon surface. The film thickness of Nafion can be estimated to be ~0.045 $\mu$m by using the density of dry commercial Nafion membranes (~2 g cm$^{-3}$). According to Higuchi’s study [95], the contribution of the film diffusion resistance, $j_f$, to the measured current, $j$, is negligible when the thickness of Nafion film is less than 1 $\mu$m for Pt/C catalysts.

In our study, the $j_f$ value was ~50 mA cm$^{-2}$ for non-contaminated electrolyte, and it decreased to ~36 mA cm$^{-2}$ for electrolyte with the highest MEK concentration. The value of $j_f$ at all conditions was much higher than the measured $j$ (0-6.7 mA cm$^{-2}$). Especially in the potential region of ORR study, 0.7 to 0.9 V vs. SHE, the measured current density is typically less than 3 mA cm$^{-2}$, which is much smaller than $j_f$. Therefore, we conclude that the contribution of the film diffusion resistance to the measured current density should be negligible, and the equation for measured apparent current density, $j$, can be simplified as:
\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_a}
\]  

(3-6)

At any potential, the cathodic kinetic current densities can be corrected for mass transport in solution using Eq 3-6 to calculate the mass-corrected current density (see below).

It is also noteworthy pointing out that the ohmic loss of electrolyte is negligible in this study. According to Dr. John Newman’s study [96], the resistance of a small electrode disk in an electrolyte solution can be calculated according to the radius of the rotating disk electrode and the conductivity of the electrolyte.

\[
R = \frac{1}{2\kappa a}
\]  

(3-7)

where \( R \) is the resistance for a RED in electrolyte solution, \( \kappa \) is the conductivity of electrolyte, and \( a \) is the radius of the disk. In this study, the conductivity of 0.5 M H\textsubscript{2}SO\textsubscript{4} solution was 200 mS cm\textsuperscript{-1} [97], and the radius of disk electrode was 0.25 cm, which yielding a resistance with a value of 5 Ω. For the entire RDE experiment, the maximum current observed was less than 7 mA cm\textsuperscript{-2}, while the ohmic voltage drop of electrolyte solution can be calculated to be 6.8 mV at this current density. The ohmic drop of the electrolyte was significantly smaller than the overpotential of rotating disk electrode and therefore can be neglected.

**3.3.2.3 Oxygen reduction reaction kinetics**

The parallel behaviour of the Koutechi-Levich lines in Fig 3-4 and in the previous literature study on Pt/C electrode in impurity-free electrolyte does not necessarily translate into an unaltered reaction mechanism in the presence of MEK contamination. One of the criteria to check this probability is the Tafel plot slope. The Tafel plots for
mass-transport-corrected (using Eq 3-6) ORR are presented in Fig 3-5 for both impurity-free and MEK-contaminated conditions. The Tafel slope changes continuously in the studied potential range, as reported in previous literature on supported Pt catalysts [98]. The Tafel slopes do not show any evidence of significant changes in the mechanism of ORR in the overpotential region investigated (0.6 to 0.85 V) upon MEK contamination. Tafel slopes were fitted through the linear part in Tafel plots between 0.62 and 0.70 V for both fresh and MEK-contaminated conditions. For clean electrode, the Tafel slope was found to be -147.7 mV decade\(^{-1}\) which is practically close to Tafel slopes for ORR on smooth Pt reported in the literature, with a value of -120 mV decade\(^{-1}\) [99-101].

Tafel slopes were found to be increase more negative with the concentration of MEK present in electrolyte, with values of -157.2 mV decade\(^{-1}\), -162.5 mV decade\(^{-1}\), and -166.3 mV decade\(^{-1}\) for 10 µM MEK, 100 µM MEK and 1000 µM MEK, respectively. The reason for change of the Tafel slope from -60 at low currents to -120 mV decade\(^{-1}\) at high currents at the smooth Pt surface was explained by the change from Temkin to Langmuir adsorption conditions (decrease in the surface coverage) [100]. A similar reason for the change in oxygen adsorption condition on Pt surface due to MEK contamination could possibly be responsible for the observed increase of Tafel slope with increasing MEK contaminant concentration. It is reasonable to assume that the oxidation product of MEK adsorbed on the Pt surface could interfere with oxygen adsorption on adjacent Pt atoms, which would change the ORR kinetics and result in a noticeable change in Tafel slope.

The significant drop in ORR kinetics at the Pt catalyst as a result of MEK contamination is readily evident from the Tafel plots in Fig 3-5. This drop can translate
to a 30 mV increase in terms of overpotential at the current density of 1 mA cm$^{-2}$. Fig 3-6 presents the mass-transfer corrected ORR kinetic current density at different overpotentials upon introduction of MEK contamination. Up to 40% ORR kinetic current density loss was found at a potential of 0.65 V for the DMFC cathode catalyst electrode when the MEK concentration reached 1 mM as compared to those measured on the clean electrolyte. This finding agrees with the H$_{\text{upd}}$-based electrochemically active surface area loss during introduction of MEK contamination, which showed ~37% ESA loss between fresh electrolyte and electrolyte containing 1 mM MEK. From Fig 3-6, dramatic kinetic current density loss commenced even at the very low concentration of MEK, as 26% kinetic current loss was already taking place when MEK concentration was only 10 µM in electrolyte (at 0.65 V). However, the kinetic current loss was not proportional to the MEK concentration, and it decreased in a much slower manner as MEK concentration increased, and this is evident at all potentials investigated in Fig 3-5. Therefore, we conclude that the Pt/C electrode was very sensitive to MEK pollution, and most kinetic activity loss occurred with the introduction of a trace concentration of MEK. Continuously increasing the MEK contamination concentration would further degrade the Pt/C electrode performance, but not in a rapid manner.

The oxygen reduction reaction is known to proceed either in a four-electron pathway to water or in a two-electron pathway to hydrogen peroxide. The four-electron pathway is generally considered as the major reaction route on polycrystalline platinum electrodes in impurity-free acidic aqueous electrolytes [102, 103]. The four electron pathway is also the major reaction pathway for Pt single crystals, except for potentials within the hydrogen adsorption/desorption region for Pt(111) and Pt(110) surfaces,
where quantitative oxygen is reduced in a two-electron pathway [98, 104]. Since the carbon supported platinum DMFC cathode catalyst consists of cube-octahedral nanocrystallites with a large portion of Pt(100) and Pt(111) for particle sizes above 2nm [105], we can assume that the ORR on Pt/C catalyst ($d_{pt}=4.6$ nm) in this study resembles the behavior mostly of Pt(111) and Pt(100). U.A. Paulus et al have investigated the ORR pathways on Pt/Vulcan catalysts deposited on a glassy carbon rotating disk electrode, and it was found the hydrogen peroxide formation was negligible above 0.6 V, and the ORR proceeded exclusively via a complete four-electron pathway [105]. Therefore, we assume that in the potential region above 0.6V in this study, all the ORR in contamination-free electrolyte proceeded in a four-electron pathway manner.

Closely following the method used by T.J.Schmidt et al [106], the turnover frequency (TOF) at different potentials was calculated from the kinetic current densities obtained (cathodic sweep of cyclic voltammetry in oxygen-saturated electrolyte, rotating rate 1600 rpm) according to the formulation:

$$TOF = \frac{i_k}{nFN_s}$$ (3-8)

in which TOF is the absolute reaction rate, defined as number of oxygen molecules being reduced per second and per active surface Pt atom, $i_k$ is the kinetic density in units of mA cm$^{-2}$, $n$ is the number of electrons participating in the ORR reaction ($n=4$ for potential above 0.6 V as explained above), $F$ is the Faraday constant, and $N_s$ is the number of active surface Pt atoms in the unit of atoms cm$^{-2}$ (data listed in Table 3-1). Fig 3-7 presents the TOF as a function of potential for ORR in electrolyte with and without MEK contaminant. An ORR activity decrease per active Pt surface atom of about 30-40% was observed for the Hispect11100 cathode catalyst electrode upon
introduction of different concentration of MEK contamination. To look more closely at the activity loss rate associated with MEK concentration, plot of TOF vs. MEK contamination concentration at different potentials are shown in Fig 3-8. Again, most of the ORR activity loss (60-70% out of total loss between impurity-free and the highest MEK contamination condition) was found to occur after introducing trace concentration of MEK in solution (10 μM MEK in acid solution at all potentials studied). This observation agree with the finding from the Tafel plot study, which confirms that even trace amounts of MEK can impair ORR activity considerably. In terms of TOF, such activity loss translates into a 27% loss at 0.6 V when 10 μM MEK was introduced into acid electrolyte. A similar degree of activity of loss was observed at all potential range (0.6-0.8 V) investigated.

3.3.3 Discussion

According to the experimental results, the presence of trace amounts of MEK caused a destructive influence on ORR at the Pt/C DMFC cathode catalyst electrode. This translated into a 30 mV increase in terms of overpotential, or 50% TOF loss when the MEK concentration reached 1 mM. Loss of Pt active surface area upon introduction of MEK impurity was observed from CV in nitrogen-enriched electrolyte. Therefore, the adsorption of MEK and its reduction /oxidation product was proposed to be one mechanism attributing for the loss of active surface Pt sites and altered ORR activity.

Surface absorbed species have been known to block active surface metal sites and impair ORR activity on Pt electrodes. Previous work by T.J. Schmidt et al.[87] has shown that the onset of ORR is shifted to higher overpotentials with increasing chloride contamination concentration in the electrolyte, with roughly a constant potential decrease of one order of magnitude for each order of magnitude increase in chloride
anion concentration. In our study, MEK impurities impair ORR in a much gentle manner compared to effect on ORR introduced by chloride ions, which suggests that MEK and its associated absorbed species have a relatively weak interaction with the Pt surface. This agrees with the finding by Zinola [82, 107] that majority of initially adsorbed species of MEK at 0.2 V would be reduced in the hydrogen adsorption/desorption potential region, and only 16% of the initially adsorbed species would remain unreduced on the Pt surface. It was also found that trace level of methane, ethane and propane were possibly formed as electro-oxidation/reduction products of MEK on Pt surface. Even though Zinola et al’s work provided very insightful information into the mechanism of MEK adsorption and electrochemical reaction on a Pt surface, the lack of information about surface absorbate species left the reaction pathway and product of MEK on Pt surface unclear.

It has been suggested [107] that the adsorption of MEK on a Pt surface is related solely to the functional group, >C=O group, and that adsorption occurs in the potential range between 0.1-0.6 V [82]. The oxidation of MEK absorbate residue occurs in the Pt oxide formation potential range [107]. The electroadsorption of organic substance with double C=C or C=O bonds on noble metals in acidic electrolytes could trigger a process leading to formation of CO-like surface species [108]. A CO covered polycrystalline Pt electrode cannot be fully oxidized by oxygen; therefore the remaining CO can essentially block the Pt sites for ORR activity [86]. Also, oxidation of CO on Pt surfaces has been associated with a significant amount of peroxide formation, attacks various fuel cell components and leads to performance loss.
It is known that Pt surface adsorbates can interact with ORR reactants. For example, it is known that the reversible adsorption of hydroxyl ions (OH\textsuperscript{-}) on Pt suppresses the ORR kinetics \[86\]. The interaction between MEK associated adsorbates on the Pt surface with ORR reactants or products may also be expected.

3.4 Summary

The oxygen reduction reaction on a typical carbon supported Pt DMFC fuel cell cathode catalyst in the presence of different concentrations of methyl ethyl ketone was investigated in this study using a rotating disk electrode method. The cyclic voltammetry study in nitrogen-enriched electrolyte showed that the Pt electro-active surface area decreased \~13-38\% upon exposure to 1 \(\mu\text{M}-1\) mM MEK contaminated electrolyte. The rotating disk data showed that the rate of oxygen reduction reaction can decrease by \~15-40\% in terms of kinetic current density (corrected for transport limitation), translating into \~15-30\ mV overpotential penalty, upon introduction of 1 \(\mu\text{M}-1\) mM MEK into the acidic electrolyte. In addition, turnover frequency analysis demonstrated that TOF value dropped by \~30-40\% after 1 \(\mu\text{M}-1\) mM MEK was added to the electrolyte solution.

The data in this study and available literature information suggest a proposed mechanism causing ORR activity loss by MEK. MEK adsorbate species act as a site-blocker which reduce the number of available active Pt surface sites for ORR activity. MEK concentration on the order of 0.7 ppm (w/w) would result in a fuel cell voltage loss of 15 mV, which would equally affect the open circuit potential.

The presented data demonstrated that MEK is indeed a pollutant for ORR on Pt/C based DMFC cathode catalysts, and could similarly cause performance degradation of DMFCs. The utilization of MEK in fuel cell manufacture should be given
special attention, either by complete removal of MEK, or by replacing MEK with a more ORR activity friendly component.
Figure 3-1. CV curves for a thin-film Hispect11100 60 wt% Pt/C electrode in nitrogen-saturated 0.5 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\) solution containing dissolved MEK at various concentrations. Pt catalyst loading 60 \(\mu\)g cm\(^{-2}\) GC; 150 cm\(^3\) N\(_2\)-satd. 0.5 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\) solution at 50 °C; sweep rate: 20 mV/s
Figure 3-2. Rotating disk electrode polarization curves for a thin-film Hispect11100 60 wt% Pt/C electrode in the presence and absence of dissolved MEK at various concentrations. Pt catalyst loading 30 µg cm$^{-2}$, O$_2$-sat. 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution at 25°C; 20 mV/s, rotation rate: 1600 rpm.
Figure 3-3. Oxygen reduction reaction polarization curves for a thin-film Hispect11100 60 wt% Pt/C electrode in the presence and absence of dissolved MEK in various concentrations and at various rotating rates. Pt catalyst loading 30 µg cm\(^{-2}\); 150 cm\(^3\) O\(_2\)-sat. 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution at 25 °C; sweep rate: 20 mV/s.
Figure 3-4. Koutechi-Levich plots of the limiting diffusion current density \( j_d \) for ORR for a thin-film Hispect11100 60 wt% Pt/C electrode in the presence and absence of dissolved MEK at various concentrations. Pt catalyst loading 30 µg cm\(^{-2}\); 150 cm\(^3\) O\(_2\)-sat. 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution at 25 °C; sweep rate: 20 mV/s.
Figure 3-5. Tafel plots for mass-transfer corrected ORR kinetic current density for a thin-film Hispect11100 60 wt% Pt/C in the presence and absence of dissolved MEK in various concentrations. Pt catalyst loading 30 µg cm$^{-2}$; 150 cm$^3$ O$_2$-sat. 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution at 25 °C; 20 mV/s; rotation rate: 1600 rpm.
Figure 3-6. Corresponding changes to the mass-transfer corrected ORR kinetic current density $j_k$ at different overpotentials on a thin-film Hispect 11100 60 wt% Pt/C electrode in Oxygen-saturated 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution as a function of dissolved MEK concentration. Pt catalyst loading 30 ũg cm$^{-2}$ GC; 150 cm$^3$ O$_2$-sat. 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution at 25 °C; 20 mV/s; rotation rate: 1600 rpm.
Figure 3-7. Turnover frequencies (TOF) for ORR on a thin-film Hispect 11100 60 wt% Pt/C electrode in Oxygen-saturated 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution at 25°C as a function of potentials without or with presence of different concentration of MEK in electrolyte. Calculated from the kinetic current densities used in Fig 3-5 using Eq 3-7. Pt catalyst loading 30 µg cm$^{-2}$ GC; 150 cm$^3$ O$_2$-sat. 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution at 25°C; 20 mV/s; rotation rate: 1600 rpm.
Figure 3-8. Corresponding changes to the turnover frequencies (TOF) at different overpotentials on a thin-film Hispect11100 60 wt% Pt/C electrode in Oxygen-saturated 0.5 mol L⁻¹ H₂SO₄ solution as a function of dissolved MEK concentration. Pt catalyst loading 30 µg cm⁻² GC; 150 cm³ O₂-sat. 0.5 mol L⁻¹ H₂SO₄ solution at 25 °C; 20 mV/s; rotation rate: 1600 rpm.
Table 3-1. $H_{udp}$ and Platinum electrochemically active surface area for a thin-film Hispect11100 60 wt% Pt/C electrode in Nitrogen-saturated 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution contain dissolved MEK at various concentrations. Pt catalyst loading 60 µg cm$^{-2}$ GC; 150 cm$^3$ N$_2$-sat. 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution at 50 °C; sweep rate: 20 mV/s.

<table>
<thead>
<tr>
<th>MEK Concentration (µM)</th>
<th>0 µM MEK</th>
<th>10 µM MEK</th>
<th>100 µM MEK</th>
<th>1000 µM MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_H$ (mC cm$^{-2}$)</td>
<td>2.42</td>
<td>1.99</td>
<td>1.96</td>
<td>1.84</td>
</tr>
<tr>
<td>Pt EAS (m$^2$ g$^{-1}$)</td>
<td>11.44</td>
<td>9.99</td>
<td>8.99</td>
<td>7.19</td>
</tr>
<tr>
<td>Active Pt atoms surface concentration ($\text{mol}_{pt}$ cm$^{-2}$)</td>
<td>2.51×10$^{-8}$</td>
<td>2.06×10$^{-8}$</td>
<td>2.03×10$^{-8}$</td>
<td>1.91×10$^{-8}$</td>
</tr>
</tbody>
</table>

Table 3-2. Parameters obtained from Levich plots of the limiting diffusion current density $j_i$ for ORR for a thin-film Hispect11100 60 wt% Pt/C electrode in Oxygen-saturated 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution in the presence and absence of dissolved MEK in various concentrations.

<table>
<thead>
<tr>
<th>MEK Concentration (µM)</th>
<th>Fresh</th>
<th>10 µM MEK</th>
<th>100 µM MEK</th>
<th>1000 µM MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$ (mA cm$^{-2}$ rpm$^{0.5}$)</td>
<td>6.64</td>
<td>6.82</td>
<td>6.70</td>
<td>6.66</td>
</tr>
<tr>
<td>$j_i$ (mA cm$^{-2}$)</td>
<td>49.74</td>
<td>49.59</td>
<td>41.31</td>
<td>36.51</td>
</tr>
</tbody>
</table>
CHAPTER 4
KINETIC STUDY OF PROPYLENE HYDROGENATION OVER A PLATINUM CATALYST USING AN IN-SITU HYPERPOLARIZED NMR TECHNIQUE

4.1 Background

Nuclear magnetic resonance (NMR) has been actively used in numerous scientific fields due to its capability to provide information about the structures of chemical and biological systems, as well as dynamic processes such as diffusion and fluid dynamics. However, the nature of low sensitivity of NMR, due to the small population differences between nuclear spin energy levels at thermal equilibrium, requires high concentrations of analyte for successful and reliable measurements. Unfortunately, NMR technique still suffers from low sensitivity, which excludes it from many applications, such as detection of biomarkers or reaction intermediates, often existing in low concentration.

During the past three decades, an emerging technique enables NMR to be applied to in detection of low concentration species. Bowers and Weitekamp first suggested that significantly enhanced NMR signals of molecules could be achieved by addition of hydrogen atoms from parahydrogen (a spin isomer of the H₂ molecule with its two proton spins aligned antiparallel) into the target molecule of interest [109]. The term “hyperpolarization” has been accepted to describe this phenomenon. This effect is known as parahydrogen-induced polarization (PHIP) [109]. The first experimental observation of PHIP was also reported by Bowers and Weitekamp [110]. A 100-200 fold enhancement of NMR signal observed when parahydrogen was added to acrylonitrile to form hyperpolarized propionitrile (CH₃CH₂CN). Eisenshmid et al.[35] and Eisenberg [111] found that the nuclear polarization from hydrogen gas enriched with parahydrogen could be transferred to unsaturated organic molecules through a catalytical
hydrogenation reaction. Each hydrogen atom in a hydrogen molecule (H₂) consists of one proton and one electron, and each proton has a magnetic moment associated with its spin. Therefore, the spins of the two protons in a hydrogen molecule couple to form a triplet state known as orthohydrogen, and a singlet state known as parahydrogen [112, 113]. Orthohydrogen and parahydrogen possess different properties in an NMR spectrum. When parahydrogen-enriched hydrogen gas is used during a hydrogenation reaction, the resulting product can exhibit hyperpolarized signals, as long as the spins are not decoupled, in NMR spectra.

The main advantage of PHIP technology is the strong signal enhancement of the target product in NMR (on the order of 10³ or higher) [114], rendering this a powerful and versatile method for NMR detection of products. For the PHIP reaction to occur, both hydrogen atoms from the former para-hydrogen nuclei must be added to the reactant molecule without lose of the spin correlation. The PHIP effect produces magnified antiphase signal patterns in NMR spectrum from two the former para-hydrogen nuclei in the resulting product. In this manner, resulting products containing para-hydrogen nuclei can be detected and characterized [115]. Because this kind of reaction enhances the signal sensitivity of the products in NMR, which enables para-hydrogen induced polarization to be a powerful analytical tool with various potential applications in chemistry [116], materials science [117, 118], biology [119], and medicine [33].

In early research, the PHIP reactions mostly employed homogenous catalysts, such as Wilkinson’s catalyst (RhCl(PPh₃)₃) [38], and Vaska’s complex (Ir(CO)Cl(PPh₃)₂) [39], because homogenous hydrogenation reactions were more likely to preserve the
spins of the two hydrogen nuclei from a parahydrogen molecule in the same resulting product molecule. The success of PHIP reactions using homogeneous catalysts demonstrated the ability of PHIP to enhance NMR signals for detection of low concentration species. However, the utilization of homogeneous catalysts in PHIP has obvious drawbacks, such as the presence of dissolved catalyst in the reaction mixture.

Heterogeneous catalysts, in contrast to homogenous catalysts, are macroscopic particles which are not dissolved in the liquid. They thus provide a solid phase which can be separated relatively easily from the solvent or gas phase reagents or products. The PHIP reaction provides a unique reaction product labeling technique. The enhanced NMR signal can only be obtained when two hydrogen atoms from a parahydrogen molecule are added to a substrate in a pairwise manner. In contrast to homogeneous catalysts, supported metal catalysts, are not expected to give enhanced PHIP signals, since the hydrogen atoms from parahydrogen can diffuse on the surface of the catalyst after dissociation.

However, PHIP has recently been observed using heterogeneous catalysts, such as highly dispersed platinum on metal oxide supports [42]. Therefore, conditions for pairwise parahydrogen addition can be achieved in heterogeneous alkene hydrogenation reactions. Despite numerous studies of heterogeneous hydrogenation of unsaturated compounds, the mechanism of PHIP hydrogenation reaction on supported metal catalysts is still not well understood.

The occurrence of PHIP in heterogeneous reactions provides several advantages over the homogeneous reactions, including production of gaseous hyperpolarized products, better control of the reaction process, and easier separation of
products from the catalyst. More than 90% of all commercial chemical processes involve heterogeneous catalysts. Therefore, considerably mature technology from existing industrial chemical process technology could be used for a heterogeneous PHIP reaction, including continuous reaction through a catalyst bed reactor instead a batch reactor.

The first reported study of the PHIP effect on supported heterogeneous metal catalysts used Pt/γ-Al₂O₃ for propylene hydrogenation in both the PASADENA (parahydrogen and synthesis allow dramatically enhanced nuclear alignment) and ALTADENA (adiabatic longitudinal transport after dissociation engenders net alignment) PHIP experiments [41]. It was tentatively suggested that numerous surface adsorbed species, including reagent, intermediates and products, would create a confined local surface area which would force two H atoms from the same parahydrogen to be adsorbed close to each other on the metal catalyst surface. Another study [42] investigated the dependence of PHIP signal enhancement on Pt particle size on different oxide supports. The results indicated that the hydrogenation reactions (non-pairwise) are mainly associated with closely packed (1 1 1) and (1 0 0) planes of the platinum surface, and pairwise hydrogen addition is more likely to occur on corner or kink platinum atoms in small Pt particles (<3 nm). Also, platinum catalysts supported on TiO₂ were found to give higher selectivity toward pairwise parahydrogen addition in propylene hydrogenation compared to platinum catalysts supported on Al₂O₃, ZrO₂ and SiO₂. Thus, metal-support interactions also influence pairwise parahydrogen addition. There is only one study on the kinetics of heterogeneous propylene hydrogenation with parahydrogen [120]. In February 2013, Salnikov et al.[120] reported that for non-
pairwise hydrogen addition, the reaction order of propylene hydrogenation over Pt/Al\(_2\)O\(_3\) catalyst is 0.1, while for pairwise addition, the reaction order is 0.7.

In this study, platinum supported on titanium (IV) oxide was employed to study the kinetics of heterogeneous propylene hydrogenation using parahydrogen and NMR. In addition, the temperature dependence of NMR signal enhancement was found for the PHIP effect on Pt/TiO\(_2\) catalyst.

4.2 Experimental Methods

4.2.1. Catalyst Preparation

The catalyst used in this study, platinum supported on titanium (IV) oxide (Pt/TiO\(_2\)), was prepared by precipitation of platinum hydroxide onto the supports from an aqueous solution of hexachloroplatinic acid hexahydrate (H\(_2\)PtCl\(_6\)·6H\(_2\)O) (Alfa Aesar) by controlling solution pH with sodium hydroxide.

More specifically for preparation of Pt/TiO\(_2\) catalyst, 1.98 g of TiO\(_2\) support (Alfa Aesar) was dispersed in 100 mL of deionized water under constant stirring. H\(_2\)PtCl\(_6\)·6H\(_2\)O (0.053 g) was dissolved in 5 mL deionized H\(_2\)O and was poured into the support/water mixture. Platinum hydroxide was deposited onto the support by dropwise addition of a 2.5 mM NaOH solution until the pH value of the catalyst dispersion mixture reached 11. The catalyst dispersion solution was then aged overnight under continuous stirring, and subsequently titrated with diluted acetic acid to pH 7. Then, the mixture was filtered, re-dispersed in deionized water, and filtered a second time after stirring overnight. The aging step was necessary to prepare a reproducible and active catalyst, and washing was necessary to remove residual sodium ions and any chloride contaminant, as these can accumulate on the surface and reduce activity. The
redispersed catalyst was dried at 105 °C overnight, and then calcined at 350 °C for 3 hours.

4.2.2 Chemisorption Measurement

Chemisorption is a powerful technique for measuring supported metal catalyst surface area. Carbon monoxide (CO) chemisorption is widely used to determine the surface area of supported platinum catalysts, the CO molecules adsorb on platinum metal atoms on the catalyst surface, and, if the stoichiometry of CO to Pt atoms on the surface is known, the number of Pt surface atoms can be calculated.

In this study, chemisorption measurements to characterize the active surface area, dispersion and particle size of platinum on the TiO₂ support was performed on a ChemBET 3000 from Quantachrome Instruments. The fresh catalysts were first oxidized using 5% oxygen in helium at 170 °C for 0.5 h and outgassed in helium before the catalyst was reduced in 5% hydrogen in nitrogen at 170 °C for 0.5 h. The oxidation and reduction cycle yield a the catalyst having a well-defined reduced. The catalyst was outgassed in helium at 170 °C for another 15 minutes in order to remove all physically adsorbed hydrogen on the catalyst surface before cooling to room temperature. The optimized temperature of 170 °C was chosen for performing the hydrogen reduction based on the information obtained from temperature programmed reduction (TPR) measurements, which indicated that most of the Pt species was reduced at 170 °C. The catalyst was then subjected to CO adsorption measurements to determine the Pt surface area.

4.2.3 NMR Studies Based on Parahydrogen Induced Polarization (PHIP)

All NMR experiments were performed using a Bruker Avance 400 MHz NMR spectrometer. A U-tube reactor cell was constructed using a ¼” glass tubing and placed
on the top of the magnet. The reaction temperature was controlled by a tube furnace, and monitored with a K-type thermocouple. The thermal couple was inserted into the outlet side of the gas flow in the reactor bed, and separated from the catalyst using a plug of glass wool. A 50 mg sample of the catalyst was used and placed at the bottom of the U-tube reactor. Prior to experiments, the catalyst was reduced and activated under constant hydrogen flow (100 mL/min) for 30 minutes at 170 °C, and then purged with nitrogen (300 mL/min) for 15 minutes at 170 °C to remove any physically adsorbed hydrogen. Following the activation step, the reactor was set to the designated experimental temperature under the same nitrogen flow. The precise delivery of reaction gas mixture of nitrogen (carrier gas), hydrogen (either normal- or para-hydrogen) and propylene was accomplished with mass flow controllers (Alicat Scientific, Inc.). Parahydrogen (p-H₂) was produced by passing normal hydrogen (n-H₂) through a ¼" copper coil filled with activated charcoal and immersed in a liquid nitrogen (77 K) Dewar, yielding a mixture consisting of 50% parahydrogen and 50% orthohydrogen isomers (hereafter referred to as p-H₂). The gas mixture flowed through the reactor at elevated temperature (50-350 °C) and then into the NMR tube positioned in the NMR probe. Since the reaction is exothermic, the reactor temperature increased upon switching from nitrogen to the reaction gas mixture. To reduce heat generation and the temperature fluctuations, a significant portion of nitrogen was introduced into the reaction gas mixture to both dissipate the heat and serve as the carrier gas. However, nitrogen dilution also significantly reduced the magnitude of signal enhancement. Obviously, with a lower concentration of nitrogen, a larger hyperpolarization effect have been achieved. NMR spectra were acquired with 128 scans using a 90 degree pulse
when steady-state reaction conditions are reached. The reactor setup was automated and controlled with a custom-designed LabVIEW program.

As the reaction was performed in a low magnetic field of outside of the superconducting NMR magnet, the resulting spectra exhibited the ALTADENA type polarization pattern. Very reproducible ALTADENA signals could be obtained through the use of precision mass flow controllers (MFCs) and a thermocouple inserted into the catalyst bed. The accurate temperature measurement is a key advantage for ALTADENA, over PASADENA [120], in which the temperature of the catalyst must be measured using an external thermocouple located in the probe outside the NMR tube. The latter is a significant problem for exothermic reactions, as it is difficult to determine the actual reaction temperature. Catalysts were re-activated between each measurement using the same hydrogen reduction method described previously to provide a fresh metal surface.

The collected NMR data were used to calculate the values of the selectivity and activity of PHIP under steady-state reaction conditions.

4.3 Results and Discussion

4.3.1 Catalyst Characterization

By titrating a known amount of adsorbate gas (CO) into a stream of inert makeup gas (helium), the titrated CO gas stream flows over the sample surface and is adsorbed onto the exposed Pt surface until the Pt surface is saturated with CO. The amount of CO gas in the makeup gas helium stream not adsorbed on the Pt surface is measured by a thermal conductivity detector (TCD). By subtracting the known amount of unabsorbed CO from the TCD signal from the total amount of titrated CO, the absorbed
CO gas can be quantitatively calculated. Estimates of the Pt particle sizes were made from these CO adsorption measurements using equation 4-1 [121].

\[ \phi_{av} = \frac{1}{S_{av} V_g} \frac{k C_m V_m}{N_a \rho_m} \]  

(4-1)

where \( \phi_{av} \) is the average particle size; \( S_{av} \) is the average stoichiometry: CO/Pt=1; \( k \) is the shape factor, 5 in this study, which is related to a cube with one side attached to the support and five sides exposed to the environment; \( V_m \) is the molar volume; \( N_a \) is the Avogadro's number; \( \rho_m \) is the metal density; \( V_g \) is the volume of gas adsorbed; and \( C_m \) is the surface density of metal atoms, and a value of 1.25 \times 10^{15} \text{ atoms/cm}^2 was used in this study. Similarly, the platinum metal surface area \( (S_{lr}) \) can be calculated according to equation 4-2.

\[ S_{lr} = \frac{S_{av} V_g}{C_m V_m N_a} \]  

(4-2)

Based on 1% nominal platinum metal loading and CO adsorption measurement, using Eq (4-1) and Eq (4-2), the dispersion and mean Pt metal particle size for 1% Pt on TiO\(_2\) catalyst were obtained, with value of 89.72% and 10.52 nm, respectively.

4.3.2 \(^1\)H NMR Spectra during Propylene Hydrogenation with Parahydrogen

For hydrogenation of propylene over Pt/TiO\(_2\) catalyst, different partial pressures of parahydrogen, propylene and nitrogen carrier gas were used while maintaining the same total gas flow rate. Keeping the constant gas flow rate ensures that travel time of the resulting product from the U-tube reactor to the NMR detector remained the same across all experiments. Therefore, the relaxation factor for different experiments remained the same, allowing the NMR signals resulting from different reactant gas mixtures to be compared.
The NMR signal of the propane product was considered to be proportional to the reaction rate, as we were detecting the NMR signal in a continuously flowing product gas stream. The reaction rate, \( r_{\text{propane}} \), can be treated as

\[
r_{\text{propane}} = C \cdot \left( \frac{I}{\Delta t} \right) \cdot \Gamma
\]  

(4-3)

where \( I \) is the NMR peak integral value of polarized \(^1\text{H}\) NMR signals of the CH\(_2\) and CH\(_3\) groups in propane product, \( C \) is the conversion coefficient, \( \Delta t \) is the detection time of a single scan, and \( \Gamma \) is the relaxation factor.

Fig 4-1 shows the ALTADENA polarized \(^1\text{H}\) NMR signals of the CH\(_2\) and CH\(_3\) groups of propane produced by propylene hydrogenation using both normal hydrogen and parahydrogen. For both normal hydrogen and parahydrogen hydrogenation reactions, the reagent mixture flow rates for nitrogen, hydrogen and propylene gas were 120, 150, 30 mL/min, respectively. The polarized \(^1\text{H}\) NMR signals of the CH\(_2\) and CH\(_3\) groups were successfully detected following the parahydrogen hydrogenation reaction, at their characteristic chemical shifts, as shown by numbers in Fig 4-1. The NMR peak positions for hydrogen in either propylene (resulting from hydrogenation of propyne, present as an impurity), or product propane are labeled with a number on the NMR spectra. The intensities of the hyperpolarized signals are strongly enhanced relative to those obtained with normal-hydrogen and propylene reaction, as evidenced by pronounced peaks of both CH\(_2\) (labeled as peak 2 in Fig 4-1 and CH\(_3\) peaks (labeled as peak 1 in Fig 4-1) on the resulting product propane. The Pt/TiO\(_2\) catalyst clearly leads to ALTADENA signals as parahydrogen flow through the reaction bed.
4.3.3 NMR Signal Enhancement of PHIP and Pairwise Hydrogen Addition Selectivity

We also observed that the PHIP enhanced NMR signal is sensitive to temperature. Fig 4-2 shows the ALTADENA polarized $^1$H NMR signals at different temperature for reactant mixture flow rates of 120, 150, 30 mL/min for nitrogen, parahydrogen and propylene gas, respectively. As the temperature increased from 100 to 250 °C, the NMR signals for both the CH$_2$ and CH$_3$ groups of propane continuously increased monotonically.

PHIP spectra were used in this study to investigate the selectivity to pair-wise addition of hydrogen in both normal hydrogen and parahydrogen hydrogenation reactions. The propane signal from $^1$H NMR spectra can be treated as a summation of both non-polarized ($I_{non}$) and polarized ($I_{polar}$) signals. The polarized signal ($I_{polar}$) is the absolute area of the polarized peak after substraction of the non-polarized ($I_{non}$) peak area. The experimental enhancement factors $\eta_{exp}$ can be calculated according to Eq 4-4:

$$\eta_{exp} = \frac{I_{polar}}{I_{non}}$$

(4-4)

The theoretical enhancement factor may be calculated using the equation [120, 122]

$$\eta_{theor} = \frac{2kT(4\chi_p - 1)}{3\gamma h B_0} \cdot \frac{1}{N_H} \cdot \frac{1}{K}$$

(4-5)

where $k$ is the Boltzmann constant, $T$ is temperature, $h$ is the reduced Planck constant, $\chi$ is the gyromagnetic ratio for $^1$H, $\chi_p$ is the fraction of $p$-H$_2$ in the mixture of supplied hydrogen, $N_H$ is the number of equivalent protons, which equals 2 for CH$_2$ group; $K$ is the ratio of the integrals of the signal intensity patterns for the entire multiplet of the
thermally polarized and hyperpolarized CH₂ group in ALTADENA experiment and is 1 in this study. In our experiment, B₀ is 9.4 Tesla, \( \chi_p \) is 0.5, \( N_H \) is 2, and \( K \) is 1.

The selectivity for pairwise hydrogen addition \( (S_{pair}) \) was estimated as the ratio of the experimental \( (\eta_{exp}) \) and theoretical \( (\eta_{theor}) \) enhancement factors, Eq (4-6)

\[
S_{pair} = \frac{\eta_{exp}}{\eta_{theor}}
\]  

Fig 4-3 presents the pairwise selectivities for propylene hydrogenation over Pt/TiO₂ catalysts at different temperatures. Parawise selectivity exhibited an increase with temperature rising from 50-150 °C, and reaches a maximum value plateau between 150-250 °C, before decreasing over the temperature range between 250 °C and 350 °C.

According to the nature of the heterogeneous catalyst reaction, the enhancement factor and pairwise addition reflects the overall apparent heterogeneous reaction mechanism, which is dictated by a combination of the intrinsic reaction mechanism, surface species adsorption and desorption, and transport processes. For the low temperature range (50-150 °C), the reaction rate for pairwise addition is likely to be controlled by the kinetic reaction rate. In the middle temperature range (150-250 °C), the signal enhancement and pairwise selectivity reached a platea, suggesting that the pairwise parahydrogen reaction is more likely controlled by a diffusion effect, which means that transport of a certain species participating in the reaction became the rate-limiting step. In high temperature range (250-350 °C), decreased pairwise selectivities were observed as the temperature increased, possibly be explained by rapid diffusion of the hydrogen on the surface, thereby decreasing the pairwise addition. The detailed reaction mechanism, including the reaction pathway dominating pairwise hydrogen
addition in propylene hydrogenation, need further investigation to reveal the reaction limiting step in each temperature range.

4.4 Summary

This work represents the study of heterogeneous propylene hydrogenation with parahydrogen employing platinum supported on titanium dioxide. It was found that the NMR signal enhancement depends on the reaction temperature, and different rate limiting steps for the pairwise parahydrogen addition were suggested for three different temperature ranges due to the observed dependency of pairwise selectivity on temperature. However, the detailed reaction mechanism of heterogeneous propylene hydrogenation with parahydrogen remains to be elucidated.
Figure 4-1. $^1$H NMR spectra of propylene hydrogenation with a) parahydrogen and b) normal hydrogen over Pt/TiO$_2$ catalyst at 150 °C and 1 atm. Gas flow rate (total 300 mL/min): N$_2$/p-H$_2$/Propylene=120/150/30 mL/min. Data were taken under steady-state conditions at 1 atm. (NMR data obtained by Ronghui Zhou through collaboration with Dr. Bowers lab in the UF Chemistry Department)
Figure 4-2. 3-D plots of 1H NMR spectra during propylene hydrogenation with parahydrogen over Pt/TiO$_2$ catalyst at different temperatures. Gas flow rate (total 300 mL/min): N$_2$/p-H$_2$/Propylene=120/150/30 ml/min. Data were taken under steady-state conditions and 1atm. (NMR data obtained by Ronghui Zhou through collaboration with Dr. Bowers lab in the UF Chemistry Department)
Figure 4-3. Pairwise selectivities for propylene hydrogenation over Pt/TiO₂ catalyst at different temperatures. Two sets of reactions were carried out with n-H₂ or p-H₂ respectively. The CH₂ group of the product propane was integrated for all calculations, and the integral from n-H₂ was subtracted from that of p-H₂, and the result was treated as pure PHIP contribution. Enhancement factors were calculated based on the ratio between the PHIP and thermal integrals with n-H₂. Pairwise selectivities were calculated based on the ratio of experimental enhancement factor over theoretical enhancement factor. Gas flow rate (total 300 mL/min): N₂/p-H₂/Propylene=120/150/30 mL/min. Pressure : 1 atm. (NMR data obtained by Ronghui Zhou through collaboration with Dr. Bowers' lab.)
CHAPTER 5
KINETIC STUDY OF PROPYLENE HYDROGENATION OVER IRIDIUM CATALYST
USING AN IN-SITU HYPERPOLARIZAED NMR TECHNIQUE

5.1 Background

Parahydrogen induced polarization (PHIP) is a method for increasing the sensitivity of nuclear magnetic resonance (NMR) signals, thereby, extending the NMR technique to potential applications requiring detection of species present at low concentration. PHIP can significantly increase the population differences between nuclear spin energy levels, as a result of addition of two hydrogen atoms from parahydrogen with correlated nuclear spins to a substrate molecule through catalytic reaction. This method can provide an enhancement of NMR signals by several orders of magnitude [35, 109, 110].

As the PHIP reaction requires pairwise addition of both atoms from the hydrogen molecule of parahydrogen to a substrate (to retain the spin correlation), the catalyst employed is a key factor in this type of reaction. As discussed in the previous chapter, PHIP reactions have traditionally utilized homogeneous hydrogenation catalysts [123]. However, an obvious problem of employing homogenous catalysts in PHIP reactions in potential biomedical applications is the presence of dissolved homogenous catalysts, which are difficult to separate from the hydrogenation product. One promising approach to overcome this difficult is to use heterogeneous catalysts in a gas-solid phase PHIP reaction. Recently, PHIP signal enhancement was discovered using a heterogeneous catalyst. The first results of this type were reported in 2008 by Kovtunov et al. [41] in propylene hydrogenation over Pt/Al₂O₃ catalyst. To our knowledge, only two kind of metals (Pt [41], Pd [124, 125]) have been studied as active supported metal catalysts for PHIP activity.
As discussed in chapter 4, supported platinum is the most investigated heterogeneous catalyst of PHIP reactions. Platinum metal particle size effects [42] and the pairwise hydrogen addition reaction order have been reported [120]. For palladium catalysts, it was found that PHIP effect over depends heavily on the support [124]. Palladium supported on TiO$_2$ exhibit strongly polarized peaks for CH$_3$ and CH$_2$ groups of propane produced through propylene hydrogenation, while palladium supported on ZrO$_2$ and SiO$_2$ shows only thermally polarized signals.

Iridium compounds are commonly used as homogenous catalysts for PHIP reactions. For example, Vaska’s complex (Ir(CO)Cl(PPh$_3$)$_2$) [39] and Ir(CO)(dppe)Br and Ir(CO)(dppe)(CN) [47] have demonstrated activity in PHIP reactions. Also, immobilized iridium complexes using [Ir(COD)Cl]$_2$ anchored on silica gels demonstrated catalytic activity towards generating a PHIP effect in the gas-phase hydrogenation of propylene.

Despite previous studies revealing that homogeneous iridium compounds are effective catalysts for PHIP reactions, there has been no study reported regarding PHIP reactions over heterogeneous iridium metal catalysts. In this study, we present the study of propylene hydrogenation reaction by PHIP using Ir on TiO$_2$ as the catalyst. This is the first time the PHIP reaction effect was has been observed and studied on an iridium metal heterogeneous catalyst. Here we report our studies of the propylene hydrogenation reaction on Ir/TiO$_2$ using the ALTADENA protocol [126], where reactions are carried out in the low magnetic field followed by transport into a high field for NMR detection. The discovery of PHIP effect on heterogeneous iridium catalyst is an important contribution to the existing pool of heterogeneous catalysts that are active to PHIP.
5.2 Experimental Methods

5.2.1 Catalyst Preparation

The catalyst used in this study, iridium metal particles supported on titanium (IV) oxide (TiO$_2$), was prepared by precipitation of hexachloroiridic acid hexahydrate (H$_2$IrCl$_6$·6H$_2$O) (Alfa Aesar) onto the supports from an aqueous solution by controlling solution pH using sodium hydroxide with the same method as described in Chapter 4.2.1 More specifically, 1.98 g of TiO$_2$ support (Alfa Aesar) was dispersed in 100 mL of deionized water under constant stirring. H$_2$IrCl$_6$·6H$_2$O (0.056 g) was dissolved deionized H$_2$O and added to the support/water mixture dropwise. The mixture was titrated with a 2.5 mM NaOH solution until the pH value reached 11. The catalyst dispersion solution was then aged overnight under continuous stirring before it was titrated with acetic acid solution to pH 7. The mixture was dispersed in deionized water again, and filtered a second time after stirring overnight. The redispersed catalyst was filtered and dried at 105 °C overnight, and then calcined at 450 °C for 3 hours.

5.2.2 Inductively-coupled Plasma-atomic Emission Spectrometry

The actual metal loadings of prepared Ir catalysts were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin-Elmer Optima 3200 RL). In short, Ir/TiO$_2$ catalyst was fused with sodium peroxide at 500°C for 1 hour, followed by dissolving in water and neutralization with hydrochloric acid. The iridium species concentration in the fusion solution was analyzed by ICP-AES, and then translated into actual iridium metal loading in the catalyst.

5.2.3 Temperature Programmed Reduction Measurements

Temperature Programmed Reduction (TPR) measurement for Ir/TiO$_2$ catalysts were performed using a Quantachrome ChemBET 3000 instrument. For the
measurement, 200 mg of the catalyst was loaded in a quartz tube reactor and secured with plug of quartz wool at the gas flow outlet end. The temperature in the catalyst bed was monitored by an Omega K-type thermocouple. The reduction was performed at a heating rate of 10°C per minute up to a temperature of 500°C. A 5% H₂/N₂ mixture at a total flow rate of 70 SCCM was used for reduction until no further hydrogen adsorption on the catalyst was observed.

5.2.4 Chemisorption Measurement

In this study, chemisorption measurements to characterize the active surface area, dispersion and particle size of the Ir/TiO₂ catalyst was performed on a ChemBET 3000 from Quantachrome Instruments. The fresh catalysts were first oxidized using 5% oxygen in helium at 350 °C for 0.5 h and then outgassed in helium, and then the catalyst was reduced in 5% hydrogen in nitrogen at 350 °C for 0.5 h. The catalyst was outgassed in helium at 350 °C for another 15 minutes in order to remove all physically adsorbed hydrogen on the catalyst surface before cooling to room temperature. The optimized temperature of 350 °C was chosen for hydrogen reduction, based on the information obtained from temperature programmed reduction (TPR) measurements, which indicated that most of Ir species was reduced at 350 °C. The catalyst was then subjected to CO adsorption measurements to determine the Ir surface area.

Estimates of the Ir particle sizes were made from the CO adsorption measurements using equation 4-1[121], in which \( S_{av} \) is the average stoichiometry: CO/Ir= 1 [127, 128]; k is the shape factor, and a value of 5 was chosen in this study, and \( c_m \) is the surface density of metal atoms, assumed to be \( 1.16 \times 10^{15} \) atoms/cm² in
this study. Similarly, the iridium metal surface area $S_p$ can be calculated according to equation 4-2.

5.2.5 Transmission Electron Microscopy (TEM) Measurement

Thin films of Ir/TiO$_2$ solutions (dispersed in isopropanol) were drop cast onto 400 mesh ultrathin carbon film supported copper grids (TED PELLA, INC, USA). TEM micrographs were obtained using a JEOL Model JEM-2010F System.

5.2.6 NMR Studies Based on Parahydrogen Induced Polarization (PHIP)

A Bruker Avance 400 MHz NMR spectrometer was employed for all NMR experiments. A ¼" glass U-tube reactor cell was placed on the top of the magnet, and a tube furnace equipped with a K-type thermocouple was used to control the reactor temperature. The thermocouple was placed in the outlet side of the gas flow in the reactor bed, separated from the catalyst with a glass wool plug. A 50 mg sample of the catalyst was used for each experiment. Prior to experiments, the catalyst was reduced and activated under constant hydrogen flow (100 mL/min) for 30 minutes at 350 °C, followed by purging with nitrogen to remove any physically adsorbed hydrogen. Precise control of reaction gas flow rates of nitrogen (as carrier gas), hydrogen (either normal- or para-hydrogen) and propylene was achieved by using mass flow controllers (Alicat Scientific, Inc.). Parahydrogen ($p$-H$_2$) was produced in-situ by passing normal hydrogen ($n$-H$_2$) through a ¼" copper coil filled with activated charcoal and immersed in a liquid nitrogen (77 K) Dewar, to produce a mixture consisting of 50% parahydrogen and 50% orthohydrogen isomers (referred this mixture as $p$-H$_2$). The gas mixture flowed through the reactor at elevated temperatures (50-350 °C) and then into the NMR tube positioned in the NMR probe. Nitrogen was introduced into the reaction gas mixture as the carrier gas and heat dissipater. NMR spectra were acquired with 128 scans using a 90 degree
pulse when steady-state reaction conditions were reached in the reactor. The reactor setup was automatically controlled with a custom designed LabVIEW program.

As the PHIP reactions were performed in a low magnetic field of and the product was transferred to the high magnetic field for detection, the resulting spectra exhibited the ALTADENA type polarization pattern. For ALTADENA experiments, this reactor setup well-controlled, very reproducible data were obtained due to the precise control of mass flow controllers (MFCs) and the reactor temperature. The measured NMR spectra were used to calculate the values of the steady-state selectivity and the activity of PHIP after the reaction reached constant condition.

5.3 Results and Discussion

5.3.1 Catalyst Characterization

Temperature programmed reduction (TPR) measurements (Fig 5-1) provided further information about the Ir/TiO₂ catalyst. Results showed that two hydrogen reduction peaks associated with iridium were detected. One peak centered at 428K, which was assigned to the Ir species, while the other peak centered at 535K, was assigned to the Ir species interacting strongly with the TiO₂ support. This observation of two separate hydrogen reduction peaks agrees well with results of previous work [129]. Starting from 570K, a broad hydrogen reduction peak appeared, and this peak was attributed to partial reduction of the TiO₂ support [129]. Based on the TPR results, we used a hydrogen reduction treatment temperature of 350°C, at which most of the Ir species would be reduced to metal but a minimum amount of the TiO₂ support would be reduced, for both CO adsorption measurements and hydrogen pretreatment for catalyst activation between hydrogenation reactions.
ICP analysis showed that the actual loading of metal iridium supported on TiO\textsubscript{2} catalyst was 0.54\% (w/w\%). Based on this metal loading and CO adsorption measurement, using Eq (4-1) and Eq (4-2), the dispersion and mean iridium metal particle size were calculated, with value of 70\% and 1.17 nm, respectively.

Fig 5-2 shows a typical TEM image of the Ir/TiO\textsubscript{2} catalyst. The iridium particles are difficult to identify by TEM, since the iridium metal loading and particle size in our catalyst are particularly small (~0.5\% metal loading, ~1.1 nm in diameter, respectively). Also, both iridium particles and the support TiO\textsubscript{2} itself are crystalline, making it more difficult to distinguish metal particles from support by crystal structure patterns. Small particles of iridium metal were highly dispersed on the outermost TiO\textsubscript{2} surface, as can be seen, referring to the arrow in Fig 5-2.

**5.3.2 Temperature Dependence of NMR Signal Enhancement Factor and Pairwise Hydrogen Addition Selectivity**

For hydrogenation of propylene over Ir/TiO\textsubscript{2} catalyst at different temperatures, the total flow rate of parahydrogen or normal hydrogen, propylene and carrier gas nitrogen was maintained. The same gas flow rates ensured that the travel time of the product from U-tube reactor to NMR detector would be the same for all measurements, resulting a constant signal relaxation rate for NMR signal (refer Eq 4-3). The NMR signal of propane product was considered to be proportional to the PHIP reaction rate, as discussed in Chapter 4.

As shown in Fig 5-3, peaks for both the CH\textsubscript{2} (labeled as peak 2 in Fig 5-3) and CH\textsubscript{3} (labeled as peak 1 in Fig 5-3) from resulting product propane molecule were pronounced and detected, providing strong evidence for the occurrence of PHIP effect during proplylene hydrogenation over Ir/TiO\textsubscript{2} catalyst. Fig 5-4 shows the ALTADENA
polarized $^1$H NMR signals of the CH$_2$ group of propane at different temperatures. The flow rates of nitrogen, parahydrogen and propylene gas were 120, 150, 30 mL/min, respectively. The polarized $^1$H NMR signals of the CH$_3$ group and CH$_2$ group from propane were successfully detected, with characteristic peaks (labeled as 1 and 2 in Fig 5-3, respectively).

Fig 5-5 presents the pairwise selectivities for propylene hydrogenation over Ir/TiO$_2$ catalyst measured at a series of temperatures. Pairwise selectivities (also enhancement factors) increase with temperature over the 50-350 °C range. Comparing the pairwise hydrogen addition reactions over Ir/TiO$_2$ and Pt/TiO$_2$ catalyst, significant differences were found. At the same temperature, Ir/TiO$_2$ demonstrated higher pairwise selectivities, as well as NMR signal enhancement factors, than that of Pt/TiO$_2$ catalyst, suggesting that Ir/TiO$_2$ is more active than Pt/TiO$_2$ catalyst towards pairwise hydrogen addition in propylene hydrogenation. Pairwise addition selectivity also increases with temperature between 50-350 °C for the iridium catalyst, while pairwise selectivity for Pt/TiO$_2$ shows a broad maximum between 150-250°C before decreasing at higher temperature (compare Fig 4-3 to Fig 5-5). It is possible that the observed difference of parahydrogen pairwise addition between two catalysts is due to differences in the metal-support interactions. The importance of metal-support interactions in TiO$_2$ supported platinum catalyst is well known, and the influence on the PHIP activity has been discussed in the literature [124].

5.3.4 NMR Signal Enhancement Factor and Pairwise Hydrogen Addition Selectivity with Respect to Hydrogen Concentration

The selectivity in hydrogenation reactions has been shown to be hydrogen concentration dependent. Studies of the relationship between pairwise selectivities and
hydrogen concentration, can provide information about the pairwise hydrogen addition hydrogenation reaction mechanism [130].

For hydrogenation of propylene over Ir/TiO\textsubscript{2} catalyst, the partial pressures of parahydrogen or normal hydrogen, propylene and nitrogen carrier gas nitrogen were varied while maintaining the same total gas flow rate, thereby ensuring the same travel time of resulting product and a constant signal relaxation rate for NMR signal. The NMR signal of the propane product was considered to be proportional to the PHIP reaction rate. The simplified calculation of experimental NMR signal enhancement factor ($\eta_{exp}$) and pairwise addition selectivity ($S_{pair}$) neglected nuclear spin relaxation of the hyperpolarized products during travel time from the reaction site and NMR detection point. Relaxation would reduce the detected hyperpolarization signal, and thus the actual pairwise selectivity values were expected to be larger than the observed values.

Fig 5-6 presents pairwise addition selectivities for propylene hydrogenation over Ir/TiO\textsubscript{2} at different hydrogen partial pressure (at 150 °C). Pairwise addition selectivities, also enhancement factors, increased in the hydrogen partial pressure range between 0.05 to 0.25 atm. Pairwise addition selectivities remain practically constant between 0.25 to 0.7 atm. In the hydrogen partial pressure range investigated (0.05 – 0.7 atm), the enhancement factor and pairwise addition selectivity were relatively insensitive to hydrogen concentration.

5.4 Summary and Discussion

This chapter presents the first observation of the PHIP effect in propylene hydrogenation using a supported iridium catalyst. It was found that on TiO\textsubscript{2} supported iridium is an effective catalyst for PHIP in propylene hydrogenation. The signal
enhancement factors and hydrogen pairwise addition selectivities were found to increase with increasing temperature over the range of temperatures investigated (50-350 °C). Also, the signal enhancement factor and hydrogen pairwise addition selectivity were found to be relatively insensitive to hydrogen concentration.

Heterogeneous catalysts, such as supported metal nanoparticles, are often known to have several different types of active sites which can operate in parallel with significantly different catalytic behavior. The pairwise pathway has been reported to occur more readily on sites with lower coordination numbers such at edges or corners [42]. The possible mechanisms [124] leading to pairwise addition of parahydrogen over Ir/TiO₂ catalyst include: 1) a purely statistical effect in which a small portion of parahydrogen molecules would add to propylene in a pairwise manner; 2) the presence of other substance absorbed on the catalyst metal surface, thereby creating a confined active area that force two H atoms from parahydrogen to stay close together on the metal surface; 3) certain types of active sites, such as corners, and edges, which can operate as isolated active centers for pairwise addition of parahydrogen; 4) physically adsorbed parahydrogen (H-H covalent bond not broken) participates in a pairwise manner in the hydrogenation reaction.

At present, the mechanism of pairwise hydrogen addition is still not well understood. Further studies of reaction orders and activation energy is for both hydrogen pairwise addition and non-pairwise addition are underway. Also, further catalyst optimization and theoretical investigation using Density Functional Theory (DFT) to determine the underlying reaction mechanism are in progress. Heterogeneous
PHIP could provide continuously flowing hyperpolarized fluids for potential applications in diffusion and novel imaging [131].
Figure 5-1. Hydrogen temperature programmed reduction profile for Ir/TiO2 catalyst. Heating rate at 10°C per minute up to a temperature of 500°C.

Figure 5-2. TEM image of Ir/TiO2 catalyst. 100,000X magnification.
Figure 5-3. $^1$H NMR spectra of propylene hydrogenation with a) parahydrogen and b) normal hydrogen over Ir/TiO$_2$ catalyst at 150 °C. Gas flow rate (total 300 ml/min): N$_2$/p-H$_2$/Propylene=120/150/30 mL/min. Data were obtained under steady-state conditions. (NMR data obtained by Ronghui Zhou through collaboration with Dr. Bowers' lab.)
Figure 5-4. 3-D plots for $^1$H NMR spectra measured during propylene hydrogenation with parahydrogen over Ir/TiO$_2$ catalyst at different temperature. Gas flow rate (total 300 mL/min): N$_2$/p-H$_2$/Propylene=120/150/30 mL/min. Data were taken under steady-state conditions (NMR data obtained by Ronghui Zhou through collaboration with Dr. Bowers’ lab.)
Figure 5-5. Pairwise selectivities for propylene hydrogenation over Ir/TiO₂ catalyst at different temperatures. Two sets of reactions were carried out with n-H₂ or p-H₂ respectively. The CH₂ group of the product propane was integrated for all calculations. Integral for n-H₂ was subtracted from that of p-H₂, which was treated as pure PHIP contribution. Enhancement factors were calculated based on the ratio between the PHIP and thermal integrals of n-H₂. Pairwise selectivity was calculated based on the ratio of experimental enhancement factor over theoretical enhancement factor. Gas flow rate (total 300 mL/min): N₂/p-H₂/Propylene=120/150/30 mL/min. (Produced from NMR data obtained by Ronghui Zhou through collaboration with Dr. Bowers’ lab.)
Figure 5-6. Pairwise selectivities for propylene hydrogenation over Ir/TiO$_2$ at different hydrogen partial pressures at 150 °C. Two sets of reactions were carried out with n-H$_2$ or p-H$_2$, respectively. The CH$_2$ group of the product propane was integrated for all calculations. The integral from n-H$_2$ was subtracted from that of p-H$_2$, and the result was treated as pure PHIP contribution. Enhancement factors were calculated based on the ratio between the PHIP and thermal integrals of n-H$_2$. Pairwise selectivity was calculated based on the ratio of experimental enhancement factor over theoretical enhancement factor. Gas flow rate (total 300 mL/min): Flow rate of propylene=30 mL/min. (Produced from NMR data obtained by Ronghui Zhou through collaboration with Dr. Bowers’ lab.)
CHAPTER 6
CONCLUSIONS

This study covered two relatively different topics: 1) platinum catalysts in direct methanol fuel cell applications; and 2) platinum and iridium catalysts in parahydrogen-induced polarization measurements. Several conclusions can be made from this research, and each of the four chapters provided a slightly different focus on these topics.

Chapter 2 presented a comparison study of four commercial direct methanol fuel cell anode catalysts in terms of performance and durability in an open-cathode design fuel cell. This project was designed to facilitate a technical choice for anode catalyst employed in an actual prototype direct methanol fuel cell with a unique open-cathode design. The low-voltage accelerated durability test revealed that the Johnson Matthey (JM) ELE170 anode catalyst had the best durability among the four anode catalysts tested. The JM ELE147 anode had the best beginning-of-life performance, but demonstrated the largest degradation rate among the four anode catalysts investigated. Cabot and Tanaka anodes both demonstrated more rapid degradation compared with the ELE170. Based on the durability test, it was shown that ELE170 is the best anode candidate among the four anode catalysts investigated in the open-cathode design fuel cell setup.

Chapter 3 focussed on understanding the effect of methyl ethyl ketone (MEK), a wetting agent commonly used in the manufacturing of direct methanol fuel cells, on the cathode catalyst, i.e. the oxygen reduction reaction (ORR) of the direct methanol fuel cell. A rotating disk electrode experimental set up and various electrochemical methods
were employed to investigate the ORR at the cathode catalyst when MEK was present. The rotating disk electrode data showed that upon introduction of 1 µM-1 mM MEK into the acidic electrolyte, the rate of oxygen reduction can be decreased by ~15-40% in terms of kinetic current density (corrected for transport limitation), translating to an overpotential loss of ~15-30 mV. In addition, turnover frequency analysis demonstrated that the TOF dropped by ~30-40% after 1 µM-1 mM MEK was added to the electrolyte solution. To explain the contamination effects, it was proposed that the MEK adsorbate acts as a site-blocking species, which reduces the number of available active Pt surface sites for ORR activity. This study is the first report on the contamination effect of MEK on DMFC cathodes, and mitigation procedures were suggested to avoid performance loss due to contamination.

Chapters 4 and 5 focus on the studies of heterogeneous propylene hydrogenation with parahydrogen over titanium dioxide supported platinum and iridium catalysts, respectively. PHIP is an important technique for enhancing the NMR signal and overcoming its inherently low sensitivity. The PHIP reaction over heterogeneous catalysts was recently discovered, and there have been very few studies reported in this field. Chapter 4 presented the study of heterogeneous propylene hydrogenation with parahydrogen over a Pt/TiO₂ heterogeneous catalyst, and Chapter 5 presented the first observation of PHIP effects in propylene hydrogenation over a heterogeneous iridium catalyst. It was found that the NMR signal enhancement depends on the reaction temperature. Because this temperature dependence, different rate limiting steps for pairwise parahydrogen addition were suggested for the three different temperature ranges. The Ir/TiO₂ heterogeneous catalyst also showed the dependency of NMR signal
enhancement and pairwise hydrogen selectivity on temperature, with both increasing with temperature between 50-350°C. NMR signal enhancement and pairwise hydrogen selectivity were found to be relatively insensitive to hydrogen concentration change (0.05-0.7 atm).

The mechanism of pairwise hydrogen addition on a heterogeneous catalyst is still not well understood at this time. A few suggestions can be made for continued work to develop an understanding of the pairwise hydrogen addition mechanism in the PHIP reaction: 1) investigation of reaction kinetics, such as reaction orders and activation energies, for both pairwise hydrogen addition and non-pairwise hydrogen addition over heterogeneous catalysts; 2) Propose possible surface reaction steps and use Density Functional Theory (DFT) to develop theoretical values of kinetic parameters of pairwise hydrogen addition for the proposed reaction steps. By comparing theoretically predicted kinetic parameters with experimental values, validation of the proposed mechanism models can be achieved; 3) Continue heterogeneous catalyst optimization and characterization to reveal relationships between metal catalyst properties and pairwise hydrogen addition in the PHIP reaction. Catalyst metal particle size, crystal planes, metal-support effects, and binary/ternary mixtures of active metals can influence the pairwise hydrogen addition reaction and should be investigated.

Understanding the relationship between various catalysts and pairwise hydrogen addition kinetics will provide important information about the underlying reaction mechanisms, and will ultimately contribute to the development of PHIP into a mature NMR signal enhancing technology for various NMR applications.
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BIOGRAPHICAL SKETCH

Wei Cheng was born in Xuancheng, China in 1983. He earned both his Bachelor of Science and Master of Science degrees both in the Department of Chemical Engineering at the University of Science and Technology in Shanghai in 2004 and 2007, respectively, under the guidance of Dr. Bo Fang. After serving in the Engineering Unit at BASF (Shanghai) Company for three months, Dr. Cheng began his doctoral studies in Chemical Engineering at the University of Florida (UF), under the guidance of Dr. Helena-Halogen Weaver. Dr. Cheng is interested in catalysis, fuel cell, and other energy related chemical engineering domains. He hopes to continue contributing his knowledge and skills learned at UF to the progress of chemical engineering research and the chemical industry.