INVESTIGATION OF THE ORR AT PEM FUEL CELL ELECTRODES: CATALYSIS, PULSE VOLTAMMETRY & HIGH TEMPERATURE APPLICATIONS

BY

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Acknowledgements

I would like to thank my advisors Dr. Thomas Zawodzinski and Dr. R. Mohan Sankaran for guidance throughout my degree program. Building up instrumentation from the barest of components for the nanoparticle work, and the understanding of nanoparticle synthesis and characterization under the supervision of Dr. Sankaran was key to my early work on catalyst synthesis. Dr. Zawodzinski’s support, patience, and keen electrochemical insight has been appreciated, and instrumental to my professional development. I would also like to thank the members of my advisory committee, Dr. Jay Mann and Dr. David Schiraldi for their insights and suggestions.

I would like to thank my funding sources of the Army Research Office’s MURI grant and Graftech, in particular Dr. Orest Adrianowycz of Graftech, as well as those companies that provided materials for my research: 3M, Graftech, and ETEK.

I would like to thank Dr. Rey Sidik for early guidance on Graftech experimental design, and Dr. Hossein Ghassemi and Dr. Vladimir Gurau for numerous conversations and reality checks during my time at Case. Finally, I would like to thank the numerous past and present students of the Zawodzinski research group for discussions, experimental assistance, and encouragement.
The cathode side oxygen reduction reaction (ORR) in a typical PEM fuel cell is the slow catalytic step. Understanding the ORR and its behavior on a Pt surface has implications for the design of fuel cell catalysts, in the choice of Pt alloys for optimizing the ORR. Measurement of ORR kinetic parameters \textit{in situ} in a fuel cell via pulse voltammetry is a means of evaluating catalyst performance under clean, surface refreshed conditions due to the potential program of a normal pulse voltammetry experiment. A Tafel slope of 98mV/decade was determined for the ORR on Pt/C fuel cell electrodes \textit{in situ}, which compares well with the literature.

A microplasma-based method for the synthesis of nanocatalysts with finely controlled composition and structure of particular interest to fuel cell electrocatalysis is developed, and found to produce high purity Pt nanoparticles. Pt nanoparticles containing Co and Fe are also synthesized, with fine size control and narrow size distributions.
High temperature (120°C) fuel cell operation is targeted in the near future for benefits in fuel choice tolerance, and sizing of balance of plant components by eliminating external humidification. The durability of a resin bonded bipolar composite plates is evaluated, and 1100 hours of runtime under 120°C and low relative humidity conditions in a functional fuel cell are demonstrated.
Chapter 1: Introduction

1.1 Fuel Cell Basics

A PEM (Proton exchange membrane) fuel cell is an electrochemical device which converts hydrogen and air into electrical energy through an electrochemical and not the thermal pathway. Fuel cells have had a long history, with W. R. Grove first developing a practical working fuel cell in 1842 (1). The electrochemical conversion of fuel and oxidant has a thermodynamic efficiency close to 80% for a liquid water product (2). Fuel cells are a promising technology for distributed and mobile power applications due to their high power density, high efficiency, fuel options, and fuel delivery options. Among fuel cell technologies are alkaline, molten carbonate, PEM, DMFC (direct methanol fuel cells), direct alcohol, and solid oxide fuel cells. Each technology is suited towards a certain chemistry, operating temperature, and power density.

The difference between a fuel cell and a battery is that a fuel cell operates continuously from externally fed reactants, whereas a battery consumes its available fuel to produce electricity, and must then be disposed of or recharged. Fuel cells have higher power density than batteries due to the fuel being outside the cell, generally light weight of the cell structure, and high energy density of the fuel (3). NASA used higher than ambient pressure, pure H₂/O₂ alkaline membrane fuel cells first in the Gemini program, and later in the Space Shuttle (4).
Figure 1.1. PEM fuel cell primary components and reaction pathway. Hydrogen is introduced on the anode (left), and oxygen is introduced on the right (cathode). Hydrogen dissociates into protons and electrons on the anode side catalyst. The protons are transported through the proton-conducting membrane while the electrons travel through the external circuit. Oxygen present at the cathode catalyst surface combines with the protons travelling through the membrane and the electrons to form water, which is then transported out of the cell.

A diagram of the primary components and reactant pathways of a PEM fuel cell operating with H₂ and O₂ is shown in figure 1.1. Hydrogen is introduced on the anode side and oxygen (usually in the form of air) introduced on the cathode in the typical PEM
fuel cell. The combined membrane and bonded electrode layers plus GDL constitute the membrane electrode assembly (MEA). Hydrogen dissociates into two protons and two electrons. The protons pass through the proton exchange membrane to combine with oxygen and electrons at the cathode. The electrons pass through the exterior circuit and power an electronic load. The overall reaction is:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$  \hspace{1cm} (1.1)

The product of the conventional PEM fuel cell reaction is waste heat and water. A typical operating condition is 80°C at a high level of relative humidity, though work on high temperature PEM fuel cells is progressing with interest at a targeted temperature of 120°C (5, 6).

The operating thermodynamic potential at the cathode is 1.23V vs. RHE, which can be observed experimentally if a conductive single monolayer of PtO covers the Pt surface(7, 8).

$$H_2 \rightarrow 2H^+ + 2e^- \hspace{2cm} E^0 = 0.000V$$  \hspace{1cm} (1.2)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \hspace{1cm} E^0 = 1.229V$$  \hspace{1cm} (1.3)

At open circuit, the theoretical potential of the fuel cell is 1.23V vs. RHE. A number of processes contribute to the measured value in the fuel cell being lower than this. At open circuit, there is a drop in the voltage due to the activation overpotential $\eta_a$. This overpotential is catalyst dependent, as there is an activation process at the catalyst surface.
that must be overcome for equation 1.1 to work. Other contributions to the drop in open
circuit voltage include the hydrogen oxidation reaction, and the mixed potential of PtO / 
Pt on the cathode surface (8-11).

1.2 PEM Fuel Cell Operation

Typical state-of-the-art PEM operating conditions are 80°C, 80-100% relative 
humidity, and 0.6V at a current density of 1.0A/cm². Such a cell requires external 
humidification, and a sufficiently high cathode air flow rate to remove excess water from 
the fuel cell. In practice, cell stacks have system components in place to maximize fuel 
usage (i.e. recirculation of the fuel line).
Figure 1.2. Typical fuel cell polarization curve, showing operating losses. The reversible potential of the cell is 1.23V vs. RHE. The fuel cell polarization curve (blue line) is lower than the reversible potential of the cell due to overpotential losses.

At high potentials and low current densities, activation overpotential for the catalysis of the ORR results in a large potential drop. The flat portion of the polarization curve is governed primarily by resistive losses primarily arising from contact resistance and the membrane resistance. At high current densities, the concentration overpotential is the reason for the potential drop, arising from mass transport limitations. The cathode polarization is the single component responsible for the largest deviation from the theoretical potential in an operating fuel cell.
The activation overpotential is the result of kinetic limitations in cell operation, where mass transport limitations are not relevant. This overpotential, $\eta$, is described by the Tafel equation (12):

$$\Delta V_{activation} = A \ln \left( \frac{i}{b} \right)$$  \hspace{1cm} (1.4)

Where $A = A_{anodic} + A_{cathodic}$, and $b = i_{0,anodic} + i_{0,cathodic}$. The constant $A$ is determined experimentally, and is known as the Tafel slope, and $i_0$ is the exchange current density. The Tafel slope is used in place of the entire Butler-Volmer equation since at high cathode overpotential, the reverse reaction current contribution is negligible (12). The Tafel slope differs for various metal catalyst compositions (13). Ohmic polarization losses are due to a simple Ohm’s law voltage drop across the cell:

$$V = IR$$  \hspace{1cm} (1.5)

The largest resistance drop present in the fuel cell is across the electrolyte membrane in the case of older, thicker (50-75µm) membranes (14). Concentration polarization losses are due to mass transport limitations in the cell, i.e., there exists a voltage where oxygen is depleted at the electrode surface, because it is insufficiently supplied to keep up with demanded current density, resulting in a substantial concentration difference between the catalyst surface and the bulk gas concentration in the electrode plenum. Transport of species to/from the boundary layer at the catalyst surface may also contribute to concentration overpotential (12).
1.3 The Hydrogen Oxidation Reaction

The hydrogen oxidation reaction (HOR) is the electrochemical dissociation of hydrogen on the surface of platinum. The hydrogen oxidation reaction (HOR) overpotential varies little over most of the fuel cell operating range. The anode side hydrogen oxidation reaction progresses sufficiently quickly that most recent research consists of reducing cost of the anode, either by reducing the catalyst loading, or by changing the catalyst morphology (15). Anode performance issues primarily arise from fuel contamination and mitigation strategies have been developed. Under typical PEM fuel cell operating conditions, the HOR proceeds sufficiently quickly in comparison to the oxygen reduction reaction that little needs to be done to enhance the catalytic activity of hydrogen. However, impurities in the fuel (i.e. CO) can strongly bind to platinum and consume surface sites, inhibiting the reaction of hydrogen (16). Minimizing the effect of impurities on fuel cell performance can be accomplished by either raising the temperature to 120°C, where the impurity is more easily stripped from the surface, or designing a catalyst that is impurity-tolerant at 80°C or injecting oxygen or air into the anode (17).

The accepted HOR mechanisms are chemical (equation 1.6), and electrochemical (equation 1.7) (18, 19):

\[
H_2 + 2Pt \rightleftharpoons 2PtH \tag{1.6}
\]

\[
H_2 + Pt \rightleftharpoons PtH + H^+ + e^- \tag{1.7}
\]
Which is then followed by the Volmer reaction discharge of the adsorbed hydrogen atom from the platinum metal surface:

\[ \text{PtH} \leftrightarrow \text{Pt} + H^+ + e^- \]  

(1.8)

For polarizations greater than 50mV, the electrochemical dissociation (1.7) proceeds faster than the chemical dissociation(1.6) (20). Mello studied the HOR on Nafion films on Pt electrodes in liquid electrolyte (21).

### 1.4 The Oxygen Reduction Reaction

#### 1.4.1 Experimental Evidence

What makes a good oxygen reduction catalyst? Underpotential deposited lead on gold is a good ORR catalyst (22). However, the lead clusters are unstable and diffuse into the gold substrate, leading to a catalyst that would be poorly suited to fuel cell use. Platinum on carbon is a remarkably stable and active electrocatalyst for ORR (23-25), though it ripens under fuel cell operating conditions (26). What is known about the state of platinum oxide(s), and the interaction of the oxides with the platinum surface in the description of the ORR on platinum arises from extensive experimental work on single crystal and bulk metal platinum surfaces and nanoparticle systems, as they pertain to fuel cell catalysis, and first principles DFT models of the reactivity of adsorbed species on simulated platinum surfaces.
Early work on the ORR focused on single crystal and “bright” solid crystalline platinum surfaces in liquid media, which mimic the conditions experienced by a PEM catalyst surface under acidic conditions present in the fuel cell. Hoare performed extensive studies of the poly- and single crystal precious metal surfaces, and the characterization of oxygen on these surfaces (27, 28). His findings were that the precious metals were more reactive than was previously had been assumed. Oxygen bound fairly strongly to the platinum surface under high potential conditions, but would also infiltrate the topmost platinum surface layers under higher potential conditions. Oxygen also dissolves in the topmost Pt layers below the surface platinum oxide (29). The implication is that the surface of the platinum is physically altered by exposure to oxygen, and leads to a slight increase in the surface area in an experiment like CV.

Hoare also catalogued the oxides of precious metals, with interesting findings as to the chemical stability and structure of oxides under normal electrochemical and ambient conditions. The status and growth of the various precious metal oxides is important work to consider when designing catalysts. DMFC catalyst technology is a good example of this effect, in that the active species for the oxidation of methanol is the RuOH surface site (16).

Considerable early debates discussed whether the potential measured at a platinum electrode versus a relative hydrogen electrode (RHE) was a direct platinum metal / oxygen couple, or whether the interaction was that of a metal / metal oxide (30-
The importance in this debate is the potential of the metal / metal oxide couple is considerably lower than that of the optimum case - PtO is conductive, whereas higher order Pt(O)_x is not(34). The consensus (7, 27, 29, 34-37) has become that a platinum metal surface does become oxidized under ambient conditions, but the coverage of this oxide is incomplete, and varies with potential. The cell potential and pretreatment cycle of the platinum surface determines the type and thickness of the platinum oxide. Under normal operating fuel cell conditions, the oxide film does not grow past a single monolayer (38). This oxide layer can be considered as an adsorbed layer consumes surface sites.

The following four main experimental observations summarize the known behaviors of the platinum oxide layer:

1) The surface coverage of oxide can be more than one monolayer, with the final oxide type determined by oxidation time and potential (39).

2) The oxide reduction charge is directly proportional to the logarithm of oxidation time over a wide range of oxidation potentials (39).

3) Increasing either the oxidation potential or the oxidation time makes is harder to reduce the resultant oxide (40).

4) The saturation coverage of platinum oxide below 1.8V vs RHE is approximately 2 layers of PtO (41).

Growth of platinum oxides on platinum black used as a PEMFC DMFC electrode was shown to continue over the course of several days (38). The oxide reduction time
remained unchanged past 2 hours, leading Eickes to the conclusion that the performance
loss at longer times is a result of the restructuring of the platinum oxide, however this
oxide was shown to be reduced at lower operating potentials (38). Paik et. al. came to the
conclusion that the accumulation of surface oxygen is limited by the slow rate of
formation at 0.85V, and not due to diffusion, due to the maximum charge passed during a
CV experiment of 0.42mC/cm² which corresponds to approximately 1 monolayer of
oxygen, versus a coulometric oxygen supply rate of 0.04 to 0.8C/cm² s (42). At 0.95,
Paik observed dependence on the cumulative oxygen introduced, and not on the
concentration of oxygen, up to 0.5 x 10²¹ molecule/cm². This was shown to be due to the
availability of surface sites – chemical growth of the surface oxide cannot occur if the
density of sites is too low. The availability of surface sites as a function of potential was
shown by Stamenkovic on Pt₃Ni (111) from CV and surface x-ray scattering
measurements (43).

The range of usefulness and types of surface reactions on platinum are dependent
on the local pH environment. Solid acid electrolyte (namely, Nafion® - Nafion® is a
registered trademark of DuPont, subsequently to be referred to as Nafion) PEM fuel cells
are a highly acidic environment for all components of the cell. Generally, the potentials at
corresponding points on the charging curves at pH values of 0 to 12 in solution shift by
59.2mV (25°C) per unit of pH (44). Obrucheva reports oxygen adsorption by platinum is
about three times higher in H₂SO₄ than in NaOH solutions (45).
1.4.2 ORR by Density Functional Theory Calculations

Density functional theory (DFT) based simulations have been used to predict stable platinum surfaces and alloys, and have been instrumental in determination of predicted binding energies for oxygen species on the surfaces of platinum (46, 47). With advances in computing power, DFT models now take into account ensembles of thousands (48) of atoms, which better simulate the extended platinum surface instead of reaction in a small, local domain. A larger model surface better captures the behavior of the entire electrode. Such advances in theoretical predictions of ORR behavior are instrumental in obtaining a better understanding of the theoretical reactivity of platinum towards oxygen. The agreement between theory and experiment appears to be good (49), up to the approximately 1.2V vs. RHE. Above 1.23V, oxygen gas evolves on the surface of platinum in aqueous solution. The surface of the platinum is also covered with a thicker, or higher order oxide which can be stable under certain (high alkalinity) conditions (34). DFT models have offered a clarification of the probabilities of ORR paths. OOH\textsubscript{ads} has a significant interaction energy with some platinum crystal faces (49, 50). The adsorbed peroxide step is energetically preferred over the direct breaking of O\textsubscript{2,ads}.

Norskov has described the observed overpotential for the ORR by DFT thermodynamics calculations, and has shown that the (111) Pt facet adsorbs oxygen strongly enough at high potentials to prevent proton and electron transfer (46). Adsorbed
oxygen and hydroxyl were found to be stable intermediates present on the platinum surface, using a simple, three step, dissociative mechanism:

\[
\frac{1}{2} O_2 + \* \rightarrow O^* \]  \hspace{1cm} (1.9)

\[
O^* + H^+ + e^- \rightarrow HO^* \]  \hspace{1cm} (1.10)

\[
HO^* + H^+ + e^- \rightarrow H_2O + \* \]  \hspace{1cm} (1.11)

Where * denotes a free surface platinum site. The adsorbed oxygen and hydroxyl species’ binding energies were determined from the reaction energies of the following reactions:

\[
H_2O + \* \rightarrow HO^* + \frac{1}{2} H_2 \]  \hspace{1cm} (1.12)

\[
H_2O + \* \rightarrow O^* + H_2 \]  \hspace{1cm} (1.13)

According to Norskov, these reactions are strongly dependent on the surface coverage of oxygen. Albu and Anderson proposed and calculated the activation energy for the following four reduction steps of the ORR: (50)

\[
Pt - O_2 + H^+_{aq} + e^- (U) \rightarrow Pt - OOH \]  \hspace{1cm} (1.14)

\[
Pt - OOH + H^+_{aq} + e^- (U) \rightarrow Pt - OHOH \]  \hspace{1cm} (1.15)

\[
Pt - OHOH + H^+_{aq} + e^- (U) \rightarrow Pt - OH + H_2O \]  \hspace{1cm} (1.16)

\[
Pt - OH + H^+_{aq} + e^- (U) \rightarrow Pt - OH_2 \]  \hspace{1cm} (1.17)

Where \( U \) is the electronic equilibrium between the transition state complex and the electrode at a particular potential. Albu and Anderson also the reduction of Pt-O to Pt-OH has very low activation energy, facilitating the low energy conversion of the oxide to the
hydroxide. Conway proposed a proton place exchange mechanism for the conversion of PtOH to PtO (40).

Recent work by Neyerlin (51) for the ORR has suggested a Tafel slope of 60mV per decade whereas simulations considering the OOH_{ads} step as the primary reaction pathway suggests a Tafel slope for the ORR of 120mV per decade (52). Norskov et. al. had to assume a symmetry factor of α=1 to explain the 60mV/decade slope, including a 1 electron rate-determining step(46). The constant α is close to 0.5 for most common electrochemical processes (12). Neyerlin also reported a reaction order of 0.5 vs. PO2, which was experimentally measured in situ. This further supports the presence of reactive surface Ox intermediates, and not a direct, 4 electron ORR. Neyerlin also developed an analytical model for the effective proton resistance in the cathode catalyst layer. Surface blocking by adsorbed species changes the observed reaction pathway from 4 electron to 2 electron production of H_{2}O_{2}, with the change in orientation in the adsorbed O\textsubscript{2} primarily being responsible (53-55).

Advancements in computational power have led to DFT models which take into account an entire ensemble of atoms consisting of the bulk crystal interacting with an electrolyte. Some models are also capable of taking into account the interaction of the water layer at the crystal surface. Models of platinum alloy catalysts have been relatively successful at predicting the alloy surface behavior. However, a model of a pure platinum cathode that is capable of describing all experimentally observable behavior does not
exist. This hampers efforts to fully understand the platinum water interaction and in establishing a DFT based platinum activity model. With an accurate model description of observed platinum surface, understanding the behavior of platinum under fuel cell conditions and designing that interaction for increased catalytic activity. The models and experimentally observed platinum surface oxides do not agree.

1.4.2 Heterogenous Catalysis

The development of a fuel cell catalyst for PEM applications is dependent on a catalyst’s performance, electrochemical stability, and cost. Platinum alloys generally have an advantage over pure Pt catalysts on cost due to platinum’s traditionally high cost. Replacement of inactive volume of the catalyst with baser metals has benefits for both the activity and cost of the catalyst. Platinum cobalt alloys, particularly in the form of Pt₃Co/C exhibit higher catalytic performance than pure Pt/C at higher potentials by way of ORR kinetic rate enhancement (56). Xu et. al. have also shown that Pt₃Co(111) has a lower binding energy towards oxygen than Pt(111) (57).
Figure 1.3. A plot of the trends in oxygen reduction activity of selected metals. Taken from Norskov (46), Figure 4.

Volcano plots are predictors of M-OH binding energy, though the plots were not understood to be as such when initially described. The goal for computational models is to optimize the M-O(H)x surface interactions to maximize the ORR activity. Figure 1.3 presents calculated trends in oxygen reduction activity of relevant metals (46). Norskov used DFT calculations to obtain bond energies of adsorbed O and OH for the metals in figure 1.3, and evaluated the free energy, ΔG to determine the overpotential of proton transfer on the metal surface. Weak bonding of oxygen to the chosen metal surface indicates the barrier for oxygen dissociation is large, as in the case of Au. By shifting the onset potential higher, the overpotential for the ORR is lower over a wider range of operating conditions, leading to efficiency gains (49).
In the intervening years, studies have primarily confirmed the presence of oxide on finely divided platinum nanoparticle fuel cell catalysts (56). The higher surface energy of platinum nanoparticles does not inhibit the formation of oxide on the surface, but does lead to a small change in the stability of the oxide species. Platinum nanoparticles have many different crystallographic orientations on each individual catalyst particle (58, 59). The catalytic activity of each platinum crystal orientation differs, as does the adsorbed oxygen bond length, activation, and kinetic parameters. The end result is that the ORR progresses faster on (111) crystal planes than either the (110) or (100) planes. This has implications for the design of a fuel cell catalyst (60-62).

1.4.4 A Note on Cyclic Voltammetry

Cyclic voltammetry (CV) is a technique by which the cell potential is swept in a triangular wave, and the resultant current response of the cell is recorded. A typical cyclic voltammogram for a PEM fuel cell operating under H₂ (anode) and N₂ (cathode) conditions is shown in figure 1.3. The peaks denoted by a and c are the hydrogen desorption region, as reported by Will (63). On clean crystal platinum, a is the desorption maximum for the (111) Pt face, and c is the (100) face. Hydrogen desorption on the (110) face was shown to be within the (100) peak by Will. Peak b and the shoulder d arise from the presence of PtO, as reported by Hoare (28). Peak b is the result of extra desorption sites present on the rough PtO surface. The e and f peaks result from the adsorption of oxygen atom precursors (OH) (28), whereas the g peak is the resultant stripping of oxide grown in peaks e and f from the platinum surface. This peak is subdued in figure 1.3 due
to the low maximum oxidation potential of 1.0V. The double layer charging region is marked as region h. Peak i is hydrogen adsorption on the (100) Pt face, and peak j is hydrogen adsorption on the (111) Pt face, stretched and including the hydrogen evolution region at potentials below 10mV (64). The cyclic voltammogram captures the majority of the operating potential range of the fuel cell, and the same adsorption and desorption processes occur during normal operation, though the anodic and cathodic processes are separated.

Figure 1.3. Cyclic voltammogram between 150 and 1000mV of a platinum fuel cell cathode. The curved arrows indicate the scan direction. The 50cm² cell was run under the following conditions: 100sccm H₂ / N₂ on the anode and cathode, respectively, 80°C, 100%RH, 0psi backpressure, with a scan rate of 50mV/sec, with the last scan of 50 preset above. Refer to text for a description of the labeled regions.
1.5 Pulse Voltammetry

Pulse voltammetry is a single technique amongst the many associated techniques of chronoamperometry. Chronoamperometry techniques measure the current-time relationship in response to applied potentials. Reverse pulse voltammetry was originally chosen first for fuel cell analysis due to the incorporation of a surface cleaning step. The intention is to pre-condition the fuel cell catalyst surface with either a thick oxide layer, or a clean platinum layer, before subsequent oxide stripping or growth. Oxide stripping or growth phases are possible during the same experiment, and are a matter of potentiostat programming and pulse mode.

Pulse polarography is an early technique analogous to pulse voltammetry, though applied to the dropping mercury electrode (DME), and later disk ultramicroelectrodes. The DME is an interesting system for the study of surface reactions due to the included surface refresh condition where a mercury drop detaches from the electrode and a fresh interface is exposed to solution. Subsequent experimentation with DME has been limited due to the use of mercury in the cell, as well as the desire to study actual catalysis reactions.

While normal and reverse pulse voltammetry are general analysis techniques similar in scope to cyclic voltammetry, differential normal pulse and square wave voltammetry
are background subtractive techniques, which are particularly useful for the detection of short lived surface species or low levels of adsorbates.

By the superposition principle, the current response to a single potential step is the result of a charging current and a faradaic, or reaction current. A first principles estimation of the charging current can be made from the reacting area of the fuel cell (obtained from an electrochemical surface area measurement technique, such as CV).

One key to understanding the proper deployment of pulse voltammetry in the fuel cell is distinguishing between charging and faradaic current measured at the electrode. Fuel cells are high surface area devices with a resulting high capacitance. Once one waits long enough to allow the charging current from a single potential step to decay, there exists a time, \( \tau \), where the faradaic current exceeds the background charging current, and ‘useful’ information can be obtained \textit{in situ} on the surface state of the catalyst layer in the fuel cell. The current density at any point in the chromatogram resulting from a single potential step is given by the sum of the charging and reaction currents:

\[
i = i_f + i_c
\]

The charging current is well characterized, and is given by:

\[
i_c = i_0 e^{-t/\tau_c}
\]

\[\text{(1.18)}\]

\[\text{(1.19)}\]
Where \( R \) is taken to be the cell resistance, and \( C \) the cell capacitance and \( i_0 \) is conventionally defined. Assuming Tafel kinetics, the current density \( i_r \) can then be calculated as a function of time from:

\[
  i_r(t) = nFk_bC_0 \exp(\lambda^2) \text{erfc}(\lambda)
\]  

(1.20)

With the dimensionless parameter \( \lambda \):

\[
  \lambda = k_b \left( \frac{t}{D} \right)^{1/2}
\]  

(1.21)

We previously showed via experiment that the faradaic and charging currents could be separated within a reasonable timeframe to allow studies of fuel cell reactions. Numerical solutions to the charging and reaction currents resultant from a single potential step are presented in figure 3, below.

![Figure 1.4. An example of numerical separation of the charging and reaction currents resulting from a single potential step.](image)
This simple model can be applied to the fuel cell case to remove the non-faradic contribution the current when determining a kinetic parameter for the surface oxidation reaction at the cathode.

1.6 High Temperature Fuel Cell Operation and Durability

Mobile power PEM fuel cell applications benefit from a higher operating temperature of 120°C from a reduced sizing in balance of plant components. US DOE technical targets for PEM fuel cell operation at 120°C are established to 2015, and include targets for low humidity operation, which further reduces the size and complexity of balance of plant components, by foregoing external humidification of gas streams (65). The operating temperature of a cell has benefits for the balance of plant thermal components, catalyst choice and operation, and decreased catalyst poisoning effects. Conversely, the rate of degradation of cell structures, primarily the membrane and catalyst layer, are enhanced, due in part to the increase thermal stresses. Developing cells for 120°C operation requires careful materials choice and development to survive the harsher conditions.

1.7 Research Objective

The main objectives of this work are (1) development of a method for high quality kinetics studies on the surface of platinum fuel cell electrodes, application of the method
and kinetics measurements of the ORR on the surface of platinum fuel cell catalysts in situ, (2) synthesis of fuel cell catalysts with properties better than current platinum catalysts. Additionally, degradation studies and considerations for high temperature operation of PEM fuel cells are presented in chapter 4. The specific interest is in the kinetics of Pt(O)x stripping, and understanding the conditions under which the oxide is present and/or removed in a fuel cell. (3) Develop and apply methods for the study of the chemical stability of natural graphite-based bipolar plates under higher than normal temperature of operation.

1.8 Plan of Work

A novel method of preparation of fuel cell catalysts for fuel cell applications with finely controlled composition and structure is presented in chapter 2. This method has applications for the development of high activity and high durability platinum alloy catalysts for fuel cell electrocatalysis.

Given the existing body of research on the use of pulse voltammetric techniques for non-fuel cell electrochemical cells, the development of the technique for fuel cells requires:

1) Understanding charging time scales in a fuel cell electrode.
2) Application of pulse voltammetry to operating PEM fuel cells.
3) ORR kinetic analysis by pulse voltammetry
4) Idealized adsorbate studies.
Fuel cell electrodes are electronically high surface area regions with both capacitive and resistive elements, with different response times. Owing to the three phase interface present in the electrode, the complex interaction between solid, liquid, and gas phases and different rates of diffusion and reaction to/at these phases results in variously timed processes coming to equilibrium on the time scale of seconds in an operating 5cm\(^2\) fuel cell.

By applying pulse voltammetry techniques to fuel cells, the catalyst performance can be evaluated \textit{in situ}, with additional parameters of time, temperature, cell chemistry, and catalyst composition as variables that can be manipulated in future projects. The higher sensitivity and tenability of pulse voltammetry versus cyclic voltammetry positions the pulse voltammetry technique to be more useful for evaluating fuel cell catalysts for development.

A testing methodology was developed for bipolar plate effluent analysis. Combined degradation and durability testing of composite resin plates is not covered in the literature, though HPLC-MS analysis of MEA degradation products has some basis (66). This was part of the high temperature bipolar plate testing due to the failure of current \textit{ex situ} resin analysis methods to adequately simulate fuel cell conditions for the composite bipolar plate.
1.9 References:

24. R. Subbaraman, A Multi-scale Hierarchical Approach for Understanding the Structure of the Polymer Electrolyte Membrane Fuel Cell (Pemfc) Electrodes


Chapter 2: Gas-Phase Synthesis of Platinum-Based Alloy Fuel Cell Catalysts via a Microplasma Reactor

2.1 Introduction

2.1.1 General Introduction

Fuel cells have emerged as a promising means of producing electricity for point-of-use applications. In particular, proton exchange membrane (PEM) fuel cells show potential for mobile applications due to higher power density than traditional batteries, and high electrical efficiency. The critical obstacles for automotive applications are cost and overall weight. At present, fuel cells cannot compete with the internal combustion engine on a cost basis. However, changing emissions standards and a shift towards electrical vehicles favors the adoption of electrical systems for automotive applications.

Platinum (Pt) metal catalysts are the current industry standard for PEM fuel cells. However, Pt catalysts suffer from several problems in a fuel cell environment including Ostwald ripening, loss of performance over extended operation due to poor durability, poor oxygen reduction kinetics, and poisoning from various fuel feeds. The focus of many recent studies has been the investigation of new catalysts for the fuel cell cathode, as the anode catalyst remains active over a broad range of conditions. In addition, lowering the total Pt content of the catalyst either by alloying or decreasing the catalyst loading could potentially decrease the total amount of precious metal required and has the potential to increase the activity of the catalyst towards the oxygen reduction reaction (1).
Core/shell type nanoparticles have been proposed as a possible catalyst architecture to address the cost and performance targets for fuel cell catalysts (2-5). A core/shell particle consists of a Pt shell a few nanometers thick on a base metal (Fe, Ni, Co) core less than 10 nm in diameter. The Pt shell prevents the direct environmental attack of the core since metals like Fe, Ni, Co dissolve in the acidic fuel cell environment and either end up in the membrane, which can lower performance by associating with sulfonic acid groups, or are removed from the cell in the humidified exhaust gases as cations (6). Loss of the core material through a thin or incomplete Pt shell also results in a long term loss in catalytic activity of the catalyst as the core is gradually attacked and dissolves.

Core/shell type nanoparticles may exhibit higher catalytic activity for the oxygen reduction reaction (ORR) than pure Pt catalysts of similar size due to the modification of the d band structure of the Pt layer by the underlying metal layer (7, 8). The d band shift results in a lower Pt-OH binding energy, thereby increasing the kinetic activity of the catalyst. Recent studies of Pt alloy catalysts have shown increased catalytic activity and durability compared to pure Pt catalysts. In particular, PtCo (i.e. Pt shell on Co core) has arisen as a high-performance fuel cell catalyst with better durability than pure Pt catalysts (1). Despite the promise of these alloy catalysts, the structure, composition, and reaction mechanism remains unknown. By synthesizing alloy catalysts with finely tuned structure, we intend to address the characterization of Pt alloy catalysts of a known structure to gain a better understanding of how these catalysts function, and in doing so, develop an optimal fuel cell catalyst with a known structure. The vapor-phase synthesis of core/shell Pt alloy catalysts by a microplasma reactor is proposed as a method to prepare well-
defined materials at low cost and scalable amounts that could lead to the availability of high performance fuel cell catalysts.

Gas-phase synthesis of catalyst nanoparticles is a means of developing nanoparticles with a finely controlled structure for specific applications. The careful control of the initial seed nanoparticle (i.e. core), along with fine control of additional precursors to deposit a shell allow catalysts to be grown with a specific structure. In addition, the continuous synthesis of nanoparticles can be monitored in situ with a differential mobility analyzer (DMA).

2.1.2 The Microplasma Reactor

A microplasma reactor can be used to produce small, high-purity, crystalline nanoparticles with a narrow size distribution in an inert environment. The microplasma, as initially developed by Sankaran, Gordon, and Giapis, is a high-pressure, efficient source of high-energy gaseous species (e.g. ions, electrons, etc.) (9, 10). The plasma microreactor itself is a low power device typically consuming a few milliwatts of power, but operating with high power density on the order of $10^5$ W/cm$^3$. Under typical operating conditions, the plasma voltage and current are approximately 250V and 2.5mA, respectively. The plasma volume is approximately 1.0nL. The energetic species created in the microplasma can be used to crack precursors such as metal-organic vapors. At high-pressures, non-thermal decomposition of the metal precursor results in the homogeneous nucleation of nanoparticles. A microreactor system is well suited to scale-up since the amount of material produced is linearly dependent on the number of reactors.
in operation. Additional reactors can be added until the desired production volume is reached.

Low-pressure plasmas are generally used for materials applications such as CVD (chemical vapor deposition) of high purity metallic films. The plasma is a highly energetic source that assists in the growth of material at low temperatures (near room temperature). When operated in a CVD process, the precursor concentration is typically kept low to prevent the formation of nanoparticles within the plasma, as particles in a film are undesirable. The precursor is typically fed into the reactor chamber with an inert gas to prevent spontaneous precursor decomposition, and to ensure a suitable environment for the formation of plasma. Reactive gases may be added to the process to either react with the precursor to produce new compounds, or to affect the plasma properties (this process is more similar to reactive ion etching, also used in the microelectronics processing industry). Thin films deposited by plasma-enhanced metal-organic CVD often yield purities on the order of 90-99% (11, 12). Metallic precursors that are available for CVD are also capable of being used in the microplasma process since these precursors have appreciable vapor pressures at ambient conditions. For nanoparticle synthesis, we have found that the precursor concentration must generally be approximately 5 ppm in the gas phase.

Alternative methods of synthesizing Pt alloy nanoparticles have typically included conventional thin film deposition methods (13-15) and colloidal methods (16). In the case of the latter, the synthesis routes rely on control over liquid chemistry and
concentration to form nanoparticles of some size distribution. In the case of thin film methods, the prepared surface is a bulk metal that is unsuitable for \textit{in situ} fuel cell catalyst studies. Liquid synthesis techniques generally produce nanoparticles with a broad size distribution, and the catalyst may be sintered during preparation. Sintering may result in a catalyst that has a final metal atom positions that could differ from an ideal structure. In the microplasma process, the catalyst can be formed at low temperature (300°C or lower), thus preserving the structure of the catalysts as it is synthesized. Useful catalysts have been synthesized by the microplasma process for other purposes (17-21).

Liquid phase synthesis techniques are also limited by the availability of catalyst precursors and the unsuitability of certain precursors to the solution chemistry. The gas phase synthesis method is generic, as long as a precursor with some reasonable vapor pressure is available. For most metals of interest to fuel cell catalysis, several organometallic precursors are available, in a range of forms / vapor pressures, owing to use of these materials in the semiconductor industry. The concentration of the precursor required for the formation of nanoparticles is low (on the order of 10-100 ppm) in an inert gas stream.
Figure 2.1. Schematic of continuous flow reactor set-up used to synthesize Pt alloyed nanoparticles. Gaseous precursors (e.g. cobaltocene) are initially decomposed in an atmospheric-pressure microplasma (1) formed between a metal capillary tube (cathode) and arbitrarily sized tube (anode) to nucleate metal seed particles (2). Core-shell nanoparticles are generated by flowing seed particles into a tube furnace (3) and adding additional gaseous precursors such as platinum acetylacetonate. Nanoparticle alloys are size classified based on their electrical mobility in a differential mobility analyzer (4) (TSI Model No. 3085). The concentration of the monodisperse aerosol (5) is measured in a condensation particle counter (not shown). \( R_b \) refers to the ballast resistor (130 k\( \Omega \)). The dashed lines within (4) denote possible trajectories of particles entering the DMA.

Figure 2.2. Closeup of the microplasma reactor. Gas flow is from the left to right (indicated by the arrow) and the microplasma is formed between the metal capillary tube and the mesh counter electrode on the right contained within the sealed quartz tube.
The gas-phase system schematically shown in figure 2.1 consists of a microplasma reactor in series with a tubular flow furnace. Non-thermal decomposition of organometallic precursors in the microplasma leads to the formation of small (1-5nm), metallic nanoparticles with a narrow size distribution. The mean particle size is controlled by the vapor concentration of the precursor, reactor residence time, and other process conditions. Argon is used as the carrier gas for the precursors and to sustain the microplasma. Dry chemical synthesis of the PtCo particles in an inert Ar atmosphere prevents and or limits the formation of oxides on the surface of the catalyst (Co oxidizes to some extent in air). Formation of the Co core and adhesion of the Pt to the core soon after limits the space time during which the pure Co crystal is exposed to potentially oxidative conditions. The complete encapsulation of the Co core by Pt prevents oxidation when the particle are subsequently exposed to air for characterization (or fuel cell applications). Additionally, a microplasma is more readily formed in argon than nitrogen, and prevents the formation of undesirable chemical species. Introduction of oxygen or nitrogen in the plasma could lead to the formation of cobalt oxide or even cobalt nitride compounds (22).

There are limits to the formation of nanoparticles in the current system, i.e. nanoparticles will not form if the precursor concentration is too low, and having too much precursor results in particle agglomeration. In the furnace, a high Pt precursor concentration could lead to nucleation of Pt particles by pyrolysis. Conditions must be carefully controlled to prevent the formation of new nanoparticles in the furnace instead of vapor deposition on existing ones. If nanoparticles are formed by pyrolysis in the furnace, the particle size distribution is observed to change by increasing in intensity.
This is consistent with our understanding of the process since nanoparticles formed by pyrolysis will create new particles and increase the overall number density. Sintering of the two populations of particles has not been investigated, though due to the usual low operating temperature of the furnace (500°C), and the short residence time (20 seconds), insufficient thermal energy is present in the furnace to force the sintering of both populations of nanoparticles.

With a single microplasma reactor, nanoparticles are synthesized at an approximate rate of micrograms per hour. The bipolar charger within the DMA charges approximately 1% of the particles in the flow. Methods of collection for the synthesized nanoparticles include filtering, electrostatic precipitation, thermophoretic precipitation, and sonic impaction. The filtering technique is intended to trap a large percentage of the nanoparticles in the flow, with the intent of studies such as XRD. Demonstrating the ability to capture macroscopic quantities of material is also necessary for the eventual preparation of a fuel cell catalyst. Various materials for filtration have been suggested, with the most promising being materials that do not have spectral lines in the same region as the alloying metals. Since most filters recommended for nanoparticles are of either a fibrous glass or organic nature, the XRD signal from Pt and heavy alloying elements lies safely away from that of the background filter material. Collection via bubbling the gas stream carrying the nanoparticles through a liquid has also been suggested, but offers very low collection efficiency.
2.2 Experimental

2.2.1 Equipment Setup

Details of aerosol size classification have been previously described by Camata (23). In general, the differential mobility analyzer (DMA, TSI Inc., Model # 3085) was coupled with a condensation particle counter (CPC, TSI Inc., Model 3076) for in situ nanoparticle sizing and counting. The DMA has a lower detection limit of 2nm. An electrostatic precipitator (TSI Inc., Model 3089) was used for sample deposition on conductive substrates (Si wafer or carbon coated TEM grid) (24). Metallocene compounds were sublimed in Ar at room temperature, with a balance of pure Ar to maintain 100sccm of gas flow through the microplasma reactor. A tube furnace with a quartz tube connected immediately after the microplasma reactor was used to deposit a different material on the nanoparticle surface. Furnace temperature was accurate in the range of ± 5°C.

An FEI Tecnai F30 high resolution transmission electron microscope (HRTEM) at 300kV and a Philips CM-20 TEM operating at 200kV were used to obtain images of nanoparticles.

Typical deposition times to prepare a TEM sample are on the order of one hour. Specimens prepared by this method have a uniform coverage of nanoparticles across both thick and thin regions of the grid. Sufficient nanoparticles are present on the grid for XEDS (X-ray Electron Dispersive Spectroscopy) on both microscopes available in the SCSAM. The Tecnai TF30 microscope has a sufficiently sensitive XEDS instrument to detect the presence of Pt in the sample, and for quantitative studies. However, due to the
position of the XEDS instrument in the F30 column, XEDS spectra also contain element characteristic information of the lens pole pieces – in particular, iron and cobalt. Thus, the quantification of alloy nanoparticle composition with the Tecnai microscope has not been possible. The Philips CM-20 XEDS instrument does not pick up the signal from the microscope pole pieces, however the instrument has a lower maximum resolution than the F30, and a sample with sufficient nanoparticle coverage for the TF30 will have far too few nanoparticles for XEDS using the CM-20.

Nanoparticles can be lost to the furnace walls by Brownian motion and thermophoretic forces. As a result, the concentration of nanoparticles present in the gas flow drops by a small amount when exiting a hot furnace. Auto thermal decomposition of the ferrocene and cobaltocene precursors in the furnace is not evident up to the furnace maximum operating temperature of 1000°C. This is most likely due to the very low concentration of the precursor in the flow. A minimum concentration of precursor vapor is required to form nanoparticles in the furnace – below this minimum concentration, nanoparticles will not form and the precursor will only deposit on the seed particles.

The original purpose of adding hydrogen to the reaction was to scavenge oxygen, water, and the organic portions of the organometallic precursors and increase the purity of the synthesized nanoparticles. Additionally, hydrogen has a higher thermal conductivity than the argon carrier gas. The reducing atmosphere could prevent core oxidation while the shell grows.
2.2.2 Fuel Cell Catalyst Synthesis

The proposed core/shell structure catalysts of 5-10nm total size will be synthesized via a microplasma reactor as described previously. Pure Pt nanoparticles will be synthesized via the microplasma to serve as a reference. Dry synthesized nanoparticles would be dispersed in liquid solution as a surface stabilized colloid, and a method of attachment similar to that used by Lim would be used to attach the stabilized Pt or Pt alloy nanoparticles to the carbon black surface (25). Platinum alloy nanoparticles of a mixed type and core/shell type will be synthesized for comparison and characterization. The mixed alloy can be grown by feeding both the Pt precursor and the alloying metal precursor into the microplasma at a fixed ratio of vapor concentration. By feeding the Pt precursor into the reactor system immediately following the plasma, the desired core/shell type structure should be formed due to the stepwise addition of the Pt precursor to the alloying metal core.

2.2.3 Catalyst Characterization

The size, shape, chemical stability, and electrocatalytic properties of as-grown Pt and Pt alloy nanoparticles were determined. The morphology of the particles was confirmed by imaging and compared with aerosol measurements. TEM histograms will be used to confirm the particle size distributions acquired by the DMA. Chemical characterization is required to determine the composition of the synthesized Pt alloy catalysts. X ray diffraction (XRD) will be used to determine average compositional and crystal information of thin films. XEDS is used to evaluate the composition of individual nanoparticles.
2.3. Results & Discussion

2.3.1 Platinum Nanoparticles

Pure Pt nanoparticles were initially synthesized as a reference catalyst for electrochemical studies. Two different CVD precursors of Pt were used—(trimethyl)methylcyclopentadienylplatinum(IV) (subsequently abbreviated to MeCpPt$^{\text{IV}}$Me$_3$), based on (26-28) and platinum acetylacetonate (referred to as Pt(acac)$_2$). The MeCpPt$^{\text{IV}}$Me$_3$ was stored below room temperature because of its low melting point of 30°C. Platinum acetylacetonate is more stable at room temperature, and required no special precautions; additionally, prior work has shown that this precursor can form Pt nanoparticles in the liquid phase (29). Of the two Pt precursors, Pt(acac)$_2$ produced narrower dispersions of particles. The higher vapor pressure allowed for tighter control over the concentration of Pt(acac)$_2$ without resorting to inadvertent decomposition of the precursor, as in the case of MeCpPt$^{\text{IV}}$Me$_3$. MeCpPt$^{\text{IV}}$Me$_3$ has a vapor pressure of 0.053Torr at 23°C and melts at 30°C (30), and Pt(acac)$_2$ has a vapor pressure of 1.0Torr at 180°C and melts at 250°C (31). Experimental data were fit with a log-normal distribution, with a geometric mean diameter $D_g$, and standard deviation $\sigma_g$. At low precursor flow rates, particles would not be detected by the DMA, whereas high precursor flow rates (high vapor concentration) would result in high particle counts, and large particles, most likely due to particle agglomeration.
Figure 2.3. Platinum nanoparticle distributions from the two different Pt precursors and a log-normal distribution fit. The Pt(acac)$_2$ distribution ($D_g = 2.75$nm) has $\sigma_g = 1.12$, and the MeCpPt$^\text{IV}$Me$_3$ ($D_g = 5.74$nm) distribution has $\sigma_g = 1.15$.

Figure 2.3 shows representative size distributions obtained for the two different Pt precursors. The particles synthesized from Pt(acac)$_2$ had $D_g = 2.75$nm, and $\sigma_g = 1.12$, whereas the smallest synthesized particles from MeCpPt$^\text{IV}$Me$_3$ had $D_g = 5.74$nm and $\sigma_g = 1.15$. Collection efforts for the MeCpPt$^\text{IV}$Me$_3$ based nanoparticles were attempted on an n-type silicon wafer, glass, and TEM grid supports via electrodeposition, but no particles were found via TEM, nor was any Pt signal seen during XRD analysis. Owing to the large organic fraction of the MeCpPt$^\text{IV}$Me$_3$ precursor, it is possible that the observed large particles are primarily carbon, with a small Pt center.

The nanoparticles synthesized from Pt(acac)$_2$ had a narrow size distribution suitable for use as a fuel cell catalyst. The smallest diameter particles in figure 2.4 below 2nm fall below the DMA detection limit, and would lead to a broadening of the observed
standard deviation. Deposition of the Pt(acac)$_2$ nanoparticles by electrodeposition onto a TEM grid was typically at -9.5kV (field strength of 3.2kV/cm) and 1.5slpm of gas flow (reactor gas with a N$_2$ balance). The deposited nanoparticles had good coverage over the TEM grid (figure 2.5). TEM images in figures 2.5 and 2.6 show nanoparticles grown under conditions detected by the DMA in figure 2.4.

![Graph](image)

Figure 2.4. Sizing data for 5.75nm ($\sigma_g = 1.15$) nanoparticles synthesized from Pt(acac)$_2$. 
Figure 2.5. HRTEM image of Pt nanoparticles formed from Pt(acac)$_2$ and deposited on a carbon coated Cu grid. The nanoparticles are small (<10nm), and show a preference of adhesion to the thicker areas of the carbon film.

Figure 2.6. HRTEM image of a Pt nanoparticle. The particle is attached to a thicker region of the stretched carbon layer over a copper mesh support, and freely hangs. The nanoparticle is crystalline, as there are varying crystal planes evident in the image.
Figure 2.7 EDS spectrum of Pt nanoparticles in figure 2.X-1. Particles were deposited in the presence of a 1.5kV electric field onto an amorphous carbon film supported by a copper grid. Copper and carbon peaks on the spectrum are the result of this TEM grid. The iron and cobalt peaks are a background characteristic of the particular microscope. Pt peaks are apparent in the spectrum of the sample. (Off-scale peaks correspond to carbon and iron).

Figure 2.6 reveals that the synthesized nanoparticles are small and crystalline, with many varying crystal facets. Whether the presence of many crystal planes on a single particle is due to the agglomeration of numerous small particles to form the $D_g = 5.75\text{nm}$ nanoparticle, or whether the particle forms in one step is unknown. EDS analysis (figure 2.7) confirms the presence of Pt in the nanoparticle, with Cu present from the TEM grid mesh, and Fe and Co resulting from the microscope.
2.3.2 Cobalt Core Nanoparticle Synthesis

Initial experiments were intended to produce an alloy of Pt and cobalt corresponding to a final nanoparticle size of about 5.0nm. This size was chosen since it is comparable to current generation fuel cell catalysts, the particles would be easily visible for HRTEM microscopy, and pure Pt nanoparticles of similar size could be produced for purposes of comparison. The precursor for cobalt was cobaltocene (bis-cyclopentadienyl cobalt), due to the use of ferrocene and cobaltocene in the literature for the formation of metallic nanoparticles for the formation of carbon nanotubes (20, 32, 33). Organometallic precursors such as ferrocene have a high vapor pressure (32). Precursors with relatively low vapor pressures at room temperature were chosen so as not to oversaturate the local plasma environment with nanoparticles, leading to possible extinction of the plasma during operation. A furnace was to be used for the second coating part of the process, operating at a sufficiently high temperature to cause the decomposition of the coating precursor in the presence of seed nanoparticles. The presence of seed nanoparticles within the furnace was seen as a more favorable location for the crystallization of the precursor gas instead of the hot reactor walls. The core/shell CoPt nanoparticle was to be formed by the stepwise addition of Pt precursor to a seed particle of cobalt formed in the plasma. The lattice mismatch between the shell and the core of the envisioned nanoparticle has not been studied, and the possibility of an inherently strained state remaining in the final nanoparticle remains a possibility. The stepwise addition of Pt to Co should result in the growth in average size of the nanoparticle distribution as measured by the DMA, without increasing the total particle number. An increase in total particle number indicates the formation of new seeds of Pt forming from the thermal
decomposition of the Pt(acac)$_2$ within the furnace. Hydrogen was added in all cases with cobaltocene to scavenge oxygen species and carbon from the surface of nanoparticle exiting the plasma.

![Particle Size Distribution Graph](image)

Figure 2.8. Particle size distributions of synthesized pure Co, CoPt (core/shell), and large diameter CoPt agglomerates at 700°C furnace temperature. $D_{g, \text{Co}} = 5.81\text{nm}$, $\sigma_{g, \text{Co}} = 1.16$, $D_{g, \text{CoPt}} = 7.95\text{nm}$, $\sigma_{g, \text{Co}} = 1.30$, $D_{g, \text{CoPt agg}} = 47.66\text{nm}$, $\sigma_{g, \text{Co}} = 1.39$.

Figure 2.8 above shows the particle size distribution for synthesized Co, and CoPt nanoparticles. The Co nanoparticles are originally synthesized at $D_g = 5.81\text{nm}$, and a narrow standard deviation of $\sigma_g = 1.16$. The synthesized Co nanoparticles were collected by electrodeposition under the same conditions as for the Pt nanoparticles on an n-type Si wafer for XRD analysis, the resultant spectrum of which is shown in figure 2.9. Nanoparticles formed from the cobaltocene are rich in Co, however, the entirety of the deposited sample is oxidized. Once the deposition time had passed, the Si wafer with the deposited Co nanoparticles was exposed to air as it was transferred between the
microplasma reactor and the XRD instrument. Oxidation of the Co nanoparticles upon exposure to air results in the observed polycrystalline Co oxides. Low-order Co metal plane peaks would have been present at $51.83^\circ$, $60.62^\circ$, and $91.083^\circ$.

![XRD spectrum](image)

Figure 2.9. XRD of Co particles deposited on a silicon wafer. All of the Co present on the wafer is present as higher order oxides of Co. No crystalline peaks for metallic Co are present.

Addition of the Pt precursor in figure 2.8 causes the observed average particle size diameter to shift by 2.14nm. In an ideal case, this would signify a 1.14nm thick Pt skin covering a Co nanoparticle. The observed shift in particle size was used to determine the start of nanoparticle collection onto a TEM grid. HRTEM images of the particles from this synthesis are shown in figure 2.10. Post collection, the observed particle size had shifted to a large $D_g$ value, with a very broad distribution, most likely as a result of the extended collection time.
Figure 2.10. TEM images of deposited PtCo clusters, and imaged at 200kV. Particle distribution on the TEM grid was consistent (upper left), however focusing on the clusters (upper and lower right) proved difficult due to the motion of the cluster in the electron beam. Small (12nm) agglomerates were also present in the sample (lower left), and strongly attached to the carbon substrate.

The agglomerates of particles presumed to contain Co and Pt are present in the HRTEM images in figure 2.10, obtained on the Philips CM-20 at 200kV. This instrument was used due to the concern about the magnetic properties of CoPt nanoparticles (16),
and the interaction of the nanoparticles in the high strength magnetic fields present within the TEM. The lower magnification images show that a significant quantity of the catalyst was deposited on the TEM grid. Focusing on a particular region of the agglomerates at higher magnification was difficult, explaining the poor quality of the obtained TEM images. The observed agglomerates were in constant motion while focusing was attempted. While part of each structure was stuck securely to the carbon film, the remainder of the agglomerate was observed to “wave” in the electron beam. This indirectly indicated the presence of CoPt within the nanoparticles, owing to the fast oxidation of exposed pure Co evident in the XRD data, and the lack of magnetic behavior of pure Pt. Only intimately bound CoPt, or a CoPt alloy is magnetic (16). XEDS (figure 2.11) confirmed the presence of Co and Pt across the sample, with carbon and Cu present from the TEM grid.
Figure 2.11. XEDS data for the agglomerated PtCo alloy from figure Copper is present in the TEM grid mesh.

Though only indirect evidence for the formation of CoPt nanoparticles was found, the results were promising. Further experiments were unable to inhibit the formation of agglomerates when Pt(acac)$_2$ was introduced into the reactor system.

### 2.3.3 Iron Core Nanoparticle Synthesis

The change from Co to Fe as the seed nanoparticle was a matter of logistics, and the need for a seed precursor with a higher vapor pressure. A higher vapor pressure precursor that did not require heating led to more stable nanoparticle size distributions. Good results for the formation of iron nanoparticles were shown by Chiang and Sankaran (33). Figure 2.12 shows the furnace temperature effect on synthesized Fe nanoparticles.
The average nanoparticle size shifts from 6.02nm to 3.87nm at the same concentration (5 ppm) of ferrocene with increasing furnace temperature, and the standard deviation also narrows. More consistent results of smaller nanoparticles at moderate conditions were seen with ferrocene versus either cobaltocene or the Pt precursors.

Figure 2.12. Iron nanoparticles synthesized from ferrocene at varying furnace temperatures. The average particle size and standard deviation is shown to decrease with increasing furnace temperature. $D_{g\text{ Fe 20.3C}} = 6.02\text{nm}$, $\sigma_{g\text{ Fe 20.3C}} = 1.25$, $D_{g\text{ Fe 100C}} = 6.62\text{nm}$, $\sigma_{g\text{ Fe 100C}} = 1.19$, $D_{g\text{ Fe 200C}} = 4.28\text{nm}$, $\sigma_{g\text{ Fe 200C}} = 1.18$, and $D_{g\text{ Fe 300C}} = 3.87\text{nm}$, $\sigma_{g\text{ Fe 300C}} = 1.15$. 
Figure 2.13. Iron and FePt nanoparticles synthesized by stepwise addition of Pt(acac)$_2$ to the $D_g = 4.12$, $\sigma_g = 1.16$ Fe nanoparticles. Two different thicknesses of Pt were coated on the Fe cores, $D_g = 7.70$, 10.05nm, with $\sigma_g = 1.26$, 1.30, respectively. There is an increase in the particle number with increasing Pt precursor concentration. Furnace temperature of 300°C.

Under carefully controlled reaction conditions, and a sufficiently low Pt precursor vapor concentration, the Pt coats the Fe shell to form the desired core/shell structure. This is indicative of the Pt coating the Fe core, and not nucleation of new Pt nanoparticles. The consistent particle density also indicates that the Pt is adding to the Fe cores and not being lost in the system. When the Pt precursor was introduced into the furnace, but the ferrocene input to the microplasma was turned off, no new particles were detected by the DMA, which indicated that either the particles thermally decomposed from Pt(acac)$_2$ are far below 2nm in size, or Pt(acac)$_2$ does not significantly decompose in the furnace at 300°C. Figure 2.13 shows the stepwise addition of Pt precursor to grow core/shell structures of two different sizes from Fe seed particles of one size. Tuning the thickness
of the Pt layer on a catalyst particle is a critical component to the design of a fuel cell catalyst. The $D_g = 7.70\text{nm}$ FePt nanoparticles were collected on a TEM grid for analysis.

Figure 2.14. HRTEM image of Pt(Fe) nanoparticles synthesized by the microplasma method. The particles deposited on the grid consist of both single nanoparticles and larger agglomerated structures.

Figure 2.15. HRTEM image of a single, crystalline, FePt nanoparticle attached to the amorphous carbon film of the TEM grid.
Figure 2.16. An HRTEM image of Pt particles prepared by the microplasma method (left), showing small, crystalline Pt particles, and an XEDS spectrum of the same sample (right). The presence of iron and cobalt in the XEDS spectrum is the result of the close proximity between the XEDS detector and the microscope pole pieces.

As shown in figures 2.14 and 2.15, the synthesized FePt nanoparticles had a crystalline structure as evidenced by the visible atom columns. The closest interatomic spacing was found to be 0.24nm in the imaged nanoparticle. This differs significantly from the expected spacing for a pure Fe particle (0.21nm) or for a pure Pt particle (0.27nm), indicating some degree of lattice mismatch and suggesting a particle composed of Pt and some other element. Sun found a lattice spacing of 0.22nm for Fe$_{52}$Pt$_{48}$ for synthesized fcc crystal structures that were thermally annealed from the fcc to the face-centered tetragonal phase (34). The EDS data from figure 2.16 indicate that a substantial Pt signal is present from the sample. An alloy of FePt is the most likely result from the synthesis conditions, as direct imaging of the difference in composition over 1-2nm in the case of a core/shell nanoparticle was not possible with the F30 instrumentation. The
highly stretched lattice may be a result in the enrichment of the particular nanoparticle in Pt. Nanoparticles were not seen to form in the absence of Fe nanoparticles, and it may also be possible that a small amount of Fe catalyzes the growth of a much larger Pt nanoparticle.

Nanoparticles in the electron beam undergo a degree of crystal rearrangement, due primarily to thermal heating of the sample (35). Thus the predicted activity of the nanoparticle based on crystallographic orientation of the faces would differ from the actual catalytic activity, depending on the number of surface defects and steps present on the synthesized nanoparticles.

2.3.4 Nanoparticle Collection by Filtration

A HEPA type filter was initially used to capture nanoparticles. The pore size of the filter is much larger than the nanoparticle size (0.3µm), however the filter had a long length, and high tortuosity, with the expectation that some of the nanoparticles would be trapped by the filter. No nanoparticles were recovered from the filtration, though several hundred hours of reactor runtime of various gas mixtures and precursors produced dark spots on the inlet side of the filter. Cutting open the filter demonstrated the dark area did not extend beyond the immediate surface of the filter, indicating the ability of the filter to trap nanoparticles, but giving little information as to the total time required to produce a visible amount of material.

Over several hundred hours of reactor runtime, the interior surface of the quartz tube used in the tube furnace was coated by a black material. Scraping the interior surface
revealed the interior facing side to be a silvery metallic color. Subsequent XRD analysis determined the surface to be pure Pt. This layer is the result of thermal decomposition of the precursor in the furnace portion of the reactor. A lower concentration of Pt precursor would have to be used to decrease the amount used coating the quartz tube with Pt. No material buildup is observed over long operation times sans post-plasma CVD precursor injection, indirectly indicating that all of the CVD precursor entering the plasma is consumed within the microplasma.

A silver membrane filter of 30mm diameter was the next material tried for nanoparticle collection. The membrane was placed in a stainless steel fixture immediately after the furnace. The large thermal mass and distance from the furnace prevented the filtration assembly from heating during operation. Nanoparticle collection was checked by analyzing the nanoparticle stream via DMA before placing the filter in series before the DMA. No particles were observed in the nanoparticle stream while sampling immediately following the filter. The backing pump on the DMA was capable of drawing a partial vacuum, thus the addition of nitrogen to the gas flow entering the DMA was adjusted to operate the entire reactor at atmospheric pressure.

2.3.5 Nanoparticle size distributions

All reported nanoparticle size distributions fit log normal size distributions. Since the furnace was used in all experimental stages, the nanoparticle distribution is probably narrower than the reported value due to the thermophoretic driving force as the warm gas and particle stream impacts the cold stainless steel fittings preceding the DMA (36).
2.4 Conclusion

2.4.1 Nanoparticle Synthesis

The microplasma reactor is an effective means of generating nanoparticles of finely tuned size. Subsequent addition of CVD precursors results in the synthesis of two component nanoparticles.

2.4.2 Future Work

The formation of high quality nanoparticles via the microplasma method has been demonstrated here, however, alternative means are needed to enable collection of testable amounts of materials for use in cells. Then extension of the work towards electrochemical characterization for long term stability of the catalyst would be a natural extension of the work. The deposition of simple core/shell and single metal catalysts is a matter of composition and time. Given a long enough collection time, a glassy carbon electrode could be directly implanted with Pt based nanoparticles and used for direct RDE-type (rotating disk electrode) electrochemistry experiments. Determination of the catalyst activity via cyclic voltammetry in acid solution is a standard test for fuel cell catalysts, which is typically used for later in situ fuel cell catalyst comparison. Comparison with other catalysts in the existing literature would then be straightforward.

Recent interest in so-called “strained” or “porous” (37) catalyst structures has shown the high initial catalytic activity of these catalysts towards the ORR. Methods of straining the nanoparticle at the time of synthesis are a way of modifying the microplasma reactor to continue as a high-throughput method of synthesis. Immersion of the nanoparticle stream immediately post synthesis into a liquid nitrogen bath may
provide sufficient thermal shock to form strained nanoparticles. An alternative is forming a bimetallic nanoparticle, and allowing for a sufficiently long time of flight through a high temperature furnace (above the material melting point) to allow the atoms within the nanoparticle to slowly move to their equilibrium positions. As the residence time in the plasma is on the order of 1 nanosecond the nanoparticles exiting the plasma reactor are assumed to have atom positions differing from the equilibrium state. This does not take into account the time to break apart the precursor, and for metal atoms to agglomerate into a seed nanoparticle.

The introduction of surface active compounds to the furnace portion of the experimental setup may be of benefit to reduce the agglomeration rate of synthesized nanoparticles while allowing for an increase in reactor throughput. For example, the addition of CO to a gas stream containing pure Pt nanoparticles should passivate the Pt surface, preventing the agglomeration of Pt nanoparticles. The addition of carbon monoxide would however limit the gas stream to temperatures below about 600°C. Carbon monoxide addition may also result in more consistently sized small nanoparticles, due to the high binding energy on smaller nanoparticles. A series of investigations would have to determine where subsequent additional precursor adds to existing nanoparticles, or whether at a certain concentration, nanoparticles of one size are made, with additional precursor resulting in new nanoparticle nucleation instead of particle growth. Gas chemistries could be tailored to force addition to the surface of a nanoparticle through an adsorbed inactive layer, to further assist in the addition of a different metal shell. The surface energy for favorable addition would have to be investigated, and tailored to
prevent the formation of new nanoparticles under the reaction conditions while making the covered in-flight metal surface most favorable for the formation of a shell.

Electrochemical characterization is a means of determining catalyst activity and hence, effectiveness as a fuel cell catalyst. Cyclic voltametry will be used to determine the specific activity of the bulk alloy and core/shell catalysts as it compares to the pure Pt and commercial catalysts. Determination of the specific catalytic activity of the catalyst is a direct measure of the catalyst performance in an *ex-situ* environment. The preparation of a fuel cell electrode precludes the need for a powder of the synthesized nanoparticles. Unsupported catalyst is attached to a carbon support by dispersing the catalyst powder in an aqueous solution containing a suspension of the carbon support. The application and testing of a supported catalyst as either an ink or direct application to an electrode allows for the testing of the catalyst in different environments. Rotating ring disk electrode studies to measure peroxide evolution can be used to determine the stability of the catalyst.

### 2.5 References


Chapter 3 Pulse Voltammetry at Fuel Cell Electrodes

3.1 Introduction

3.1.1 General Introduction

Fuel cell electrocatalysis, especially for the oxygen reduction reaction, is a central theme of ongoing research (1-7). The catalyst utilization in fuel cells as well as catalyst optimization affect the economics of fuel cell applications. By applying the techniques of pulse voltammetry to a fuel cell electrode, the interesting kinetic behavior of the cathode catalyst can be observed in situ. Experiments with similar information content to an RDE or RRDE can be performed within a fuel cell. The high inherent capacitance of the fuel cell, due to its high surface area, does not preclude the application of pulse voltammetry techniques to the fuel cell. We can manipulate the experiment to discriminate between the charging and faradaic current response of the cell at different time scales.

Osteryoung applied pulse voltammetry to microdisk electrodes for the detection of reactive intermediates (8). Mercury drop electrodes have a built-in surface refresh step in that the electrode surface is completely replaced as soon as the mercury drop detaches from the capillary electrode. The benefit of a constantly refreshed surface is a high
sensitivity due to the clean surface before each experiment, and the ability to detect reaction intermediates. This serves as the basis for the application of pulse voltammetry to the fuel cell. Osteryoung introduced normal pulse and reverse pulse voltammetry and the description of said techniques. Pulse voltammetry is an array of sampled current techniques, the most common of which are normal pulse, reverse pulse, differential normal pulse, and square wave voltammetry. Normal and reverse pulse voltammetry are suited as general analysis techniques similar in scope to cyclic voltammetry, while differential normal pulse and square wave voltammetry are background subtractive techniques, which would be particularly useful for the detection of short lived surface species or low levels of adsorbates (9). Square wave voltammetry has favorable characteristics for multiple step surface reactions and the discrimination between surface reactions (10). Reverse pulse voltammetry is particularly useful for determining the stability of a reaction product over a potential range (11). As applied to microdisk electrodes, pulse voltammetry consisted of a gradually increasing set of potential steps. Normal pulse voltammetry was chosen due to the nonplanar surface renewal behavior at shorter time scales at the microdisk electrode surface than with a pumped or stirred system. A fuel cell electrode is considered to be a triple-phase boundary, in that reactant gases interact with the solid electrode surface. The electrode surface contacts or is considered to be covered with a wetted ionomer.

The use of a pulse voltammetry technique may allow for better control over the growth conditions of the platinum oxide over an electrochemically clean surface. In reverse pulse voltammetry, the electrode is held at a separate conditioning potential to
grow or strip the platinum oxide before a pulse is applied. This conditioning potential controls the initial thickness of the oxide, and leads to a uniform electrode surface condition before each pulse ‘experiment’, i.e. at each point along the i-V curve. The sensitivity of reverse pulse voltammetry to reactive intermediates approaches that of a rotating ring disk electrode but also allows the arbitrary control of the timescale over which these intermediates are probed. If we can deploy reverse pulse voltammetry in the fuel cell, we can study such intermediates in the cell, probing the effects of the much drier environment present in a hydrated gas phase electrode.

Recent concern over the sluggishness of the oxygen reduction reaction (ORR) on the fuel cell cathode has led to a renewed interest in the cathode catalytic process and the suitability of platinum and platinum alloy catalysts for use in hydrogen / air fuel cells. Owing to the fast reaction kinetics on the typical fuel cell anode (on an order of magnitude faster than the cathode kinetics), there is little concern for catalyst improvement at the anode. A better understanding of the cathode kinetics could lead to catalysts that make better use of available platinum, to address the platinum loading and current high cost of fuel cell catalysts. The use of high power density fuel cells for vehicular or mobile applications in particular shows promise for near term implementation in specialized applications.

Platinum hydroxide and platinum oxides form on platinum in the presence of water and/or oxygen and under high potentials versus RHE in a fuel cell environment.
Both oxides inhibit the diffusion of gas to the surface of the catalyst, and limit the number of reaction surface sites available, and thus the subsequent rate of reaction. The problem is especially pronounced on the cathode in a hydrogen / air fuel cell due to the sluggishness of the oxygen reduction reaction (ORR) kinetics. The fuel cell particularly experiences high potentials which favor platinum oxide formation during startup and shutdown. Experimental evidence in the literature suggests a initial formation of PtOH at potentials over 0.84 V vs. RHE (12), as well as the following reactions of platinum to form different oxides in the following sequence (12-15):

\[
\text{Pt} + \text{H}_2\text{O} \rightarrow \text{PtOH} + \text{H}^+ + e^- \quad 0.85 - 1.10V \quad (3.1)
\]

\[
\text{PtOH} \rightarrow \text{PtO} + \text{H}^+ + e^- \quad 1.10 - 1.40V \quad (3.2)
\]

\[
\text{PtO} + \text{H}_2\text{O} \rightarrow \text{PtO}_2 + 2\text{H}^+ + 2e^- \quad >1.40V \quad (3.3)
\]

The development of a technique for in situ measurement of the onset potential for platinum oxide formation provides a means of characterizing catalyst performance in the fuel cell. The effect of varying catalyst compositions and morphologies can also be studied, in the development of the pulse voltammetry. The transition potential from PtOH to PtO₂ is also an interesting regime that can be studied by pulse voltammetry to better understand when and at what potential the transition occurs, as well as the kinetics of platinum oxide removal. The growth rate of platinum oxides is dependent on the catalyst composition. Thus different catalysts will change the onset potential for PtOH formation from that of pure Pt.
Figure 3.1. Potential diagram of a single step and current response. The current is measured at some time \( \tau \), \( t_p \) is the pulse duration, and \( t_w \) is the time between successive pulse experiments.

Figure 3.2. Each normal pulse experiment is a single potential step. The normal pulse waveform is composed of a discrete number of normal pulse experiments.
Pulse steps and durations are chosen to electrochemically clean the electrode surface, preparing it for the subsequent step to some reaction potential. The electrode is conditioned in normal pulse voltammetry to delay the initial faradaic reaction before the current is sampled. The Cottrell equation defines the current decay characteristic for the system, and the difference between the measured current decay and theoretically calculated decay current can be attributed to the current of reaction. The electrode cleaning step occurs sufficiently quickly that the electrode remains clean for the short duration of the pulse experiment. In normal pulse voltammetry, a square wave voltage pulse of time duration $t_p$ is applied to the cell. Subsequent voltage pulses are applied with an increasing potential from $E_i$ to $E_{puls}$ in fixed potential steps. The current response of the cell is measured at the end of the wait time, $t_w$. Typical current response to a normal pulse experiment is shown in figure 3.1.

Figure 3.3. Reverse pulse waveform and current response. $E_{cond}$ is the conditioning potential, $E_s$ is the step potential, $t_p$ is the pulse time, $E_{puls}$ is the pulse potential, $t_w$ is the wait time between pulses, and $E_i$ is the initial or base potential.
In reverse pulse voltammetry, the electrode starts at the limiting current for some reacting species before being stepped to a lower reaction or non-reaction condition. This enables the detection of intermediates and adsorbates on the surface of the electrode due to the fast reaction and measurement time. Deviation from the limiting current allows for discrimination of the reaction current and leads to the high sensitivity of this technique. Under carefully controlled conditions, pulse voltammetry mimics cyclic voltammetry, i.e. the shape of a pulse voltammogram can be recreated with pulse voltammetry, with higher sensitivity due to the surface refresh effect. Pulse voltammetry is also a qualitative technique. Spectroscopic techniques would have to be applied to the system to determine exactly what sort of chemical species are present at the electrode surface. The pulse pattern and current response is shown in figure 3.3.

![Diagram](image)

**Figure 3.4.** General normal pulse voltammogram response and observed reaction directions. The normal pulse experiment steps from a non-reaction condition to a reaction condition.
A better understanding of when the platinum oxide begins to form, and what conditions favor oxide formation or removal in a fuel cell environment would be beneficial in determining optimal conditions for fuel cell operation. Additionally, the development of a technique for in situ measurement of the onset potential for platinum oxide formation provides a means of characterizing catalyst performance in the fuel cell. The effect of varying catalyst compositions and morphologies can also be studied. The transition potential from PtOH to PtO$_2$ is also an interesting regime that can be studied by pulse voltammetry to better understand when and at what potential the transition occurs, as well as the kinetics of platinum oxide removal. Growth rate of platinum oxides is dependent on the catalyst composition, thus different catalysts will change the onset potential for PtOH formation from that of pure Pt. The different regions of voltage limited platinum oxide growth overlap with the oxidation of carbon.

Experiments in the presence of H$_2$ and N$_2$, or just non-reactive gas on the Pt electrode of interest are primarily studying the activation of water at the Pt surface. However, if the pulse potential is sufficiently high, the Pt-OH$_{ads}$ should convert and behave as Pt-O. Potentials over 0.85V vs. RHE are common in fuel cell operation, particularly during startup and shutdown. Moreover, the presented pulse voltammetry experiments are performed over the range of 250 to 950mV vs. RHE, and should encompass the Pt-O conversion behavior and therefore the Pt-O surface coverage encountered by a H$_2$ / air fuel cell.
3.2 Experimental

Fuel cell membrane electrode assemblies (MEA) were prepared in house. The catalyst layer was composed of ETEK 50 wt% Pt/C at a loading of 0.4mg/cm² at both the anode and cathode, combined with Nafion 1100EW ionomer for a total catalyst ionomer loading of 20wt%. Prepared catalyst inks were hot pressed onto Nafion® 117 or 115 membranes. All fuel cell experiments were carried out on a Precision Flow Technologies test stand. A Solartron SI 1280B and an Eco Chemie Autolab PGSTAT 302 potentiostat was used for CV and normal pulse voltammetry experiments. An example pulse potential program is shown in figure 3.5.

Cells were conditioned for 24-48 hours before testing. Most testing was carried out in hydrogen anode and nitrogen cathode conditions to limit the amount of oxygen present in the system. High absolute current densities are mitigated by having small (1-5cm²) fuel cells.
3.3 Results & Discussion

3.3.1 Observed Pulse Voltammetry Fuel Cell Behavior

The potential window for pulse voltammetry is limited by the materials properties in the cell. Very low potentials (<100mV) vs. RHE are in the hydrogen evolution region of Pt behavior. Extending the potential range far above 1.0V, results in oxygen evolution on the Pt electrode (figure 3.6). The magnitude of the oxygen evolution current is significantly greater than that of water activation past 1.2V vs. RHE. Thus, the effective potential window for pulse voltammetry experiments in a fuel cell is limited to between 0.150V and 1.0-1.1V vs. RHE.
Figure 3.6. Cathode scan of H₂ (anode) / N₂ (cathode) 1cm² fuel cell with 50sccm H₂/N₂, 100%RH, 0psi backpressure experimental conditions. Extending the potential range of the pulse voltammogram eventually leads to oxygen evolution on the cathode as water is consumed at high potentials. 50mV start potential, 250mV base potential, 5mV/step.

3.3.2 Potential Dependence

Figure 3.7. Cathode side normal pulse voltammogram obtained from a 1cm² fuel cell operating on H₂ / air (anode / cathode). A well developed steady state current is observed below 0.5V. 50mV initial potential, 250mV base potential, 10mV/step.
Initial experiments were conducted to determine the optimal pulse time, width, and delay between subsequent pulses. The fuel cell electrode has a large electrochemical surface area. The capacitive elements of the resulting post-pulse current can be taken into account with the Cottrell equation, resulting in a measurable reaction current. A time of 1-5 seconds for the pulse width was found to be optimal for most experiments, as longer times were found to decay to the background current level. At open circuit potential (approximately 70-100mV, depending on the membrane) with a hydrogen anode / nitrogen cathode, there is a residual current present in the system; the hydrogen crossover current. At potentials higher than the open circuit potential, a hydrogen pumping mechanism is present in the cell. Pulse times shorter than 5 seconds resulted in erratic cell behavior and current reversal in the cell if the cells were not sufficiently conditioned beforehand. Maximum peak currents observed exceeded 2.5 amps, and the step potential was limited by the potentiostat at approximately 800mV, as potential steps greater than this limit exceeded the current rating of the instrument, even when operating the cell with hydrogen and nitrogen.

An initial oxidation onset potential of approximately 550mV for the formation of PtOH was measured in the reverse pulse experiment which is substantially lower than the experimentally determined value of 0.85V present in the literature (16). The measurement of such a low oxidation potential for platinum was due to the fast measurement and reaction times directly at the fuel cell electrode, and the use of a reverse
pulse technique to clean the electrode before each experiment. Platinum oxide formation is the most likely reaction occurring at the investigated potentials, and under the conditions present in the fuel cell. However, pulse voltammetry can measure reaction currents, but provides no information about the reacting chemical species.

Figure 3.8 above details a sequence of pulse voltammograms obtained from a fuel cell from varying initial potentials of 50, 250, 500, and 750mV. Though initially the shape of the voltammograms appears consistent with initial and expected results, the interpretation...
of the voltammogram leads to slightly different information. The purpose of the particular experiment was to determine the effect of the initial potential on the shape of the voltammogram, which relates to the expected reactions occurring on the surface of the platinum in the fuel cell. At 50mV, no initial reaction is expected (other than hydrogen crossover) since the surface of the platinum is initially covered with adsorbed hydrogen species (PtH) under this low potential condition. During the course of a single normal pulse, the cathode starts at open circuit hydrogen / nitrogen potential (70mV). At the start of the experiment, the electrode potential is lowered to 50mV (this potential is chosen), where no reaction is expected – this is the baseline or initial potential for the experiment. A potential pulse is then applied to the cell by the potentiostat. This higher potential immediately facilitates a reaction to occur at the electrode surface, if the potential step is to a reaction potential, and leads to a high measured initial current. The enhancement in catalytic activity from 250 to 500mV was most likely due to surface roughening of the Pt surface. Alternating current directions rapidly roughens a bare-metal Pt surface considerably (17, 18). Furthermore, a single crystal Pt surface which is cycled restructures and new adsorption sites are introduced (19, 20).

The voltammograms at 50 and 250mV have similar shape to the idealized voltammogram presented earlier. The progression from the hydrogen evolution region to the pseudo steady-state hydrogen crossover dominated region is clear, as is the step to the PtOH stripping region above 600mV. Once the initial potential is raised to 500 and 750mV, the initial measured current shows an approximately 2.5 times enhancement over the 50 and 250mV cases. The only parameter that changes between each voltammogram
is the initial potential from which the pulse sequence starts. This enhancement in the measured current is most likely due to a surface roughening effect due to the rapid cycling at the cathode surface, and the amplitude of the potential steps past 250mV.

3.3.3 Pulse Time dependence

Figure 3.9 below shows a current density (i) versus $1/t^{1/2}$ plot obtained from the chronoamperometric curve from the reverse pulse experiment. The non-linearity of the curve relates to the two previously mentioned measurement of a charging and faradaic current.

![Figure 3.9](image)

Figure 3.9. Fuel cell current short term current response from a single applied potential pulse to a 5cm$^2$ cell at 60°C with 50sccm H$_2$ anode / 50sccm N$_2$ cathode.

Measurement of the current occurs at some time, $\tau$, where $0< t < \tau$. The potential step occurs at time $t$. A further step down to the base potential also contains useful
information. The wait time must be sufficiently long to allow for the reaction current belonging to the previous step to decay before the next pulse is applied to the cell. Techniques similar to differential normal pulse or square wave voltammetry can potentially discriminate against this background current and allow for shorter time between pulses. As can be seen in figure 3.10, the cell charging behavior dominates at short time scales.

Figure 3.10. Pulse time dependence on measured normal pulse voltammogram – cathode scans. 1cm² cell, 50sccm H₂ (anode) / N₂ (cathode), 80°C, 50mV initial potential, 250mV base potential, 5mV/step. Charging behavior dominates at short pulse times.
3.3.4. Alloy Catalysts

In Figure 3.11, the pulse voltammograms for platinum and platinum cobalt alloy electrodes are shown. It is clear that the electrodes yield different responses. There are also qualitative differences in the shapes of the voltammograms as a result of the gas fed to the working electrode (the cathode side of the fuel cell). The relationship of the gases present to the oxide formed, and the removal behavior of that oxide is not readily apparent.

![Figure 3.11](image_url)

Figure 3.11. Normal pulse voltammograms of PtCo and Pt catalyst with H₂-anode (auxiliary electrode)/N₂ cathode (working electrode) at 80°C and 100% relative humidity conditions in the fuel cell. The left voltammogram is the result of 1 second pulse and wait times, whereas the right voltammogram is the result of 0.1 second pulse and wait times. 50mV initial potential, 250mV base potential, 5mV/step.

Figure 3.11 above shows normal pulse voltammograms obtained from a fuel cell at two different pulse durations. As these voltammograms are in the absence of oxygen on the cathode, the predominant reaction is that of the catalyst with water. In both cases, the high activity of pure platinum towards the oxidation of water is observed, while the oxidation of water in the platinum cobalt catalyst case is suppressed and shifted to higher
potentials. The 0.1 second pulse voltammogram considers a pulse time that is still close to the scale of the charging current. The inflection point on the 1 second voltammogram corresponds to a potential of 600mV. This is lower than the literature value for the onset of platinum hydroxide formation on platinum (16). This is a consequence of the higher sensitivity of the pulse voltammetry technique towards adsorbed surface species. The initial catalyst oxidation potential is shifted to approximately 700mV in the PtCo case, owing to the higher stability of PtCo to surface hydroxide formation. Figure 5 shows another normal pulse voltammogram obtained from a 5cm² fuel cell operating on H₂ / N₂ on the anode and cathode, respectively. Moving along the voltammogram from low potential to high step potential, initially, hydrogen evolution is observed, leading to a gradually increasing current, before platinum hydroxide formation begins around 650mV.

![Figure 3.12. Cathode scan normal pulse voltammogram for Pt catalyst in a 5 cm² cell, 50sccm H₂ (anode) / 50sccm N₂ (cathode), 60°C, 100%RH, 50mV initial potential, 250mV base potential, 5mV/step.](image)
Again, an initial oxidation onset potential of approximately 550mV for the formation of PtOH was measured which is substantially lower than the experimentally determined value of 0.85 volts present in the literature. The measurement of such a low oxidation potential for platinum was due to the fast measurement and reaction times directly at the fuel cell electrode, and the use of a reverse pulse technique to prepare the electrode before each experiment. Platinum oxide formation is the most likely reaction occurring at the investigated potentials, and under the conditions present in the fuel cell.

3.3.5. Determination of Tafel Slope

The general reaction of interest in normal pulse voltammetry is:

\[
O + n e^- \rightarrow R
\]

During which the diffusion limited current measured at time \(\tau\) after the potential step is given by the Cottrell equation

\[
i_d(\tau) = nFAD_O^{1/2} C (\pi \tau)^{-1/2}
\]

Where \(n\) is the number of electrons transferred, \(F\) is the Faraday constant, \(A\) is the active electrochemical area, \(D_O\) is the diffusion coefficient, and \(C\) is the bulk concentration of the species \(O\). The current as a function of potential at the electrode surface is given by the Butler-Volmer equation:

\[
I_c = I_{c0} \left( e^{\frac{n_a a_0 F \eta}{R T}} - e^{\frac{n_a (1-a_0) F \eta}{R T}} \right)
\]
Where $i^0$ is the exchange current density, $R$ is the gas constant, $T$ is the temperature, and $\alpha$ is the dimensionless symmetry factor describing the preference for the anodic or cathodic reaction at the electrode. At large overpotentials, the reverse reaction current is small, and equation 3.6 can be simplified to

$$I = i^0 e^{\frac{n\alpha F \eta}{RT}}$$

Equation 3.7 is normally rewritten as:

$$\eta_c = a + b \log(i)$$

Where $\eta_c$ is the cathode overpotential, $a$ is the exchange current density, and $b = RT/\alpha n F$. The constant $b$ is the Tafel slope, and is approximately 60mV/decade at 80°C with $n=1$ and $\alpha=0.5$ at high cathode overpotential and low current density.

The scan rate in the following voltammograms is extremely low, under 1mV/second due to the pulse program. The pulse amplitude was incremented by 1mV per step, and the pulse time and wait time between pulses was equivalent, at 1 second. This gives an effective scan rate of 0.5mV/second. At such a slow scan rate, the system can be considered to be almost at equilibrium, and the current measurement is conducted near quasi-steady-state conditions.
Figure 3.13. Normal pulse voltammogram of the cathode in an H₂ (anode) / air (cathode) fuel cell, 60°C, 100%RH, 0psi backpressure, 1 second pulse time, 1 second wait time between pulses. The potential sequence starts at 50mV. Effective scan rate 0.5mV/second. 50mV initial potential, 250mV base potential, 1mV/step.

Figure 3.14. Normal pulse voltammogram of the cathode in an H₂ (anode) / air (cathode) fuel cell, 60°C, 100%RH, 0psi backpressure, 1 second pulse time, 1 second wait time between pulses, post background subtraction. 50mV initial potential, 250mV base potential, 1mV/step.
The voltammogram obtained in figure 3.14 is the normal pulse voltammogram from figure 3.13 minus the same voltammogram obtained under H₂ (anode) / N₂ (cathode) conditions. Subtracting the H₂ / N₂ voltammogram obtained under the same reaction conditions removes the effect of hydrogen crossover and water activation at high (over 0.65V) potentials. Thus the voltammogram shown in figure 3.14 is purely the effect of oxygen and adsorbed oxygen species not formed by the activation of water on the Pt cathode in a fuel cell. At low high potentials (high η), Tafel-like behavior is expected, and the Tafel slope can be determined from a plot of η versus log(i).

![Graph](image)

**Figure 3.15.** Cathode overpotential in the potential range of 0.85 to 0.90V RHE, vs. log of current density for the voltammogram in figure 3.14, with the linear fit shown in red. The Tafel slope in this case is 98mV/decade.

Taking the linear portion of figure 3.15, in the range of 0.85 to 0.90V gives a Tafel slope of 98mV/decade, which gives a corresponding i₀ value for Pt of 2.52 x 10⁻⁵ A/cm² electrode. This is between the 60mV and 120mV reported in the literature for the fuel
cell Tafel slope (21). The determined Tafel slope corresponds to an $\alpha$ value of 0.29 assuming the number of electrons transferred in the slow step is one. This is a low value for $\alpha$, indicating the slow reaction kinetics on the cathode catalyst surface. The rate-limiting one electron ORR intermediate step is most likely (22):

$$\text{Pt} + \text{O}_2 + \text{H}^+ + e^- \rightarrow \text{Pt-O}_2\text{H}$$  \hspace{1cm} (3.9)

Discrepancies in the determined Tafel slope are less sensitive to the magnitude of the overpotential over the low current density region of measurement (0.85-0.90V vs RHE). An error in the overpotential will however effect the exchange current density for Pt.

Why does the pulse voltammetry technique show enhanced detection limits for water activation, followed by result differing than the literature for the electrode kinetics? Subtraction of the voltammogram obtained in $\text{H}_2 / \text{N}_2$ conditions removes the charging effect at each potential step, since the cell capacitance is not dependent on the chemical species present, as well as the water activation behavior. Parthasarathy and Martin attributed a Tafel slope of 60mV/decade to a situation where the ORR occurs on a PtO$_x$ surface, while the 120mV/decade slope occurs on oxide-free Pt surfaces (22). The temperature difference between fuel cell operation between 60 and 80°C accounts for an approximately 6mV/decade change in the Tafel slope. A determination of the Tafel slope on the original pulse voltammogram, ignoring the background correction, results in a 80mV/decade slope. The 18mV/decade shift in the Tafel slope as a result of background
correction is the combined effect of water activation and hydrogen crossover in the fuel cell. The 98mV/decade Tafel slope is close to the 97mV/dec (experimental) and 95mV/dec (theoretical) values obtained by Banham et al. for 40wt% Pt/C at 25°C on RDE (23).

3.3.6. Reverse Pulse Voltammetry

Figure 3.16. Cathode side reverse pulse voltammogram of a 5cm² Pt fuel cell, 50sccm H₂ (anode) / 50sccm N₂ (cathode), 100%RH, 80°C, 5 second pulse time, 10 second wait time, 50mV/step, 50mV initial potential, 50mV base potential, 500mV conditioning potential. The initial onset of oxidation occurs at approximately 550mV as measured by the reverse pulse technique.

Reverse pulse voltammetry of a 5cm² fuel cell running on 50sccm H₂ (anode) / 50sccm N₂ (cathode) at 80°C and 100%RH yielded a lower onset to water activation than
observed under CV conditions due to the applied waveform of the reverse pulse method. Due to the surface cleaning step incorporated into each reverse pulse waveform, the sensitivity of the reverse pulse technique towards surface adsorbates is higher.

The red points in figure 3.16 refer to the currents measured at a potential hold condition after 5 minutes at the indicated potential. The measured reverse pulse currents differ significantly from the currents measured at the cathode at steady state, as seen in figure 3.16. At steady state, the measured current density is primarily the result of hydrogen crossover from the anode to the cathode, in addition to the current measured as a result of water activation at higher potentials, as in the normal pulse voltammetry discussed earlier.

### 3.4 Conclusions & Future work

Pulse voltammetry is an effective means of determining reaction currents in a fuel cell, and is not limited by the high inherent capacitance of a fuel cell system. The technique reveals features of the electrode similar to that of RDE type experiments, without the need for an exterior RDE setup. Additionally, the high sensitivity of pulse voltammetry is well suited for the detection of reactive intermediates at the fuel cell electrode, as well as in situ kinetics measurements with similar results to that shown by other methods.
In light of the previously mentioned initial results, pulse voltammetry for use in fuel cells is a viable means of probing the cathode catalyst layer. Owing to past work on the synthesis of various platinum alloy catalysts and interesting set of experiments would include pulse voltammetry with commercially available platinum alloy catalysts, particular PtRu catalysts for organic fuel cells. Particularly, application of the pulse voltammetry technique for the determination of reaction steps and kinetics for the methanol, methyl formate, or formic acid reaction (or related fuels) on platinum alloys would be beneficial towards further possible extensions of the MURI project, and/or assist with current understanding of ways to improve current platinum alloy catalysts for DMFC. We would intend to further break down the organic reaction of hydrocarbons on platinum. It is likely that previous work on the kinetics of the methanol has covered all possible reactions on the platinum surface. Due to the fast pulse times available with pulse voltammetry, some finer granularity of the reactions on the platinum surface within a fuel cell may be possible. Normal pulse voltammetry on Pd/C catalysts in formic acid fuel cells has been shown, but this experiment was performed \textit{ex situ} (24). Pulse voltammetry experiments considering reactions of interest on the electrode catalyst do not require an external setup, if the experimental conditions are tailored as they are here, to the specific geometry of the fuel cell.
Figure 3.17. Normal pulse voltammograms, cathode scan, of H₂ saturated MeOH vs. 100sccm N₂, 60°C. Current maxes at pulse times above 2 seconds for the given cell geometry and area.

With an array of catalysts of various compositions available, a possible application of pulse voltammetry would be the confirmation or determination of the initial onset potential for the formation of platinum oxide on the platinum alloy catalysts. Such information would be beneficial for the study of the ORR on platinum alloy catalysts, as well as in the development of alloys for various other fuel systems (e.g. MeOH, EthOH, methyl formate, gasoline). The organic fuel series in particular has an array of interesting intermediates and possible adsorbates in the fuel cell system. Being able to see and measure the kinetics of these possible reactions in situ in the fuel cell is a powerful means of determining catalyst suitability and in future catalyst design criteria.
Normal pulse voltammetry was presented as a more sensitive technique versus cyclic voltammetry. The use of normal pulse voltammetry as a direct substitute for CV type measurements (e.g. CO stripping) is a possible application of the technique. Refinements in pulse parameters lead to high cleanliness of the catalyst surface during pulse experiments, leading to lower detection levels of contaminants such as CO. Slow scan CV may yield similar detection levels to normal pulse voltammetry, but the pulse voltammetry technique is arguably faster. In such a mode of operation, normal pulse voltammetry is a diagnostic technique.

When dealing with multiple carbon liquid fuel streams, i.e. ethanol, glycerol, the number of intermediate steps for the oxidation of each carbon is quite complex (25-29). Pulse voltammetry is presented as a method for analyzing reactive intermediates in these liquid fed fuel cells, particularly as a means of evaluating catalyst new catalyst compositions for fuel cell suitability. In this case, pulse voltammetry type experiments can be used as a screening technique to either find a catalyst with favorable reaction kinetics in situ. Though full fuel cells would have to be prepared for such studies, the interaction between catalyst and other cell components are present and identifiable with pulse voltammetry. Choosing reverse pulse voltammetry for a set of experiments allows for the study of reactive intermediates. Choosing normal pulse voltammetry allows for studying adsorption / desorption kinetics. Kinetics measurements of catalyst behavior with liquid fed fuel cells will be critical for the development of such technology, and can
be fed into deterministic type models of fuel cell catalysis, for the development of future catalysts.

In the case of glycerol oxidation, a number of reactive intermediates are known (30). By breaking down the sequence of reaction steps through pulse range potential control, the interactions and kinetics of each step could be studied, and quantitative values for the reactivity of reaction intermediates in the oxidation of glycerol could be determined. Running a similar study over several catalysts of interest would benefit in identifying important reaction pathways in glycerol oxidation, which would be of benefit in designing future catalysts to take advantage of favorable reaction pathways, as well as whether or not these catalysts actually work. This analysis is not exclusive to liquid fed cells. For PEM fuel cells, the potentials of interest are those over which surface oxides form. The stability of platinum oxides is potential and catalyst dependent.

The use of differential normal pulse, and square wave voltammetry are not precluded for use in fuel cell systems, though the charging behavior of the fuel cell electrode becomes more of an issue for square wave voltammetry.

Non fuel cell applications of pulse voltammetry are relatively well covered in the literature. A half MEA system with a fuel cell electrode on Nafion backed against an aqueous solution could function as a sensor. The enhanced sensitivity of the pulse
voltammetry technique coupled with the selectivity of a Nafion separator would result in a high sensitivity detector towards an electroactive species, for example, alcohol content in wastewater.

### 3.6 References


Chapter 4:

Graphite Composite Flow Field Plate High Temperature Durability Testing & Effluent Analysis

4.1 Introduction

The typical PEM fuel cell for automotive applications operates at 80°C, which is a balance between materials and thermodynamic efficiency considerations. High temperature operation of PEM fuel cells is a desirable goal due to the benefits afforded to balance of plant components and thermodynamic considerations. However, the change from 80°C to 120°C requires a number of materials considerations, particularly in the choice of MEA materials (1, 2). For comparison, a typical automobile engine operates at 170-195°C. A PEM fuel cell requires cooling as well as external humidification to keep the membrane humidified and the cell at temperature. For the cooling loop, the temperature delta between the fuel cell and exterior environment determines component sizing and cost. A higher temperature difference reduces the required size of the heat exchanger for the fuel cell, compared to operation at 80°C which results in a reduction of component weight and cost. Higher temperature operation increases CO tolerance on the anode, allowing lower grade hydrogen to be used in the case of a vehicle application(3). DOE technical targets from 2010 onward require low relative humidity inlet gas feeds, which put additional strain on membrane development and the conditions experienced by the entire fuel cell stack (4).
The operation at 120°C also has benefits for the cathode, improving the kinetics of the ordinarily slow oxygen reduction reaction (ORR), due to the temperature dependence of $i_0$ (5). An increase in the temperature on the cathode results in an increase of the exchange current density (6). Operation at 120°C also assists in the removal of water from the cathode at high current densities (when cathode flooding is most likely due to the water production rate) due to evaporative transport of the water away from the cathode as water vapor instead of liquid water(7).

The supplied Graftech composite plates consist of expanded graphite bound by epoxy in the shape of a typical PEM fuel cell flow field plate (FFP). The Graftech composite plates have a high thermal conductivity, dimensional stability, and thermal stability, as they have been specifically designed for 120°C operation. A goal of testing was to demonstrate operation of a fuel cell with the Graftech plates at 120°C for 1000 hours. The solid graphite plates used as standard FFPs in laboratory fuel cells are too thick, heavy, and expensive to manufacture for a commercial mobile power fuel cell stack. Composite graphite plates could be molded to cheaply produce a thin, high thermal tolerance FFP. US Department of Energy (DOE) targets for the composite plate material are shown in table 4.1.
Table 4.1: DOE Technical Targets: Bipolar Plates (From Table 3.4.14.(8))

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2010/2015</th>
<th>Program 2008 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost^a</td>
<td>$/kW</td>
<td>5/3</td>
<td>TBD</td>
</tr>
<tr>
<td>Weight</td>
<td>kg/kW</td>
<td>&lt;0.4</td>
<td>TBD</td>
</tr>
<tr>
<td>H₂ permeation flux</td>
<td>cm³ sec⁻¹ cm⁻² @ 80°C, 3 atm</td>
<td>&lt;2 x 10⁻⁶</td>
<td>TBD</td>
</tr>
<tr>
<td></td>
<td>(equivalent to &lt;0.1 mA/cm²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion</td>
<td>μA/cm²</td>
<td>&lt;1ᵇ</td>
<td>&lt;1ᵇ</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>S/cm</td>
<td>&gt;100</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Resistivity^c</td>
<td>Ohm-cm</td>
<td>0.01</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Flexural Strength^d</td>
<td>MPa</td>
<td>&gt;25</td>
<td>&gt;55</td>
</tr>
<tr>
<td>Flexibility</td>
<td>% deflection at mid-span</td>
<td>3 to 5</td>
<td>TBD</td>
</tr>
</tbody>
</table>

^a Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).
ᵇ May have to be as low as 1 nA/cm if all corrosion product ions remain in ionomer for metal plates.
Corrosion of flexible graphite plates is not an issue.
^c Includes contact resistance.
^d Developers have used ASTM C-651-91 Using Four Point Loading at Room Temperature.

Chemical analysis of the resin material was not provided by GTI, therefore a variety of chemical exposure tests were required to broadly characterize the characteristics of the supplied resin composites for HPLC-MS analysis.

No existing procedures exist for the quantification of degradation products of fuel cell operation on the time scale of thousands of hours. There are existing guidelines for long term testing, as well as DOE targets for performance on this time scale, but the capture and analysis methods remain undefined. While fluoride release has been used to track MEA decay with time (9, 10), this technique cannot be used to track the degradation of the graphite plate, as fluoride is not present in any of the composite plate materials, nor is it an expected decomposition product of any of the plate materials.

Organic and inorganic leachates arising from either the graphite or the resin epoxy are expected to be present in the fuel cell effluent stream, if the composite plate is
degraded under the experiment conditions. Ex-situ analysis methods are used to determine the presence of leachates. High pressure liquid chromatography with a mass spectrometer for mass detection (HPLC-MS) is the proposed method of determining the presence of leachates in the effluent. The HPLC-MS technique should be capable of distinguishing between the membrane degradation products, and the effluent components resulting from the composite FFP.

### 4.2 Experimental and Procedural Considerations

Two different resin formulations were supplied by GTI: named 2G and 2H in the following sections. Both machined 50cm$^2$ (active area) sized bipolar plates and 1” x 1” coupons of the 2G and 2H resin samples were used. Materials were washed and sonicated in diluted (50:50 water : isopropanol) solutions to clean them before and after each use. An expanded view of the cell setup for coupon and single cell testing is shown in figures 4.1 and 4.2, respectively.

Autolab Eco Chemie PGSTAT 302 potentiostats were used for all electrochemical testing. Fuel cell tests were carried out on Fuel Cell Technologies test stands for the coupon testing. A Precision Flow test stand was used for all 50cm$^2$ testing. The Precision Flow test stand was incapable of high temperature humidifier operation, thus reducing the testing conditions to 24% relative humidity (RH) at 120°C. Cells were conditioned at 80°C and 100% RH for 24 to 48 hours before being set to the high temperature conditions. Each cell was checked for less than 5% variability over a chosen sample period at 600mA/cm$^2$ and 80°C. Co-flow operation was used for all fuel cell tests. While
on the Precision Flow test stand and at high temperature, cells were shut down once daily for cell resistance and performance characterization.

Extended durability membranes were supplied by 3M. These membranes have no special properties toward high temperature operation, were used as supplied, and consisted of a 0.002” thick membrane with platinum catalyst based anode and cathode electrodes. ETEK 1500 gas diffusion layers were used throughout testing. A stock graphite plate was used for the anode side wherever required opposite the GTI composite plate.

Resin composite testing was initially of the coupons in fuel cell hardware. An example of the coupon testing setup is shown in figure 4.2. The coupon was sandwiched between the bipolar plate, with PTFE gaskets used to either isolate or center the coupon in the cell. A half cell setup was used for high potential testing. A potential of 1.2V was applied during high potential testing.

Hydrogen crossover was measured under hydrogen (anode) / nitrogen (cathode) conditions at a potential of 0.4V vs. the anode, and the last 30 second current average of a 5 minute potential hold was used. The crossover current under these conditions took approximately 1 minute to reach a steady-state.

A Hypersil C18 column (5μm, 120 A, 250mm x 4.6mm diameter) was used for all HPLC experiments. A Thermo Scientific Accela Pump and Autosampler were used in
conjunction with a Thermo Scientific LCQ Fleet Mass Spectrometer for all HPLC-MS analysis. All samples had an injection volume of 5μL, 125μL/min flow rate. The flow program was 0-30 minutes: 5-100% acetonitrile, balance water, 30-45 minutes, 100% ACN. The MS operated in negative polarity mode, over a range of 50-1000m/z. The NIST Chemistry Webbook was used to identify MS data (11).

![Single Cell Schematic](image)

Figure 4.1. Single cell expanded view, showing conventional PEM fuel cell components and relevant dimensions. The cathode side FFP was replaced with a Graftech unit in the 1000 hour testing protocol.
Figure 4.2. Half cell, half-MEA fixture diagram. The coupon was inserted on the “cathode” side of the cell, with direct contact against the non electrode-coated side of the half MEA. GDL material backs the coupon to ensure good electrical contact between the stock FFP and the coupon of interest.

Half MEA coupon experiments were conducted at 90°C to slightly enhance possible thermal decomposition pathways versus operation at 80°C, but were kept below 100°C due to the complete lack of high temperature tolerance of the half MEAs. A diagram of the physical cell setup for half MEA tests is shown in figure 4.2.

All components in direct contact with the plate and coupon materials were subjected to cleaning before and after individual tests. When liquid samples were collected, the first two samples of the collection phase were discarded. Collection of liquid samples from coupon testing was accomplished by diverting the high pressure
exhaust of the fuel cell into a glass vial immersed in an ice water bath. Thus the collected coupon effluent consisted of liquid and condensed vapor portions of the fuel cell effluent. A collection time of 30 minutes resulted in 10-15mL of condensed liquid.

4.3 Results and Discussion

4.3.1 Coupon Testing

The supplied coupons were exposed to environments best representing fuel cell conditions encountered at 120°C. The conditions judged most likely to lead to measureable degradation were:

1) Prolonged exposure to a reducing atmosphere.

2) Prolonged exposure to an oxidizing atmosphere.

3) High potential (1.2V) in the presence of pure oxygen.

Conditions were chosen to be exceedingly harsh on the composite plate materials. The test parameters were temperature, environment (oxidizing or reducing), and potential. Coupons were exposed to oxidizing (pure oxygen) and reducing (pure hydrogen) environments, to mimic conditions encountered at the cathode and anode, respectively. Hydrogen and oxygen were supplied at 100% relative humidity at both 80°C and 120°C. The cell fixture was operated at 0 atm backpressure at 80°C, and 2.0 atm backpressure at 120°C (the steam pressure at 120°C). Though a low humidification level is expected in the final stack setup, gases were fed at 100% RH to maximize liquid
contact time with the coupons, as collected liquid was the means of assessing degradation products. A summary of collected samples and conditions is presented in Table 4.2.

<table>
<thead>
<tr>
<th>Test</th>
<th>2G</th>
<th>2H</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>O₂</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>O₂ + 1.2V</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.2 Summary of sampling intervals for coupon tests, and exposure conditions. Samples were collected approximately every 24 hours, except for the first hydrogen exposure test with the 2G coupon, which was extended.

For high potential testing, half of the cell was the coupon, and the other side was a standard fuel cell electrode in humidified oxygen. The cell diagram for half MEA experiments is shown in figure 4.2. A carbon cloth was located between the graphite plate and the coupon. The coupon was in direct contact with the non-catalyst coated side of the half MEA (the “cathode”), although the gasket fit around the coupon was not air-tight, to allow some flow of O₂ around the coupon. Gas flow rates for the half MEA experiment were 50sccm O₂ (cathode), 50sccm H₂ (anode), with the cell polarized to 1.2V versus the anode (RHE). Typical current under these conditions fluctuated between 25 and 35mA/cm². No physical changes in the surface of coupon were seen during any testing. The carbon cloth in contact with the coupon exhibited a change from hydrophobic to hydrophilic behavior with time at high potential, which was observed by placing a water droplet on the carbon cloth ex situ post experiment completion. This behavior is
consistent with carbon loss and direct oxidation of the carbon cloth. Half MEA electrodes were missing sections of the Pt/C catalyst which was observed once the cells were disassembled. These areas did not correspond to any visible changes in the surface of the coupon in contact with the half MEA. The primary mechanism for carbon loss from the electrode and carbon cloth was thought to be via the oxidation of carbon to CO$_2$ (12).

![Graph](image)

Figure 4.3. HPLC-MS spectrum of 2H coupon sample, post background subtraction. This is a sample spectrum similar to that obtained for most coupon samples. The measured intensity is approximately 2 orders of magnitude below that seen later in later HPLC-MS experiments.

HPLC-MS was not an effective means of analyzing the liquid samples collected during the coupon tests. A sample spectrum from a 2H coupon sample is shown in figure 4.3. The signal intensity in this spectrum is very low, and it is noisy. Fuel cell effluent testing was based on Zhou’s thesis and some work using an HPLC-UV Vis spectrometer by Wang (13, 14). The lack of existing literature on the topic of fuel cell effluent analysis
led to the development of in house methods for the analysis of collected effluent. With no literature reference for expected fragment sizes, and with the intention of distinguishing between membrane and balance of plant components of the effluent, significant time was spent on exploratory HPLC-MS, with Wang's procedure as the only reference for a separation study that was able to identify degradation products from a membrane. Stability between samples was not always present. Samples were stored in the dark at room temperature for several weeks between collection and actual HPLC analysis.

4.3.2 Resin Degradation

Owing to the lack of observable degradation products in the collected effluent from the coupon tests, and the unknown class of the resin during coupon effluent analysis, a number of chemical exposure and chemical attack methods were applied to a sample of cured resin. Intentional degradation of a resin sample at high apparent concentrations was carried out to determine the properties of the resin, to understand how the resin would interact with the HPLC column, or in what form the degraded resin would present in a liquid solution (if any). A summary of the solvents used and results of solvent exposure are present in Table 4.4.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Result</th>
<th>Solvent</th>
<th>Result</th>
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</thead>
<tbody>
<tr>
<td>1M HF</td>
<td>wets</td>
<td>DMSO</td>
<td>swells</td>
</tr>
<tr>
<td>1M Na + 1M HF</td>
<td>wets</td>
<td>NMP</td>
<td>swells</td>
</tr>
<tr>
<td>0.5M H₂SO₄</td>
<td>wets</td>
<td>chloroform</td>
<td>swells</td>
</tr>
<tr>
<td>1M KOH</td>
<td>wets</td>
<td>MeOH</td>
<td>does not wet</td>
</tr>
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</table>

Table 4.3. Summary of resin exposure conditions at 21°C and solvent-resin interaction results.

For the solvent-resin interactions described in table 4.3, approximately 10mg of a finely divided, shaved resin sample was stirred overnight with 10mL of the chosen solvent. The DMSO solvent sample was also heated to 120°C, but no apparent increase in the dissolution of the solid resin was observed. Strong organic solvents were seen to swell the resin sample, whereas the highly acidic and basic aqueous solvents simply wet the surface of the polymer. Addition of water to methanol was observed to wet the resin.

None of the solvents used in table 4.3 dissolved the resin sample to any appreciable extent. A Fenton’s reagent at a concentration of 100mM was prepared to rapidly degrade the resin sample. The ordinarily dark brown resin dissolved vigorously in the presence of the Fenton’s reagent and turned the liquid solution a dark orange-brown. After 24 hours at room temperature, no solid portion of the resin remained, but a yellow powder had settled to the bottom of the solution vial. A further 24 hours did not result in an increase in the amount of solids present. The dark orange liquid portion of the solution
was filtered and diluted to 10mM. A further aliquot of H$_2$O$_2$ was added to the solution, and after a further 24 hours, a bright yellow powder had accumulated at the bottom of the vial, indicating that the initial resin sample was soluble in the solution, but not degraded entirely by the 100mM Fenton’s reagent. Further filtration and dilution of the 10mM solution to 1mM also resulted in a bright yellow settled powder after the addition of H$_2$O$_2$. Separate 1mM Fenton’s solution containing the degraded resin became and remained (dissolving the precipitate) clear after the addition of H$_2$SO$_4$ to a final concentration of 0.5M. Addition of KOH to 0.5M did not dissolve the precipitate.

The conclusion from the chemical exposure tests is that strongly acidic conditions in the presence of H$_2$O$_2$ and metal cations are most likely to lead to degradation of the resin binder.
Figure 4.4. Background subtracted HPLC-MS spectrum for the 1mM Fenton’s reagent degraded 2G resin sample. An initial peak is present at a RT = 16.19 minutes, with two further peaks at RT = 29.31 and 29.87 minutes, respectively.
Figure 4.5. Background subtracted HPLC-MS composite spectrum over the first peak in figure 4.4, at a retention time range of 15.40 to 16.93 minutes of the 1mM Fenton’s reagent degraded 2G resin sample. ‘Light’ masses are most evident, with a spectrum of heavier masses between 400 and 900 amu.

The Fenton’s reagent degraded resin sample shows a small peak at a retention time of 16.19 minutes in figure 4.4, along with two sharp peaks at a 29.31 and 29.87 minutes. All spectra from the peaks (figures 4.4, 4.5) exhibit a wide distribution of fragments of various weights from approximately 350 to 900 amu.
Figure 4.5 shows the MS spectrum over the peak at 16.19 minutes. The highest intensity moieties occur at 96.96 and 79.95 amu. The 96.96 amu moiety is attributed to the bisulfate anion (HSO$_4^-$), which occurs due to the use of FeSO$_4$ for the Fenton’s Fe cation source. The 79.95 amu moiety is a result of C$_2$Si$_2$ present in the sample. The small peak at 113.01 amu can be attributed to either C$_2$H$_3$F$_2$O$_3^-$ or 2,2,2-trifluoro-acetamide, C$_2$H$_2$F$_3$NO. Higher intensity mass peaks in figure 4.5 at 508.91, 518.93, 682.58, 782.02, 764.13, and 824.82 amu are unknown. The 469.98 amu moiety is C$_9$HF$_{19}$, a likely decomposition product of PTFE components included in the sample (e.g. seals, stir bar), and is eluted quickly due to a low level of interaction within the HPLC column. The 562.24 amu peak is C$_{27}$H$_{46}$O$_5$Si$_4$, which would suggest that portions of the heavier mass spectrum are the result of interaction with the glass vial wall, or the immobile phase of the HPLC column.
Figure 4.6. HPLC-MS spectrum agglomerate over the highest single intensities in figure 4.4 at a retention time of 29.17 to 30.54 minutes of the 1mM Fenton’s reagent degraded 2G resin sample.

Figure 4.6 shows the MS spectrum over the two high intensity peaks at RT = 29.31 and 29.87 minutes. The small peak at 97.09 amu represents a group of N containing amine, cyano, nitrile, and azano compounds, e.g. 2-cyanopentane and 3-methylpentanenitrile. The strong peak at 249.11 and the smaller peak at 173.16 amu are both due to N containing compounds as well, e.g. 1-hexanamine, mon-TMS (C₉H₂₃NSi) for 173.16 amu, and 2,4,6-triallyloxy-1,3,5-triazine for 249.11 amu. The peaks at 89.28, 117.18, 157.17, 383.82, 499.61, 569.23, and 779.55 amu are unknown, nor are they
recognizable as species with a +2 charge. The identifiable compounds in the figure 4.6 spectrum are complex, with multiply bonded N atoms, which are eluted more slowly by the HPLC instrument, or interact more strongly with the immobile phase due to the potential hydrophobicity of the compounds.

4.3.3. Fuel Cell Operation and Degradation

The fuel cell polarization curves for Cell 01, assembled with the 2G cathode plate are shown in figure 4.7. Cell performance at 120°C is considerably worse than at 80°C.

![Figure 4.7. Fuel cell polarization curves for Cell 01, assembled with the 2G cathode plate. A stock graphite plate was used on the anode. Note the lower performance at 120°C due in part to the lower relative humidity versus the 80°C result. 3M stock MEAs.](image)

Cells were set to operate in continuous voltage mode at 600mV vs. the anode (RHE) to better mimic operational requirements. As seen in figure 4.7, the typical current
draw at 600mV is below 100mA/cm$^2$. This is approximately an order of magnitude reduction in current density versus ideal operation at 80°C, which is primarily caused by the reduction in membrane conductivity.

Owing to the harsh operating conditions, MEAs failed after approximately 100 hours of runtime, thus a considerable portion of testing time was dedicated to breaking in and qualifying the cells before a short operational time at 120°C. Upon disassembly, all of the MEAs used exhibited pinhole formation. The formation of pinholes is consistent with the drop in open circuit potential with time, and the increase in measured hydrogen crossover current with time.
Figure 4.8. Hydrogen crossover and cell high frequency resistance for all cells assembled with the 2G plates at 120°C. The cell resistance is shown to increase with time for each fresh cell. Hydrogen crossover increases over the lifespan of an individual MEA.
Figure 4.9. Potential and current density performance of cells assembled from the 2G plate over time. As each individual cell ages a drop in the cell potential at a particular current density is observed, as well as a reduction in the maximum current density attainable by a particular cell.

Figure 4.9 above is a timeline of the individual cell potential performance as a function of the 1100 hour test of the 2G cathode plate at 120°C. The maximum current drawn by an individual cell drops with time. The open circuit potential of each cell drops nearly linearly for most cells as a function of time. While shutting cells down while maintaining inert gas flow can improve cell performance at 80°C, the same is not the case at 120°C. At 80°C and operation with hydrogen / nitrogen (anode / cathode) gas flows, the membrane has time to return to equilibrium with the humidity of the incoming gas streams. At 120°C, the cell shutdown is probably more damaging to the long term life of
the membrane. Operation at 120°C and low current densities produces water at the cathode that enhances the local membrane conductivity. Owing to the low current densities and high active cell area, the formation of localized hot spots that progress along the channel length of the cell with time is also a possibility. Sequential damage to the membrane would explain the gradual performance decay of each membrane and resultant performance loss. The co-flow operation mode of the cell exacerbates this problem.

The final test of the 2G plate before it was returned to Graftech was a potential hold at open circuit as an accelerated test to failure condition. Under normal fuel cell operating parameters, the potential at the cathode during startup and post-shutdown (if air infiltration of the anode is permitted while the cell is shutdown) is the open circuit potential of the operating cell, or higher (15). The membrane performance and potential drop over the potential hold is shown in figure 4.10. The cell exhibits a rapid loss in open circuit potential over the first few hours of operation before settling into a linear rate of decay over the next 3 days. A decay rate of 242mV/hour at open circuit was observed over days 2-4. It is unknown why a step transition occurs just past the 1 day mark, as the cell was running without interruption for the duration of the test.
Figure. 4.10. OCV potential hold for the 2G cathode plate operating at 120°C, 24%RH, 100sccm H₂ (anode) / 332sccm air (cathode), cell broken in for 24 hours before start of test. The cell suffers an initial large drop in performance before stabilizing to exhibit a linear decline in further open circuit potential.

A background sample of pure HPLC grade water (Fisher) was used as the reference against the effluent samples.
Figure 4.11. HPLC-MS spectrum post background subtraction for Cell 01 with the 2G resin from effluent collected after 99 hours of runtime. One peak is evident at a retention time of 8.54 minutes, along with lower intensity peaks at retention times of 9.11 and 9.65 minutes.

Figure 4.11 is the entire HPLC-MS spectrum for Cell 01 with the 2G resin plate from a sample of the cell effluent post 99 hours of runtime, which is further broken down for the peak at a retention time of 8.54 minutes in figure 4.12. A grouping of peaks is present in figure 4.11 from 7.99 to 9.52 minutes. A summary of the highest peaks and corresponding compounds is present in table 4.4, along with empirical formulas for compounds corresponding to unknown mass fragments.
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<tr>
<td>101.45</td>
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<td>CO2N2FSi4</td>
</tr>
<tr>
<td>113.19</td>
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<td>C4H9N4</td>
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<tr>
<td>157.13</td>
<td>ident.</td>
<td>C8H19NSi, 1-[2-(trimethylsilyl)ethyl]-azetidine</td>
</tr>
<tr>
<td>249.12</td>
<td>ident.</td>
<td>C13H19NO2Si, dimethyl(4-cyanophenoxy)isobutoxy-silane</td>
</tr>
<tr>
<td>338.15</td>
<td>ident.</td>
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<td>384.92</td>
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<td>520.95</td>
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<td>C23O10N2F3</td>
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</table>

Table 4.4. Identified compounds at a retention time of 8.54 minutes for the 2G resin Cell 01 after 99 hours of operation. Unknown compounds have an assigned empirical formula, and have a charge value of 1 unless otherwise specified.

Figure 4.12. MS spectrum post background subtraction for Cell 01 with the 2G resin plate from effluent collected after 99 hours of runtime at a retention time of 8.54 minutes.
Figure 4.13. MS spectrum post background subtraction for Cell 01 with the 2G resin plate from effluent collected after 99 hours of runtime at a retention time of 7.99 to 9.52 minutes. A high intensity of high weight fragments are present across the 8.54 minute peak.
Figure 4.14. HPLC-MS spectrum post background subtraction for Cell 04 with the 2G resin from effluent collected after 240 hours of runtime. Three peaks are apparent in the spectrum, with the highest intensity peak occurring at a retention time of 11.75 minutes.
Figure 4.15. HPLC-MS spectrum post background subtraction for Cell 08 with the 2G resin from effluent collected after 1104 hours of runtime. One peak is evident at a retention time of 11.90 minutes.

Further summary tables of collected MS data along with identifiable compounds for cells 04 and 08 with the 2G resin sample are present in the appendix.

4.3.4 Fuel Cell Teardown Observations

The 2H plate exhibited deformation around both of the gas inlets after 300 hours of runtime at 120°C. As the transfer line temperatures were below that of the cell (90°C vs. 120°C), the deformation was not the result of plate erosion by the incoming gases. The other possible results of deformation are overly high compression, or local heating of the inlet leading to thermoplastic deformation of the plate, which is exacerbated by the
co-flow operation of the cell. The gas crossover of the cell was measured over the lifetime of the cell, and increased throughout testing of the 2H plate. Additionally, the surface of the 2H plate exhibited large pores (figure 4.15). The most likely explanation is that the 2H resin material began decomposing or offgasing, forming the visible pores, and increasing the porosity of the plate. The 2G plate did not exhibit physical changes with time.

Figure 4.15. Light optical image of the 2H cathode plate. The imaged surface faced the MEA. The dark band in the upper left corner is a channel. A change in the brightness across the surface is a result of the incident (off-axis) light source used to illuminate the depth of the pore, and high reflectivity of the plate surface.

The end of life average hydrogen crossover for all cells using the supplied MEAs was 11.3mA/cm². The expected hydrogen crossover for Nafion 112 at 120°C and 25%RH is 2.1mA/cm² (16). The low initial conductivity and high hydrogen crossover of
the membranes is not unexpected, due to the low relative humidity of the incoming gases. Water is required to transport protons in Nafion-type membranes, and with low relative humidity comes poor conductivity. The low operating current density of the 50cm² cells was insufficient for complete wetting of the membrane. Additionally, the membrane was not specifically engineered to encourage water retention. The stable phase of water at 120°C is as a gas, which precludes the full hydration of the membrane.

4.4 Conclusion and Future Work

Prior to each experiment, the HPLC column was continuously flushed, while the MS was run in scan averaging mode for several column volumes. Fragments were detected exiting the HPLC column, but these fragments did not resolve into a peak. Nor were the detected fragments of any specific mass value. Components of the HPLC effluent exiting the column consist of the injected sample, the introduced solvents, and possible long retention time fragments strongly bound to the column medium.

None of the fragments common to the samples containing the Graftech plate samples were found in the coupon HPLC-MS results. The coupon testing effluent was indistinguishable from the background spectra. This would indicate the collected fluid was insufficiently concentrated in degradation products, or the onset of plate binder degradation does not occur over the time scale of the coupon tests. The flow field plate used for durability testing was run for substantially longer than any of the individual coupon tests.
The resin is a benzoxazine, formed from the reaction of amine, phenol, and formaldehyde (17). A figure of the general structure of the benzoxazine backbone is shown in figure 4.16. In light of this information, and the unknown status of the side chains (R, R’) attached to the phenolic or amine groups, the presence of the amine group and any nitrogen containing R groups would be responsible for the observed N containing compounds to some extent. Some of the N containing compounds detected in the fuel cell effluent would appear too complex to be attributable to decomposition of a single benzoxazine monomer unit. However, the amine functional group is subject to attack by protonation under acidic conditions, resulting in the detachment at the amine group. Hydrogen adsorbs on the surface of graphite (18). The stability of both the amine and phenol groups is dependent on the exact structure of the side groups.

Other sources of nitrogen within the system may have been the result of the acetonitrile mobile phase associating with membrane polymer or resin binder effluent products. Though effluent samples were stored in PTFE containers, samples were transferred to glass vials for HPLC-MS analysis. No silicone based adhesives were used
in the construction of the fuel cells, thus the observed silicon containing compounds are the result of interaction with sample vial side walls, or destructive reaction with the HPLC column substrate. There are many fragments of various atomic weights present in the HPLC-MS results that are not accounted for by background subtraction nor are the fragments part of the identifiable resin degradation products. Empirical formulas for the heavier fragments are tabulated based on elements present in the identifiable components of the mass spectra.

Long chain fluorocarbons or group fragments containing sulfonic acid were not detected under the experimental conditions, but were expected in the effluent based on past investigations of membrane decomposition products (9). Most identifiable compounds contained nitrogen in the form of -amines, -amides, or -azines, as well as large fragments containing silica side groups. The only identifiable compound found in multiple spectra was daniquidone (C₁₅H₁₁N₃O), in the 2G Cell 04 and 08 MS data, after 240 and 1104 hours time at 120°C. Approximately one half of the compounds present in the cell effluent samples were identifiable compounds, with the remainder described only empirically in Appendix A.

At the cathode, hydrogen is present as a crossover gas, and though the rate of hydrogen crossover is low under normal operating conditions, the long life expected life of the stack may result in substantial degradation of the bipolar plate. The work presented here has used membranes that were unsuited to high temperature operation, and had abnormally high hydrogen crossover rates. The rate of hydrogen crossover was
consistently increasing with time. Thus the test conditions were a worst case scenario for the resin plates, combining high temperature, low relative humidity, and high potential by operation as the cathode, and high hydrogen crossover. No suggestion is made as to the rate of degradation of the resin binder, as hydrogen present at the cathode can be consumed partially or fully in the cathode catalyst layer. In a fuel cell stack designed for operation at 120°C and with high temperature membranes, the rate of hydrogen crossover with, for example, PBI membranes can be comparable to the values obtained in this work, approximately 7.8mA/cm² at 800 hours (19).

Alternatively, a fuel cell assembled with the Graftech plate as the anode would probably be a better simulation of the harshest conditions experienced during operation at 120°C, due to the resolved structure of the resin binder, and its susceptibility to proton attack under acidic conditions. Hydrogen peroxide is generated under some conditions within the electrode of a PEM fuel cell at both the anode and cathode (20). Whether the peroxide manages to reach the anode plate, and whether metal cations are present in the effluent at the anode and are capable of interacting with the peroxide at the plate surface at an appreciable rate remains to be determined. It is possible that the rate of decomposition of the resin binder is low enough within the fuel cell over the lifetime of the plate to limit concerns of resin degradation. Quantifying the rate of decomposition in situ over a long duration experiment is necessary to determine whether the 2G resin is sufficiently stable over the stack design life.
4.5 References

Chapter 5: Conclusion

5.1 Catalysis

It is important to understand the properties of the ORR as it pertains to fuel cell cathode catalysts for designing improved catalysts for PEM fuel cells. Normal and reverse pulse voltammetry are shown to effective means of analyzing cathode catalyst parameters in situ, and can provide similar information as ex situ RDE and RRDE experiments, particularly in the case of reverse pulse voltammetry, due to the incorporation of a surface refresh step. Additionally, kinetic parameters can be obtained from the pulse voltammetry data: a Tafel slope of 98mV/decade was determined for the ETEK 50wt% Pt/C catalyst used to make the experimental fuel cell electrodes.

Determination of the Tafel slope from the normal pulse voltammetry results for catalysts synthesized by the microplasma process is a means of evaluating catalysts for ORR activity within a fuel cell. Since the Tafel slope is dependent on the electrocatalyst composition, normal pulse voltammetry is a high sensitivity and high precision technique for the evaluation of ORR catalysts. Reverse pulse voltammetry is also a high sensitivity technique for the study of adsorption processes on fuel cell electrodes. PtO\textsubscript{x} is treated as an adsorbate for the purpose of the pulse voltammetry experiments.
With the prior means of synthesis of Pt alloy nanoparticles presented earlier in this work, optimized catalysts can be developed for the ORR in a PEM or liquid fed fuel cell. A wide variety of organometallic compounds have been found to work for CVD processes. Adapting a CVD precursor to the microplasma reactor for nanoparticle synthesis involves choosing a precursor that has a low vapor pressure, or introducing a heating or cooling element to the reactor setup to keep the precursor concentration in the single ppm level.

The electrochemical properties of the catalyst synthesized by the microplasma process can be evaluated for performance by the methods of pulse voltammetry discussed earlier. The microplasma reactor can produce experimental quantities of catalyst, suitable for small fuel cell electrodes.

Catalyst of some chosen composition can be produced by the microplasma method, i.e. Pt:Co, 1:4, and this catalyst can be analyzed by normal pulse voltammetry. Producing a series of catalyst of varying compositions and establishing a library of electrochemical properties based on composition and Pt:M ratio, and identifying the character of the oxide surface coverage as a function of potential can provide a useful tool for further catalyst development, or useful information that may further be fed into catalyst simulations.
5.3 High Temperature Bipolar Plates

Compounds containing portions of the resin material were identified in the effluent of the fuel cells built with the Graftech resin bonded bipolar plates. No investigation as to the rate of degradation of the resin was carried out. Thus the suitability of the 2G resin for use as a binder in the bipolar plate is dependent on the rate of degradation of the binder. A sufficiently low rate of degradation for a few thousand hour design life may already be achievable with the current plate materials. No visible erosion or surface deformities were seen with the 2G resin plate post 1100 hours of testing, unlike the 2H resin plate.
Appendix A

HPLC-MS results and spectra from selected experiments in chapter 4 are presented for further detail.

Figure A.1. Background spectrum, HPLC grade water.
Figure A.2. MS spectrum cell 4, 6.37 minutes. MS spectrum post background subtraction for Cell 04 with the 2G resin plate from effluent collected after 240 hours of runtime at a retention time of 6.37 minutes. The three highest intensity peaks are of relatively light moieties.

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Table A.1. Identified compounds at a retention time of 6.37 minutes for the 2G resin Cell 04 after 240 hours of operation, from figure A.2. Unknown compounds have an assigned empirical formula, and have a charge value of 1 unless otherwise specified.
Figure A.3. MS Spectrum at a retention time of 11.75 minutes. (Cell 4). MS spectrum post background subtraction for Cell 04 with the 2G resin plate from effluent collected after 240 hours of runtime at a retention time of 11.75 minutes. The highest intensity peak of 249.18amu is of an unknown compound, an empirical formula for which is given in table A.2.

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Table A.2. Identified compounds at a retention time of 11.75 minutes for the 2G resin Cell 04 after 240 hours of operation, from figure A.3. Unknown compounds have an assigned empirical formula, and have a charge value of 1 unless otherwise specified.
Figure A.4. MS spectrum post background subtraction for Cell 04 with the 2G resin plate from effluent collected after 240 hours of runtime at a retention time of 25.11 minutes. Compositions of the 249.09amu and 117.11amu fragments are given in table A.3.

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<td>C9H5O6N9F6Si2</td>
</tr>
<tr>
<td>733.34</td>
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<td>C21H60O2N9F5Si6</td>
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</tbody>
</table>

Table A.3. Identified compounds at a retention time of 25.11 minutes for the 2G resin Cell 04 after 240 hours of operation. Unknown compounds have an assigned empirical formula, and have a charge value of 1 unless otherwise specified.
Figure A.5. MS spectrum post background subtraction for Cell 08 with the 2G resin plate from effluent collected after 1104 hours of runtime at a retention time of 11.90 minutes.
<table>
<thead>
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<th>status</th>
<th>name or formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>117.22</td>
<td>unknown</td>
<td>C7H19N</td>
</tr>
<tr>
<td>157.15</td>
<td>ident.</td>
<td>C9H19NO, n-isobutyl pentanamide</td>
</tr>
<tr>
<td>249.09</td>
<td>ident.</td>
<td>C15H11N3O3, daniquidone</td>
</tr>
<tr>
<td>329.12</td>
<td>ident.</td>
<td>C17H19N3O2S or C16H18F3NO3</td>
</tr>
<tr>
<td>431.04</td>
<td>unknown</td>
<td>C13H10ON7F5Si2</td>
</tr>
<tr>
<td>521.04</td>
<td>unknown</td>
<td>C14H13O9N10Si2</td>
</tr>
</tbody>
</table>

Table A.4. Identified compounds at a retention time of 11.90 minutes for the 2G resin Cell 08 after 1104 hours of operation, from figure A.5. Unknown compounds have an assigned empirical formula, and have a charge value of 1 unless otherwise specified.

Figure A.6. MS spectrum post background subtraction for Cell 08 with the 2G resin plate from effluent collected after 1104 hours of runtime at a retention time of 11.55 to 21.64 minutes.
Table A.5. Identified compounds at a retention time of 11.55 to 21.64 minutes for the 2G resin Cell 08 after 1104 hours of operation. Unknown compounds have an assigned empirical formula, and have a charge value of 1 unless otherwise specified.

<table>
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<th>status</th>
<th>name or formula</th>
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<td>C8H19NSi</td>
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<tr>
<td>249.08</td>
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<td>C16H11NO2</td>
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<tr>
<td>329.14</td>
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<td>C19H20FNO3</td>
</tr>
<tr>
<td>570.10</td>
<td>ident.</td>
<td>C15H33Cl2IrO2P2</td>
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</tbody>
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