ELECTROCATALYTIC AND FUEL PROCESSING STUDIES FOR PORTABLE FUEL CELLS

DISSERTATION

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ABSTRACT

In the field of catalysis, the development of alternative catalysts for the oxygen reduction reaction (ORR) in Polymer Electrolyte Membrane Fuel Cell (PEMFC) cathodes has been an ongoing task for researchers over the past two decades. PEM fuel cells are considered to be potential replacements for internal combustion engines in automobiles, and their reduced emissions and better efficiency would have huge payoffs for our environment, and in reducing our nation’s dependence on foreign oil. To date, PEMFC cathode over-potentials are still significant, and the only materials discovered to be highly active and stable catalysts in an acidic environment are platinum-based. Despite several major advances in recent years in reducing platinum loading in fuel cell electrodes, the high expense and low availability of platinum will hinder the large-scale commercialization of PEM fuel cells. The most hopeful advances being made in replacing platinum are related to pyrolyzed organic macrocycles with transition metal centers (such as Fe or Co porphyrins and phthalocyanines). Encouragingly, it has recently been discovered that active electrodes could be prepared by heat-treating metal and nitrogen precursors (not necessarily organic macrocycles) together in the presence of a carbon support.
In the first study of this dissertation, catalysts for the Oxygen Reduction Reaction (ORR) were prepared by the pyrolysis of acetonitrile over various supports. The supports used included Vulcan Carbon, high purity alumina, silica, magnesia, and these same supports impregnated with Fe, Co, or Ni in the form of acetate salt. The catalysts were characterized by BET surface area analysis, BJH Pore Size Distribution (PSD), conductivity testing, Transmission Electron Microscopy (TEM), Temperature Programmed Oxidation (TPO), Thermo-Gravimetric Analysis (TGA), X-Ray Diffraction (XRD), X-ray Photo-electron Spectroscopy (XPS), Mössbauer Spectroscopy, Rotating Disk Electrode (RDE) half cell testing, and full PEMFC testing. The most active catalysts were formed when Fe was added to the support before the pyrolysis; however, samples in which no metal was added still showed elevated activity for oxygen reduction. The alumina-based samples showed the best activity, although they were less conductive, even after exposed alumina was dissolved away with hydrofluoric acid. Within a support family, the more active catalysts had a higher amount of pyridinic nitrogen, as determined from XPS. A theory has been proposed to explain this trend based on the formation of different nano-structures depending on which support material is used for the acetonitrile decomposition. According to this theory, nitrogen-containing carbon samples with nano-structures that result in more edge planes being exposed (the plane in which all pyridinic nitrogen is found) will be more active for the ORR. Recommendations for further research in this area are presented.

In volume II of this dissertation, Cu-based catalysts for hydrogen production from methanol and water were studied. These catalysts have applications for mobile fuel cells that rely on hydrogen production from easier to store liquid fuels, such as methanol.
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VOLUME I:

NANOSTRUCTURED NITROGEN-CONTAINING CARBON
CATALYSTS FOR THE OXYGEN REDUCTION REACTION IN
PROTON EXCHANGE MEMBRANE FUEL CELL CATHODES
CHAPTER 1

INTRODUCTION

1.1 Advantages of Fuel Cells

Fuel cells are promising alternative energy devices that convert the chemical energy of a fuel directly into electricity without combustion. There are several types of fuel cells, with the name usually indicating the type of electrolyte the cell uses. The Proton Exchange Membrane Fuel Cell (PEMFC) is a low operating temperature (typically 60 to 100°C) fuel cell being considered as a potential replacement for Internal Combustion Engines (ICE’s) in vehicles and for other mobile power applications. Since the electrolyte of a PEMFC works at such low temperatures, these fuel cells are unique from the other commercially viable types of fuel cells, like the Solid Oxide Fuel Cell (SOFC), the Phosphoric Acid Fuel Cell (PAFC), and the Molten Carbonate Fuel Cell (MCFC). Consequently, fast start-up times are achievable only with the PEMFC. Further, the thin electrolyte membrane allows PEM fuel cells to produce relatively high power while occupying a minimal amount of volume. These characteristics of fast start-up time and high power density make PEM fuel cells the best candidate for use in
portable power applications, such as laptop computers, cell phones, and automobiles. Most vehicle manufacturers recognize PEM fuel cells as the number one candidate to replace combustion engines in automobiles in the future [1].

There are several factors driving fuel cell development. First, a key advantage of fuel cell technology is the potential for higher fuel efficiency and thus a reduction or potentially a complete elimination of greenhouse gas emissions. Because fuel cells operate like batteries and do not burn their fuel, their efficiency is not constrained by Carnot efficiencies, unlike heat engines. In a heat engine, chemical energy is converted to thermal energy which is then converted to mechanical work. The conversion of heat to mechanical energy is where the Carnot heat engine efficiency is imposed, and therefore, the theoretical best efficiency for a typical ICE is around 50%. Contrastingly, in a fuel cell, only entropy differences between the reactants and products limit the efficiency. This fundamental difference means the theoretical efficiency of a PEMFC is near 90% (using H₂ as the fuel), and allows such fuel cells to operate at efficiencies not possible with internal combustion engines. For a PEMFC system operating off of hydrogen produced by an onboard methanol reformer, the experimental tank to wheel efficiency of the system is approximately 45%, whereas a gasoline powered ICE has an efficiency of only 25% [2]. The well to wheel efficiencies of H₂ powered PEM fuel cells and gasoline ICE’s are comparable since the various production processes for hydrogen are not as efficient as refining oil. However, the use of fuel cells could potentially yield a 100% reduction of CO₂ emissions if a renewable source of H₂ were developed (i.e. ethanol or methanol produced from CO₂ consuming plants or biomass, or electrolysis of water with solar energy), and even if H₂ were produced onboard from gasoline, the estimated energy
efficiency would be 37% for PEMFC’s versus 25% for ICE’s [2].

A second, and equally important advantage of PEMFC’s, is the potential reduction in byproducts typically formed by ICE’s. Combustion engines are a major source of pollution in the form of nitrogen oxides (NO\textsubscript{x}), sulfur oxides (SO\textsubscript{x}), Volatile Organic Chemicals (VOC’s), and particulate matter. Both NO\textsubscript{x} and SO\textsubscript{x} emissions, which lead to acid rain, could be reduced if clean sources of hydrogen are developed. Nonetheless, nearly half of NO\textsubscript{x} emissions do not originate from the fuel, but rather from “thermal NO\textsubscript{x}”, which forms when nitrogen in the air reacts directly with oxygen inside of the high temperature combustion chambers. Additionally, VOC’s form from unreacted fuel that is expelled in the exhaust, and particulate matter originates from incomplete combustion of the fuel. Both NO\textsubscript{x} and VOC’s are precursors to smog, and particulate matter is a source of respiratory problems. Thermal NO\textsubscript{x}, VOC’s, and particulate matter are all forms of pollution that could be virtually eliminated by using the cleaner form of energy conversion provided by fuel cells, which does not rely on combustion.

A third advantage of fuel cell systems, and arguably the most important to our nation, is their fuel flexibility. Lessening our nation’s dependence on foreign oil would have huge economic impacts, and reducing our involvement with volatile, oil rich governments of the Middle East would promote world peace. Currently, nearly half of the oil consumed in the United States is imported. This number will rise as demand increases and domestic supplies dwindle, therefore, alternative power sources must be developed to sustain the current quality of life. Fortunately, hydrogen gas could be produced from the reforming of almost any hydrocarbon, from our nation’s vast coal
supply, and from renewable sources such as biomass and landfill gases. Furthermore, solar, wind, nuclear, and hydroelectric energy could even be employed to produce hydrogen from the electrolysis of water.

1.2 How a PEM Fuel Cell Works

Although fuel cells operate by the same principles as a battery, PEMFC’s use a replenishable fuel and a source of oxygen (usually air) to produce energy. PEMFC’s typically operate off of pure hydrogen as the fuel, but can also produce electricity directly from fuels such as methanol or formic acid. Figure 1 shows a schematic demonstrating how a PEMFC works. Hydrogen enters at the anode side, where it reacts to form protons and electrons on the anode catalyst. Alternatively, in a Direct Methanol Fuel Cell (DMFC), an equimolar methanol and water mixture can be used as fuel for the anode, where they react to form protons, electrons, and carbon dioxide. In a formic acid PEM fuel cell, formic acid (HCOOH) reacts at the anode to form two protons and carbon dioxide. The solid polymer electrolyte has low permeability to the reactants and electrons; however, protons can travel across the electrolyte to the cathode. Typically, a dense acidic polymer, such as Nafion, is used as the electrolyte to achieve this function. Electrons are forced through an external circuit to produce electricity before reaching the cathode. At the cathode, protons and electrons react with oxygen to form water. The reduction of oxygen in the cathode is the most challenging reaction in a PEM fuel cell, as will be discussed in the following sections.

Currently, few materials possess the necessary properties for use as a fuel cell
electrode. The electrode of interest in this study is the cathode. Here are the five basic attributes that a PEMFC cathode must have for successful operation of the cell:

i.) High electrochemical activity for the Oxygen Reduction Reaction (ORR) – The cathode catalyst must be active for oxygen reduction, where oxygen reacts with protons and electrons to form water. The reaction is shown here:

\[
O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O \quad (1.2 \text{ V vs. NHE})
\]

Thermodynamically, this reaction could occur at a voltage as high as 1.2 V vs. Normal Hydrogen Electrode (NHE), if a catalyst with infinite activity existed.

ii.) Chemical stability – Obviously to function as a catalyst, the material must be stable in the cathode environment for an extended period of time. This is not trivial considering the low pH of the electrolyte, the high oxidizing potential under normal operation, and the active oxygen intermediates that form during the reaction. Therefore, oxidation and/or dissolution of the catalysts and support is often an issue.

iii.) Electrical conduction – the electrodes of the fuel cell must be able to conduct electrons to produce a usable current.

iv.) Proton conduction/mobility – protons must travel from the H₂ adsorption sites to the anode/electrolyte interface, through the electrolyte to the cathode, and then meet up with activated oxygen species. Typically, the electrodes are doped with a proton conducting polymer (such as Nafion) that serves as a binding agent and connects the catalyst layer to the electrolyte.

v.) Morphology – At low current densities, having a higher surface area catalyst
allows for more available active sites and a higher kinetic current. At high current densities, good porosity allows for better mass transfer of oxygen into the cathode, while water must be transferred out. Therefore, having a mix of hydrophobic and hydrophilic pores is desired.

If the cathode lacks any of these properties, then it will have a detrimental effect on the efficiency and maximum power of the cell. For instance, resistance from slow reaction kinetics contribute significantly to voltage losses, as will be discussed in the following paragraph. While the kinetics for the oxidation of hydrogen are fast and contribute minimally (< 5% of the kinetic losses) [3], the same cannot be said for the cathode reaction. In the case of the ORR, the kinetics are exponentially dependant on the voltage in the cathode, as is the case for electron transfer reactions [4]. As current is drawn from the cell, the voltage drops from the open circuit value, and the kinetic current increases exponentially. However, since the kinetics for the ORR are slow over all known catalysts, a large potential drop always occurs before the current is measurable. The worse the catalytic activity, the larger the potential drop incurred, meaning less efficiency and power. Similarly, resistance to proton conduction through the membrane or electrical resistance in the electrodes will decrease the voltage proportionally to current. With regards to morphology, poor mass transfer of oxygen into the cathode increases the mass transfer resistances, and inability to transfer water out of the cathode causes flooding, which completely cuts off the catalyst accessibility to oxygen.

Figure 2a shows individual contributions for potential losses due to kinetics, ohmic resistances, and mass transfer in a typical PEM fuel cell. Figure 2b shows a typical
characteristic curve of current versus potential for a PEM fuel cell, where the potential drop from the theoretical voltage of 1.2 V is a summation of the losses in Figure 2a. Figure 2c shows the power density curve for a PEM fuel cell, which is obtained from the data in Figure 2b using the equation:

\[ P = I \times V \]

The efficiency of the conversion of chemical energy into electrical energy was obtained from the equation:

\[ \varepsilon = \left( \frac{E_{\text{cell}}}{E_{\text{theoretical}}} \right) \times 100\% . \]

From this series of graphs it is apparent how the required properties previously are necessary for high power output and high efficiency. The red line in the figures shows the effect of have better ORR kinetics. Better kinetics would mean the kinetic current takes off with less of a voltage drop. Correspondingly, the cell would operate with a higher electrical potential at equivalent currents. From Figure 2c, it is apparent that the improved kinetics improve both the power density of the fuel cell, and efficiency. If there are large ohmic resistances in the cell, then the voltage will drop steeply with increasing current. Correspondingly, efficiency and power density would be lost. If mass transfer is poor in the cathode, then the onset of mass transfer voltage losses will become significant at lower currents, and again, the same negative effects would result. Therefore, all the required properties discussed effect the power density and efficiency of the cell.
Figure 1: Schematic drawing of how a PEM fuel cell works.
Figure 2: Characteristic curves for a typical PEM fuel cell.
1.3 Shortcomings of Current PEM Fuel Cells

Fuel cells have several economical obstacles to overcome before they can be commercialized. One setback is that they are competing against a very cheap and well-developed source of energy in gasoline combustion engines. However, as the demand for oil increases, and its supply decreases, fuel cells will become a more economical option. The world’s production of oil is expected to peak before 2050, and as early as next decade [5], therefore it is important to consider alternative energy sources now. Although current prototype fuel cell systems are expensive, according to principles of mass production this cost will drop once large-scale production is initiated. Most experts in the automotive industry, agree that the cost of building a H₂ powered PEM fuel cell vehicle would be close to the cost of building a gasoline powered automobile if done on a larger scale.

Before large-scale production of PEMFC’s could begin there are other obstacles that must be overcome. One very important issue is that a source of fuel for the cells and the corresponding infrastructure must be developed. Since fuel cells are merely energy conversion devices, they are only as clean and efficient as the upstream fuel source. An extensive amount of research is being carried out, particularly by catalysis researchers, on the production of fuels for fuel cells, but this complicated issue will not be discussed here (VOLUME II: of this thesis deals with hydrogen production).

In addition to fuel source issues, the reliance of PEMFC’s on scarce materials poses a problem. Because of the low temperature of operation, catalysts play an important role in the electrodes and represent one of the biggest challenges to
commercialization. Currently, it appears that the low availability of platinum will hinder the inauguration of PEMFC’s as replacements for ICE’s. State-of-the-art PEMFC’s use platinum supported by carbon black as electrocatalysts in both the anode and the cathode. The lowest loading of platinum achievable (before performance is reduced) using state-of-the-art methods is 0.05 mg/cm² in the anode and 0.4 mg/cm² in the cathode [3]. The cathode requirements present a more difficult challenge compared to the anode, as evident from the high platinum loadings. Estimates show that the maximum possible production of platinum in the world would barely be high enough to allow 10-20% of the automobiles being produced annually to be powered by PEM fuel cells [6-8]. Furthermore, even if breakthroughs in platinum-based catalysts are achieved, there are other concerns with relying on platinum-based materials. One particular concern is that most of the world’s platinum is mined in unstable regions, such as Africa and the Ural Mountains region in the former Soviet Union [9]. Additionally, beyond the geopolitical and availability shortcomings of platinum, it is still not an ideal material for use in a PEM fuel cell cathode because of poor performance compared to what may theoretically be attainable.

A large amount of research has focused on reducing platinum loadings in PEMFC electrodes. However, it seems unlikely that required platinum loadings could be reduced by another order of magnitude by simply developing better preparation techniques. Figure 3 shows a magnified drawing of a PEMFC electrode. Particles of platinum are supported by carbon black and covered by a thin film of Nafion. Only the platinum particles that are in contact with the so-called “triple boundary phase” are electrochemically active. This means platinum must be connected electrically to the
external circuit through the conductive carbon support, it must be connected to the
electrolyte through the proton conductive film, and must be exposed to the reactant all at
the same time. The largest difficulty with platinum utilization is from it being covered by
too thick of a layer of Nafion for fast H\textsubscript{2} or O\textsubscript{2} diffusion [10], or with too large of
platinum particles leaving a high percentage of platinum atoms in subsurface layers [11].
Moreover, sintering of platinum particles occurs during normal operation, causing the
active surface area to decrease with time [12]. Platinum can also be poisoned by
impurities in the reactant stream, thus rendering it inactive. This is especially a problem
for carbon monoxide, often found in hydrocarbon derived fuel streams, which can hurt
activity in concentrations as low as 10 ppm [13]. In state-of-the-art fuel cell technology it
is estimated that between 25\% to 50\% of the platinum is in contact with the triple
boundary phase [14], and thus electrochemically active (before deactivation). Therefore,
while optimizing platinum usage could potentially yield a 4-fold reduction in the required
platinum loadings, world-wide platinum supplies will still be drained.

As discussed in the previous section, the use of platinum as the PEMFC cathode
catalyst also contributes extensively to inefficiencies in the cell because of poor activity.
The slow ORR kinetics typically contribute the most out of all sources to inefficiencies in
a H\textsubscript{2} fueled PEMFC operating at maximum power [3].

Because of the problems facing current PEMFC technology, researchers are
focusing on improving many aspects of the current technology, from anodes with better
carbon monoxide resistance, to better performing electrolyte membranes. However, the
use of platinum in the cathode of PEM fuel cells is an issue that must be resolved since it
drastically hurts the efficiency of the cell, and limits the possibility for wide-scale
production. Alternative cathode catalysts to platinum has been the objective of many researchers over the past four decades [15]. Still, an acceptable replacement for platinum-based cathodes has yet to be developed. This volume of work focuses on bettering the understanding of alternative catalysts to platinum for use in a PEM fuel cell cathode.

Figure 3: Drawing of a PEMFC electrode demonstrating the triple boundary phase.
2.1 Non-Noble Metal Cathode Materials

2.1.1 Macrocycles

In the mid 1960’s a new class of ORR catalysts for PEM fuel cell cathodes was reported by Jasinski [16, 17]. In this class of materials, a metal ion is stabilized by an organic macrocycle. It should be noted that these catalysts are related to the active sites that living organisms use to transport and activate oxygen at low temperatures, therefore, perhaps it is not that surprising that such materials could be used to activate oxygen in a PEM fuel cell cathode. Since Jasinski’s report on the activity of cobalt phthalocyanine (CoPc), a large number of other transition metal N₄-chelates (particularly Fe and Co) have been shown to be active ORR catalysts, and consequently research in this area has been reviewed extensively elsewhere [18-24]. While these materials can be active in a fuel cell environment, long-term activity is poor compared to pyrolyzed macrocycles (discussed in the following section). Therefore, considering the previous reviews on this topic, and the poor stability compared to heat treated versions, only some of the major
findings for non-pyrolyzed transition metal N₄-chelates will briefly be reviewed here.

The most well studied types of macrocycles include porphyrins, phthalocyanines, and tetraazaannulenes, all of which are depicted in Figure 4. Several different properties can affect how the ORR proceeds. The activity and selectivity varies depending on the metal ion, the chelate, and to a lesser extent, any functional groups attached to the chelate [19, 20]. The most active materials are N₄-chelates with Fe or Co metal centers [19]. Other metals, such as Ni and Cu, and other chelating elements, such as oxygen or sulfur, do not yield the same level of activity [19]. Selectivity in the full range of 2 electrons (where oxygen is reduced to peroxide) to 4 electrons (oxygen is reduced to water) has been reported depending on the material used, with Fe centers typically having the highest selectivity to water [20]. Interestingly, Collman et al. studied a series of face to face Co porphyrins and reported that selectivity is dependant on the distance separating the active sites [25, 26]. The studies concluded that the a separation of about 4 Å facilitates bridged oxygen adsorption, which allows the reduction to proceed to water [25, 26]. Furthermore, the electrolyte properties can effect activity and selectivity of an ORR catalyst [27] and the voltage can have an influence on the selectivity for the 4 electron reduction of oxygen to water [20].

To work in a functional fuel cell these semi-conducting macrocycles must be adsorbed onto a conductive electrode support. Typically, some form of carbon black is used, and the choice of carbon can affect activity [19]. However, as mentioned previously, the long-term stability of these catalysts under operating conditions is poor, particularly in acidic media [20, 23]. In an operating electrode, oxidation of the macrocycle by ORR intermediates is believed to cause the quick degradation of the
catalyst [20]. Most recent research related to ORR catalysts has focused on pyrolyzed metal N₄-chelates (see the following section); however, those wishing to obtain more information on recent work regarding macrocycle ORR catalysts could look to the work of Collman et. al and references therein [28] and a recent review by Zagal [20] as a good starting point.
Figure 4: Depiction of common transition-metal chelates (or transition metal complexes of macrocyclic N₄ ligands).
2.1.2 Pyrolyzed Macrocycles

In 1976, approximately a decade after the first reports on macrocycle ORR activity, Jahnke et al. reported the improved activity and stability of pyrolyzed macrocycles (macrocycles heat treated in an inert environment) [19]. Since that time a large amount of work has been carried out on pyrolyzed Fe macrocycles [29-49], Co macrocycles [43-48, 50-71], mixed Fe/Co macrocycles [72-74], other transition metal macrocycles [45, 48, 74, 75], and non-metal macrocycles [43, 53, 54, 69, 76]. Several reviews have also discussed the results in this body of literature [18, 20-24, 75, 77, 78]. In general there is agreement that Fe and Co starting materials produce the most active non-noble metal catalysts [48]. The choice of the ligand and it’s functional groups effect the activity and selectivity after pyrolysis [55, 68, 75]. Selectivity near n = 4 is commonly obtainable [36, 37, 55]. Materials such as Ir and Ru macrocycles have high activity as well [75, 79], but are less studied. Active and stable materials can be produced from pyrolysis temperatures ranging anywhere between 400°C and 1000°C. Generally, the macrocycles are placed on a high surface area support prior to the pyrolysis to generate a better performing catalyst. Optimal loadings somewhere between 2% and 10% typically exist, where the optimal loading is often referred to as a “monolayer coverage of the support” [30, 38, 56, 58, 80, 81]. To produce highly active catalysts, the metal, the organic nitrogen-containing macrocycle, and the conductive support must all be present together during the heat treatment [38, 43, 62]. However, the metal species does not necessarily have to be situated inside the macrocycle [43, 62]. Active catalysts produced from non-macrocyclic starting materials are discussed in the
following section. Characterization of post-pyrolysis macrocycles has included analysis by numerous techniques, which are overviewed in Table 1. Techniques used to measure activity have included various half-cell set-ups, Rotating Ring-Disk Electrode (RRDE) arrangements, and full PEM fuel cells. Selectivity has been measured directly by RRDE experiments or indirectly by Rotating Disk Electrode (RDE) experiments using Koutecky-Levich plots. Agreement between activity testing results in half-cell and full fuel cell systems has been verified [57]. Characterization has been performed by a variety of techniques, including: Electron Spin Resonance (ESR), Infra-Red (IR) spectroscopy, Mössbauer spectroscopy, Nuclear Magnetic Resonance (NMR), Raman spectroscopy, Secondary Ion Mass Spectrometry (SIMS), Ultra Violet-Visible (UV-Vis) spectroscopy, X-ray Absorption Spectroscopy (XAS), X-ray Photo-electron Spectroscopy (XPS), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), as well as various elemental or thermal analysis techniques.

The nature of the active site formed during pyrolysis of transition metal chelates has been the focus of much debate in the literature, and all the theories put forward to this point will be discussed here. First off, researchers from several different groups have reported that the metal center remains intact during the pyrolysis, but that the peripheral structure of the chelate reacts with the carbon support [46, 75, 82]. Better stability and in most cases better activity is obtained and is generally attributed to the binding of the active site to the carbon surface [75]. Similarly to how functional groups on the macrocycle effect activity of untreated macrocycles, the binding of the metal center to the support changes electron density of the metal ion, effecting activity [75]. Since the
reactive parts of the ligands are removed in the process, oxidative attack by intermediate species cannot occur as easily, thus improving stability as well [75].

A second possibility is that the metal center remains intact, but the macrocycle ligands react with each other. In macrocycles treated in the absence of a support, there is evidence that polymerization of the macrocycles occurs [44, 83]. Likewise, in the presence of a carbon black support, such polymerization could occur during pyrolysis and could possibly affect activity and stability for similar reasons to the ones mentioned in the previous paragraph [44, 60]. However, above a treatment of 400°C (which produces a more active material) the macrocycle polymer is thought to decompose [60]. Another possibility is that the heat treatment helps disperse the macrocycles on the support surface and leads to strong chemisorption rather than physisorption [82].

The types of macrocycles most studied in which the active metal center is believed to be retained include Co, Fe, Ru porphyrins and related macrocycles. In these studies the optimal pyrolysis temperature is often reported to be between 400-800°C. Above these temperatures, the active site begins to be destroyed, and activity decreases [39]. An array of characterization techniques have been used to support these claims. XPS analysis has demonstrated that at the highest activity of samples, the surface composition of metal and nitrogen is also at its highest [46, 64]. Above the optimal treatment temperature, nitrogen and metal begins to disappear from the surface. Furthermore, Mössbauer spectroscopy and XAS has been used to determine that the coordination of the metal ion does not change in the active samples after pyrolysis up to 700°C, above which changes occur and activity is lost [39, 66, 67].

On the contrary, many opposing views have suggested the belief that the metal
center is completely destroyed during the pyrolysis. In these studies, the optimal heat treatment can fall between 400-1000°C, at which point samples show good stability and activity in electrochemical testing, but characterization reveals an absence of metal-N₄ centers [34]. In these studies, the full range of Co and Fe macrocycle precursor were examined, and a significant number of the works have shown, using an array of techniques, that after pyrolysis, metal particles are abundantly present in the active catalysts. TEM imaging has shown the formation of metal particles in active heat treated samples [35, 56, 58, 84], and both Mössbauer spectroscopy [69] and XAS [84] have shown the change in the coordination and oxidation state of the metal species [33]. XPS results have even shown complete demetallization of the surface during the pyrolysis in an active sample [35, 53]. Gouerec et al. studied heat treated cobalt porphyrins for the oxygen reduction reaction and observed the same beneficial effects of heat treating the nitrogen, carbon, and metal together that others have observed [68]. The group also characterized catalysts with ESR, and observed a (P)Co³⁺O₂ species for samples heat treated under 600°C. However, samples treated above 600°C were ESR silent, despite still being active for the ORR, indicating the nature of the ORR mechanism is different on these samples. Further, using electrochemical tests Bae et al. have shown that CO can adsorb onto untreated macrocycles, but the pyrolyzed materials cannot adsorb CO, despite having better ORR activity [33]. In the next section, catalysts prepared from the pyrolysis of metal/carbon/nitrogen precursors where the metal is not located within a N₄-chelate will be discussed, thus demonstrating the initial metal center is not required. Clearly this volume of work justifies claims that a new active site for the ORR must be proposed to explain the activity of materials formed from the high temperature pyrolysis
of organic macrocycles.

It should be noted that the two explanations of activity for heat treated materials do not necessarily disagree. Some researchers have concluded a combination of the theories discussed, in that the more active metal-N$_4$ center can remain intact for treatments between 400-700°C, but a new more stable site forms with higher temperature treatments [40, 47, 60, 61]. In fact, in one of the earliest reports of an ORR active heat treated macrocycle discussed the fact that the optimal treatment temperature was 600°C, but higher treatments up to 1000°C created a more stable, though slightly less active catalyst [19].

The active site that forms upon the destruction of the metal center is in itself a topic of much debate. One possible active site that has been proposed is the metal particles that form during the high temperature heat-treatment of these organo-metallic materials [20, 58, 60, 84]. These particles become completely encased in layers of carbon as pyrolysis temperature is increased, as TEM imaging has shown [35, 47, 58-60, 84]. XAS results also corroborate that the metal centers have been destroyed and only metallic particles remain in at least some active heat treated materials [84]. The carbon envelopes prevent the metal from dissolving in the electrolyte, a problem that prevents most transition metals from being used as catalysts. However, it is not clear how O$_2$ could reach the surface of the metal particles. One possibility is that the underlying metal improves the catalytic activity of the carbon shell above. This active site assignment does not explain the observations that nitrogen must be present during the pyrolysis to achieve high catalytic activity, since encased metal particles can also be formed from treatments without nitrogen. Furthermore, this theory does not explain why activity is
often lower in samples with higher metal loadings.

Another possible explanation for activity in these materials is that metal centers can reform once the catalyst is placed in the electrolyte. It has been established that a portion of the metal dissolves when pyrolyzed samples are placed in an acidic solution, and interestingly, such a wash improves activity [38]. It is thus possible that the dissolved metal ions could re-adsorb to nitrogen coordinated sites [20, 85, 86]. Lefevre et al. has proposed just such a site for heat treated materials [87], which is discussed in detail in the following section.

In a different line of thought, researchers have proposed that the metal is no longer part of the active site for the ORR, but instead catalyzes the formation of a new active site. Gruenig and Weisner were the first to draw this conclusion when analyzing pyrolyzed N₄-chelates with Fe, Co, or H₂ centers [54, 88, 89]. The researchers clearly demonstrated that the same properties could be obtained with metallic and non-metallic precursors, except that there was an approximate 350°C shift in the required pyrolysis temperature. The properties that were identical in the metallic and non-metallic pyrolyzed macrocycles included ORR activity, selectivity, BET surface area, and x-ray diffraction patterns [54]. In this case, nitrogen groups on the surface or nitrogen-doped carbon could explain the increased activity [53]. Activity of a pure carbon support improves after pyrolysis of nitrogen-containing H₂ macrocycles on the support. In some cases skeptics attribute this to metal contamination in the carbon. In one instance the results of non-metallic nitrogen-treated carbon activity could not be reproduced with a purified carbon support [69]. However, in another case a completely metal free carbon support (formed from PVDC decomposition) showed increased activity compared to pure
carbon upon pyrolysis of non-metal macrocycles [75]. For pyrolyzed Fe porphyrins, Gojkovic et al. proposed that nitrogen groups form during pyrolysis from the reaction of the macrocycle with the support, and that the metal only catalyses the formation of the active site [79]. Expanding on this sentiment, a theory proposed by the authors of the thesis in hand (Matter et al.) stated that nitrogen-containing carbon is itself more active than carbon for the ORR, and the metal particles catalyze the formation of nitrogen-doped carbon with more exposed edge planes during pyrolysis, which is thought to be more active than the basal plane for the ORR [90]. This theory is discussed in detail in the following section. It should be mentioned that this theory may hold for pyrolyzed macrocycles, since the pyrolysis of Fe phthalocyanine has been shown to catalyze the formation of nitrogen-doped carbon nanofibers with increased edge exposure, and consequently, the resulting material showed good ORR activity in a neutral pH electrolyte (acidic electrolyte was not reported) [41]. Furthermore, mass spectrometry has demonstrated that during the pyrolysis of N₄-chelates, metal particles improve the retention of nitrogen, which could be another possible catalytic effect [76].

More specific non-metallic nitrogen-based active sites have been proposed in the past [53, 79, 91]. Gouérec et al. proposed protonated nitrogen groups on the carbon surface are part of a redox mechanism for the reduction of oxygen [53]. XPS analysis verified that both demetallation occurred in active samples and protonation of nitrogen occurs in samples during activity testing [53, 91]. Gojkovic et al. suggested that a N-O type site could be the source of activity [79]. Interestingly, there have been reports in the literature of a pyridinic-N⁺-O⁻ species formed from exposure of nitrogen-doped carbon to the atmosphere [92-94], and modeling has even verified the potential for such a species to
form [95, 96]. Since the proposed nitrogen-based non-metal active sites, and even the metal-center active site proposed by Lefevre et al., all involve nitrogen groups on the edge plane of carbon, the theory proposed by Matter et al. could be complimentary to any of them.

Despite the uncertainty regarding the exact nature of the active site for oxygen reduction, researchers have managed to produce catalysts based on heat treated macrocycles with comparable activities to state-of-the-art platinum catalysts. In numerous cases researchers have shown activity close to or better than platinum catalysts [29, 37, 40, 73, 81]. Moreover, these materials have an enormous upside, since the active site for the ORR is not fully understood. There is still enormous potential for breakthroughs in their development. A second plus to this class of materials that should be mentioned is their inactivity for methanol oxidation, which makes them better suited than platinum for use in direct methanol fuel cell cathodes where methanol crossover to the cathode can occur [34, 72, 74, 97-99]. In terms of stability, although the long-term activity of heat treated materials is significantly better than unpyrolyzed macrocycles, long-term stability uncertainty still exists. In a full fuel cell environment slow deactivation has been observed by some researchers [38], while others have reported constant current over a 200 hour period [52]. In the next section, pyrolyzed non-macro cyclic materials will be discussed. Considering the same activity can be obtained with the simpler and less expensive non-macro cyclic materials, research has shifted focus to that area in recent years and commercialization with the non-macro cyclic precursors seems more feasible based on cost.
Table 1: Overview of pyrolyzed macrocycle research.

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2.1.3 Non-macrocyclic Heat Treated Catalysts

Not only is it unnecessary for a metal ion to be located in the macrocycle before pyrolysis [43, 62], as mentioned earlier, but it is also unnecessary to begin with organic macrocycles to produce active ORR catalysts. Johansson and Larsson first reported the thermal activation of a Co polymer complex in 1986 [107]. Prior to heat treatment, the Co was not believed to be present in a N₄-chelate environment, and the material showed no activity for the ORR. After heat treatment above 600°C, the material became active for oxygen reduction. Thereafter, researchers have demonstrated that nitrogen-containing polymers, such as polypyrrole (PPy) and polyacrylonitrile (PAN) can be activated by pyrolysis in the presence of Co or Fe salts and a high surface area carbon support [85, 108, 109]. Furthermore, a tremendous amount of work from the Dodelet group has demonstrated that even simpler starting materials can be used to form active catalysts, such as carbon, ammonia (NH₃) or acetonitrile (CH₃CN), and Fe or Co salts [87, 102, 104, 106, 110-119]. In direct comparisons to pyrolyzed macrocycles, these simple precursors can display equivalent or better activity and selectivity [87, 102, 104, 106, 120]. For reference, an overview of the precursor materials that have been activated for the ORR, and techniques used to study these materials are shown in Table 2, similar to the table presented in the previous section for pyrolyzed macrocycles. Other recently developed related materials that will be discussed in this section, which have demonstrated high ORR activity, include pyrolyzed PAN aerogel (mixed with Fe or Co salt) [121, 122], pyrolyzed Fe phenantroline complexes [80, 123], and nitrogen-
containing carbon nanofibers grown during CH$_3$CN pyrolysis over supported metal particles [90, 124-127].

To generate a highly active ORR catalyst, the requirements are generally identical to pyrolyzed macrocycles. A nitrogen source, a carbon source, and the metal (typically Fe or Co), must be heated together to a maximum temperature between 600 and 1000°C [112, 114]. However, there are several caveats to this statement that should be pointed out. First, Martin-Alves et al. reported that active materials formed from pyrolysis of Co acetate and a non-nitrogen polymer that could complex with the cobalt [128]. However, while the activity of this material had twice the current reported for pure carbon, considering the voltage of the comparison was only –0.15 V vs. SCE, this material cannot be considered highly active [128]. Second, numerous reports have shown that the ORR activity of pure carbon can be improved by treatment with ammonia or hydrogen cyanide [90, 113, 120, 129]. In many of these cases, metal contamination in the carbon support is suspected [113], and adding more metal generally improves activity [90, 113, 120]. However, there is overwhelming evidence that nitrogen-containing carbon has better ORR activity than pure carbon, as will be discussed in the following paragraphs, and must at least be considered to contribute to ORR activity.

The objective of most research in the area of pyrolyzed metal/N/C materials has centered around understanding the nature of the active site for the ORR. Similar to heat treated macrocycles, there has been parallel controversy over the nature of the active sites and the role of Fe or Co in these metal-nitrogen-carbon catalysts. Based on the activity attainable from a wide-range of precursors, it seems safe to assume that above a certain temperature, the active site formed is the same regardless of the metal-nitrogen-carbon
starting material (macrocycle or otherwise). Initially, some researchers believed that the metal clusters protected by a layer of carbon (which prevented leaching of the metal in the acidic electrolyte) were the source of catalytic activity [128, 130]. The main argument presented was that protected clusters were seen in TEM imaging, and no evidence of metal-nitrogen bonding could be detected by Extended X-ray Absorption Fine Structure (EXAFS) [128, 130]. However, this theory seems to have been discredited, since there is usually a maximum in activity obtained with very low Fe loadings (as low as 0.2-wt%) [102]. It should be mentioned however, that metal oxide and/or hydroxide particles, observed in post-pyrolysis materials have been labeled as catalysts for 2 electron reduction of oxygen to peroxide in recent work [120].

The most widely accepted theory is that the active site formed is the same in nature to the pyrolyzed metal chelates, and consists of M-N4 and/or M-N2 centers. The main evidence for the existence of M-Nx sites was presented by Lefèvre et al., who reported ToF-SIMS evidence that there are two ions in heat-treated materials that can be correlated to activity; one is a Fe-N4 center similar to what is formed by the pyrolysis of metal chelates, and the other is a more active Fe-N2 site [87], which could be the second site formed during high temperature pyrolysis of macrocycles. In the latter case it is believed that the nitrogen atoms are part of a pyridine structure. Further ToF-SIMS results showed a correlation between the FeN4C8 and FeN2C4 groups and activity [102]. There has also been evidence from EXAFS results, which detected metal-nitrogen bonds in active catalysts [131]. Moreover, evidence from XPS performed by Faubert et al. detected pyridinic nitrogen (at the edge of a graphene layer contributing one e\textsuperscript{-} to the \pi band), and pyrrolic nitrogen (at the edge of a graphene layer contributing two electrons to
the π band) [115]. A shift in the pyridinic nitrogen peak was observed upon addition of Fe, while no shift was observed for the pyrrolic or any other nitrogen. It seems plausible that nitrogen is inserting itself into the carbon support to form pyridine structures that are part of the support, and then the pyridinic nitrogen stabilize the metal. This stabilization occurs in phenantroline molecules used to detect Fe ions in aqueous solutions. An example of how this may occur for nitrogen-containing carbon was proposed by Lefevre et al. [87], and is shown in Figure 5. In a more recent paper ToF-SIMS was used to analyze pyrolyzed Co catalysts [106]. Using different precursors of Co acetate and NH₃ treated carbon or Co porphyrins on carbon, it was possible to obtain active catalysts for the ORR. Contrastingly, SIMS results did not yield the same consensus to the nature of the active site as the Fe counterpart. The presence of a Co phenanthroline-type site could neither be confirmed nor discredited. Although characterization often does not detect such a site in post-pyrolysis catalysts, one hypothesized reason for discrepancies is that in an acidic media the metal is soluble, and can move (or leach) until it is adsorbed by electron donating nitrogen sites [20, 86].

![Proposed representation of an M-N₂ active site with pyridinic nitrogen species on the edge of the graphene plane.](image)

**Figure 5:** Proposed representation of an M-N₂ active site with pyridinic nitrogen species on the edge of the graphene plane.
Several variations to the site presented in Figure 5 have been proposed by other authors. Schulenburg et al. proposed a six coordinated Fe active site based on Mössbauer spectroscopy results. In this site, Fe is coordinated to 4 nitrogen atoms in addition to an unknown coordination below and oxygen above [103]. Jain et al. modeled nitrogen substitution on graphite edge planes and bonding of Fe to the edge. In the presence of hydrogen passivation, the site proposed by Lefevre et al. was energetically favorable, but when there was no hydrogen passivation on the carbon edge plane, Fe preferred to be coordinated to one nitrogen and one carbon atom on the edge [132].

Labeling nitrogen stabilized metal centers as the source of activity is not a foregone conclusion. Besides reports of activity increases by treating carbon with a nitrogen source, which may be questionable because of metal contamination [90, 116, 129], the authors of this chapter have prepared highly active catalysts by decomposing acetonitrile over a high purity (< 1 ppm metal contamination) alumina support [124, 125]. The alumina was subsequently leached from the sample using HF acid. The purified acetonitrile char had activity for the ORR within about 200 mV of a commercial 20-wt% Pt/VC catalyst in 0.5 M H₂SO₄. If Fe was added to the alumina prior to the pyrolysis, then activity within 100 mV of the commercial catalyst could be obtained. Based on XPS, TEM, and hydrophobicity measurements, the Fe-containing sample was determined to have more pyridinic nitrogen, and more edge plane exposure. Therefore, the role of Fe was determined to be that of a catalyst for the formation of nitrogen-doped carbon with more edge plane exposure. The active site was hypothesized to be on the edge of nitrogen-doped carbon. Since pyridinic nitrogen can only be located on the edge of a carbon plane, it may be part of the active site, or conversely, simply an indication for
more edge exposure in the sample. This theory falls in line with the hypothesis presented by Gouerec et al. [53], and Gojkovic et al. [79] for heat-treated macrocycles, as discussed in the previous section.

There is strong theoretical support to the hypothesis that nitrogen-doped carbon edge sites are the source of activity for the ORR. Several modeling studies have verified the improved electron-donating properties of nitrogen-doped carbon [133-135]. Additionally, the edge plane of carbon is known to be more catalytically active for a number of electrochemical reactions [136-138], including the reduction of oxygen in basic electrolytes [139]. Furthermore, numerous studies have demonstrated the Fe catalyzes the formation of nitrogen-doped carbon fibers with edge exposure during the pyrolysis of precursors, such as pyridine [140], acetonitrile [90, 125], and macrocycles [41]. Similarly, a study has reported that nitrogen-doped carbon fibers prepared from melamine are enriched with nitrogen on the surface, and that using Fe catalyzes the formation of more pyridinic type nitrogen than using Ni as the catalyst [141].

Still, there are several weaknesses to labeling nitrogen-containing carbon edges as the sole source of activity in heat treated materials. First, catalysts that contain Fe or Co as of now still always show higher activities. Until a more active catalyst is prepared without metal, it is difficult to dispel the theory that metal-center active sites improve activity. Second, metal particles are not always reported to catalyze the formation of fibers, and in some cases, metal particles were not visible by TEM in the active catalyst even though metal was present [123]. In these cases, it is difficult to visualize how the metal in the sample could be improving edge exposure. However, considering the volume of work conducted to date, it is apparent that nitrogen-containing carbon is more
active than pure carbon for the ORR, thus some activity improvement after pyrolysis must be attributed to it. To conclude the active site discussion, based on what is known to this point, it is possible that the role of metal particles in highly active ORR materials could be as a catalyst for the formation of active sites during the pyrolysis of nitrogen-carbon precursors and/or as part of the active site for oxygen reduction on nitrogen-containing carbon.

In attempts to improve the performance of these materials, alternative avenues of research have been investigated other than active site characterization. The Dodelet group has investigated the effect of carbon support choice, and effects of support pre-treatment [113, 116, 117]. In one paper, over 19 different carbon supports were tested [116]. In order to prepare active materials through pretreatment of the support with NH₃ prior to pyrolysis, it is important to choose a support that can retain nitrogen species on the surface. Other ideas that have been exploited to improve performance were based on using novel precursors. Ye and Vijh have demonstrated that highly active ORR catalysts can be prepared from the pyrolysis of an aerogel PAN and metal salt mixture [121, 122, 142]. Activities near commercial platinum could be obtained without the use of a carbon support. Alternatively, Matter et al. prepared highly active ORR catalysts by growing nitrogen-containing carbon nanofibers from supported Fe or Co particles using acetonitrile vapors [90, 124-126]. The inorganic supports and metal particles could be removed with subsequent washes topurify the nitrogen-doped carbon char. This resulted in a highly active high surface area material, with activity within 100 mV potential drop from a commercial 20-wt% platinum catalyst.

Considering the high activity, surface area, and conductivity of the heat-treated
Fe/N/C catalysts, these materials could be viable replacements for platinum catalysts in PEM fuel cell cathodes. Consistently samples can be prepared within a 100 mV overpotential of commercial platinum catalysts. This means that the alternative catalysts with a similar total loading in the cathode could potentially perform with an equivalent current density as the commercial catalyst while operating at an additional 100 mV of overpotential. This additional overpotential corresponds to only about 8% lower fuel efficiency and 18% more waste heat (when operating the non-metal catalyst at 0.55 V versus 0.65 V for a noble metal cathode at identical current densities). These values seem small considering the potential to completely replace platinum in the PEMFC cathode, which is one of the major obstacles to automotive fuel cell commercialization, unlike fuel efficiency. Moreover, because of the potential to produce the catalyst using inexpensive methods, higher loadings of catalyst could be used in the cathode layer with no economic drawback (with only mass transfer effects eventually limiting the acceptable loading) improving performance even further. However, in a recent review article the validity of comparisons between alternative catalysts and platinum has been questioned [6]. The authors of that article stated that activity comparisons were being made using poisoned or less active (than state-of-the-art) platinum catalysts. In some cases it is true that researchers compare catalysts on an equal metal basis, i.e. heat treated 2% Fe/carbon compared to 2% Pt/carbon. In these cases the platinum sample is not as active as state-of-the-art high platinum loading catalysts. However, in several cases the non-noble metal catalysts faired well compared to state-of-the-art samples tested in the same system [123, 125, 143]. The activity of such samples are still said by the authors of the criticizing article [6] to be much worse compared to commercial catalysts when the turnover
frequency was extrapolated from the alternative catalyst testing conditions to the state-of-the-art testing conditions. However, the alternative catalysts were tested at room temperature with in oxygen saturated sulfuric acid, which is far from the conditions used to test commercial catalysts (80°C, 400 kPa, full PEM fuel cell). To perform the extrapolation an unknown activation energy had to be assumed to account for the temperature difference, and the concentration of oxygen in the electrolyte was assumed to be 100 kPa (over 100 times higher than the actual saturated oxygen concentration in 1 M sulfuric acid). Thus the extrapolation of the activity is likely erroneous, and cannot be used to discredit the high performance of these non-noble metal samples. Furthermore, with regards to the automotive industry, it is not fair to hold alternative catalysts up to the standard of what is attainable with state-of-the-art platinum catalysts, because state-of-the-art platinum catalysts could not be produced on this large of a scale due to the limited availability of platinum. However, until full fuel cell preparation conditions for the alternative catalysts are optimized, and performance is demonstrated at industrial standard conditions, their potential to replace platinum may remain in question.

A final issue that faces this class of catalysts is stability in the fuel cell environment. Deactivation of materials in a fuel cell environment has been shown to be minimal in some studies [111, 114], and severe in others [104, 119]. More active catalysts seem more susceptible to deactivation. Deactivation has been linked to the formation of peroxide and the loss of metal from the catalyst [104]. On the other hand, demetallization has also been observed in pyrolyzed samples that did not lose activity with time [52]. Another possible mode of deactivation could be due to the oxidation of the carbon surface. However, it seems reasonable that a complete understanding of the
deactivation mechanism would first require a well-developed understanding of the active site for oxygen reduction. It should be mentioned that stability is also a major issue facing platinum based catalysts, so this issue is not a unique issue for alternative catalysts. However, in platinum-based catalysts, deactivation occurs through sintering [12], which is not likely the case in carbon/nitrogen materials, so the mechanisms for deactivation are most likely completely different in nature.
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</table>

**Table 2:** Overview of non-macrocyclic pyrolyzed ORR catalyst materials.
2.1.4 Conducting Polymers

Polymers have served roles in PEM fuel cell cathodes such as modifiers to macrocycle-based electrodes to improve conductivity and stability [146], as composite materials with heteropolyacids [147], and as precursors to pyrolyzed catalysts [84, 85, 108, 109]. However, in the previous section the activity of nitrogen-containing carbon was discussed, raising the possibility of non-metal electrodes functioning in a cathode environment. Likewise, researchers have noted ORR activity for various non-pyrolyzed conducting polymers containing nitrogen, and recently studies on their potential use in PEM fuel cell cathodes have come to light.

In 1985 Jakobs et al. studied polypyrrole (PPy) covered platinum and gold electrodes for the ORR [148, 149]. One interesting results of the work was that compared to a bare gold electrode, the PPy covered gold reduced oxygen at a lower overpotential [149]. Further, the PPy covered electrodes, when in the oxidized state, catalyzed peroxide decomposition and thus improved selectivity to water [149].

In recent years, work in Ukraine has investigated the ORR capabilities of a number of conducting polymers [150-152]. Researchers demonstrated that an additional reduction reaction occurs over polyaniline (PANI) during cyclic voltammetry sweeps in acid solutions when oxygen is present. This reaction is not a part of the normal redox reactions that PANI undergoes in argon sparged solution [150, 151].

A recent publication by Khomenko et al. has modeled and tested the activity of an array conducting polymers for the ORR [152]. The observed activity was explained by quantum-chemical modeling of conductive polymers, most notably polyaniline (PANI)
and polypyrrole (PPy), modeling of adsorbed oxygen complexes, and calculations of the electronic structure. The work noted that oxygen adsorbs on active carbon sites within the polymers, and that the unique electronic structure of the polymers leads to activation of the oxygen molecule (weakens the O-O bond). Based on calculations, electron density is donated from PANI to the adsorbed O₂, causing the breaking of the O-O bond.

Conductive polymers do not perform particularly well as ORR catalysts compared to the most active pyrolyzed samples. While a measurable ORR current is often observed at potentials as high as 0.6 V vs. NHE, the current is generally slow to take off [152]. The PANI samples are only active when the polymer is in its reduced state, and high conductivity is dependant on the oxidation state, thus there is a narrower voltage range that the polymer can be subjected to. Long-term stability is also a concern that needs to be further investigated. However, there is no doubt that such work is fundamentally important and could potentially lead to breakthroughs in understanding the ORR mechanism and developing more active catalysts. Additionally, advances are being made in the manufacturing of high surface area conducting polymers, such as PANI, that could improve the performance potential to use such materials as electrocatalysts [153, 154].

2.2 Nitrogen Surface Species

An alternative theory to the Fe Nₓ-chelate active ORR site discussed in the previous section was that nitrogen species in the carbon are responsible for activity, and that Fe is somehow acting as a catalyst for the formation of the active site. There are many possible nitrogen species in carbon, and researchers have thoroughly studied the
nitrogen functional groups in nitrogen-containing carbons using XPS [92-94, 155-157]. Original work was aimed at seeing if certain nitrogen functionalities played a role in NO\textsubscript{x} formation during coal combustion [92, 156], however, more recently researchers have examined carbons formed by decomposing compounds like acetonitrile and pyridine [93, 94, 155]. The most thorough work by Pels \textit{et al.} reports that for nitrogen/carbon compounds heat-treated above 600\degree C, there are 4 main types of XPS peaks. The first, and seemingly one of the most stable, is pyridinic-N at 398.6 ± 0.3 eV. This assignment is widely accepted by others, and represents nitrogen in six member rings on the edge of graphite planes. Pyrrolic-N is widely assigned to peaks at 400.5 ± 0.3 eV. However, it must be said that pyridone-N (pyridinic-N next to OH group) has a similar assignment, and the two are thought to be indistinguishable. Both of these functionalities have been shown to decompose at temperatures above 600\degree C to pyridinic-N (mentioned above) and quarternary-N, which is found in the region of 401.3 ± 3 eV. Quarternary-N is similar to pyridinic-N; however, it is contained within the graphene plane, not on the edge, meaning it is bonded to three carbons (all part of a 6 member ring) instead of two. The last nitrogen functionality identified in these types of carbon are pyridinic-N\textsuperscript{+}-O\textsuperscript{−} in the range of 402-405 eV. This is the most controversial assignment, and always the weakest of the peaks. Even the presence of a peak in this region is not conclusive. Shown in Figure 6 is a representation of the various nitrogen functionalities.
Figure 6: Depiction of the types of nitrogen species commonly present in pyrolyzed nitrogen-containing carbon.

The possibility of a pyridinic-$N^+\cdot O^-$ is very interesting for cathode applications. It has been hypothesized that this species must form at ambient conditions when the material is removed from the inert atmosphere of the furnace and exposed to $O_2$ for the first time. The ability of the surface nitrogen to activate oxygen may explain some of the reported trends in activity. In fact, some have even hypothesized that pyridinic-$N^+\cdot O^-$ is the site of oxygen activation [79]. However, this research work was not followed up, and the XPS evidence of the existence of a pyridinic-$N^+\cdot O^-$ bond is still not conclusive.

Assigning the higher binding energy shoulder present in $N$ 1s XPS spectra to oxidized pyridinic nitrogen is not unanimous in the literature. Casanovas et al. reported a different assignment for the high binding energy nitrogen species often observed by XPS
[157]. The group modeled nitrogen-containing aromatic compounds and determined that high binding energy peaks (around 403 eV) could be obtained from graphitic nitrogen without oxygenating nitrogen. The group concluded that the expected peaks in pyrolyzed nitrogen and carbon would be pyridinic-N (~399 eV), pyrrolic-N (~400.3 eV), and graphitic-N (~401-403 eV). This work is strong evidence that the pyridinic-N\(^+\)-O\(^-\) peak may not exist.

Even if the pyridinic-N\(^+\)-O\(^-\) assignment is incorrect, such a species could form during the oxygen reduction process, and lower the energy barrier for the reaction. Montoya \textit{et al.} has studied the combustion of nitrogen-containing carbon in oxygen using molecular modeling [95, 96]. Their work has concluded that it is reasonable to assume pyridinic-N\(^+\)-O\(^-\) species forms exothermically during the combustion of carbon, and it is a relatively stable intermediate.

However, there is another possible theory to how nitrogen species could improve the ORR in nitrogen-containing carbon, in which nitrogen does not directly interact with oxygen. Strelko \textit{et al.} modeled the electron donating abilities of carbon doped with boron, nitrogen, and phosphorous [133, 134]. The studies concluded that nitrogen within the carbon plane improves the ability of the material to donate electrons. A simplified explanation of this concept is that nitrogen is a similar atom to carbon, except it has an additional electron in its outer shell. If you replace a carbon atom in a carbon matrix with a nitrogen atom, the matrix will have an extra electron that it wants to get rid of. The results of the modeling are not surprising, since nitrogen-containing carbon materials are generally known to be basic, and the definition of a Lewis base is a material that donates electrons. Since the ORR requires donation of four electrons from the cathode to oxygen
in order to form water, improving electron donation capabilities of the cathode would logically be beneficial to the ORR.

2.3 Potential Role of Nanostructure

An intriguing possibility to how Fe could catalyze the formation of particular nitrogen species mentioned in the previous section is that Fe may catalyze the formation of specific nitrogen-containing carbon nanostructures that favor a certain nitrogen surface species. For instance, there are a wide range of possible carbon nanostructures, several of which are depicted in Figure 7. Some of these structures have more edge plane exposure than others, such as stacked platelet carbon, which has carbon edge plane exposed up and down the length of the tube. On the other hand, multi-walled nanotubes (MWNT’s) only have edges exposed at the end of the tubes, and perfect nano onion structures have no edges. An intermediate structure, stacked cups, have periodic edges exposed down the length of the fiber. Graphitic ribbon structures (stacked platelets extending in a perpendicular direction) have about half edge plane exposure and half basal plane exposure up and down the fiber axis. Therefore, edge plane exposure can vary between 0% up to nearly 100% depending solely on the nanostructure present. This is significant since the most abundant nitrogen species in pyrolyzed materials, pyridinic-N and quarternary-N are found in different carbon planes, the edge plane and basal plane respectively.
Figure 7: Depictions of common carbon nanostructures. The arrows indicate the direction the structure extends.

Metal particles are well-known to catalyze the formation of various carbon nanostructures. Perhaps not so coincidentally, the conditions for fiber growth are strikingly similar to the pyrolysis conditions necessary to form active ORR catalysts. A wealth of literature has been published by the Baker and Rodriguez (now husband and wife) groups on the growth of structured carbon fibers [158-172]. Other groups contributing work on this topic include Park (formerly of Rodriguez’s group) and Keane [160, 173-175], the de Jong and Bitter group [176], Dresselhaus and co-workers [177-
Rather than writing a review of all these works, Table 3 shows an overview of the catalysts tested, the atmosphere used, and if mentioned in the paper, the yield of carbon and its nanostructure. The most common catalysts tested are Ni and Fe based, with Cu often used as an additive. Although Cu does not catalyze the growth of fibers by itself, it enhances the growth rate and affects the resulting structure when alloyed with Fe or Ni. The temperature used for growth usually falls between 600 and 900°C, with many sources of carbon available for fiber growth. The growth rate of the carbon is controlled by the diffusion of carbon through the particles, which is a function of temperature and crystalline size and structure. The crystalline size and structure is likewise a function of the catalyst composition, temperature, and the atmosphere. The structure of the resulting carbon is also a function of the crystalline structure and its orientation if on a support. Only the more recent works report on the structure of the carbon and the orientation of the planes. Hydrogen is often added to the feed gas to remove non-graphitic carbon (wax, hydrocarbon chains, etc.) although it is not always necessary.
<table>
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<th>T (°C)</th>
<th>Catalyst</th>
<th>Carbon yield</th>
<th>Described structure</th>
<th>Reference</th>
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<td>Fe-Ni</td>
<td></td>
<td>diamond fiber</td>
<td>[162]</td>
</tr>
<tr>
<td>C2H4 / H2</td>
<td>600</td>
<td>Cu-Fe</td>
<td></td>
<td>diamond fiber</td>
<td>[162]</td>
</tr>
<tr>
<td>C2H4 / H2</td>
<td>600</td>
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<td></td>
<td>diamond fiber</td>
<td>[161]</td>
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<tr>
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<tr>
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<td>Cu-Ni</td>
<td>high</td>
<td>herring bone</td>
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<tr>
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<td>stacked</td>
<td>[193]</td>
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</table>

**Table 3:** Preparation conditions for the formation of various types of carbon nanostructures.
In Table 3 the reactant and temperature columns are self-explanatory. Catalysts were typically prepared from precipitation of nitrate (N) or acetate salts and then reduced prior to the carbon fiber growth. To form alloys the bi-metallic samples were generally reduced for several hours. The yield indicates the weight of carbon obtained per weight of catalyst used. Several types of structures can form during the treatments, some of which were not depicted previously. “Coils” indicates a morphology where the fibers formed are heavily coiled and possesses spring-like quality. The arrangement of the carbon planes in this structure was not reported. These materials may have applications for elastic composite materials. “Diamond fiber” indicates fibers that grew bi-directionally from a diamond-shaped metal particle, without any indication of the carbon plane orientation, although later work indicates that such growth can result in herringbone fibers. “Fibers” indicates that fiber structures formed, but the structures were not specified. “Herringbone” fibers have planes oriented at an angle to the central fiber axis, like a stack of folded papers, and these structures have nearly 100% edge plane exposure. In some cases these structures were hollow. “Multi-directional hexagonal” resembled the diamond fibers only with growth in six directions from a hexagon, “MWNTs” possessed a tube structure with little edge planes exposure, and “shell” carbon describes the case when metal particles are encased in carbon and no fiber growth occurred. Finally, “stacked” refers to the stacked platelet structure where the planes are perpendicular to the fiber axis and edge planes comprise nearly 100% of the exposed surface. These structures grow bi-directionally from a rectangular particle.

Several other types of fiber structures were reported, although their preparation procedure was not clear. Some papers by the Baker group report on the selective
formation of graphite ribbons. In these structures the carbon planes are aligned parallel to the central axis, but are not tubular like the MWNT’s. Therefore, about 50% of the surface will consist of exposed edges. Despite the lesser amount of exposed edges compared to stacked platelet carbon, these materials may be of interest to electrode research because of the longer range of high conductivity (up and down the central axis rather than across the structure). Unfortunately the review papers sited in the procedure to grow such structures does not report the structure of the carbon formed from the various procedures used, so the procedure to form this particular structure is not clear. Another type of structure of interest for the same reason is the hollow herringbone structure filled with amorphous carbon. This type of fiber was the first discovered in Baker’s group’s early studies on fiber growth [194], and discussed in more detail along with a schematic by Rodriquez [195]. However, the procedure for preparing this structure is not clear from the papers published.

From these many studies several facts can be concluded regarding the catalytic formation of carbon nanofibers. Firstly, it is apparent that a wide range of nano-structures can form from metal particles. The most studied metals are Fe, Co, and Ni, and these metals are active for fiber growth in a wide range of conditions. Seemingly slight changes in the preparation conditions, such as feed composition, support used, and temperature can call have an effect on the structure that forms.

Some researchers have studied the growth of carbon nano-fibers using a nitrogen source in the preparation [155, 196]. Although these researchers did not report on the nano-structure of the fibers, the XPS results can be used to infer the edge plane exposure based on the ratio of quarternary to pyridinic nitrogen. Nakajima and Koh showed that
nitrogen-containing carbon fibers with a high percentage of edge planes could be prepared using unsupported Ni or Co catalyst particles and acetonitrile at 800°C [155]. The total concentration of nitrogen was rather low (2.5%). At higher temperatures more nitrogen was incorporated, but the formation of quarternary nitrogen was favored. At lower temperatures fiber growth was “insignificant”. Kvon et al. published a brief article on the growth of fibers from a mixture of CH₄, H₂, band pyridine over alumina supported Ni/Cu alloy [196]. At very low temperatures (550°C) the group obtained a high edge plane percentage with up to 3.2-wt% nitrogen. At higher temperatures (750°C) more nitrogen was incorporated into the carbon at the expense of the pyridinic to quarternary nitrogen ratio. The researchers declined to report the amount of catalyst used, the time of the treatment, the feed ratios, and the growth rate of the carbon. Even within the ORR literature, there have been reports by the Dodelet group of nanofiber formation [110, 111, 114], although the structure of the fibers and their potential role in activity was never investigated. Undoubtedly, catalytic nitrogen-containing nanofiber formation is possible, and is likely as intricate and complicated as the wide-array of pure carbon nanofiber structures.

Since the inception of the theory that nanostructures are playing a role in the ORR activity of nitrogen-containing carbon materials, several ongoing studies on other systems have come to light that appear to be closely related to our proposed theory. In a presentation and discussion with van Dommele and Bitter (of the de Jong group) the researchers reported the preparation of nitrogen-containing carbon fibers to use as solid base catalysts [197]. The group prepared this series of catalysts from the pyrolysis of acetonitrile over various Co and Fe supported catalysts at various temperatures. The
catalysts were characterized by XPS and TEM. The activities of the samples were gauged with a model reaction, a Knoevenagel condensation of benzaldehyde and ethylcyanoacetate, which is known to proceed over solid base materials. A sample prepared from acetonitrile pyrolysis over silica supported cobalt had the highest activity for the model reaction. Consequently, this material had the largest composition of pyridinic nitrogen of all the samples.

Perhaps the most relevant research is being carried out by Maldonado and Stevenson at the University of Texas [41, 140]. In their first published work the group demonstrated that pyrolysis of iron(II) phthalocyanine supported on a Ni support leads to the formation of nanofibers (40-60 nm in diameter) with a large amount of defects and edge plane exposure. These resulting materials were found to be active for oxygen reduction in neutral to basic pH solutions. The group sited a paper by Ohio State’s own McCreery group to explain the mechanism for ORR over these materials [198], in which the reaction was studied on glassy carbon in basic solutions. The focus of this work seemed to be for applications to oxygen sensors, although the authors notes possible implications to fuel cell and battery research.

In a subsequent paper the authors prepared active catalyst fibers for the ORR using a floating catalyst technique with ferrocene and pyridine [140]. The activity of these materials were compared to carbon materials prepared from xylene by the same method, which leads to pure carbon fibers without nitrogen. The sample that did not contain nitrogen had more order, as determined from Raman spectroscopy and TEM. However, the nitrogen-containing fibers had more disorder, edge plane exposure, and a 100-fold increase in peroxide reduction kinetics, and an increase in the kinetics of $O_2$ to
The importance of having carbon edge planes exposed on the surface for improving activity is a well-known concept. Particularly, the text *Carbon, Electrochemical and Physiochemical Properties* by Kinoshita [136] explains how the combustion of carbon occurs at edge planes. This occurs because edge planes are the most active sites of oxygen chemisorption according to the text. Further, the text notes the improved performance of carbon edge planes compared to basal planes for oxygen reduction in basic electrolytes. The 100 to 1000-fold increase in kinetics of the edge plane was attributed to the ability of the edge plane to adsorb oxygen, not the $10^4$ increase of electrical conductivity in carbon planes versus basal plane to plane conduction. The book even cites work that reported improved activity for oxygen reduction for carbon in basic electrolytes after treatment in ammonia above 600°C. Other researchers, including the McCreery group, have noted the improved activity of carbon edge planes compared to the basal plane for various other reactions [137-139, 199].

While these insights are very interesting, and may have implications to PEMFC cathode materials, these results cannot be directly applied to ORR catalysts in fuel cells. First, the Texas group’s papers did all their ORR testing in basic electrolytes [41, 140], which are not models for PEM acidic electrolytes, and the researchers say nothing about activity in acidic electrolytes. This is significant since some catalysts may only be active for an electrochemical reaction in a single type of electrolyte (for example, pure carbon is only active for the ORR in alkaline electrolytes) [136]. Secondly, all the researchers studying the ORR used samples that were contaminated with Fe and Ni, so they really cannot discount the theory proposed by other researchers, such as the Dodelet group, that
attributes activity to Fe stabilized by edge plane nitrogen groups. Third, the materials prepared were not compared to a commercial standard, so from an engineering standpoint these papers discussed are not extremely informative, although they are extremely strong fundamentally.

To review, based on the work discussed regarding alternative non-noble metal catalysts for the ORR, several facts are apparent. First, it is apparent that the active site for oxygen reduction over nitrogen-containing carbon materials is not yet known. The source of activity could possibly involve a metal center stabilized by nitrogen groups, similar to organic macrocycles that are active for the ORR. However, there is significant evidence that suggests metal particles may merely act as catalysts for the formation of ORR active sites. For example, metal particles could catalyze the formation of nanostructures that have greater carbon edge plane exposure. A number of proposed active sites would be found on carbon edge planes. To develop more active alternative catalysts to platinum, the active site in nitrogen-containing needs to be identified.
CHAPTER 3

EXPERIMENTAL METHODS

3.1 Catalyst Preparation

In order to study the active site in nitrogen-containing carbon catalysts for the ORR, several series of catalysts were prepared to examine further with characterization and activity testing techniques. In the first series, carbon black was used as the support for decomposition (pyrolysis) of acetonitrile. In some cases, Fe or Ni was added to the support prior to the pyrolysis. Because carbon black inherently contains Fe contamination, a second series of catalysts was prepared using high purity alumina as the support for acetonitrile decomposition. While alumina is an insulator, and therefore cannot be used as an electrode material, it can be removed from the carbon that forms during the treatment by washing with a strong acid. Additionally, to provide extensive comparisons, catalysts were prepared using two other commercial supports, silica and magnesia, which can be removed with even milder washes. The procedures for catalyst preparation are as follows.
3.1.1 Carbon Supported Materials

For carbon-based catalysts, Vulcan Carbon XC-72 (as received from Cabot) was used as the support for acetonitrile decomposition. Vulcan Carbon, henceforth notated by VC, is a high surface area (230 m²/g) carbon black often used for electronic applications because of its good conductivity. In fact, the support of choice for Pt in PEMFC electrodes is typically VC. In some cases as received VC was used as the support, but additionally, the effect of doping the carbon with Fe or Ni before the treatment was examined. To dope the support, Ni(II) acetate or Fe(II) acetate was dissolved in 10 mL demineralized water, using the required amount of salt to add 2-wt% metal to the support. Next, the salt solution was added to 2 g of VC while being stirred vigorously in 100 mL of demineralized water. It was necessary to stir the carbon vigorously since it can otherwise separate from the water and form a film on the surface. The carbon was then dried overnight at 100°C, and crushed before being used as the support for the decomposition of acetonitrile.

Acetonitrile decomposition, or pyrolysis, was carried out by first adding 2.0 g of support to a quartz calcination boat, and sealing it inside a quartz tube furnace. The temperature was then ramped at 10°C/min up to the treatment temperature under the carrier gas (N₂ unless noted otherwise) flowing at 150 sccm. Once the furnace reached the desired treatment temperature, the room temperature carrier gas was saturated with acetonitrile (P_{vap} = 72.8 mm Hg) using a bubbler before being sent to the furnace. After the treatment was complete (times varied) samples were cooled to room temperature under the carrier gas. Additionally, one sample was prepared by decomposition of
acetonitrile in the absence of a support. The same conditions were used, but the treatment time lasted 18 hours and the resulting graphite flakes had to be scraped off the side of the tube walls.

Two samples were also prepared within a sealable quartz tube for controlled atmosphere XPS analysis. Both VC and 2-wt% Fe on VC were used as precursors. Each support (100 mg) was placed in its own ¼” I.D. quartz tube with quartz wool packed on each side. The tubes were then placed in an in-house built horizontal high temperature tube furnace. Valves were connected to each end of the quartz tube using graphite ferrules. The valves were far enough away from the furnace to prevent their seals from failing. The temperature was then raised to 900°C at 10°C/min under N₂ flow at 50 sccm. At that point the N₂ was sent through a room temperature bubbler to saturate the feed with acetonitrile. After 4 hours, the flow was switched back to N₂, and the temperature was allowed to cool to 100°C, then the samples were sealed in the quartz tube by closing the valves, and taken to a glove box for XPS sample preparation.

3.1.2 Alumina Supported Materials

In order to prepare samples with no Fe contamination, and to prepare samples where the support material can be removed, in-house alumina was prepared. The high purity alumina was prepared by a sol-gel technique [200], in which aluminum tri-sec-butoxide (Aldrich, 97%, < 1 ppm metals contamination) was mixed with ethanol (HPLC grade) in a 1:2 mass ratio. After stirring vigorously for 5 minutes, water (demineralized) was added using a syringe pump at 0.5 mL/min while stirring to obtain the final water to
ATB mole ratio of 4:1. The pH of the gel was then adjusted to 5 using several drops of concentrated HNO$_3$. The sample was dried overnight at room temperature. The resulting solid was crushed then calcined at 800°C in air for 2 hours. All glassware that came in contact with the alumina was cleaned beforehand with nitric acid (Fisher, 0.04 ppm Fe) and double distilled water to limit metal contamination.

In the cases where the support was doped with a metal prior to acetonitrile deposition, the desired amount of metal acetate salt was dissolved in 100 mL of double distilled H$_2$O, then the support was added to the solution while stirring vigorously. The sample was then stirred an additional 30 minutes and sonicated 20 minutes before drying overnight at 100°C. In one case the support was doped with Fe(II) acetate using an incipient wetness technique. For this sample, enough Fe(II) acetate to yield a 2-wt% product was dissolved with just enough water to fill the pore volume of 2 grams of alumina. The acetate solution was then added drop-wise to the alumina while gently mixing the powder in a manner typical for incipient wetness preparations.

The acetonitrile pyrolysis procedure was identical to the VC supported samples procedure outlined in the previous section.

Some selected samples, prepared using alumina as the support, were subjected to a HF acid treatment to remove any exposed metal and alumina. Approximately 0.5 g of sample was placed in a Nalgene beaker, wetted with a couple mL of water, and then 10 mL of concentrated HF was added slowly. The mixture was stirred lightly and allowed to sit for 2 hours. Finally, 500 mL of demineralized H$_2$O was added slowly, and the undissolved carbon sample was washed by suction filtration using an additional 1000 mL of double distilled H$_2$O.
3.1.3 SiO₂ Supported Materials

Nitrogen-containing carbon fibers were prepared from silica (SiO₂) supported Ni, Co, or Fe. The silicon oxide high surface area catalyst support (215 m²/g, from Alfa Aesar) was used without further treatment. The SiO₂ was impregnated by incipient wetness with an aqueous solution of the metal acetate salt. A concentration of the acetate solution was chosen such that the final metal loading would be 2-wt% (unless otherwise noted), and the total volume of water used would be equivalent to the total volume of the support pores. The precursor was dried at 100°C overnight. TGA was used to determine the weight loss incurred during temperature ramping in an inert atmosphere to accurately determine the carbon yield during the acetonitrile treatment. A total of 2 grams of precursor was used for fiber growth. The precursor was placed in a 6 inch quartz boat inside a quartz tube furnace, and the temperature was ramped to the treatment value (550°C or 900°C) at 10°C/min under N₂ flow at 150 sccm. For treatment temperatures of 550°C the metal salt was reduced in situ with 5% H₂ in N₂ prior to sending acetonitrile to the precursor, while for temperatures of 900°C, the salt was simply allowed to be reduced by the acetonitrile. The acetonitrile treatments lasted 2 hours, using nitrogen flowing at 150 sccm saturated with acetonitrile (Pᵥap = 72.8 mm Hg at 25°C) by means of a room temperature bubbler. After the treatment the temperature was lowered under N₂ flow to room temperature.

The fibers prepared using silica-based supports were purified by subsequent KOH and HCl washes. First, the product from the acetonitrile treatment was refluxed in 1 M...
KOH for 6 hours, then washed with distilled water by suction filtration. Next, the material was refluxed in 1 M HCl for 6 hours, then washed with distilled water by suction filtration. The recovered fibers were dried overnight at 100°C. XPS analysis was used to determined the composition of the fiber surface after washing, and showed very little silica or chlorine remained on the sample surface.

3.1.4 MgO Supported Materials

Nitrogen-containing carbon fibers were prepared from MgO supported Ni, Co, or Fe. Two different types of MgO support were used. The first MgO support had a surface area of 55 m²/g, and was used as received from Leco Co. The second type of MgO “nanopowder” was used as received from Sigma-Aldrich and had a surface area of 150 m²/g. The metal impregnation and acetonitrile pyrolysis procedures were identical to the procedure used for the silica materials outlined in the previous section.

Fibers prepared using magnesia-based supports were purified by a subsequent HCl wash. The product from the acetonitrile treatment was refluxed for 6 hours in 1 M HCl, then washed with distilled water by suction filtration. The recovered fibers were dried overnight at 100°C. XPS analysis was used to determined the composition of the fiber surface after washing. No detectable MgO remained on the surface.

3.1.5 Unsupported Materials

A series of materials were prepared using a number of unsupported metal
particles. The list of metal particles examined included unsupported Fe(II) acetate, a Ni:Cu 70:30 alloy, a Fe:Cu 95:5 alloy, and ferrocene as a carrier to form floating unsupported iron nanoparticles [201]. Fe(II) acetate was used since this material was the dopant used for the supported samples. An unsupported Ni:Cu alloy was used by Kvon et al. to grow fibers from pyridine, therefore, this material was examined for growth with acetonitrile as the carbon and nitrogen source [196]. The preparation of the alloy has been described in more detail elsewhere [202], but briefly, it involved co-precipitation of Ni and Cu hydroxides from their respective nitrate salts, followed by calcinations and reduction prior to acetonitrile treatment. Additionally attempts were made to prepare carbon fibers from an Fe:Cu alloy. Rodriguez and Baker patented a process to prepare stacked platelet carbon from CO and H₂ using this unsupported alloy as a catalyst [203]. Again, this material was prepared through a co-precipitation technique described elsewhere [161]. In addition to treatment of this alloy with acetonitrile, stacked platelet carbon fibers were prepared from CO and H₂ using the procedure outlined in the patent. These fibers were subsequently and/or concurrently subjected to treatment with ammonia. This procedure was used since ammonia treatment of carbon adds nitrogen groups [204], and even improves activity of pure carbon for the ORR [129]. Since platelet carbon has nearly 100% edge plane exposure, the hope was that the ammonia treatment would be even more effective.

3.2 Catalyst Characterization

A variety of characterization techniques were employed to examine the catalysts
throughout the stages of their preparation. The objective of these techniques is to identify differences in the properties of the materials, and to see which properties are related to ORR electrocatalytic activity. The techniques used are as follows.

### 3.2.1 Thermo-Gravimetric Analysis of in situ Pyrolysis

Acetonitrile deposition for catalyst preparation was performed in situ while following weight changes with a Setaram TGA-DSC 111 for selected catalyst precursors. The instrument was placed in corrosive gas mode, and approximately 10 mg of support was loaded in a quartz crucible while an empty quartz crucible was used on the reference side of the balance. To study temperature dependence the temperature was ramped from 20°C to 800°C at a rate of 5°C/min while flowing N₂ saturated with acetonitrile at room temperature (50 sccm split between both sides), then held at 800°C for 2 hours before ramping back down to 20°C. To study weight changes as a function of treatment time the temperature was ramped from 20°C to 800°C at a rate of 5°C/min under N₂ flow. At 800°C, the N₂ was saturated with acetonitrile (at room temperature) before being sent to the sample and reference. After 12 hours the temperature was lowered to 20°C. In some cases samples were reduced in situ with 5% H₂ in N₂ at 650°C before the treatments described above. Post-deposition samples were saved for further analysis by XPS.

### 3.2.2 Thermo-Gravimetric Analysis of Precursors

Using the same TGA equipment the weight loss of all precursor materials was
examined. Experiments were carried out in nitrogen (flowing at 40 sccm) to determine the percentage of mass lost during the initial temperature ramp, which was set at 5°C/min.

3.2.3 Temperature Programmed Acetonitrile Pyrolysis

Temperature Programmed Acetonitrile Pyrolysis (TPAP) analysis of the byproducts of the carbon deposition were performed with an online Cirrus Mass Spectrometer (MS). For these experiments 100 mg of catalyst precursor was placed loosely (with a channel to prevent plugging) in a quartz tube and placed horizontally in a furnace with the MS sampling the exit stream. The temperature was ramped from room temperature to 900°C at 10°C/min while flowing He (20 sccm) saturated at room temperature with acetonitrile. The MS scanned for ions between 1 and 100 AMU.

3.2.4 Weight Change Analysis

Before and after acetonitrile pyrolysis the respective precursor and the newly formed catalyst was weighed to determine the effect of the treatment on the samples mass. The percentage of weight gain is defined as the weight increase during the treatment divided by the original weight, then multiplied by 100%. The carbon yield per metal is defined as the weight increase during the treatment divided by the weight of metal in the precursor. In these calculations, the weight lost during the temperature ramp (measured by TGA) was accounted for.
3.2.5 \textit{N}_2 \textit{Physisorption Experiments}

BET surface area measurements were made by \textit{N}_2 \textit{physisorption} using both a Micromeritics ASAP 2010 and a Micromeritics Accusorb 2100E. With the ASAP 2010 instrument the full nitrogen adsorption and desorption isotherms were obtained. From the adsorption and desorption data the BJH Pore Size Distributions (PSD) were obtained. The BJH cumulative pore volume was calculated from the desorption.

3.2.6 \textit{X-Ray Diffraction}

X-ray diffraction patterns were obtained with a Bruker D8 diffractometer using Cu K$_\alpha$ radiation. Samples were supported by poly-ethylene holders with a 0.5 mm deep reservoir for the powder samples. Patterns were recorded between 10$^\circ$ and 90$^\circ$ 2$\Theta$.

3.2.7 \textit{Temperature Programmed Oxidation}

The VC-based samples were characterized by Temperature Programmed Oxidation using an on-line Shimadzu QP-5050 GC-MS. In the experiments, 10 mg of sample was placed in a $\frac{1}{4}$” I.D. quartz U-tube between pinches of quartz wool. The sample was then flushed with 10\% O$_2$ in He flowing at 30 sccm for 20 minutes. Next, the temperature was ramped from room temperature to 800°C while flowing the same gas mixture. A Gas Chromatograph/Mass Spectrometer (GC/MS) was used to detect the oxides of hydrogen, carbon, and nitrogen.
Temperature programmed oxidation of non-carbon supported samples was carried out in a Setaram TG-DSC 111 with the product stream being analyzed by a Cirrus Mass Spectrometer (MS). Approximately 10 mg of sample was loaded into the TGA and the temperature was ramped at 5°C/min to 750°C in 10% O₂ in He flowing at 60 sccm (split evenly between the reference and sample side). Both the TG and DSC signals were recorded. The MS was used to follow oxides of nitrogen and carbon that formed from the combustion. Products were quantified using ionization probabilities of the products provided by the manufacturer. These values were also verified experimentally using a known feed of CO₂ and NO.

3.2.8 Raman Spectroscopy

Raman spectra were obtained with the Kaiser spectrometer in Dr. McCreery’s lab, using low power to prevent sample heating, and an argon 514.5 nm laser. The spectra was calibrated using a Naphthalene standard.

3.2.9 Mössbauer Spectroscopy

To carry out sample analysis with Mössbauer spectroscopy, ⁵⁷Fe enriched precursors were prepared. First, ⁵⁷Fe metal (Cambridge Isotope Labs, Inc.) was dissolved in glacial acetic acid. Then water was added to the solution until the color of the ⁵⁷Fe acetate solution matched the color of the 0.0046 M Fe acetate solution used in previous non-enriched samples for wet impregnation. For wet impregnation samples the enriched
solution was then diluted with the normal aqueous Fe acetate salt solution such that the final weight percent of the alumina supported precursor would contain 0.08-wt% $^{57}$Fe, but still 2-wt% Fe overall. For incipient wetness precursors, the necessary amount of $^{57}$Fe solution to make the 0.08-wt% $^{57}$Fe precursor was mixed directly with non-enriched iron acetate salt, then water was added until the solution had a volume equivalent to the pore volume of the mass of alumina to be used. From this point the normal procedure was followed for sample preparation. It should be noted that the $^{57}$Fe samples lost a large amount of mass during the temperature ramp (40% compared to the typical 24%) presumably from the loss of acetic acid (used to dissolve $^{57}$Fe) in the sample. The distinct smell of acetic acid was apparent in this precursor prior to the treatments.

Mössbauer spectroscopy was conducted using $^{57}$Co as the gamma ray source, and by vibrating the samples in the range of –5 to 5 mm/s. The isonomer shift corresponds to a $\alpha$-Fe standard. All of the samples were exposed to the atmosphere and were at room temperature during the analysis.

3.2.10 Hydrophobicity Testing

The ability of selected samples to be dispersed in water was compared to several standard forms of nanostructured carbon. In each test, approximately 1.0 mg of sample was dispersed in 10 mL of deionized water by sonicating for 30 minutes. Photographs were taken 1 minute after removing the samples from the sonication bath. The standard forms of carbon that were tested included Vulcan Carbon XC-72, Multi-Walled Nano-
Tubes (MWNT’s) as received from Pyrograf Products Incorporated (PR-24 PS), and stacked platelet carbon prepared in our laboratories by a well-established technique [205].

3.2.11 X-ray Photoelectron Spectroscopy

XPS was carried out with a Kratos Ultra Axis on samples to determine surface composition of the elements present, and to gain clues about the nature of their structures on the surface. The powder samples were supported with double-sided carbon tape or steel disk pellet holders. For each sample a survey was performed from 1200 to 0 eV using a Mg anode at 14 kV, and a 10 mA current. Next, 5 sweeps were carried out for each element concurrently, with the C 1s, N 1s, and O 1s regions always being scanned. Air sensitive samples were transferred into the instrument using a glove box and a controlled atmosphere transfer chamber. The estimated oxygen concentration in the glove box was below 10 ppm, and each sample was exposed to this environment for less than 20 minutes. In some cases, sample analysis was repeated using steel disk supported catalyst pellets for comparison to the carbon tape supported samples. The steel disks were used for all the carbon fibers grown from inorganic supports.

3.2.12 Transmission Electron Microscopy

Transmission electron microscopy was performed with a Phillips CM300 Ultra-Twin FEG TEM and also a Phillips Tecnai TF20. Samples were supported with lacey-formvar carbon, which was supported by a 200 mesh copper grid. Samples were
dispersed with excess ethanol by sonicating for 30 minutes prior to being deposited on
the lacey-formvar support. For distributions of fiber diameters and fiber types, about 50
different fibers were chosen randomly within each sample.

3.3 Electrochemical Testing

Several tests were carried out to determine if a catalyst is usable in a PEM fuel
cell. Since electrode materials must be electrically conductive, conductivity
measurements were performed on all samples, as described in the following subsection.
Additionally, the catalytic activity of all samples was gauged using half-cell Rotating
Disk Electrode (RDE) experiments. These experiments give an estimate of the potential
loss that will be incurred in a real fuel cell using that particular sample, in addition to
other kinetic information. Further, selected samples were analyzed using a Rotating
Ring-Disk Electrode (RRDE) technique, which can determine activity for the ORR as
well as selectivity for the complete four electron reduction to water. Samples that had
acceptable conductivity and good catalytic activity were tested in a full lab-scale PEM
fuel cell system, as described in the following subsections.

3.3.1 Conductivity Testing

Rough estimates of the conductivity were obtained to determine the electrical
resistance of the materials in a fuel cell environment. For these measurements a 1:1 mass
ratio of sample to 5-wt% Nafion in aliphatic alcohols solution was mixed with an
additional 10 mass equivalents of ethanol, then sonicated for 30 minutes. This process mimics the catalyst ink preparation commonly used for fuel cell cathode preparation. Next the ink was distributed evenly on a copper plate covered with Teflon tape that had a small hole punched through the tape to act as a reservoir for the catalyst ink. Enough ink was added to overfill the reservoir. After the catalyst dried, the plate was then clamped to a bare copper plate using a force of approximately 100 psi with only the catalyst making electrical contact between the plates, as the Teflon tape is not conductive. The plates were then connected to a PAR 263A potentiostat, and the voltage was swept from 0 to -0.1 V to determine conductivity. Resistance in the Cu plates was accounted for in the conductivity calculation. Each sample was measured 4 times and the average standard deviation was roughly ± 10%.

3.3.2 Rotating Disk Electrode Half Cell Testing

The activity of all samples for the ORR was gauged with Cyclic Voltammetry (CV) experiments using a PAR 263A Potentiostat/Galvanostat with a 616 RDE set-up. Figure 8 shows a schematic of the half-cell RDE set-up. First, the theory behind the set-up should be explained. The half-cell acts as a model for a fuel cell environment, in which the catalyst is placed in an oxygen-saturated electrolyte. The electrolyte (0.5 M H₂SO₄) provides protons to the reaction at the cathode similarly to a Nafion membrane providing incoming protons from the anode to the cathode in an actual PEM fuel cell. Oxygen within the solution diffuses to the surface of the electrode and reacts to form water, consuming electrons and producing a measurable current. The potentiostat not
only measures the current, it also controls the voltage in the cathode, therefore giving a measure of the voltage at which the reduction current increases. A smaller voltage drop from the theoretical voltage for the ORR corresponds to a better catalyst. By rotating the electrode at different rates, the mass transfer effects of oxygen diffusion through the solution can be accounted for, and the pure kinetic current can be calculated, giving a true measure of catalytic performance at specific voltages. Additionally, if the surface area of the cathode is known, the number of electrons transferred per mole of oxygen reacting ($n = 4$ for complete reduction to water) can be calculated.

To test the samples, a 10 $\mu$L drop of catalyst ink (prepared for conductivity testing) was placed on the glassy carbon RDE so as to cover the glassy carbon current collector but not the Teflon, and was then allowed to dry. After the ink dried a small drop of water was placed on the surface of the catalyst and the surface tension was broken to wet the catalyst before placing it in the electrolyte. For the activity testing a 0.5 M solution of H$_2$SO$_4$ was used as the electrolyte. The solution was purged with pure O$_2$ flowing at 50 sccm at room temperature for 30 minutes before performing an initial test sweep from 1.2 to 0.0 V (vs. NHE) at 10 mV/s to remove gaseous O$_2$ from the catalyst pores and allow the pores to fill with solution. Next, the solution was sparged with argon for 30 minutes to remove O$_2$. Then, 5 consecutive CV’s were run from 0.0 to 1.2 to 0.0 V (vs. NHE) at 50 mV/s to confirm that there is no oxygen remaining, and to obtain a steady current by cleaning reducible and oxidizable contaminants off the electrode. Next, the baseline was obtained by sweeping from 1.2 to 0.0 to 1.2 V (vs. NHE) at 10 mV/s in the argon sparged solution at a 0 rpm rotation rate. Finally, the solution was saturated with O$_2$ until consecutive CV’s match (0.0 to 1.2 to 0.0 V at 50
mV/s), and slow CV’s (10 mV/s) were then taken with rotations from 0 up to 2000 rpm with 250 rpm increments in an alternating order converging on 1000 rpm (0, 2000, 250, 1750, etc.). After testing the RDE was polished with an alumina and water slurry. The electrolyte was usually changed before every sample, particularly after a sample with Fe was analyzed or before a metal free sample was analyzed. The voltage of the peak oxygen reduction current at 0 rpm is reported as a measure of activity. Additionally, Koutecky-Levich plots of $1/I$ (mA$^{-1}$) vs. $1/\omega^{1/2}$ (s$^{1/2}$ rad$^{-1/2}$) were constructed from data to obtain the parameter n and the kinetic current, as described in the results and discussion.

Figure 8: Schematic drawing of a RDE half-cell set-up.
3.3.3 Rotating Ring-Disk Electrode Testing

The activity and selectivity of samples for the ORR was gauged with Cyclic Voltammetry (CV) experiments using a PAR Bi-Stat with a model 636 Rotating Ring-Disk Electrode (RRDE) set-up. First, a catalyst ink was prepared using one part (by mass) of catalyst and ten parts of 0.5-wt% Nafion in aliphatic alcohols. After sonicating the ink, approximately 10 µL was dispensed on the glassy carbon disk so as to completely cover the glassy carbon current collector with a thin film of catalyst, but not cover the platinum ring or Teflon casing of the RRDE.

For the testing, a 0.5 M solution of H₂SO₄ was used as the electrolyte. The solution was purged with pure O₂ before performing an initial test sweep from 1.2 to 0 V (vs. NHE) at 10 mV/s to remove gaseous O₂ from the catalyst pores and allow the pores to fill with solution. Next, the solution was sparged with argon for 30 minutes to remove O₂ from the electrolyte. Then, five consecutive CV’s were run on the disk from 1.2 to 0.0 to 1.2 V (vs. NHE) at 50 mV/s to confirm that there is no oxygen remaining, and to obtain a steady current by cleaning reducible and oxidizable contaminants off the electrode. Next, a baseline for the disk was obtained by sweeping from 1.2 to 0.0 to 1.2 V (vs. NHE) at 10 mV/s in the argon sparged solution at a 100 rpm rotation rate. Simultaneously, a background for the ring was obtained while holding the voltage of the platinum ring at 1.2 V vs. NHE. Finally, the solution was saturated with O₂ until consecutive CV’s for the disk match (1.2 to 0.0 to 1.2 V at 50 mV/s), and slow CV’s (10 mV/s) were then taken at rotations of 0 rpm, 100 rpm, and 1000 rpm. The peak in reduction current on the disk during the sweep without rotation is reported as a
measurement of ORR activity. During the CV at 100 rpm, the ring potential was held at 1.2 V vs. NHE, and its current was monitored to detect any H₂O₂ production originating from the sample (on the disk). A higher amount of current in the ring indicates higher selectivity of the sample to peroxide, an undesirable byproduct. The RRDE manufacturer reports the collection efficiency of the ring to be 20% under laminar flow conditions. The reported ring currents were multiplied by 5 to correct for this efficiency.

3.3.4 Lab Scale Proton Exchange Membrane Fuel Cell Testing

Promising samples with high activity and conductivity were tested in an operating PEM fuel cell. Electrodes were made by first preparing a catalyst ink from 50 mg of catalyst, 50 mg of 5-wt% Nafion in aliphatic alcohol, 0.9 g of ethanol, and several drops of glycerol. The ink was sonicated for 30 minutes, then applied to one side of a 5 cm² square of Teflon treated carbon cloth using a painting technique. Next the electrode was dried by ramping the temperature to 70°C at 1°C/min and holding for 1 hour. The Membrane Electrode Assembly (MEA) was made by hot pressing the electrode together with a Nafion 115 membrane and a Nafion doped Pt anode using 2000 psi of force for 3 minutes at 130°C. The MEA was placed in an in-house built test stand and connected to a PAR 263A Potentiostat/Galvinostat. The temperature of the MEA was held steady at 60°C, and H₂O saturated O₂ (60°C) was sent to the cathode at a rate of 50 sccm and a pressure of 20 psi, while H₂O saturated H₂ (70°C) was sent to the anode at a rate of 50 sccm and a pressure of 20 psi. The potentiostat cycled the voltage from 1.2 to 0 V vs. NHE at 10 mV/s until identical characteristic curves were obtained. Power density
versus voltage (or current) plots could then be constructed from this data, although comparison of I-V curves provide the most useful information on performance (see Figure 2 as an example).
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Carbon Supported Catalysts

4.1.1 Effect of Fe on Acetonitrile Pyrolysis

The growth of carbon nano-fibers from a carbon source has been well-studied using Fe, Co, and Ni-based catalysts [155, 161, 195, 196]. Depending on the catalyst, fiber growth usually initiates near a temperature of 600°C, the temperature at which carbon can adsorb on the metal surface, diffuse through the metal particle, and deposit out the opposing side of the particle in the form of elemental carbon [195]. Some researchers have prepared nitrogen-containing carbon fibers although the presence of nitrogen generally requires higher temperatures for fiber growth. These fibers can be grown from acetonitrile or other vapors using Ni and Co based catalysts [155, 196]. In ORR catalyst studies a loading of 2-wt% Fe on the support has been found to be the optimal loading to form active catalysts from acetonitrile pyrolysis [38, 110, 114]. However, since active ORR catalysts have only been reported for nitrogen and carbon decomposed in the presence of Fe, it was decided to compare catalysts made in the
presence of both Ni and Fe, since Ni is also known to lead to fiber growth.

Determining the temperature necessary to initiate carbon growth was the first step for catalyst preparation. TGA experiments were run to see what temperature carbon deposition takes off on the various supports as the temperature is increased. Table 4 shows the temperature at which sample weight began to increase in the presence of acetonitrile saturated N₂. The presence of 2-wt% Fe or Ni on the support decreased the temperature at which fiber growth commences, with the Ni sample taking off at the lowest temperature. Interestingly, researchers studying Fe/N/C chars as catalysts for the ORR have observed that pyrolysis temperatures between 600°C and 900°C yield active catalysts [102], the same temperature range in which fiber growth can possibly occur.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan Carbon (VC)</td>
<td>610</td>
</tr>
<tr>
<td>2% Fe / VC</td>
<td>560</td>
</tr>
<tr>
<td>2% Ni / VC</td>
<td>532</td>
</tr>
</tbody>
</table>

**Table 4:** Acetonitrile decomposition light-off temperatures for VC supported samples.

The next TGA experiments carried out sought to determine what an acceptable treatment time would be for catalyst preparation. In these experiments the temperature was raised to 800°C, and left for 12 hours to observe the weight increase trend. Figure 9 shows the comparison of Fe-doped Vulcan Carbon to pure Vulcan Carbon. Both samples continue to increase in weight through the duration of the treatment; however, the metal doped sample gains weight at a much faster rate than the non-metal sample.
Based on these trends a series of catalysts were prepared using the supports of interest with treatment temperatures varying between 600°C and 900°C, and treatment times from 20 minutes to 12 hours. For all these samples some initial properties were measured, including weight gain during the treatment, BET surface area, nitrogen content, and ORR activity. The weight increase during the treatment is defined as the difference between the weight of the sample before and after the sample, divided by the weight before (an identical definition to the value used for the y-axis of the TGA plots). The percentage of the surface that is composed of nitrogen atoms was determined from XPS analysis, which will be discussed in more detail in the following sections. A quick and easy estimate of the activity of these samples for the ORR was also performed using a RDE half-cell set-up where the catalyst is placed in a 0.5 M H₂SO₄ electrolyte saturated at room temperature with O₂. The voltage is then cycled while recording the current. A peak in the current is observed as the O₂ in the vicinity of the catalyst is used up. This peak occurs at a voltage closer to the theoretical ORR voltage of 1.2 vs. NHE for more active catalysts. This technique is commonly used by ORR catalyst researchers for gauging activity, and moreover, additional kinetic information can be obtained from these experiments by rotating the sample, as is explained in the activity testing section. At this point it is only important to note that more active catalysts will have a higher ORR peak. A more detailed discussion of activity testing is contained in the activity testing results section. As a reference, a 20-wt% Pt/VC commercial catalyst (Electrochem, EC20PTC), had an ORR peak potential of 750 mV vs. NHE.

The properties of the initial series of catalysts are shown in Table 5. Untreated Vulcan Carbon, which contains no nitrogen, is a poor catalyst for the ORR. However,
treating the sample with acetonitrile results in a weight increase (dependant on time), an uptake of nitrogen, and an improvement in catalytic activity, with a 2-hour treatment giving the most active catalyst. The same trend holds true if 2-wt% Fe is present on the carbon before the treatment. In the case of the Fe-containing samples, the weight gains are much higher, the final surface areas are higher, and the activities are higher. At lower temperatures the activities of the Fe samples do not match the activity of the samples treated at 900°C, likely because despite having similar weight gains and surface area, these samples have lower nitrogen content. Treatments were not carried out above 900°C, but other researchers have reported that treatments at temperatures of 1000°C yield a catalyst with lower nitrogen content and lower activity than samples treated at 900°C [21, 102]. Ni is also a common catalyst for fiber growth, but treatment of 2-wt% Ni on Vulcan Carbon did not give the favorable properties and activity seen in the Fe-containing samples. Other researchers have hypothesized that Fe is part of the active site for the ORR, and that samples supported by Vulcan Carbon that show some activity are active because of the inherent Fe contamination (70 ppm) in the commercial carbon. However, this initial characterization shows there may be an additional role Fe is playing considering the higher weight gains and surface area of the Fe-doped samples. Figure 10 clearly demonstrates for samples treated at 900°C that despite undergoing higher weight gains, the Fe-based samples maintain a higher surface area.

Before examining more physical characterization, it is interesting to note what happens if samples are prepared without a support or heated in the absence of acetonitrile. Table 6 shows the properties of such samples. When Vulcan Carbon is treated in pure N₂ rather than acetonitrile saturated N₂ the activity for oxygen reduction
does not improve. If Fe is present on the support before the N₂ treatment then the activity improvement is very small versus plain carbon, showing acetonitrile is necessary for significant catalytic improvement. If acetonitrile is decomposed in the absence of a high surface area support the final product has very low surface area and little activity for oxygen reduction. When Fe acetate alone is treated in the presence of acetonitrile there is a significant weight increase, however, the final surface area and activity is low. These results together with the initial series of catalysts support the belief that active catalysts need to be a carbon material with high surface area and contain nitrogen, but do not necessarily have to contain iron to have elevated activity, unless the 70 ppm Fe contamination is enough to contribute activity.

Pore Size Distribution (PSD) analysis of some selected samples show a unique feature for samples in which Fe was present during the decomposition of acetonitrile (see Figure 11). After 2 hours of treatment the Fe-doped sample has a higher distribution of smaller pores, and a peak in its distribution at 4 nm. This feature at 4 nm is likely arising from nano-fiber growth from Fe particles. Apparently such fiber growth does not occur in Ni-doped or non-doped Vulcan Carbon samples. Interestingly, Figure 12 demonstrates that fiber growth likely occurs on unsupported Fe as well, since unsupported Fe acetate treated in acetonitrile at 900°C resulted in a sharp peak at 4 nm. The nature of this peak at 4 nm will be discussed more in the discussions of alumina samples. In contrast to using metal particles in the furnace, graphitic flakes formed from acetonitrile pyrolysis in an empty furnace had very little pore volume and no interesting features in the pore size distribution, also shown in Figure 12.
Both Figure 13 and Figure 14 show the changes occurring in the PSD with treatment time for both pure VC and 2-wt% Fe/VC respectively. The pure VC sample undergoes very little change in the PSD throughout the treatment. In the Fe-containing sample the 4 nm peak appears after only 20 minutes of treatment time, but fades after the 12 hours of treatment time. The total pore volume also appears to drop after 12 hours in the Fe sample, however, it still has significant pore volume, especially compared to the alumina supported samples that will be shown in the following section.
Figure 9: TGA of weight gains versus treatment time for VC samples being treated at 800°C with acetonitrile.

Table 5: Initial properties tested for all the acetonitrile-treated VC-based samples.
Figure 10: Effect of Fe on the surface area as a function of weight gain using VC as a support for acetonitrile decomposition at 900°C.

<table>
<thead>
<tr>
<th>Support</th>
<th>Atmosphere</th>
<th>% weight increase</th>
<th>BET S.A. (m²/g)</th>
<th>N composition from XPS</th>
<th>ORR current peak (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC</td>
<td>N₂ only</td>
<td>-0.6%</td>
<td>228</td>
<td>0.0%</td>
<td>10</td>
</tr>
<tr>
<td>2% Fe / VC</td>
<td>N₂ only</td>
<td>-2.1%</td>
<td>234</td>
<td>0.0%</td>
<td>165</td>
</tr>
<tr>
<td>none</td>
<td>CH₃CN</td>
<td>undefined</td>
<td>1.5</td>
<td>3.3%</td>
<td>5</td>
</tr>
<tr>
<td>Fe acetate</td>
<td>CH₃CN</td>
<td>43.2%</td>
<td>9</td>
<td>1.5%</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 6: Properties of unconventional samples treated at 900°C.
Figure 11: Pore size distributions of various VC supported samples treated for 2 hours at 900°C with acetonitrile.

Figure 12: Pore size distributions of unsupported samples treated for 2 hours at 900°C with acetonitrile.
Figure 13: Pore size distributions of VC after various treatment times at 900°C with acetonitrile.

Figure 14: Pore size distributions of 2% Fe/VC after various treatment times at 900°C with acetonitrile.
4.1.2 Bulk Physical Characterization

Further physical characterization provides some insight to the nature of the carbon that is forming during the treatments. The XRD patterns for a series of carbon-derived samples are shown in Figure 15. Amorphous Vulcan Carbon has a very broad characteristic [002] peak corresponding to a d-spacing of 0.363 nm. The nitrogen-containing graphite flakes formed from the decomposition of acetonitrile without a support have a [002] peak corresponding to a d-spacing of 0.338 nm. The peaks for all the samples analyzed were very broad, indicative of small crystallite size (<10 nm) or amorphousness. The samples that underwent higher weight gains were the ones that displayed a shift in the C [002] peak from that of Vulcan Carbon to the peak consistent with nitrogen-containing graphite flakes formed in the absence of a high surface area support. There is no correlation between this peak and activity (since there are apparently other important properties for activity), however, it does show how 2% Fe/VC treated for only 2 hours in acetonitrile (the best catalyst shown thus far) leads to a shift in the [002] peak unlike the other samples treated for 2 hours, and that a new type of carbon forms during the treatments. The identical d-spacing for the carbon that forms shows that Fe is not effecting the carbon plane spacing, which would be expected if Fe intercalation were occurring.
Figure 15: XRD patterns for acetonitrile-treated VC supported samples.
There are further consistencies among the carbon that forms during acetonitrile pyrolysis independent of the catalyst/support used. XPS confirmed that the nitrogen content of the carbon is a function of treatment time, and not of the support, as shown in Figure 16. It should be pointed out that this is a surface sensitive technique. Additionally, there may be differences in the nitrogen species present on the surface, but this will be examined in the surface characterization section.

Raman spectroscopy is often a useful technique for analyzing carbon nanostructures. Graphitic carbon has two characteristic bands near 1575 cm\(^{-1}\) and 1355 cm\(^{-1}\), known as the G and D bands respectively. The band near 1575 cm\(^{-1}\) is a measure of defects within a graphite plane, while the band at 1355 cm\(^{-1}\) is attributed to a particle size effect [206]. In Raman analysis more ordered carbon has a much higher intensity for the G band, thus the ratio of the I\(_D\) to I\(_G\) band intensities are often reported as a measure of disorder within a graphitic material [140, 206, 207]. The Raman spectra are reported in Figure 17 for the series of materials prepared from acetonitrile. Evidently, the nitrogen-containing carbon that forms is very disordered, regardless of the catalyst used. This is not surprising since nitrogen is known to create disorder within a graphite plane [208].

Another characterization technique typically employed to study carbon is Temperature Programmed Oxidation. Such experiments were carried out in this study to see if results correlated to the activity of samples for oxygen reduction. It is conceivable that samples which are more active for the ORR will activate oxygen at a lower temperature, and therefore combust more quickly. In comparing “as received” Vulcan Carbon and acetonitrile char (shown in Figure 18) it is apparent that the nitrogen-containing carbon combusts at a much lower temperature. This is especially surprising
Figure 16: XPS analysis of the nitrogen content versus treatment time for VC supported samples treated at 900°C with acetonitrile.

Figure 17: Raman spectra of VC supported samples treated at 900°C with acetonitrile.
since the acetonitrile char has a very low surface area, which one would expect would make it combust more slowly. Both carbon samples combust to form both CO (28 AMU) and CO₂ (44 AMU and a small 28 AMU contribution); however, only CO is shown in the figure. The patterns were similar for CO₂ and CO except when the combustion rate is high, at which point CO₂ formation plateaus (likely from a drop in O₂ concentration) while the CO abundance forms a smooth peak. For both samples the CO₂ intensity was slightly higher than CO. The combustion of Vulcan Carbon did not lead to the formation of any nitrogen oxides, while some NO (30 AMU) but virtually no NO₂ (46 AMU) was formed during the combustion of the acetonitrile char. Interestingly, although nitrogen oxide was released simultaneously with the carbon oxides, the majority of the NO was produced towards the final stage of the char combustion.

Figure 19 shows that the presence of a metal decreases the combustion temperature and causes a sharp spike in the amount of CO and CO₂ being released, with Fe decreasing the combustion starting temperature more than Ni. Again, the patterns were identical for 44 AMU and 28 AMU, with 44 AMU being about 50% more intense. The fragmentation of pure CO₂ would predict that 44 AMU have 10 times the intensity of 30 AMU if only CO₂ were formed, so obviously CO was forming together with CO₂. Nitrogen oxides peaks (not shown) accompanied the much larger carbon oxide peaks with no major differences other than intensity. The Vulcan Carbon sample treated in acetonitrile without metal addition combusted at a higher temperature than the metal-containing samples and even acetonitrile char. During preparation, this sample only received a 20% weight gain from the acetonitrile decomposition, so the majority of the sample may just be Vulcan Carbon. The other samples may also consist mostly of
Vulcan Carbon, but the metal is likely acting as a catalyst for combustion, making the samples burn at much lower temperatures than the pure carbon would. To really characterize carbon fibers, the metal must be removed by extensive washing to prevent any effect on the combustion profile [175]. Because of this catalytic combustion effect of the metal, TPO is limited in the characterization it can provide for the metal containing samples.
Figure 18: TPO comparison of VC and unsupported acetonitrile char.

Figure 19: TPO of VC supported samples treated for 2 hours at 900°C with acetonitrile.
Although Fe appears to be effecting catalyst morphology, the bulk physical characterization techniques did not reveal any differences in the properties of the carbon that forms. Likewise, the first electrochemical test, conductivity testing, which is essentially a bulk characterization technique, did not reveal many differences either. The conductivity results are shown in Table 7. Conductivity improves from Vulcan Carbon after the treatment, but there are no trends apparent related to the precursor support used. The conductivity results could be skewed somewhat by differences in the density of the carbon materials. For instance, the 20-wt% platinum sample is more dense and unexpectedly had lower conductivity. Since roughly equal catalyst weights were loaded into the testing apparatus, the less dense materials had the advantage of being compressed more tightly. Coincidentally, the acetonitrile treated samples were noticeably more fluffy. However, it is also possible that the measurements are accurate, and the improved conductivity results from chemical changes occurring during the treatment. Regardless, the high conductivities are apparent, and indicate that these samples could potentially function in a PEM fuel cell cathode if they have sufficient ORR activity.

The activities for all the carbon samples were reported previously in Table 5. To obtain the oxygen reduction peak, a baseline for each sample had to be obtained. To do this CV’s were run in the argon sparged electrolyte until a steady baseline was obtained. Figure 20 shows the baseline CV’s for an Fe-containing sample. During the first CV, a small oxidation peak typically appeared around 0.3 V. This is likely from the dissolution of exposed Fe into the solution, which occurs through the reaction of Fe° to Fe²⁺
<table>
<thead>
<tr>
<th>Metal/support</th>
<th>Treatment</th>
<th>Conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None/VC</td>
<td>As received</td>
<td>71</td>
</tr>
<tr>
<td>20% Pt/VC</td>
<td>Commercial</td>
<td>47</td>
</tr>
<tr>
<td>None/VC</td>
<td>CH₃CN for 2 h, 900°C</td>
<td>111</td>
</tr>
<tr>
<td>None/VC</td>
<td>CH₃CN for 12 h, 900°C</td>
<td>165</td>
</tr>
<tr>
<td>2% Fe/VC</td>
<td>CH₃CN for 2 h, 900°C</td>
<td>117</td>
</tr>
<tr>
<td>2% Fe/VC</td>
<td>CH₃CN for 12 h, 900°C</td>
<td>98</td>
</tr>
<tr>
<td>2% Ni/VC</td>
<td>CH₃CN for 2 h, 900°C</td>
<td>119</td>
</tr>
</tbody>
</table>

**Table 7:** Conductivity testing results for VC supported samples.

**Figure 20:** Typical background CV taken in the argon sparged electrolyte for an Fe-containing sample.
(theoretical $V = -0.44$ vs. NHE [4]). It is not clear what triggers this dissolution, since Fe should dissolve in the same manner in an open circuit. After Fe dissolves into the solution, it can react reversibly between the 2+ and 3+ oxidation states, a reaction that occurs at 0.68 V in aqueous 1 M $\text{H}_2\text{SO}_4$ solutions [4]. The beginning of another very large oxidation peak is seen as the voltage approached 1.2. This peak was present for every carbon sample, and usually did not go away until 4 or 5 CV’s were run. The tentative initial assignment for this peak is the oxidation of the carbon surface by the electrolyte. After a steady baseline was obtained, the electrolyte was sparged with O$_2$, and more CV’s were run until the CV’s were repeatable, indicating the solution was completely saturated with oxygen. The difference between the reduction current for the oxygen saturated solution and the reduction current in the argon sparged solution indicates current caused by the reduction of oxygen. Figure 21 demonstrates what this difference typically looks like. If the electrode is not being rotated, then the current peaks. This peak is caused by the temporary reaction of oxygen within the pores of the sample. Since the current is proportional to the area of the electrode, the electrochemically active area and current are initially very high, however, eventually the reduction kinetics become very fast and all the oxygen within the sample reacts, making the oxygen concentration zero at the front edge of the sample. At this point the active electrode area is the same as the two dimensional geometric area of the electrode (a smaller area than the three dimensional sample area), and the current becomes limited by the diffusion of oxygen from the bulk of the solution. Figure 22 demonstrates how the oxygen concentration profile changes with time. If the sample is being rotated then the oxygen diffusion limited current is much higher, since rotating the sample improved mass
**Figure 21:** Typical changes in the reduction current upon O$_2$ addition over an active ORR catalyst.

**Figure 22:** Depiction of the changes in the electrolyte O$_2$ concentration with time during a CV over an active and conductive ORR catalyst layer.
transfer of oxygen to the electrode surface. As can be seen in Figure 21, if the electrode is rotated the limiting current is much higher, and the peak is no longer apparent. Rotating the sample can be used to extract important kinetic data out, as will be discussed in section 4.2.10 Electrochemical Testing Results.

The voltage at which the oxygen reduction current peaks is higher for more active materials. A comparison of reduction currents for some samples are shown in Figure 23. The commercial Pt catalyst is the most active sample, but the most active Fe derived samples apparently has good activity as well. Even the sample derived from pure VC treated with acetonitrile performs better than untreated VC. The peak voltages are plotted as a function of the pyrolysis temperature for Fe and Ni samples in Figure 24. From this figure it is apparent that there is not a strong correlation between treatment temperature and activity. The Fe sample treated at 900°C performed the best of all the samples. In Figure 25 the ORR peak voltage is graphed as a function of temperature for pure VC and Fe samples. Similarly, there is not a strong correlation, but the 2 hour treated samples perform the best in each case.

When all the data is examined, one thing is very apparent; the Fe-containing samples perform better than the non-Fe samples. From physical characterization of the carbon this cannot be explained, since there were no apparent differences; however, one may assume that the morphological improvements observed in the pore volume and surface area analysis may explain why the Fe samples perform better. Therefore, the activity of the samples was plotted versus the nitrogen surface area (defined as Fe composition from XPS multiplied by the BET surface area) in Figure 26. This plot shows dramatically that even when the samples are normalized to surface area and
Figure 23: ORR current peaks for selected VC supported samples.

Figure 24: ORR peak voltages plotted versus treatment temperature for VC supported samples.
Figure 25: ORR peak voltage plotted versus treatment time for VC supported samples.

Figure 26: ORR peak voltage plotted versus nitrogen surface area for VC supported samples.
nitrogen content, the Fe-derived samples function at a higher level of activity, regardless of preparation time or temperature. Obviously, there must be an explanation beyond the morphology of the samples to account for the better activity of the Fe-based samples.

4.1.4 Surface Characterization

To find differences between the Fe and non-Fe samples a more detailed analysis of the species on the surface needs to be carried out. XPS is the ideal characterization technique for examining species on the surface of solid carbon materials. In analysis of the O 1s region there was a rough correlation between decreasing oxygen concentration and treatment time, but no apparent link to activity. Additionally, deconvolution of the O 1s peak is very difficult because of the multiple species that can be present on the surface. Typically there were multiple oxygen species with binding energies ranging from 532-534 eV. On the other hand, nitrogen, which is suspected to be the source of improved activity in these materials, revealed interesting results from the XPS analysis of the N 1s region. A great deal of analysis has been carried out on nitrogen-containing carbons, particularly with XPS, for coal and Li ion battery electrode applications as discussed in the literature review. It has been shown that nitrogen functionalities in carbon decompose at higher temperatures to form two species, quarternary nitrogen and pyridinic nitrogen. Quarternary nitrogen can be described as “graphitic nitrogen”, in which nitrogen is within a graphite plane and bonded to three carbon atoms. This type of nitrogen is known to have a characteristic N 1s peak in the XPS spectra around 401.3 ± 0.3 eV. Pyridinic nitrogen exists on the edge of graphite planes, where it is bonded to
two carbon atoms, donates one p electron to the aromatic π-system, and has a resulting N
1s binding energy near 398.6 ± 0.3 eV. Therefore, XPS can be used to differentiate
between the abundance of these species based on differences in the N 1s spectra.

Before examining the XPS spectra for samples, the assignment of the high
binding energy shoulder in the N 1s region should be discussed. After reading the work
of Casanovas et al. [157] and performing in situ XPS of samples that were never exposed
to the atmosphere, it is apparent that the high binding energy peak does not originate
from oxygenated nitrogen species. Figure 27 shows the spectra for samples that were
never exposed to oxygen, fit with a high binding energy shoulder. This shoulder is likely
from a distribution of graphitic nitrogen groups, as described by Casanovas [157]. For
instance, it has been documented that the presence of nitrogen in graphite stretches the C
1s peak to higher values [112]. Figure 28 shows an example of this phenomenon in
comparing VC to acetonitrile treated VC. It is possible that because some carbon atoms
are closer to a nitrogen atom in the graphite matrix than others, some carbon will
inherently have a higher C 1s binding energy. The C 1s peak has been shown to get
wider as more nitrogen is added to graphite [112]. A similar phenomenon may be
occurring in the N 1s spectra. Some nitrogen atoms will be closer to others, and therefore
have a higher binging energy than others. Similarly, calculations by Casanovas et al.
revealed that the “graphitic nitrogen” (quarternary-N) can have a binding energy ranging
between 401-403 eV, even in the absence of oxidized nitrogen, depending on its location
in the carbon plane. Since the cause of the higher energy N 1s shoulder is not obvious,
this area was ignored in deconvolution and when calculating the ratio of quarternary to
pyridinic nitrogen in the spectra that are reported. Additionally, contributions to the N 1s
Figure 27: Controlled atmosphere XPS analysis of the N 1s regions for (a) 2-wt% Fe/VC and (b) pure VC treated at 900°C with acetonitrile.
spectra from pyrrolic nitrogen (or pyridone) were ignored for the samples treated at 900°C, since such species are not thought to be stable at this temperature [94], and during deconvolution appeared to only contribute minimally if at all. With the exception of the high binding energy shoulder, two peaks fit the data well. However, for samples treated shorter times and at lower temperatures it was difficult to deconvolute the N 1s spectra since the nitrogen content was typically lower and perhaps because pyrrolic nitrogen was more abundant. Consequently, only samples treated at 900°C for 2 hours or longer are compared, and for the purpose of this study the ratio of quaternary to pyridinic nitrogen is of the greatest importance, since this will give some indication to the extent of edge plane exposure and the corresponding nanostructure.

![Figure 28: XPS analysis of the C 1s region comparing carbon to nitrogen-containing carbon.](image)

**Figure 28:** XPS analysis of the C 1s region comparing carbon to nitrogen-containing carbon.
XPS analysis revealed there was a correlation between the amount of pyridinic nitrogen and ORR activity. The best carbon supported sample made from 2% Fe/VC had a higher proportion of pyridinic-N (0.48) compared to the treated Vulcan Carbon (0.36) and 2% Ni/VC (0.27) samples, as shown in Figure 29a-c. If the 2% Fe sample was treated for 12 hours the activity decreased along with the abundance of pyridinic nitrogen (down to a 0.39 ratio) as seen in Figure 29d. The acetonitrile char and Vulcan Carbon treated 12 hours (neither shown) have nearly identical N 1s spectra to the Vulcan Carbon sample treated for 2 hours with respect to peak ratios. It should be noted that the higher binding energy shoulder does not change with the size of the pyridinic nitrogen peak. In addition to the controlled atmosphere tests mentioned earlier, this is further evidence that Cassanovas’s assignment of this peak as graphitic nitrogen is correct.

The samples treated at lower temperatures and shorter times were more difficult to deconvolute because of their lower nitrogen content. There is some indication that for shorter treatment times the pyridinic ratio is even better than the more active samples treated for two hours, based on approximate peak intensities. A possible reason these samples are actually less active would be the fact that they contain less of the nitrogen-containing carbon derived from acetonitrile because of the shorter treatment time. However, it is also possible other nitrogen species are present in the samples, like pyrrolic nitrogen, at the lower temperatures or during the initial stages of carbon growth, which makes deconvolution more difficult.

At this point, it is important to note that pyridinic-N is not being labeled as the active site for the ORR. It seems reasonable based on the data presented thus far and the work of others to say that the active site for the ORR is on the edge plane of the nitrogen-
containing graphite. Therefore, the more active samples may contain more pyridinic nitrogen only because these samples have a higher proportion of edge planes exposed, not necessarily because pyridinic-N itself is the source of activity. Therefore, TEM imaging was carried out to investigate the nanostructure since high resolution TEM is useful for directly observing the orientation of graphite planes within nanostructures.

**Figure 29:** XPS analysis of the N 1s region for (a) 2-wt% Ni/VC treated 2 hours, (b) pure VC treated 2 hours, (c) 2-wt% Fe/VC treated 2 hours, and (d) 2-wt% Fe/VC treated 12 hours.
4.1.5 TEM Imaging

TEM samples were obtained for some selected samples to see if there was a correlation between the trends seen in XPS and the nano-structure of the carbon. Figure 30 shows a comparison of 2% Ni/VC, and 2% Fe/VC after acetonitrile treatment for 2 hours at 900°C. In the Ni sample (Figure 30a) no fibers formed and the carbon particles appeared to be larger than the ones in the Fe sample (Figure 30b). The Fe sample had fibers in addition to carbon and metal particles. Figure 31 shows higher magnification images of acetonitrile treated Vulcan Carbon and 2% Ni/VC. No real structures were apparent in the Vulcan Carbon sample, only amorphous particles and some weakly graphitic particles (Figure 31a) were observed. Likewise, the Ni sample had similar carbon particles to this, in addition to Ni particles that apparently became encased in an envelope of carbon (Figure 31b). However, when Fe was added to the Vulcan Carbon, nano-structures resembling tubes of various diameters were present. Some of the fibers were typical multi-walled nano-tubes, but most had a hollow stacked cup structure (schematic shown previously in Figure 7). This type of structure has carbon graphite planes that terminate at the outside of the tube, as can be seen in Figure 32. The core of this type of structure is electron transparent and likely hollow or possibly filled with amorphous carbon. The diameter of the cores of the observed fibers were on the order of 3-10 nm, potentially accounting for the peak in pore diameter distributions for Fe-containing samples reported earlier. As a result of the terminating planes, such a structure will have a large amount of edge exposure, explaining the differences seen in XPS. These structures obviously formed from the metal particles that were about the
same diameter, and often were encased in the end of the fiber (Figure 33). Overall, the nano-structures and alignment of carbon planes seen in this series of catalysts appear to correlate well with the XPS and activity results.
Figure 30: TEM images of (a) 2-wt% Ni/VC, and (b) 2-wt% Fe/VC, both treated for 2 hours at 900°C with acetonitrile.

Figure 31: TEM images of (a) pure VC, and (b) 2-wt% Ni/VC, both treated for 2 hours at 900°C with acetonitrile.
**Figure 32:** TEM image of 2-wt% Fe/VC treated for 2 hours at 900°C with acetonitrile showing the orientation of graphite planes in the fiber structures.

**Figure 33:** TEM image of 2-wt% Fe/VC treated for 2 hours at 900°C with acetonitrile showing the shape of an Fe particle.
4.1.6 PEM Fuel Cell Testing

The most active samples were tested in a full PEM fuel cell set-up. Assembling the MEAs proved to be difficult. Similar activities to a commercial MEA could be achieved by in-house pressing commercial electrodes with a membrane, thus the pressing procedure was determined to be acceptable (see Figure 34). However, the process of depositing the catalyst onto the backing layer proved to be difficult. Often, it was difficult to disperse the catalyst in the ink (the ink would be chunky), obtaining a smooth layer was tedious and challenging, and when the ink dried it would often leave cracks behind. An operational cell was prepared with the 2% Fe/VC treated for 20 minutes in CH$_3$CN at 900°C. The potential drop from kinetics was about what half-cell testing would predict, but ohmic and/or mass transfer losses were much worse than a commercial electrode. The maximum power was about $1/5^{th}$ the power of the commercial MEA.

![Figure 34: PEM fuel cell testing results showing characteristic I-V curves for various samples.](image-url)
4.2 Alumina Supported Catalysts

4.2.1 Determination of Acceptable Treatment Parameters using TGA

The active ORR catalysts studied in previous section were prepared using carbon as a support for an Fe salt, since carbon is conductive. Using carbon as a support is more practical for use in an actual fuel cell; however, alumina is better suited for theoretical studies for several reasons. First, alumina can be made in the lab with well-defined characteristics and high purity, unlike commercial carbons that will contribute Fe contamination and a plethora of ill-defined and potentially reactive surface carbon-oxide species. Second, the alumina itself cannot be made active for the ORR since it is not conductive. Third, it is possible to selectively remove the alumina after the pyrolysis by treatment with a strong acid (HF) leaving behind only the nitrogen-containing carbon formed during the pyrolysis, allowing for easier characterization of the pyrolysis product.

In this section pure alumina, and alumina supported Fe and Ni are examined as supports for acetonitrile decomposition. Determining the temperature necessary to initiate carbon growth is the first step for catalyst preparation. TGA experiments were run to see what temperature carbon deposition takes off on the various supports as the temperature is increased. Table 8 shows the temperature at which sample weight began to increase in the presence of acetonitrile humidified N₂. Light-off temperatures were slightly higher than for the Vulcan Carbon supported catalysts in the previous study, although again all samples are within +/- 100°C of 600°C. Metal containing samples began to increase their mass at a lower temperature than pure alumina, with Ni having the
most favorable effect.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure $\text{Al}_2\text{O}_3$</td>
<td>684</td>
</tr>
<tr>
<td>2% Fe / $\text{Al}_2\text{O}_3$</td>
<td>627</td>
</tr>
<tr>
<td>reduced 2% Fe / $\text{Al}_2\text{O}_3$</td>
<td>606</td>
</tr>
<tr>
<td>2% Ni / $\text{Al}_2\text{O}_3$</td>
<td>576</td>
</tr>
<tr>
<td>reduced 2% Ni / $\text{Al}_2\text{O}_3$</td>
<td>545</td>
</tr>
</tbody>
</table>

Table 8: Acetonitrile decomposition light-off temperatures for alumina supported samples.

Reducing the samples prior to the acetonitrile treatment lowered the take-off temperature 21$^\circ$C and 31$^\circ$C for the Fe and Ni samples respectively. Figure 35 and Figure 36 compare the alumina supported Fe and Ni sample growth profiles during the temperature ramp with and without pre-reduction. Because the ability of the alumina support to adsorb water, the samples undergo a weight loss during the beginning of the temperature ramp. Since the pre-reduced sample was already subjected to a temperature of 650$^\circ$C, its weight loss is less significant. However, after the weight increase initiates, the rate of weight gain is essentially identical for the two samples. The alumina supported Fe sample also had the same trend in growth rate with or without pre-reduction. Because of the negligible difference in fiber growth rates, further prepared catalyst samples were not reduced before the acetonitrile treatment. Additionally, the carbon-supported samples were not pre-reduced with hydrogen (because the carbon could gasify), therefore, for comparison it is beneficial that the treatment parameters match exactly. Furthermore, activity testing also showed negligible differences between the pre-reduced and non-reduced samples.
A second series of experiments carried out on the precursors with TGA was necessary to determine carbon yields during sample preparation. The TGA of the initial weight loss during the temperature ramp is shown for all the different Fe-doped supports of this study in Figure 37. The differences in the TGA profile are dependant on how the Fe is introduced to the sample. For instance, the 2% Fe and 10% Fe samples both had Fe acetate introduced through wet impregnation, then they were dried at 100°C overnight. Therefore, both samples have similar profiles with little weight loss below 100°C, and a total weight loss of about 24% once the temperature reaches 800°C. Most of the mass loss is believed to be coming from water desorbing from the alumina surface. There are two possible modifications to the preparation procedure that effect this profile. First, incipient wetness catalysts were not dried, so they contain more water, and lose more mass at lower temperatures. However, the overall weight loss is only slightly higher. Second, the ⁵⁷Fe enriched samples were also consequently enriched with the acetic acid used to dissolve the ⁵⁷Fe. Therefore these samples undergo more of a mass loss at higher temperatures presumably from the acid decomposing. The total mass lost is much higher for these samples. The total mass lost for each support was accounted for when the weight changes were calculated, and the term “dry support weight” reflects that the weight lost during the temperature ramp has been applied.

The next TGA experiments carried out sought to determine what an acceptable treatment time would be for catalyst preparation. In these experiments the temperature was raised to 800°C, and left for 12 hours to observe the weight increase trend. The alumina had much higher carbon uptake than the other samples (including the Vulcan Carbon samples in the previous study), although the rate did slow after 6 hours of
treatment, as Figure 38 shows. The figure also demonstrates that adding a metal to alumina will cause the weight gain to level out after 2 hours of treatment. Further characterization will attempt offer some clues to help explain this trend.

Despite some small differences, the decomposition of acetonitrile over an alumina support generally seems to be a similar process to the decomposition over Vulcan Carbon. In the Vulcan Carbon study, the most active catalysts resulted from treatments at 900°C for 2 hours. Therefore, for comparison sake, samples were prepared using the three different supports (pure alumina, 2% Fe on alumina, and 2% Ni on alumina) under the same conditions. Additionally, a pure alumina support was treated for 12 hours, since TGA indicated the support was capable of weight increases for extended treatments.

![Figure 35: TGA profile for 2-wt% Fe/Al₂O₃ during temperature ramp in acetonitrile with and without pre-reduction.](image)
Figure 36: TGA profile for 2-wt% Ni/Al₂O₃ during temperature ramp in acetonitrile with and without pre-reduction.

Figure 37: TGA profile of weight loss during temperature ramp in inert atmosphere for some various Fe-doped alumina precursors.
4.2.2 By-Products of Acetonitrile Pyrolysis

In accord with TGA of in situ pyrolysis experiments, Temperature Programmed Acetonitrile Pyrolysis (TPAP) experiments were designed to shed light on to what reactions are occurring during the acetonitrile pyrolysis and provide complementary information. The precursors studied by these techniques include pure Al₂O₃, 2-wt% Fe/Al₂O₃, and 2-wt% Ni/Al₂O₃. There is strong evidence from these experiments that the samples undergo reduction during temperature ramping in acetonitrile. Figure 39 and Figure 40 show results obtained over undoped-alumina. As seen in Figure 39a, there is a low temperature CO₂ (44 AMU) evolution around 150°C, which is likely due to
desorption of CO$_2$ adsorbed from the atmosphere. When alumina was treated with 10% H$_2$ in He, a similar low temperature CO$_2$ desorption was also present (data not shown). However, for the alumina treated in H$_2$ there were no more desorption products produced below 900$^\circ$C, other than water being desorbed at the same temperature as the CO$_2$. In the case of acetonitrile, however, a significant amount of oxygenated carbon products are released between 300$^\circ$C and 700$^\circ$C, including CO$_2$ (44 AMU), and concurrently acetone (58 and 43 AMU) and acetaldehyde (43 AMU), as shown in Figure 39a. Carbon dioxide formation is accompanied by water formation. Figure 39b shows H$_2$O desorption from the surface. As expected, the low temperature H$_2$O evolution is much larger since there is more water adsorption at room temperature than CO$_2$ adsorption, but the high temperature feature for H$_2$O is similar in magnitude to that of CO$_2$. These results show that CH$_3$CN reacts with lattice oxygen from alumina and leaves it in a partially reduced state. In the complementary *in situ* TGA experiment during CH$_3$CN treatment, shown in Figure 39c, it is apparent that the alumina loses about 3% of its initial weight in the same temperature region as the oxygenated carbon desorption, in addition to losing weight at lower temperatures from desorption of CO$_2$ and H$_2$O. In a blank TGA run in helium (data not shown), the alumina lost about 7% of its mass from water and CO$_2$ desorption below 300$^\circ$C, but experienced no significant weight loss above this temperature.

After the high temperature CO$_2$ peak subsides (Figure 39a) a small spike is observed that corresponds to fragments of higher hydrocarbons. One particularly good match for the fragments observed during this spike is methallyl cyanide. The trends observed were completely reproducible in a repeat run, and the temperature of this spike was within 2$^\circ$C of the first run. For temperature-programmed acetonitrile pyrolysis
experiments over metal-doped alumina, the trends were similar (data not shown). The only major difference was that the metal-doped samples release about 50% more CO$_2$ in the 300°C-700°C range, presumably because acetate salts are also being reduced in addition to small percentage of the alumina.

The major products of the pyrolysis of acetonitrile over alumina are shown in Figure 40a-c. Acetonitrile is not consumed significantly until the instance when the higher hydrocarbon spike is observed (Figure 40a). Ammonia is also produced (see 16 AMU and 17 AMU in Figure 40c), with both a low temperature and higher temperature peak. Around 700°C, the point where CO$_2$ production subsides, the main products of the pyrolysis are formed. The main products include HCN (27 AMU), H$_2$ (2 AMU), N$_2$ (28 AMU), and CH$_4$ (16 AMU, but not 17 AMU). At the point where acetonitrile is abruptly consumed, there are disturbances in some of these signals caused by changes in the baselines or fragments from other species present in the hydrocarbon spike. After these disturbances the HCN signal levels out, the N$_2$ and H$_2$ signals continue to increase, and CH$_4$ drops. An approximate quantification of the products based on the total ion count for each species shows that, for each mole CH$_3$CN, 0.56 mol HCN, 0.30 mol CH$_4$, 0.10 mol N$_2$ and 0.23 mol H$_2$ can be accounted for. Based on mole balances, the species not quantified or not detected by MS contain approximately 1.14 moles of C, 0.23 moles of N, and 0.80 moles of H. The undetectable species likely include tars and nitrogen-containing solid carbon. After a typical acetonitrile treatment, deposition of elemental carbon is apparent from the black color of the treated samples and their increased mass, while brown tar is apparent near the exit of the furnace and in the exit stream water trap. Based on the feed used for actual sample preparations, after a 2 hour treatment, 1.0 g of
carbon would still be unaccounted for in the products detected by the MS. Since samples typically gain about 0.5 g during a 2 hour pyrolysis process, it is apparent that both a significant amount of solid carbon products and a significant amount of volatile tar are forming as products of the treatment, with a ratio on the order of 1:1.
Figure 39: (a and b) Oxygenated products and higher hydrocarbons formed during acetonitrile pyrolysis over alumina detected by MS, and (c) the corresponding weight changes occurring during a similar TGA experiment performed in situ.
Figure 40: Major by-products of acetonitrile pyrolysis over alumina; (a) main fragments for CH$_3$CN, (b) fragments for HCN, H$_2$, and N$_2$, and (c) fragments for NH$_3$ and CH$_4$. 
4.2.3 Treatment Parameters Examined

The properties of the carbon doped with nitrogen, denoted CNx, that was deposited on the alumina supports during the acetonitrile pyrolysis were characterized by several techniques. The most crucial properties for an ORR catalyst to be used in a gas diffusion electrode are activity for the ORR, conductivity, and surface area. Proton conductivity is also essential within the catalyst layer, but this is typically achieved by impregnating the catalyst with Nafion or another proton conducting binder. The ORR activity of samples was measured in a half cell set-up, and the conductivity was measured in a set-up that simulated PEM fuel cell conditions, both of which were described in the experimental section. To gauge ORR activity we report the voltage at which the oxygen reduction current peaks during a reduction sweep, signifying a transition from kinetic limited current to mass transfer limited. More active catalysts will peak at a higher voltage (at less of a voltage drop from the theoretical voltage of 1.2 V vs. NHE). As a reference, a 20-wt% Pt/VC commercial catalyst was tested in our system and peaked at 750 mV. While reporting the reduction current at a constant voltage is a more accepted method for gauging ORR activity of platinum catalysts, this method cannot be employed here because the wide range of catalyst activities prevents the choice of a voltage where all of the samples have a measurable current.

The properties of supports that underwent the acetonitrile pyrolysis treatment for 2 hours at 900°C, but were not washed are shown in Table 9. All of the samples have similar weight increases during the treatment from the deposition of nitrogen-containing carbon. The CNx from pure alumina sample maintains a higher surface area after 2 hours
of acetonitrile decomposition than any other sample. This may explain why alumina maintains a high rate of mass increase for longer treatment times, as shown in Figure 38. The alumina sample has an order of magnitude lower conductivity, which is likely related to it having smaller particles (thus giving it a higher surface area). However, the activity of the samples for the oxygen reduction reaction is not dependant on the carbon uptake, the surface area, or the conductivity within this series of samples. The samples prepared from Fe-impregnated supports showed the highest activity; however, there is no correlation between the percentage of Fe added and activity. In fact adding too much Fe was seen to reduce the activity. Although not as high as the Fe-doped CNx samples, the pure alumina CNx sample had good activity, showing Fe is not required. The properties of the carbon that most strongly influence ORR activity will be discussed later.

In order to improve the properties of the samples, and in order to better characterize the CNx that forms during the pyrolysis, exposed alumina in the sample can be washed away using HF acid. Table 10 shows physical properties of samples after they have been washed. The 0.5% and 1% Fe-derived CNx samples were not included since their properties were very similar to CNx from 2% Fe. However, two new samples were prepared by adjusting treatment conditions for the CNx from 2% Fe. Based on the results presented in Table 10, all of the samples lose a significant amount of mass during the wash. From XPS analysis (data not shown), the unwashed samples of CNx-Al2O3, CNx-2% Ni, and CNx-2% Fe contained 19.6%, 6.9%, and 10.1% aluminum on the surface respectively. A portion of this aluminum was in nitride form, as reported elsewhere (see section ‘4.2.7 Surface Characterization’). After being washed the samples all contained less than 0.3% alumina, confirming that the exposed aluminum was effectively removed.
XPS analysis of other regions will be discussed in following sections. In every case the surface area, conductivity, and activity increased upon the removal of alumina. The conductivity of the washed fibers approaches that of Vulcan Carbon XC-72, which was measured in the same system to be 71 S/m. The activity of the washed samples maintained the same trends as the unwashed samples. Altering the treatment conditions, such as the amount of precursor in the furnace, and the treatment time had very little effect on the activity. It is important to note, however, that increasing the Fe content to 10% provided no improvement in activity. In fact, the activity of the CNₓ sample from 10% Fe was significantly lower than that of Fe-free CNₓ sample. Other researchers have reported the disadvantageous effect of adding too much iron in similar heat treated ORR catalysts [115]. The lack of a correlation between iron content and activity supports our assertion that an iron phase formed during the heat treatment is not the primary source of ORR activity in these samples.

The parameter n (determined from RRDE testing), which represents selectivity to water versus hydrogen peroxide, seems to be related to activity in the washed samples, but these results will be discussed in more detail in the discussion of parameters affecting ORR activity, in the subsections ‘4.2.10 Electrochemical Testing Results’, and ‘4.2.11 RRDE Selectivity Testing’.
4.2.4 Morphological Characterization

Reporting just the surface area of a sample does not fully characterize its pore structure. The morphology of different samples can be better portrayed through Pore Size Distribution (PSD) analysis. Figure 41a follows the PSD of alumina being treated with acetonitrile. As the treatment time is increased the support loses volume throughout the entire pore diameter range. After the sample is washed with HF acid (in this case the
sample treated for 2 hours), a large volume of very small pores are opened, explaining the high surface area of this sample. The other washed samples have a similar PSD, as Figure 41b shows. Since the PSD’s are calculated from the BJH desorption isotherm, it is possible that the sharpness of the peak around 4 nm originates from the tensile strength of nitrogen effect as is discussed in the following paragraph. The pore size distribution of the Fe samples subjected to different treatment conditions or prepared using different batch sizes are also very similar (see Figure 41c). Among the washed catalysts, 10% Fe sample had a lower pore volume as reflected in the lower surface area. Overall it is fair to say that all of the washed samples, based on their pore size distributions, have structure at the nano-scale. While some morphological differences exist among the samples, these differences alone cannot explain the differences in ORR activity.

The PSD’s reported to this point have all been calculated based on BJH desorption isotherms. However, it has become apparent that the feature at 4 nm in many of the fibers containing materials may be an artificial feature due to a meniscus effect of liquid nitrogen. During discussion of our work, Bitter brought up the point that the 4 nm peak observed in our BJH desorption distribution could be non-physical in nature, and may be resulting from what is known as the Tensile Strength Effect (TSE) of nitrogen [197]. A letter to the editor was uncovered which confirmed the non-physical nature of a sharp desorption peak at 3.9 nm [209]. The letter suggested that adsorption analysis coupled with other characterization is necessary to confirm pore sizes in this range. Moreover, several works were uncovered that analyzed the validity of using the BJH desorption model (which assumes cylindrical pores) to determined pore volume and pore diameter in materials with positive curvature (such as cylindrical fibers) that have the
opposite of cylindrical pores [210, 211]. Generally, using the BJH model will lead to larger apparent pore diameters than the actual spacing between the fibers [211]. Figure 42 shows the BJH adsorption distributions for the HF washed materials. In the desorption distributions there was a sharp peak in all the alumina grown samples around 4 nm (coming from a single data point), however, this peak was much broader in the adsorption distribution and the peaks shifted from the 4 nm value. Obviously, the adsorption isotherms seem more realistic, however, further characterization may be required, such as TEM fiber diameter distributions and low angle XRD, in order to confirm the nanostructure size distributions.
Figure 41: PSD analysis for (a) alumina subjected to various acetonitrile treatments, (b) samples prepared from acetonitrile pyrolysis at 900°C over various supports then washed with HF acid, and (c) treated and washed samples with variations from the standard treatment of 2 g of 2-wt% Fe/Al₂O₃ for 2 hours.
Figure 42: PSD from the BJH adsorption isotherm for CN$_x$ from alumina supported samples washed with HF acid.

4.2.5 Bulk Physical Characterization

Similar to the VC supported samples, the nature of the carbon with respect to most bulk characterization techniques is not influenced by the support combination used. The XRD patterns of these samples shown in Figure 43 all have the same carbon [002] peak in addition to alumina peaks. The carbon peak, which matches the d-spacing found for nitrogen-containing graphite, does not correlate to activity or weight gain. There is no carbon diffraction apparent in the alumina sample treated for 2 hours, although it does become apparent after a longer treatment time. The alumina peaks present in the
unwashed samples match patterns in the PDF database for cubic Al$_2$O$_3$ (PDF# 74-2206) [212] and also partially nitrided alumina (PDF# 18-51) [213].

XRD patterns of the carbon materials after the HF acid wash (shown for the CN$_x$ from 2% Fe/Al$_2$O$_3$ sample and the 2% Ni/Al$_2$O$_3$ sample in Figure 44) were identical to the non-treated samples except for the absence of the alumina peaks; however, XPS of post-TPO samples revealed that some alumina (and the respective metal) remains in the sample even after the HF treatment. This can seemingly be explained if carbon encases alumina and metal particles, thus protecting them from the acid wash. However, based on the weight change during the treatment and the XRD patterns, a majority of the alumina and metal was removed. XPS analysis showed that fluorine could be removed from the sample surface as long as the post acid treatment filtration was thorough, while its presence does not effect activity.

In identical results to the VC supported samples, Raman spectroscopy concurred that the alumina-grown carbon is highly disordered (see Figure 45). No other information can be obtained from the spectra since they are essentially identical.

TPO results were also similar to the carbon supported counterparts, although less intense (see Figure 46). This was expected since an equal weight of the alumina based samples contain less combustible carbon than the nearly entirely combustible Vulcan Carbon samples. For the metal containing samples the release of nitrogen oxide mimicked the carbon oxides; however, for the non-metal sample, nitrogen oxide peaked after the carbon oxides, similarly to acetonitrile char shown previously in Figure 18. For all these samples, at least some of the respective metal and alumina particles remained in the reactor after the oxidation treatment based on post oxidation residue observations and
XPS analysis. After being washed with HF acid the TPO patterns changed slightly, with some of the minor changes in the pattern likely being attributed to the absence of exposed metal particles (see Figure 47). A small low temperature feature was seen in the samples along with the simultaneous release of water. This feature is likely coming from combustion of hydrocarbon species. No fluorine containing species could be detected by the mass spectrometer during the oxidation. The carbon oxide production peaked at a higher temperature for the samples, however, this may be from the fact that there is a higher concentration of carbon in these samples compared to the mostly alumina samples. There is also a difference in the shape of the peaks after HF washing. The Ni loaded sample formed one peak, while the Fe loaded sample now has three peaks. It is possible that the Fe-based sample has several types of carbon, as TEM imaging will investigate. However, the presence of some metal after the treatments makes it difficult to draw concrete conclusions. The release of NO mirrored the carbon oxides in the metal loaded samples, but the non-metal sample released most NO after the carbon oxides peaked, the same trend seen in the samples that were not treated with HF acid.
Figure 43: XRD patterns of alumina supported samples.
Figure 44: XRD patterns of CN₅ prepared from metal/Al₂O₃ treated for 2 hours at 900°C with acetonitrile and washed with HF acid.

Figure 45: Raman spectra of CN₅ grown from alumina-supported samples.
Figure 46: TPO profiles of nitrogen-containing carbon formed on alumina supports.

Figure 47: TPO profiles of nitrogen-containing carbon formed on alumina supports and washed with HF acid.
4.2.6 Characterization of the Fe phase with Mössbauer Spectroscopy

At this point characterization of the Fe phase of the samples has not been possible using the techniques discussed thus far. The Fe particles are too small and sparse for analysis with XRD, and XPS cannot be used to detect such a small amount of Fe, especially when the particles are covered with carbon. TEM could provide insights into the Fe phases, but would be an expensive and time consuming technique to get a wide distribution of Fe particles. However, Mössbauer spectroscopy is a powerful technique for analyzing Fe, even if the Fe composition is low, since $^{57}$Fe enriched samples can be prepared to allow characterization of low Fe compositions. For this study, precursor materials were partially enriched with $^{57}$Fe to improve the response, and this variable did not effect sample properties.

Mössbauer spectroscopy, like any spectroscopy, measures absorption of electromagnetic radiation in a sample. In the case of Mössbauer spectroscopy, the radiation is gamma rays created from the decomposition of a radioactive source, typically $^{57}$Co. The energy of the source is varied by vibration via the Doppler effect. Therefore, rather than reporting the energy of the radiation on the x-axis (as is usually done for other spectroscopy techniques), the velocity of the source is given on the x-axis. Various coordination, oxidation states, and magnetic field strengths (affected by grain size in iron) have an effect on the absorption spectra of samples. A discussion of the theory behind the different absorption characteristics can be found elsewhere [214].

A typical Mössbauer spectra for the materials discussed here is shown in Figure 48. The spectra had to be fit to 4 species. Table 11 shows the typical ranges for some
common species in similar materials (based on the knowledge of an experienced collaborator, Dr. Jean-Marc Millet of the Institut de Recherches sur la Catalyse, Lyon, France), coincidentally the 4 deconvoluted species fit well within the known ranges for $\gamma$-Fe, $\theta$-Fe$_3$C, Fe$^{3+}$, and Fe$^{2+}$. Table 12 reports the parameters for all the fits that are presented. Gamma Fe is a high temperature phase of metallic Fe, that is apparently stabilized, perhaps, because it is covered by carbon. Baker et al. observed $\gamma$-Fe using Mössbauer in samples where fibers grew from graphite supported Fe [215]. The determined mechanism for fiber growth in these materials began with Fe spreading on the support surface, followed by adsorption of carbon, and then elemental carbon growth from the Fe, while the Fe remained on the surface. $\theta$-Fe$_3$C is another species that should not be stable at room temperature while open to the atmosphere, so this species is likely encased in carbon. This species has been observed by Audier [216] and Millet [217] in materials where carbon fibers grew from Fe particles. The mechanism in this case involved the adsorption of carbon onto the metal, diffusion of carbon through the particle, and deposition of carbon out the other end, resulting in the metal being lifted off the support surface during fiber growth [218]. The partially oxidized Fe species may be from the previous species which were not completely encased in carbon, and therefore reacted with oxygen in the atmosphere. It is possible the oxidation proceeds through Fe$^{2+}$, explaining the presence of this species. However, since a carbide species is present, one may also expect a nitride species to be present, since acetonitrile was used to carry out the treatment, and both nitrogen and carbon were present in the fibers. This could be an alternative explanation for the Fe$^{2+}$ species, although a literature search of Fe nitride species could not uncover a species that has a similar Mössbauer spectra.
The Mössbauer spectra contained the same 4 species regardless of treatment time, although the relative intensities of the species changed. Figure 49 clearly shows the change in the relative intensities of the sextet yielding carbide species for treatments of 20 minutes, 2 hours, and 12 hours. The deconvolution results of the spectra in Figure 49 are shown in terms of relative compositions in Figure 50. From this figure it can be seen that the carbide contribution grows with treatment time, while the gamma Fe phase decreases. The oxidized Fe phases as a whole remain relatively constant, although the Fe$^{3+}$ decreases with time. There are two possible explanations for this. First, if Fe$^{2+}$ is an oxide, then apparently the amount of exposed Fe remains constant with treatment time, but it gets harder to fully oxidize the Fe after longer treatment times. This could be caused by larger particle sizes after longer treatments, or more carbon coverage. It should be noted that each sample was exposed to atmospheric conditions several weeks before being analyzed. A second theory is that the Fe$^{2+}$ is a nitride phase, forming in a similar manner to the carbide phase, and thus increasing for the same reason the carbide phase increases. It should be pointed out that we have yet to find a nitride phase reported in the literature that has a similar isonomer shift and quadrupole splitting as the observed Fe$^{2+}$ phase. However, there are a large number of possible nitrides with a wide range of different Mössbauer spectra [219, 220].

Interestingly, when the Fe was supported by carbon rather than alumina, the spectra contained the same species, but had significantly different contributions from these species. A comparisons of the spectra are shown in Figure 51. When Fe is supported by Vulcan Carbon, it appears that Fe carbide is less likely to form, and $\gamma$-Fe is
preferred. The Fe$^{2+}$ is only slightly larger in the sample with more carbide, so little can be said of its nature based on these results.

The Mössbauer spectra also changed after the alumina supported sample was washed with HF acid. The spectra after HF washing is shown in Figure 52. Again, the same species could be fit to the deconvolution, however, the ratio of the species changed. Specifically, the oxidized phases, and the carbide phases decreased after the wash. Apparently, the carbide phase is not protected as well as the $\gamma$-Fe phase. Again, nothing can be said of the origin of the Fe$^{2+}$ phase based on the results. It should be noted that when these species contribute such a small amount to the spectra that deconvolution becomes difficult, especially with the noise present in the signal. The relative compositions for the samples are shown in pie graph form in Figure 53 for ease of comparison. It should also be noted that the ORR activities of the $^{57}$Fe enriched samples were the same as the un-enriched samples prepared by the same treatments.
Figure 48: Deconvolution of Mössbauer spectra for 2-wt% Fe/Al₂O₃ treated for 2 hours at 900°C with acetonitrile.

Table 11: Parameter ranges for Mössbauer spectra of common Fe species.
<table>
<thead>
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<th>Sample</th>
<th>Species</th>
<th>% of Fe</th>
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<th>$\Delta$ (mm/s)</th>
<th>H (kO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe / Al$_2$O$_3$ - 2 hours</td>
<td>$\theta$ Fe$_3$C</td>
<td>46%</td>
<td>0.204</td>
<td>0.016</td>
<td>203.9</td>
</tr>
<tr>
<td></td>
<td>$\gamma$ Fe</td>
<td>30%</td>
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<tr>
<td></td>
<td>Fe$^{2+}$</td>
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<td></td>
<td>Fe$^{3+}$</td>
<td>10%</td>
<td>0.702</td>
<td>0.574</td>
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<tr>
<td>Fe / Al$_2$O$_3$ - 20 min</td>
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<td>40%</td>
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**Table 12:** Values for deconvoluted Mössbauer spectra.
**Figure 49:** Changes in the Mössbauer spectra with treatment time for 2-wt% Fe/Al₂O₃.

**Figure 50:** Fe phase composition plotted versus treatment time for 2-wt% Fe/Al₂O₃ treated at 900°C with acetonitrile, as determined by Mössbauer spectroscopy.
Figure 51: Comparison of Mössbauer spectra for VC and alumina-supported Fe samples treated 2 hours at 900°C with acetonitrile.

Figure 52: Comparison of Mössbauer spectra for HF washed and unwashed alumina-supported Fe samples treated 2 hours at 900°C with acetonitrile.
Figure 53: Comparison of Fe phase compositions for (a) 2-wt% Fe/Al₂O₃ – 2 hours, (b) 2-wt% Fe/Al₂O₃ – 2 hours, HF washed, and (c) 2-wt% Fe/VC – 2 hours.
4.2.7 Surface Characterization

To characterize the surface of these carbon materials derived from alumina supports, XPS proved to be an especially useful tool. In the samples that were not washed with HF, a small amount of alumina (around 10%) was exposed at the surface, but any exposed metal could not be detected. The pure alumina differed in the fact that it had more alumina exposed (20%), and the N 1s peaks contained an additional large feature at a low binding energy around 397 eV, as Figure 54 shows. This peak may be derived from aluminum nitride or the interaction of nitrogen in the carbon with alumina. After 12 hours of treatment this extra nitrogen feature diminished leaving a normal N 1s spectra (not shown), in concurrence with the disappearance of any exposed alumina. The Al 2p region for the treated pure Al₂O₃ sample also had 2 peaks (shown in Figure 55), which would be consistent with a mixture of aluminum oxide and nitride.

When the HF washed samples are examined it becomes possible to compare the entire series of nitrogen-containing carbon materials that were prepared. Figure 56 shows the three samples that were treated with HF acid. Of these samples the one derived from 2% Fe on alumina performed the best, with a reduction current peak at 688 mV vs. NHE. This sample also had the most pyridinic-N, with 0.65 pyridinic-N for every quarternary-N. The next most active sample (grown from pure alumina) had a pyridinic to quarternary ratio of 0.58, while the least active sample of the three (2% Ni/Al₂O₃) had a ratio of 0.52. XPS analysis showed that the samples sometimes contained a small amount of fluorine on the surface (< 1%), but no detectable metal or alumina.
Figure 54: XPS spectra of the N 1s region for pure alumina treated for 2 hours at 900°C with acetonitrile.

Figure 55: XPS spectra of the Al 2p region for pure alumina treated for 2 hours at 900°C with acetonitrile.
Figure 56: XPS analysis of the N 1s region for CN$_x$ samples prepared using (a) pure Al$_2$O$_3$, (b) 2-wt% Fe/Al$_2$O$_3$, and (c) 2-wt% Ni/Al$_2$O$_3$, treated 2 hours at 900°C with acetonitrile, and washed with HF acid.
<table>
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<td></td>
<td>B.E. (eV)</td>
<td>%</td>
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<td>2 hrs, 900°C</td>
<td>398.6</td>
<td>1.9%</td>
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<tr>
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<td>1.4%</td>
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<td>2 hrs, 900°C</td>
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<td>2.0%</td>
</tr>
<tr>
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<td>10% Fe / Al$_2$O$_3$</td>
<td>2 hrs, 900°C</td>
<td>398.6</td>
<td>1.4%</td>
</tr>
</tbody>
</table>

**Table 13:** XPS analysis of the N 1s region for washed CNx prepared from various alumina-based supports.

4.2.8 TEM Imaging

At this point, it should be noted again that pyridinic-N is not being labeled as the active site for the ORR. It seems reasonable based on the data presented thus far and the work of others to say that the active site for the ORR is on the edge plane of the nitrogen-containing graphite. Therefore, the more active samples may contain more pyridinic nitrogen only because these samples have a higher proportion of edge planes exposed, not necessarily because pyridinic-N itself is the source of activity. High resolution TEM is a useful technique for directly observing the orientation of graphite planes within the nanostructures.

TEM images were obtained for some selected samples to see if there was a correlation between the trends seen in XPS and the nano-structure of the carbon. Some major structural differences were also observed in the alumina-supported samples, despite the similar bulk carbon characterization results. Figure 57 shows structures
present in carbon grown from 2% Fe/Al₂O₃ after HF acid wash. Most of the carbon formed was in the shape of rough fibers shown in Figure 57a. There were some cases where carbon was covering alumina particles, explaining the fact that some alumina remained in the sample even after the HF treatment (not shown). A closer look at the fibers show there are short periodic discontinuous tubes, and a sort of “stacked cups” structure shown in Figure 57b. The stacked cups structure is somewhat of a mixture between a stacked platelet and low angled herring-bone structure. These “compartmentalized” stacked cup structures have been observed by Trasobares et al. in their study on the growth of nitrogen-containing carbon fibers [141]. This works also noted that fibers grown using Fe as a catalyst preferentially incorporated nitrogen in the form of pyridine in the graphite layers [141].

The carbon grown from alumina supported Ni did not contain as high of a ratio of pyridinic-N as the Fe samples according to XPS. Although this correlates to XPS results, this is somewhat surprising since Ni is often used a catalyst for the growth of carbon fibers with herringbone structures [160, 175, 195]. However, TEM images confirmed that such structures were not present in the samples grown from Ni using acetonitrile. Figure 58a shows that a large amount of long fibers formed from the Ni particles with a similar diameter to the ones formed from the Fe particles; however, Figure 58b shows that the graphite planes in these structures mostly run parallel to the central axis of the tubes. While this was not generally consistent with carbon fibers grown with Ni particles, this type of fiber has been observed by researcher who used a nitrogen source to the reactant feed [141]. Moreover, it was noted in the work of Trasobares et al. that nitrogen is preferentially incorporated into carbon within the graphite layer, not in the
form of pyridine, when Ni is used as a catalyst [141]. Similar to the Fe samples, there were alumina particles covered by carbon present in this sample even after washing with HF.

The pure alumina sample led to the formation of blotches of carbon that contained several types of nanostructures (see Figure 59 and Figure 60). Surprisingly, stacked cup structures were found in the pure alumina sample, as seen in Figure 59b. While the Fe-doped alumina formed more of these structures, apparently they can form on pure alumina as well. Additionally, structures with a low amount of edge planes exposure were found. Figure 60a shows structures resembling nano onions, which consist of a series of concentric graphite spheres [221]. The graphitic ribbons that often covered the alumina particles were also seen in the pure alumina sample, and an image of these ribbons is shown in Figure 60b. In a less magnified image of the CNx derived from pure alumina, the various types of carbon are displayed (see Figure 61). This clearly shows the presence of fibers in addition to a large portion of non-fibrous carbon.

For the fibers prepared from Fe and Ni particles distributions of the fiber diameters were obtained by TEM. This type of distribution was not obtained for the pure alumina-supported sample because the majority of the samples was composed of non-fibrous carbon. The distributions for the metal-containing samples are shown in Figure 62. The average diameter of the Fe-grown fibers was 16 nm, versus 35 nm for the Ni-grown fibers. The higher surface area of the Fe-grown CNx agrees with this result. Further, the size distribution for the Fe sample is much more narrow. Distributions of the types of fibers present (stacked cups versus MWNT’s) will be discussed in subsection ‘4.3.6 TEM Imaging’.
The unwashed alumina-based samples were not significantly different from the washed samples, other than the presence of exposed alumina in the unwashed samples. In the unwashed Fe-doped alumina sample it is interesting to note that the alumina particles seemed to have a high affinity for the carbon fibers, as there was often alumina particles stuck to the side of fibers (images not shown). This could explain how this sample quickly lost its surface area during the heat treatment. The fibers may be acting as a glue, causing agglomeration of alumina particles to form larger particles with a lower surface area. In the Vulcan Carbon based samples there were no sign of agglomeration of carbon particles, possibly explaining how these materials kept a higher surface area and weight gain even after extremely long treatments.

Both the washed and unwashed samples contained encased metal particles that were apparently not affected by the acid wash. It is not believed that these metal particles contribute to ORR activity, as discussed in the literature review, because activity is not proportional to metal loading beyond a couple percent. Images of some of these particles formed from various supports are shown in Figure 63 and Figure 64. In some cases these particles were inside the tip of the fiber, and had a larger diameter than the fiber itself. In other cases particles were observed periodically within a fiber. Some MWNTs, had metallic cores. In other cases, metal particles were found attached to the supports, but encased with several layers of graphite. Based of the unusual shapes and locations of the metal particles associated with fibers, it seems likely that the metal particles are in the form of a liquid during the fiber formation. However, based on the images, to this point not much can be said of the mechanism for fiber formation.
In Table 9 we reported that when an excess of Fe was loaded on the alumina the final surface area was lower after the acetonitrile pyrolysis and HF wash. TEM imaging confirmed that the sample still contained stacked cup structures (see Figure 65a), however, the fiber diameters were larger. Additionally, many metal particles apparently did not catalyze the formation of nanofibers, but rather became encased in a layer of carbon, as Figure 65b displays. These observations provide further evidence that Fe particles are acting as catalysts for the formation of active structures, but are not themselves active catalysts for the ORR. Other researchers have also reported that the addition of an excess amount of Fe to samples prior to pyrolysis in a nitrogen and carbon atmosphere adversely affects activity [111]. Based on these images and the PSD results reported earlier, it is apparent that using too much Fe reduces its effectiveness to catalyze the formation of small fibers. If metallic iron or iron carbide were itself an active catalyst for the ORR, then one would assume that using 5 to 20 times as much Fe in the precursor would produce a more active catalyst, which is not the case based on results reported in Table 9 for samples with various Fe loadings.
Figure 57: TEM images of HF washed 2-wt% Fe/Al₂O₃ grown fibers.
Figure 58: TEM images of HF washed 2-wt% Ni/Al$_2$O$_3$ grown fibers.
Figure 59: TEM images of HF washed Al$_2$O$_3$ grown fibers.
Figure 60: TEM images of HF washed Al$_2$O$_3$ grown CN$_x$. 
**Figure 61:** Lower magnification TEM image of HF washed Al$_2$O$_3$ grown CN$_x$.

**Figure 62:** Diameter distributions observed from TEM analysis for CN$_x$ fibers grown from metal doped alumina.
Figure 63: TEM images of encased iron particles formed during heat treatment at 900°C in acetonitrile, using various supports for iron.
Figure 64: TEM images of encased iron particles formed during heat treatment at 900°C in acetonitrile.
Figure 65: TEM image of acetonitrile-treated and washed 10% Fe/Al$_2$O$_3$.
4.2.9 Hydrophobicity Testing

In the previous section we reported the unique nano-structures that formed when either Al$_2$O$_3$, 2-wt% Fe/Al$_2$O$_3$, or 2-wt% Ni/Al$_2$O$_3$ is used as a support for acetonitrile decomposition. Although the bulk properties of the carbon are the same, these different structures could have significantly different surface properties originating from differences in edge plane exposure. One particular property that is strongly effected by differences in the carbon plane exposed is hydrophobicity.

Water dispersibility testing supports the TEM observations that Fe and pure Al$_2$O$_3$ catalyze the formation of structures with greater edge plane exposure. Carbon structures with mostly basal plane exposure, such as MWNT’s, are known to be hydrophobic. In initial experiments we observed that commercial MWNT’s could not be dispersed in water, while Vulcan Carbon and stacked platelets, which both have significant edge plane exposure, could easily be dispersed (see samples A-C in Figure 66). Likewise, the CN$_x$ fibers grown from Ni/Al$_2$O$_3$ did not disperse in water to the same extent as the CN$_x$ prepared from Al$_2$O$_3$ or Fe/Al$_2$O$_3$ (see samples D-F in Figure 66), although they were not as hydrophobic as the commercial MWNT’s as seen when sample (B) and (E) are compared.
Figure 66: Images comparing dispersibility in water for standard samples of (A) Vulcan Carbon XC-72, (B) commercial MWNT’s, and (C) stacked platelet carbon, and CN$_x$ samples prepared from acetonitrile pyrolysis over (D) pure Al$_2$O$_3$, (E) 2% Ni/Al$_2$O$_3$, and (F) 2% Fe/Al$_2$O$_3$.

4.2.10 Electrochemical Testing Results

There are numerous properties that a material must posses to function as a fuel cell electrode (see the introduction for a complete list). One essential property of electrode materials in a fuel cell is good electrical conductivity. Table 9 and Table 10
previously reported the conductivities of the unwashed and washed alumina-grown CN\textsubscript{x} materials respectively. Since alumina is an insulator, it is not surprising these materials do not have as high of conductivity as carbon black. However, enough carbon is deposited on the supports that the conductivities are within a couple orders of magnitude of commercial PEMFC electrode materials. As has been shown, washing the samples with HF acid can remove most of the alumina from the samples; however, only small improvements in conductivity resulted. A possible reason the conductivities are still low in the HF acid washed samples is that the small fiber diameters lead to more particle to particle contact resistances. The contacts between particles within a powder carbon material are well-known to be a major source of resistance [136]. If methods can be developed to improve the conductivities of these materials they would likely be good candidates to replace platinum in PEMFC cathodes, especially considering the most active material (HF washed CN\textsubscript{x} fibers from Fe/Al\textsubscript{2}O\textsubscript{3}) had an ORR peak within 80 mV of the commercial platinum catalyst. The activities of all the alumina-grown samples were reported previously in Table 10.

It is possible that the poor conductivities of the samples effect the activity measurements in the half-cell set-up. Figure 67 and Figure 68 compare the oxygen reduction currents for the washed and unwashed alumina grown samples. The more conductive Ni samples have a larger peak in each case, and all the peaks become larger and sharper for similar samples, after they are washed with HF acid. An explanation for this phenomenon is that in less conductive materials the only part of the sample that is active for the reaction is particles which are directly touching the current collector. Therefore, the oxygen concentration profile is different from the one shown in Figure 22,
and more likely resembles the one shown in Figure 69. In this case, the large peak in the current never comes about, because the active surface area of the sample always remains close to the surface area of the current collector, rather than including the 3-dimensional area within the pores that becomes active in conductive materials.

It is not currently believed that the conductivity of the material greatly effects the voltage at which the oxygen reduction current peaks. Washing the samples with HF acid improved the conductivity of the samples by roughly an order of magnitude, but only improved activity by 60-73 mV. This improvement in activity may just be from more active sites being freed up when the approximate 10% alumina on the surface was removed. The improved conductivity should only make the reduction peak larger and sharper, but not effect its location, at least not significantly considering the approximate ± 25 mV error in the measurement.

There is another possible effect of having less conductive samples related to activity testing. Figure 70 shows the reduction currents for the 10 mV/s CV’s taken for the pure alumina supported nitrogen-containing carbon sample that was washed with HF. The lowest current was obtained from the sweep in the argon-sparged electrolyte, in which case the double-layer capacitance of the sample is the only cause for any current. The next current up from the argon current shows that the addition oxygen does lead to more current, proof the oxygen is being reduced. This is especially significant since this sample is the first to contain such a small amount of metal (<1 ppm). As the rotation rate of the electrode is increased, the mass transfer of oxygen to the sample increases, thus increasing the mass transfer limited current. When the current becomes completely mass transfer limited it should level out to be parallel with the baseline taken in argon, and not
dependant on voltage. Other researchers have also observed a slight upward slope with voltages perhaps caused by an uneven distribution of active sites in the catalyst [79]. It is possible this upward slope is caused by poor conductivity. This slope is generally more apparent in less conductive samples. Other researchers have investigated the origins of this slope, and attributed it to “a distribution of active sites within the catalyst” [222]. Having a less conductive material could create just such a distribution, because there will be a voltage distribution within the catalyst layer. The reaction kinetics take off as the voltage drops, but some parts of the catalyst layer in a less conductive catalyst will lag behind in terms of electrical charge. In highly conductive materials the voltage will be very evenly distributed since the material can easily transfer electrons around.

More significant information can be obtained from the RDE experiments. Koutecky-Levich plots can be constructed from the data to determine the kinetic current and the number of electrons being transferred per mole of oxygen reacting. First, the reaction order with respect to O₂ must be verified using the following relationship:

\[
\log(I) = \log(I_{\text{kin}}) + p \log\left(1 - \frac{I}{I_l}\right)
\]

where \(I\) is the reduction current, \(I_{\text{kin}}\) is the kinetically controlled current, \(p\) is the reaction order, and \(I_l\) is the limiting current taken at \(V = 0\) when the current levels out. A plot of \(\log(I)\) versus \(\log(1 - I/I_l)\) made using data from two different voltages for the HF washed alumina based sample had a slope of approximately unity (not shown). The other samples also had slopes close to one, although these plots could only be constructed if the sample had high activity for oxygen reduction (peak above 300 mV), otherwise the mass transfer limiting current is not reached by 0 V at increasing rotation rates. Gupta et al.
confirmed that the reaction order was one with respect to O₂ over pyrolyzed Fe-
macrocycle samples using the same technique [79].

Since the reaction order is one, the Koutecky-Levich equation can be applied as a
model for the reduction current:

\[
\frac{1}{I} = \frac{1}{I_{\text{kin}}} + \frac{1}{I_{\text{c}}} \quad \text{Koutecky-Levich Equation [4]}
\]

The mass transfer controlled current is equal to:

\[
I_{\text{c}} = 0.62 \, n \, F \, A \, D_0^{2/3} \, \nu^{-1/6} \, C_0^* \, \omega^{1/2} \quad \text{Levich Equation [4]}
\]

where \( n \) is the number of electrons transferred per reaction, \( F \) is Faraday’s constant, \( A \) is
the electrode surface area (discussed in the following paragraph), \( D_0 \) is the diffusion
coefficient of oxygen though the electrolyte, \( \nu \) is the kinematic viscosity of the
electrolyte, \( C_0^* \) is the bulk concentration of oxygen in the electrolyte, and \( \omega \) is the
rotation rate of the RDE. All these parameters are constant over the voltage range with
the possible exception of \( n \), so both \( n \) and \( I_{\text{kin}} \) can be determined at a particular voltage by
plotting \( I^{-1} \) versus \( \omega^{-1/2} \). Using the data presented in Figure 70, Koutecky-Levich plots
were made for voltages from 0.6 to 0.0 vs. NHE, as shown in Figure 71. The intercept is
slightly greater than zero at higher voltages indicating some kinetic limitations above 0.0
V. However, the lines are parallel indicating that if the surface area and other parameters
are constant then the number of electrons per mole of oxygen reacting does not change
either between these voltages.

Unfortunately, the exact surface area is not known for the electrode due to
imperfections (such as gaps and surface roughness) in the catalyst layer caused by the
imperfect application process. However, the parameter \( n \) can still be estimated if the
slopes are compared to values obtained for platinum on the same electrode, since the
commercial platinum electrodes are known to have nearly full conversion of O₂ to water. Gouérec et al. estimated the active surface area of their rotating disk electrodes and the corresponding deposited powder catalysts using a reaction with a known value for n [68]. A variance of +/- 10% was measured, so there will be some error in this technique for determining n. Moreover, a value of exactly 4 for n is not always obtained with Pt electrodes, although it is usually close [223]. Fortunately, differences in the internal catalyst surface area do not affect the active surface area as long as the current is limited by the diffusion of oxygen through the solution to the catalyst, which is the case when the kinetic current is high. Therefore, this method can provide an estimate of the number of electrons being transferred in the reaction. Considering the average Koutecky-Levich slope for 20% Pt/VC was found to be 7900 A⁻¹ s⁻¹/₂, the pure alumina sample would have an approximate n of 3.4, correlating to 70% of the O₂ reacting to water, assuming n = 4 for Pt. When the calculation was carried out for the other non-noble samples of sufficient activity values of n varied between 3.3 and 4.0. Although it appears platinum is still a better catalyst for complete reduction than the nitrogen-containing carbon samples, it is encouraging to see good selectivity to water (closer to 4 than 2) for the non-noble metal samples. All things considered this method only provides a rough estimation of n. Rotating-ring disk testing is a technique that is better suited for studying the extent of the conversion of O₂ to H₂O₂, and will be employed in the future to study these catalysts. However, these estimates of n show that these catalysts can facilitate complete reduction of O₂, even in the absence of metal.

While the features of the ORR current for the alumina based sample shown in Figure 70 are representative of the other less conductive samples (other than the peak
position), it is important to note the differences seen in the ORR currents of the more conductive samples. Figure 72 shows the ORR current at different rotation rates for the 2% Fe/VC sample treated for 2 hours in acetonitrile. The current in the argon-sparged solution caused by double-layer capacitance is much lower for this sample because this sample has lower surface area than the alumina based HF-washed sample. Approximately the same weight was used for each sample, on the order of 300 µg, but the 2% Fe/VC sample has one-sixth the surface area. Apparently though, the area of the ORR peak is much larger for the more conductive sample. This is because electrons can conduct throughout the powder sample more quickly and react with oxygen within the pores of the catalyst, giving the sample a much larger active surface area. In the less conductive sample oxygen can apparently only react on sites very close to the current collector, since electrons cannot travel far through the sample because of resistance. As the reaction kinetics increase the active surface area decreases since the current will be limited by the diffusion of oxygen through the solution. When oxygen reaches the sample it will react quickly and the internal surface area cannot come into play. The corresponding Koutecky-Levich plot for the 2% Fe/VC sample confirms this (see Figure 73). At 0.4 V the line has an intercept of 1070 A⁻¹, indicating kinetic limitations are present, and consequently the slope of this line is very small. The active surface area is the only parameter that can change such a large extent to cause this low of a slope, as explained by the reaction of oxygen within the pores. This low slope was not seen in the other sample because it is not conductive enough to allow oxygen to react significantly within its pores. At lower voltages the slope returns to a reasonable value as the kinetic limitations become insignificant, and oxygen cannot reach the inside of the pores. The
slope of the Koutecky-Levich plots for this sample corresponds to approximately complete conversion of $O_2$ to water.

Although the voltage of the oxygen reduction current peak may be an effective way to compare the activities of samples, it does not necessarily correlate to how a catalyst will perform in an actual fuel cell. In addition to being catalytically active, cathode materials must be electrically conductive, proton conductive, and possess acceptable mass transfer properties to allow $O_2$ to diffuse into the electrode and water to diffuse out. Therefore, fuel sized fuel cells were prepared using various catalysts in the cathode. It was observed that the electrical conductivity of the alumina deposited samples was too low for use in an actual fuel cell, as no significant current could be drawn from a fuel cell made with these samples. Future work will focus on improving the conductivity of these materials and optimizing the electrode preparation procedure for these new materials. An operational fuel cell was prepared using the catalyst made from 2-wt% Fe/VC treated for 2 hours at 900°C with acetonitrile. The maximum power that could be obtained from the cell was about one fifth the power that was obtained from a commercial Membrane Electrode Assembly (MEA) (using 20-wt% Pt/VC electrodes) in the same test stand under identical conditions. However, the MEA preparation conditions have not been optimized for the non-noble metal catalysts. Additionally, if the more active high surface area samples can be made more conductive, such a sample would not have much of a power loss compared to the commercial Pt MEA. Still, there are questions as to whether or not non-noble metal catalysts can remain stable in the fuel cell environment [104], and whether or not such an active, high surface area and conductive sample can be prepared.
**Figure 67:** Oxygen reduction currents for unwashed samples.

**Figure 68:** Oxygen reduction currents for HF washed samples.
Figure 69: Depiction of the changes in the O₂ electrolyte concentration with time during a CV over an active but less conductive ORR catalyst layer.
Figure 70: Oxygen reduction currents for HF washed pure alumina treated for 2 hours at 900°C with acetonitrile.

Figure 71: Corresponding Koutecky-Levich plot for HF washed pure alumina treated for 2 hours at 900°C with acetonitrile.
**Figure 72:** Oxygen reduction currents for 2-wt% Fe/VC treated for 2 hours at 900°C with acetonitrile.

**Figure 73:** Corresponding Koutecky-Levich plot for 2-wt% Fe/VC treated for 2 hours at 900°C with acetonitrile.
4.2.11 RRDE Selectivity Testing

Although the voltage of the oxygen reduction current peak discussed previously may be an effective way to compare the activities of samples, it does not necessarily correlate to how a catalyst will perform in an actual fuel cell. In addition to being catalytically active, cathode materials must be electrically conductive, proton conductive, and possess sufficient mass transfer properties to allow O₂ to diffuse into the electrode and water to diffuse out. To prevent corrosion of cell components and achieve better efficiency, ORR catalysts should also be highly selective to the formation of water, not hydrogen peroxide.

Rotating Ring-Disk Electrode (RDE) experiments can be used to measure selectivity of catalysts for the complete ORR, in addition to indicating relative ORR activity of samples [104], providing complimentary information to the results presented in the previous section. The selectivity of the reaction is monitored with the platinum ring of the RRDE. When held at a potential of 1.2 V vs. NHE, the ring cannot reduce O₂, but can reduce any H₂O₂ formed from the disk. Two possible reactions occurring on the disk during a CV are shown here:

\[
\begin{align*}
O_2 + 4 e^- + 4 H^+ &\rightarrow 2 H_2O \quad (1.23 \text{ V vs. NHE at STP}) \\
O_2 + 2 e^- + 2 H^+ &\rightarrow H_2O_2 \quad (1.76 \text{ V vs. NHE at STP})
\end{align*}
\]

The collection efficiency of the ring is known to be 20% when the RRDE is operating in a laminar flow regime, therefore, the ring current was only collected at 100 rpm of rotation in order to remain under laminar flow conditions. The results of these RRDE experiments are shown in Figure 74, Figure 75, and Figure 76 for HF washed CNₓ.
prepared with 2% Fe/Al₂O₃, pure Al₂O₃, and 2% Ni/Al₂O₃ respectively. The ring current in these figures is multiplied by 5 to correct for the collection efficiency.

For the more conductive samples, the disk current undergoes a peak during the transition from kinetic limitations to mass transfer limitations. This is because the higher conductivity allows for a three dimensional active catalyst region in the thin catalyst film. Once mass transfer limits the reaction, then the current is proportional to the two dimensional geometric area of the disk. Since the electrodes all have approximately the same geometric area, the currents eventually level out to the same value in the mass transfer limited region. However, the current also depends on the number of electrons being transferred in the reaction, so the currents are not identical. Such trends are discussed in more detail elsewhere [4].

The ring currents follow similar trends to the disk currents, although the relative intensities vary from sample to sample. The number of electrons being transferred per mole O₂ consumed can be determined from the equation:

\[ n = 4 \left( \frac{I_{\text{disk}}}{I_{\text{disk}} + \left( \frac{I_{\text{ring}}}{N} \right)} \right) \]

where \( N = 0.20 \), the efficiency of the ring. For the more active Fe/Al₂O₃ derived CNₓ sample, \( n \) is on average 3.91 after the currents level out, indicating nearly complete conversion to water. For the Ni/Al₂O₃ derived CNₓ sample, \( n \) is only 3.56, indicating significant peroxide formation, while the pure alumina sample has an average \( n \) of 3.70. Thus the correlation between activity and edge plane exposure also seems to hold for selectivity to water versus peroxide. Researchers have previously reported differences in the activity and selectivity of different carbon crystallographic planes for other reactions [137, 138], including the ORR in non-acidic electrolytes [41, 136, 140]. Further, several
modeling studies of oxygen reduction on nitrogen-doped carbon arrived at different conclusions depending on the plane were the researchers had oxygen adsorb. The basal plane of nitrogen-doped carbon was reported to catalyze the reduction of oxygen to hydrogen peroxide [135], while the edge plane has been shown to catalyze complete oxygen reduction to water (better than non-doped carbon) [133, 134].

Figure 74: RRDE reduction currents for CN$_x$ prepared from 2% Fe/Al$_2$O$_3$ treated 2 hours at 900°C with acetonitrile and subsequently washed with HF acid. The ring potential was held at 1.2 V and ring currents have been corrected for the collection efficiency.
Figure 75: RRDE reduction currents for CN$_x$ prepared from pure Al$_2$O$_3$ treated 2 hours at 900°C with acetonitrile and subsequently washed with HF acid. The ring potential was held at 1.2 V and ring currents have been corrected for the collection efficiency.

Figure 76: RRDE reduction currents for CN$_x$ prepared from 2% Ni/Al$_2$O$_3$ treated 2 hours at 900°C with acetonitrile and subsequently washed with HF acid. The ring potential was held at 1.2 V and ring currents have been corrected for the collection efficiency.
4.2.12 Methanol Oxidation Activity

In direct methanol fuel cells, significant voltage is lost due to methanol crossover, where methanol passes through the electrolyte membrane and reacts directly with O\textsubscript{2} in the cathode. However, if the cathode catalyst were not active for methanol oxidation, then methanol crossover would not be an issue. Therefore, based on reports of inactivity for methanol oxidation for heat-treated macrocycles [97], an active CN\textsubscript{x} sample was tested for methanol oxidation activity. Tests on CN\textsubscript{x} from 2% Fe/Al\textsubscript{2}O\textsubscript{3} were run in argon sparged electrolyte, then in the electrolyte mixed with methanol. The CVs were compared to two commercial catalysts. The first is 10% Pt / 10% Ru / VC, which is used as an anode catalyst in direct methanol fuel cells. The second was the standard 20% Pt/VC commercial cathode catalyst.

The results of the experiment are shown in Figure 77. The Pt/Ru catalyst had an oxidation peak that resembled what is typically observed for the ORR, except that the sign of the current in opposite. The Pt catalyst had large peaks both during the reduction and oxidation sweeps. This could be caused by adsorption and subsequent reaction of species, unlike the complete reaction that was seen for Pt/Ru. For the non-metal catalyst no activity for methanol oxidation was observed. The baseline does change from the addition of methanol to the electrolyte, so the backgrounds don’t match perfectly.
Figure 77: Methanol oxidation activity testing for (a) Pt/Ru/VC, (b) Pt/VC, and (c) CNₓ from 2% Fe/Al₂O₃ treated with CH₃CN at 900°C.
Active catalysts for the ORR were prepared by the pyrolysis of acetonitrile over pure alumina, and alumina impregnated with Fe or Ni. Most of the alumina support could be removed from the sample by washing with a strong acid (HF acid), leaving behind the nitrogen-containing carbon, which was characterized extensively. All of the samples had higher activity for the ORR than would be expected for unmodified carbon. The high activity of the pure alumina-derived sample demonstrates that metal is not required for oxygen activation in acidic electrolytes using nitrogen-containing carbon. The role of metal particles, such as Fe, in these samples is likely that of a catalyst for the formation of more active carbon nano-structures during pyrolysis. The most active nanostructures both contain nitrogen and have higher edge plane exposure. Characterization techniques including XPS, TEM, and hydrophobicity measurements all support the claims that the more active catalysts have greater edge plane exposure. While we have demonstrated that nitrogen-containing carbon free of any significant Fe contamination is active for the ORR, we have not unequivocally ruled out the possibility that the presence of Fe enhances activity through a parallel mechanism beyond increasing edge exposure. For example, Fe-based particles or Fe ions adsorbed on edge sites (such as the phenanthroline-type site [87]) could be enhancing activity further in the Fe-containing samples. Interestingly, the more active samples with more edge plane exposure were also more selective for complete reduction of oxygen to water. These results are in line with several recent modeling studies for oxygen reduction on nitrogen-doped carbon [133-135].
4.3 Silica and Magnesia Supported Catalysts

4.3.1 Pyrolysis By-Products

Before reporting information about the solid carbon product that forms during pyrolysis treatments, it is important to note the gaseous products of the pyrolysis treatments. Temperature programmed acetonitrile pyrolysis byproducts were analyzed using an online MS. The samples examined by TPAP included the bare silica and magnesia, and the supported doped with 2% Fe, 2% Co, 10% Co, and 2% Ni. During the temperature ramp, oxygenated gases were released from the surface of all the samples. The results were similar to the ones reported for TPAP over alumina. While it could not be confirmed that reduction of the supports were occurring (as was the case for alumina), it was apparent that metal particles are reduced well below 900°C due to the presence of additional oxygenated species when metal was present.

After the furnace temperature reached 900°C, there was little difference in the products being produced over the range of supports tested. Quantification of the products based on the total ion count for each species revealed that at 900°C, on average over all the samples for each mole of acetonitrile (CH₃CN) sent to the furnace, 0.48 moles of HCN, 0.35 moles of CH₄, 0.10 moles of N₂ and 0.53 moles of H₂ are produced. Based on mole balances, the species not detected by the MS comprise approximately 1.17 moles of C, 0.32 moles of N, and 0.06 moles of H per mole of acetonitrile fed.
4.3.2 Preparation Parameters

A wide range of conditions were used for the pyrolysis of acetonitrile to prepare CN\textsubscript{x} catalysts for the ORR. Table 14 overviews all of the samples prepared, the amount of mass gained during the pyrolysis, the conditions used to wash the carbon product and the mass of product remaining after this wash, and if enough sample was available, the BET surface area. Temperatures as low as 550\degree C are reasonable for nanofiber growth from a carbon source [166]; however, this low of temperature is apparently insufficient for decomposition of acetonitrile. For all the samples treated at 550\degree C, very little weight gain was observed after 4 hours of treatment. At 900\degree C, a better deposition rate was obtained over all the supports tested. The MgO supports had higher deposition rates than SiO\textsubscript{2}. The mass gains were similar to the mass gained using alumina supported particles reported previously in Table 10. The results of acetonitrile deposition in the absence of a support or in the presence of unsupported metal particles were presented previously as well in Table 6.

Based on the amount of mass lost during the washing step, the respective wash techniques were effective at removing a majority of the support. The respective wash techniques easily dissolved untreated supports in trial runs, however, it is possible for metal particles and even the metal oxide support particles to become encased by carbon during the pyrolysis, making it impossible to remove them during the wash. Thus, not all of the support is removed during the wash. In one instance, for 2\% Co/SiO\textsubscript{2}, the carbon product was washed with HF acid to compare the effectiveness of the procedures.
Further characterization will assess the extent of the support removal obtained by the washing techniques.

<table>
<thead>
<tr>
<th>Support</th>
<th>Metal Loading</th>
<th>CH$_2$CN Pyrolysis Conditions</th>
<th>Pyrolysis Mass Gain</th>
<th>Wash Conditions</th>
<th>Post Wash Mass Remaining</th>
<th>BET Surface Area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>none</td>
<td>550°C, 4 hrs</td>
<td>1.7%</td>
<td>KOH, HCl</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
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<td>2% Fe</td>
<td>550°C, 4 hrs</td>
<td>3.0%</td>
<td>KOH, HCl</td>
<td>N.A.</td>
<td>N.A.</td>
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<td>2% Co</td>
<td>550°C, 4 hrs</td>
<td>2.4%</td>
<td>KOH, HCl</td>
<td>1%</td>
<td>N.A.</td>
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<td>KOH, HCl</td>
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<td>288</td>
</tr>
<tr>
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<td>2% Fe</td>
<td>900°C, 2 hrs</td>
<td>18.9%</td>
<td>KOH, HCl</td>
<td>25%</td>
<td>255</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2% Co</td>
<td>900°C, 2 hrs</td>
<td>13.6%</td>
<td>KOH, HCl</td>
<td>19%</td>
<td>465</td>
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<tr>
<td>SiO$_2$</td>
<td>10% Co</td>
<td>900°C, 2 hrs</td>
<td>18.8%</td>
<td>KOH, HCl</td>
<td>22%</td>
<td>214</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2% Ni</td>
<td>900°C, 2 hrs</td>
<td>5.8%</td>
<td>KOH, HCl</td>
<td>9%</td>
<td>N.A.</td>
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<td>MgO</td>
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<td>900°C, 2 hrs</td>
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<td>HCl</td>
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<td>HCl</td>
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<td>128</td>
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<td>HCl</td>
<td>25%</td>
<td>256</td>
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<td>28.7%</td>
<td>HCl</td>
<td>28%</td>
<td>241</td>
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</table>

**Table 14**: Samples prepared from the pyrolysis of acetonitrile over silica and magnesia supports.

4.3.3 N$_2$ Physisorption Analysis

The surface area of the final carbon material obtained (see Table 14) was much higher than the original support in all cases. Using higher surface area MgO (150 m$^2$/g versus 55 m$^2$/g) only resulted in a modest increase in surface area of the carbon produced. In general, the surface areas obtained were not as high as the ones obtained from HF washed acetonitrile char deposited on alumina shown previously in Table 10.
The effect that washing had on the pore structure of the samples is apparent from some representative Pore Size Distribution (PSD) plots in Figure 78. For the SiO$_2$ samples there was little difference between unwashed SiO$_2$, and the treated samples. Washing the samples opened smaller pores and reduced the larger SiO$_2$ pores, although a significant portion of larger pores still remained. A spike in the distribution at 4 nm has been observed in the alumina-derived CN$_x$ samples containing nanofibers. As was discussed previously, this feature is a characteristic of nanostructures, but in reality the distribution may not be so narrow. The other washed SiO$_2$ samples that contained metal had similar distributions, while the treated and washed pure SiO$_2$ sample was similar in the larger pore diameter region, but did not have a pronounced spike at 4 nm in the smaller pore diameter region (data not shown).

The pore distributions for the MgO supported samples behaved somewhat differently than the SiO$_2$ samples. The addition of metal to MgO, and the treatment in an acetonitrile atmosphere at 900°C for 2 hours reduced the pore volume (see Figure 78b). Washing the samples greatly increased the pore volume for both large and small pores, as shown for the carbon derived from 2% Fe/MgO. Again, the characteristic peak at 4 nm was present in all samples, however, it was smallest in the sample that did not contain metal. It should also be noted that the treated and washed Ni/MgO sample had considerably less pore volume in the larger pore diameter region compared to the other samples (data not shown).
Figure 78: PSD analysis of samples throughout their preparation process for (a) Co/SiO₂, and (b) Fe/MgO, treatments were carried out at 900°C.
4.3.4 X-ray Diffraction Analysis

X-ray diffraction patterns demonstrate the effectiveness of washing samples in addition to information about other phases present, and the crystalline properties of the carbon. Figure 79 compares the diffraction pattern of treated, but unwashed Fe/MgO to all of the washed carbon samples derived from MgO-based supports. In the pattern for the unwashed sample it is apparent how crystalline the MgO phase is, as the only peaks present are from cubic MgO. In the pure MgO sample, a small amount of MgO is still apparent even after the wash, but for the metal-containing samples all of the detectable MgO was removed. The only peaks remaining can be attributed to poorly crystalline graphitic, the main peak being C [002], and various phases of the metal (peaks between 42° and 46° 2Θ). The metal phases present will be discussed elsewhere, but for similar materials, carbide, metallic, and oxide phases are typically observed. The only major differences between the samples is in the patterns attributed to the metal phases. Also shown in Figure 79 is the pattern for the carbon derived from 2% Fe/SiO₂. The diffraction pattern is nearly identical to the pattern for the carbon obtained from 2% Fe/MgO. Since the SiO₂ was not crystalline, patterns of the unwashed samples resembled diluted versions of the washed samples, thus this data is not shown.
4.3.5 Bulk Analysis Using Temperature Programmed Oxidation

The nitrogen-containing carbon materials obtained after the washing step were characterized by TPO with \textit{in situ} TGA-DSC and gaseous product analysis with a MS. These experiments served several functions. First, from the gravimetric analysis, the amount of non-combustibles in the samples can be determined, giving an indication of how much of the metal catalyst or inorganic precursor remains entrapped in the sample after the wash. Second, based on the amount of carbon oxides and nitrogen oxides released during the combustion and detected with the MS, an estimate of the amount of
nitrogen in the bulk sample can be made. Third, from the combination of all the signals being followed during the TPO, the nature of the carbon can be characterized based on the oxidation profile.

The signals from a typical analysis are displayed in Figure 80 for the sample prepared from Fe/MgO-(HSA). The DSC signal begins to become positive around 300°C, indicating the onset of oxidation. Significant oxidation does not occur until above 400°C, at which point the TG signal drops. The derivative of the TG signal (derivative is not shown) exactly mirrors the DSC signal, as expected. There are two separate oxidation peaks for this sample. All of the samples containing metal-containing had multiple oxidation peaks, while the samples prepared on non-metal supports contained only one oxidation peak similar to pure acetonitrile char or acetonitrile char deposited on alumina shown previously. It is not clear if the multiple peaks originate from multiple types of carbon, or if they are caused by metal particles in contact with carbon thus catalyzing combustion of that carbon. The sample shown in Figure 80 lost 92% of its mass, as is apparent from the TG signal.

The products of the combustion were monitored with a MS. Only CO₂ formed in the excess oxygen environment, although small amounts of CO would be difficult to differentiate from the fragment at 28 AMU for CO₂, which has an intensity of 12% of the 44 AMU signal. As Figure 80 shows the 44 AMU signal matches the DSC signal. Additionally, NO was detected as a product of the combustion with the main fragment being 30 AMU. The NO production did not follow the CO₂ production in every sample, for instance, in the figure it is apparent that more NO is produced during the first oxidation peak. In the samples that do not contain metal particles, NO was consistently
released more heavily at the end of the combustion. The samples containing metal typically released more NO early in the combustion, similar to Fe/MgO-(HSA), with the exception of the carbon deposited on Ni/SiO₂. Previously we reported that for carbon formed on alumina supports from acetonitrile pyrolysis the NO and CO₂ production followed one another. However, these TPO experiments were carried out under different conditions, and there were not as well-defined multiple combustion peaks in the TPO of the alumina samples.

The TPO profile for CNₓ prepared with Fe/MgO (data not shown) was similar to the profile for CNₓ prepared from Fe/MgO-HSA. The profile for CNₓ deposited on pure MgO (shown in Figure 81a) or pure SiO₂ (data not shown) is similar to single peak profile of acetonitrile char shown previously. Two separate peaks were apparent in the Ni/MgO derived fibers, although the lower temperature oxidation peak was much smaller, as Figure 81b shows. It is possible that the Ni sample contains a smaller percentage of fibers that combust at low temperature. Interestingly, the TPO profile for CNₓ from Co/MgO was similar to CNₓ from Fe/MgO, considering that it had two peaks of similar size (see Figure 82a); however, the shapes of the peaks were slightly different from the Fe sample. Again, it is dangerous to read too much into these differences in profiles, since the metal particles still entrapped in the samples could catalyze combustion. When the Co/SiO₂ sample was washed with HF acid (instead of KOH and HCl as Figure 82b shows) a drastically different TPO profile resulted (see Figure 83). Clearly the washing conditions have a significant effect on the carbon product.

These experiments also served as a bulk elemental analysis technique. Using a standard mixture of NO and CO₂, the MS response was calibrated; therefore, the relative
intensities of the 30 and 44 AMU signals could be used to quantify the amount of carbon and nitrogen in all of the samples tested. The results from this analysis as well as the total mass lost is reported for all of the samples tested in Table 15. There are two trends in this data worth noting. First, from the mass lost it is apparent that removing SiO$_2$ is more difficult than removing MgO. Even if a SiO$_2$ sample is washed with concentrated HF acid the percentage of combustion is lower than any of the MgO samples. This seems to indicate that a significant portion of SiO$_2$ is protected from the wash by carbon. Second, from the MS signal integrations, it is apparent that the nitrogen contents of the samples vary. In particular, the Co/SiO$_2$ samples produce carbon contained more nitrogen than the other samples. Since the nitrogen content does not increase with Co loading, it is unlikely that the additional NO being produced in this sample originated from cobalt nitride. The Fe-containing samples consistently have the least amount of nitrogen. The nitrogen contents of the samples detected by TPO is less than what was reported for alumina-derived samples, determined by X-ray Photoelectron Spectroscopy (XPS). In a later section we will show that XPS analysis of the same samples detects more nitrogen than TPO, perhaps because the surface is enriched with nitrogen.
Figure 80: TPO analysis of HCl washed carbon prepared from acetonitrile pyrolysis over 2% Fe/MgO; (a) thermogravimetric and calorimetry signals, and (b) major oxidation products detected by the mass spectrometer.
Figure 81: TPO products detected by the mass spectrometer for HCl washed CN$_x$ prepared from acetonitrile pyrolysis over (a) pure MgO, and (b) 2% Ni/MgO.
Figure 82: TPO products detected by the mass spectrometer for CN$_x$ prepared from acetonitrile pyrolysis over (a) 2% Co/MgO (HCl washed), and (b) 2% Co/SiO$_2$ (KOH washed).
Figure 83: TPO products detected by the mass spectrometer for HF washed CNₓ prepared from acetonitrile pyrolysis over 2% Co/SiO₂.

<table>
<thead>
<tr>
<th>Support</th>
<th>Metal Loading</th>
<th>Wash Conditions</th>
<th>% of Mass Combusted</th>
<th>% Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>none</td>
<td>KOH, HCl</td>
<td>61%</td>
<td>1.1%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2% Fe</td>
<td>KOH, HCl</td>
<td>83%</td>
<td>0.8%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2% Co</td>
<td>KOH, HCl</td>
<td>60%</td>
<td>2.9%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2% Co</td>
<td>HF</td>
<td>72%</td>
<td>2.9%</td>
</tr>
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<td>10% Co</td>
<td>KOH, HCl</td>
<td>44%</td>
<td>2.1%</td>
</tr>
<tr>
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<td>2% Ni</td>
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<td>49%</td>
<td>1.5%</td>
</tr>
<tr>
<td>MgO</td>
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<td>HCl</td>
<td>81%</td>
<td>1.6%</td>
</tr>
<tr>
<td>MgO</td>
<td>2% Fe</td>
<td>HCl</td>
<td>93%</td>
<td>0.9%</td>
</tr>
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<td>2% Co</td>
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<td>86%</td>
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</tr>
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<td>2% Fe</td>
<td>HCl</td>
<td>92%</td>
<td>0.7%</td>
</tr>
</tbody>
</table>

Table 15: Results of oxidation analysis for washed samples prepared from CH₃CN pyrolysis at 900°C for 2 hours over silica- and magnesia-based supports.
4.3.6 TEM Imaging

Electron microscopy imaging confirmed that nanofibers formed during acetonitrile pyrolysis over most of the supports examined. However, unlike pure alumina, which catalyzed the growth of some fiber structures during acetonitrile pyrolysis, the pure SiO₂ and pure MgO samples did not lead to the formation of any fibers. There was not strong evidence that reduction of SiO₂ or MgO occurred during TPAP experiments, unlike the alumina experiments reported previously. Images of the carbon deposited on the SiO₂ support (see Figure 84) showed that the sample contained short strands of graphitic carbon often layered on amorphous particles of silica. Amorphous carbon particles were also present throughout the sample. The carbon deposited on the MgO maintains much better defined structures after being washed. Figure 85 shows the hollow cubes of nitrogen-containing carbon that were left behind after MgO crystals were removed. In some cases the MgO still remained inside of the carbon after the wash.

The metal-doped supports all catalyzed fiber formation during the pyrolysis. Distributions of the fiber diameters are reported in Figure 86 for all the samples, except for Ni/SiO₂, which only contained a few fiber structures. The silica-supported Fe and Co samples formed fibers with an average diameter of 62 and 36 nm respectively. The distribution was much more broad for the Fe sample, as

Figure 86a shows. For the MgO samples the fiber diameter distributions were similar to one another, with the exception of the Ni/MgO sample. The average diameters
for the fibers formed from 2% Co/MgO, 2% Fe/MgO, and 2% Fe/MgO-HSA were 32 nm, 36 nm, and 42 nm respectively. The Ni/MgO formed fibers with an average diameter of 59 nm.

Some exemplary images of fibers grown from silica-supported metals and magnesia-supported metals are shown in Figure 87 and Figure 88. The majority of Fe and Co grown fibers for both the SiO₂ and MgO supports were compartmentalized and stacked together like a stack of cups. This is the same type of structure that formed during the same pyrolysis conditions over Fe/Al₂O₃. Multi-walled nanotubes and solid fibers were also found in all of the Fe and Co samples to a lesser extent. For the Ni/SiO₂ sample, only a small amount of short fiber structures, such as the one pictured in Figure 87c. These fibers contained a relatively high amount of large metal encased inside of them. The structure of these fibers were hollow with sporadic and disordered carbon planes inside the fiber. Similarly structured fibers were reported from the same pyrolysis conditions over Ni/Al₂O₃. With Ni/MgO the same broken multi-walled nanotubes formed along with conventional multi-walled nanotubes and solid fibers.

While the figures in this subsection show representative images of fibers that formed during acetonitrile pyrolysis over the respective supports, it should be mentioned that the various types of fibers discussed could be found in any of the samples. Thus, distribution of the different fiber types within the samples were obtained using TEM. The four major types of fibers observed were defined as stacked cups (see Figure 57, Figure 87 a and b, and Figure 88 a and b), solid fibers (see Figure 89a), MWNT’s (see Figure 89b), and broken MWNT’s (see Figure 58, Figure 87c, and Figure 88c). Some fibers counted half towards MWNT’s and half towards stacked cups because their
structure changed down the axis (see Figure 90a for examples), or the spacing between compartments was large (see Figure 90b for an example). The distribution for all fiber-containing samples is shown in Table 16. This table shows to what extent the various fiber types were found in each sample. Clearly, Fe and Co samples preferentially catalyze the formation of stacked cup fibers, while Ni samples favor the broken MWNT’s. In general, there were only a few trends with respect to fiber type and fiber diameter. Solid fibers always had very large relative diameters compared to other fibers in the samples, while MWNT’s had smaller diameters.

At this point an explanation of the mechanism for the formation of the different fiber types from the different metal particles cannot be provided. However, there were some interesting observation regarding the metal particles in the samples that are worth mentioning. Often within MWNT’s, metal particles could be observed within the hollow core. In some cases the particles were spherical and in other cases the metal was apparently cylindrical and completely filled the tube core. In the stacked cup structures, in some cases metal particles could be found at the end of the fibers, in other cases no metal could be found, or metal particles could be found repeatedly in every compartment. Other researchers have discussed mechanisms for carbon fiber growth from metal particles [161, 166] and even nitrogen-doped carbon fiber growth [141]. Further work is required to explain the observations reported here, however, this work was not initiated since it does not pertain directly to fuel cell cathode research.
Figure 84: TEM images of washed acetonitrile char formed on pure SiO$_2$. 
Figure 85: TEM images of washed acetonitrile char formed on pure MgO.
Figure 86: TEM fiber diameter distributions.
Figure 87: TEM images of fibers formed during acetonitrile pyrolysis at 900°C over (a) 2% Fe/SiO₂, (b) 2% Co/SiO₂, and (c) 2% Ni/SiO₂.
Figure 88: TEM images of fibers formed during acetonitrile pyrolysis at 900°C over (a) 2% Fe/MgO, (b) 2% Co/MgO, and (c) 2% Ni/MgO.
Figure 89: TEM images of (a) solid CN$_x$ fiber grown from Fe/SiO$_2$, and (b) MWNT grown from Fe/MgO.

Figure 90: TEM images of CN$_x$ fibers counted as half MWNT, and half stacked cups formed from (a) Fe/SiO$_2$, and (b) Fe/Al$_2$O$_3$. 
### Table 16: Distribution of fiber types in all samples examined by TEM.

<table>
<thead>
<tr>
<th>CN&lt;sub&gt;x&lt;/sub&gt; Precursor</th>
<th>Stacked Cups</th>
<th>Fibers</th>
<th>MWNT's</th>
<th>Broken MWNT's</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe / Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>54%</td>
<td>10%</td>
<td>21%</td>
<td>15%</td>
</tr>
<tr>
<td>Ni / Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6%</td>
<td>17%</td>
<td>17%</td>
<td>60%</td>
</tr>
<tr>
<td>Fe / SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>71%</td>
<td>7%</td>
<td>18%</td>
<td>4%</td>
</tr>
<tr>
<td>Co / SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>66%</td>
<td>0%</td>
<td>13%</td>
<td>21%</td>
</tr>
<tr>
<td>Fe / MgO</td>
<td>42%</td>
<td>14%</td>
<td>9%</td>
<td>35%</td>
</tr>
<tr>
<td>Co / MgO</td>
<td>54%</td>
<td>10%</td>
<td>21%</td>
<td>15%</td>
</tr>
<tr>
<td>Ni / MgO</td>
<td>13%</td>
<td>25%</td>
<td>18%</td>
<td>45%</td>
</tr>
<tr>
<td>Fe / MgO-HSA</td>
<td>60%</td>
<td>10%</td>
<td>20%</td>
<td>10%</td>
</tr>
</tbody>
</table>

#### 4.3.7 Surface Characterization

To characterize the composition of the sample surfaces, all of the nitrogen-doped carbon materials prepared were analyzed by XPS. Table 17 shows the results of this analysis for the washed samples prepared from acetonitrile pyrolysis over silica-based supports. Several important trends are apparent in this data.

First, silicon is always present in the samples to some degree (usually as silica evident from the Si 2p peak near 103.5 eV), showing that the KOH wash is not entirely effective at removing silica. Some samples may contain nitrided silicon (B.E. of 102.0 eV [224]) rather than silica. When HF acid is used as the leaching agent then more silica is removed from the surface. It is possible that some of the silica remaining in the samples is below several layers of carbon, since XPS is not entirely surface sensitive.
Consequently, the samples that contain more silica on the surface also contain more oxygen. A very small amount of chlorine (or fluorine) typically remained in the samples after the wash.

The majority of all the samples surfaces are composed of carbon. The binding energies are slightly higher than what is typical for elemental carbon due to the doping of the carbon with nitrogen. This effect is typically reported in pyrolyzed nitrogen-containing carbon materials. The nitrogen species present were deconvoluted in the same manner as the alumina- and carbon-supported materials reported previously. The two main peaks can be attributed to pyridinic (398.6 +/- 0.3 eV) and quarternary (401.2 eV +/- 0.2 eV) nitrogen. The quarternary nitrogen always had a higher binding energy shoulder; however, since it is believed that this shoulder is derived from various quarternary species (see discussion in section ‘2.2 Nitrogen Surface Species’), this shoulder was lumped with the quarternary assignment, and was not reported separately. Clearly, the nitrogen content is higher on the surface than what is reported for the bulk of the samples by TPO elemental analysis. The nitrogen surface enrichment of catalytically grown nitrogen-doped carbon nanofibers has been reported elsewhere [141].

For the alumina- and carbon-supported samples, there was a relation between nanostructure and the ratio of the nitrogen types. This sort of trend is weakly apparent in the silica-derived materials. The CN_x deposited on pure silica contains the least amount of pyridinic nitrogen, while the Fe and Co samples contain the highest ratio of pyridinic nitrogen. Surprisingly the Ni sample contains the most nitrogen, but the lowest ratio of pyridinic nitrogen.
The XPS analysis results for the HCl washed magnesia-derived CN\textsubscript{x} samples are shown in Table 18. Only a small amount of magnesia remained in the treated and washed pure magnesia sample. The metal doped samples were completely free of magnesia after being washed. Chlorine was not detected in the samples. Again the majority of the composition was composed of carbon, with a slightly higher binding energy than pure elemental carbon. Around 3% oxygen was present in all of the samples.

The nitrogen contents and the relative ratios of nitrogen species varied from sample to sample. The most nitrogen was found in CN\textsubscript{x} that had been deposited on pure MgO. However, this sample contained a low ratio of pyridinic to quarternary nitrogen. Based on the nanostructure of this sample reported previously, the low ratio of pyridinic nitrogen could be expected since the sample did not have significant edge plane exposure. The sample was not highly graphitic, and had many defects, which could explain the presence of some pyridinic nitrogen. The Fe and Co samples both had structures that would be expected to have exposed edges, and these samples had a higher pyridinic nitrogen ratio. The Ni sample also had a similar ratio of pyridinic:quarternary nitrogen, although its nanostructure would not lead to one predicting this. The total nitrogen content of the Ni sample is much lower than the other samples. Still, all of the samples have a higher nitrogen content on the surface than in the bulk when one compares XPS to TPO elemental composition.

Although the carbon- and alumina-derived samples showed a strong correlation between pyridinic nitrogen and nanostructure, this is not necessarily the case for the silica- and magnesia-derived CN\textsubscript{x} just discussed. Further, despite the fact that Fe-doped samples have a similar nanostructure regardless of the support used, the CN\textsubscript{x} formed from
alumina supported Fe has a much higher content of pyridinic nitrogen than the other Fe samples. Several hypothesis could explain these trends. First, XPS is not entirely surface sensitive, since subsurface layers will contribute to the analysis to some extent (on the order of 5 nm). Fibers with thin walls have a higher percentage of atoms on the surface than thicker fibers. Thus, the analysis of samples containing thicker fibers may be diluted more by subsurface layers than samples containing fibers with walls that are so thin that there are not enough subsurface layers to dilute the analysis. This would explain why the CN\textsubscript{x} from Fe/Al\textsubscript{2}O\textsubscript{3} (with smaller fibers) has a higher pyridinic nitrogen ratio than CN\textsubscript{x} of the same nanostructure formed from Fe supported silica or magnesia.

Second, it is possible for pyridinic nitrogen to be present at defects in the carbon plane in addition to being located at the edge of a plane. Therefore, some of the precursors could catalyze the formation of pyridinic nitrogen by means other than orientation of carbon planes within the fiber. Since all of the fibers contain pyridinic nitrogen to some extent, despite the fact that some have structures with little or no edge exposure such as the cubes formed on MgO, this hypothesis is likely true to some extent. Have a structure with more edge exposure could still account for more pyridinic nitrogen in this case. It should be mentioned that Trasobares et al. noted that more pyridinic nitrogen formed from Fe particles than Ni particles, but the researchers did not attribute this observation to any nanostructure difference [141].

A third possibility is that other forms of CN\textsubscript{x}, such as amorphous carbon, that cannot be quantified easily by TEM or other means is contributing to the XPS analysis. Amorphous particles were seen in all the samples (although not a abundant as the fibers).
Additionally, in the metal-doped MgO samples, the nano-cube structures were observed along with the fibers and likely contributed to the XPS analysis to some extent.

<table>
<thead>
<tr>
<th>pure SiO₂</th>
<th>Region</th>
<th>BE (eV)</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>532.9</td>
<td>27.2%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>401.1</td>
<td>3.5%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>398.6</td>
<td>1.2%</td>
<td></td>
</tr>
<tr>
<td>C 1s</td>
<td>285.0</td>
<td>61.2%</td>
<td></td>
</tr>
<tr>
<td>Cl 2p</td>
<td>200.1</td>
<td>0.6%</td>
<td></td>
</tr>
<tr>
<td>Si 2p</td>
<td>103.7</td>
<td>7.6%</td>
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<table>
<thead>
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<th>BE (eV)</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>532.5</td>
<td>6.9%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>401.2</td>
<td>3.9%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>398.7</td>
<td>1.7%</td>
<td></td>
</tr>
<tr>
<td>Cl 2p</td>
<td>200.4</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>Si 2p</td>
<td>103.3</td>
<td>1.5%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2% Co</th>
<th>Region</th>
<th>BE (eV)</th>
<th>% Composition</th>
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</thead>
<tbody>
<tr>
<td>Co2p</td>
<td>778.4</td>
<td>0.2%</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>532.9</td>
<td>12.4%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>401.3</td>
<td>4.4%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>398.8</td>
<td>1.7%</td>
<td></td>
</tr>
<tr>
<td>C 1s</td>
<td>284.9</td>
<td>77.6%</td>
<td></td>
</tr>
<tr>
<td>Si 2p</td>
<td>103.5</td>
<td>3.7%</td>
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<table>
<thead>
<tr>
<th>2% Ni</th>
<th>Region</th>
<th>BE (eV)</th>
<th>% Composition</th>
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<tbody>
<tr>
<td>Ni2p</td>
<td>854.3</td>
<td>0.8%</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>532.2</td>
<td>5.5%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>401.2</td>
<td>5.9%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>398.7</td>
<td>1.8%</td>
<td></td>
</tr>
<tr>
<td>C 1s</td>
<td>284.8</td>
<td>85.4%</td>
<td></td>
</tr>
<tr>
<td>Si 2p</td>
<td>102.0</td>
<td>0.5%</td>
<td></td>
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<table>
<thead>
<tr>
<th>2% Co - HF washed</th>
<th>Region</th>
<th>BE (eV)</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co2p</td>
<td>778.5</td>
<td>0.4%</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>532.3</td>
<td>4.9%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>401.0</td>
<td>4.2%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>398.6</td>
<td>1.7%</td>
<td></td>
</tr>
<tr>
<td>C 1s</td>
<td>284.7</td>
<td>86.4%</td>
<td></td>
</tr>
<tr>
<td>F 1s</td>
<td>685.8</td>
<td>0.7%</td>
<td></td>
</tr>
<tr>
<td>Si 2p</td>
<td>101.9</td>
<td>0.5%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10% Co</th>
<th>Region</th>
<th>BE (eV)</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co2p</td>
<td>778.4</td>
<td>0.6%</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>532.7</td>
<td>14.8%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>401.1</td>
<td>4.5%</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>398.8</td>
<td>2.0%</td>
<td></td>
</tr>
<tr>
<td>C 1s</td>
<td>284.7</td>
<td>74.9%</td>
<td></td>
</tr>
<tr>
<td>Si 2p</td>
<td>103.3</td>
<td>3.1%</td>
<td></td>
</tr>
</tbody>
</table>

**Table 17:** XPS analysis results for CNₓ formed from acetonitrile pyrolysis over silica supports.
Table 18: XPS analysis results for CN$_x$ formed from acetonitrile pyrolysis over magnesia supports and washed with HCl acid.

### 4.3.8 Hydrophobicity Testing

The dispersibility of CN$_x$ samples in water was compared as a measure of hydrophobicity, similar to what was conducted on the alumina-derived samples. For these tests, 1 mg of sample was sonicated in 10 mL of water for 30 minutes, then a photograph was taken within one minute. The photographs for the silica- and magnesia-derived CN$_x$ are shown in Figure 91. The magnesia samples were similar to the results obtained from the alumina samples. The stacked cup structured carbon formed from Fe and Co particles was the most easy to disperse, while the broken MWNTs formed from Ni particles did not disperse as well. For the CN$_x$ grown from silica, none of the samples
dispersed particularly well in water. These samples all contained a significant amount of silica, as was determined from TPO/TGA experiments, so this may be a contributing factor to this observation.

Figure 91: Hydrophobicity testing for CNₓ prepared form CH₃CN pyrolysis over (A) pure MgO, (B) 2% Fe/MgO, (C) 2% Co/MgO, (D) 2% Ni/MgO, (E) pure SiO₂, (F) 2% Fe/SiO₂, (G) 2% Co/SiO₂, and (H) 2% Ni/SiO₂.
4.3.8 Electrochemical Properties

To determine how the samples would perform in a PEM fuel cell, the conductivity was measured using an in-house built set-up described previously, and the ORR activity and selectivity were measured with a RRDE set-up. The results for all of the washed samples are shown in Table 19. Unlike pure alumina, the CN\textsubscript{x} deposited on pure silica and magnesia supports did not for nanofibers, and likewise were not highly active for the ORR. The pure silica sample had very poor conductivity as well. This sample contained a large amount of silica, as TPO experiments indicated.

The Ni-doped supports did not lead to highly active CN\textsubscript{x} either. The fibers formed from Ni (regardless of the support used) were mostly of a nanostructure with a low number of edge planes exposed, such as broken MWNT’s. In the case of CN\textsubscript{x} from Ni/SiO\textsubscript{2} the activity and conductivity was significantly higher than the CN\textsubscript{x} deposited on pure silica. There was little difference between the properties of CN\textsubscript{x} prepared on pure MgO compared to Ni/MgO.

The CN\textsubscript{x} samples with the highest activity were consistently formed from supported Fe and Co particles. These samples also had good conductivity. The conductivity of Vulcan XC-72 was measured to be 71 S/m in the same set-up under the same conditions. The most active sample was formed from acetonitrile pyrolysis over 2\% Fe/SiO\textsubscript{2}. The sample contained larger diameter fibers (average of 62 nm), mostly of a compartmentalized stacked cup structure (71\% of the fibers). The activity of this sample was within a 100 mV potential drop of a state-of-the-art 20-wt\% Pt/VC commercial catalyst tested in the same set-up using the same conditions. The CN\textsubscript{x}
prepared from Fe/SiO₂ was also almost completely selective for complete oxygen reduction to water. The reduction currents for the ring and the disk for this sample are shown in Figure 92. To compare the performance of the most active sample to the most active alumina-derived sample, and to the commercial state-of-the-art catalyst, Tafel plots for these samples were constructed, and are shown in Figure 93. The slopes of the non-metal catalysts are the same as the commercial catalyst, indicating that these samples all likely have the same rate determining step. On an equal current basis, there is only an additional 100 mV potential drop, on an equal voltage basis, the alternative catalysts have about 1/10th the current of the commercial sample.

Interestingly, there is an apparent loose correlation between activity for the ORR and selectivity of the materials for the complete 4-electron reduction to water. The highest values for n are generally samples with high activity. One particular outlier from this trend in the sample prepared using 10% Co/SiO₂. While this sample had high activity, it’s selectivity was rather modest. This could be related to the large amount of cobalt in this sample. Researchers generally report that catalysts prepared from the pyrolysis of cobalt-containing precursors have poorer selectivity for the 4-electron ORR compared to samples prepared from the pyrolysis of Fe precursors. This includes precursors, such as organic macrocycles, polymers, or nitrogen-containing hydrocarbon feeds. Therefore, it is possible that Co is part of and active site for hydrogen peroxide formation, and adding more cobalt increases selectivity to peroxide. The activity for the complete ORR would then be attributed to the nanostructured CNₓ formed from the Fe or Co particles.
Washing the Co/SiO₂ derived CNₓ with HF acid did not affect activity, however, it did improve selectivity for the 4-electron reduction. The only significant change in surface properties that were brought about by the HF acid wash was the removal of additional silica, as determined by XPS.

<table>
<thead>
<tr>
<th>Support</th>
<th>Metal</th>
<th>BET SA (m²/g)</th>
<th>Conductivity (S/m)</th>
<th>ORR peak (mV vs. NHE)</th>
<th>Average n</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>-</td>
<td>290</td>
<td>0.2</td>
<td>100</td>
<td>3.3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2% Fe</td>
<td>255</td>
<td>11</td>
<td>655</td>
<td>3.95</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2% Co</td>
<td>465</td>
<td>26</td>
<td>615</td>
<td>3.92</td>
</tr>
<tr>
<td>SiO₂</td>
<td>10% Co</td>
<td>214</td>
<td>26</td>
<td>640</td>
<td>3.6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2% Ni</td>
<td>141</td>
<td>7</td>
<td>405</td>
<td>3.7</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>180</td>
<td>8</td>
<td>370</td>
<td>3.3</td>
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<td>MgO</td>
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<td>32</td>
<td>580</td>
<td>3.8</td>
</tr>
<tr>
<td>MgO</td>
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<td>3</td>
<td>570</td>
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<tr>
<td>MgO</td>
<td>2% Ni</td>
<td>130</td>
<td>12</td>
<td>400</td>
<td>3.3</td>
</tr>
</tbody>
</table>

**Table 19:** Electrochemical testing results for CNₓ formed from silica and magnesia supports.
Figure 92: RRDE reduction currents for CN$_x$-Fe/SiO$_2$.

Figure 93: Tafel plot of most active non-metal catalysts compared to commercial 20-wt% Pt/VC.
Nitrogen-containing carbon nanostructures were prepared from the decomposition of acetonitrile at 900°C over silica and magnesia supports. For the carbon grown from supported Fe and Co particles, compartmentalized fibers with a stacked cup structure predominantly formed, while mostly broken multi-walled nanotubes formed from Ni particles. These observations are consistent with the structures formed from alumina supported Fe and Ni. The diameter of the fibers varied significantly depending on the support used, and the total nitrogen content varied depending on the metal/support combination used. Washing the silica-derived samples removed some of the silica, but based of TPO/TGA results, about half of the sample still consisted of silica. This was likely caused by the complete encapsulation of silica particles in carbon, since washing with HF acid did not yield much of an improvement. Conversely, the magnesia particles could easily be removed by washing with HCl acid, leaving behind only carbon and encapsulated metal particles.

Activity for the ORR was highest over CN$_x$ fibers grown from supported Fe and Co particles. These fibers had compartmentalized stacked cup structures, which would be expected to have a higher degree of edge plane exposure than MWNTs. The most active materials were generally the most selective catalysts as well. The most active alternative non-noble metal catalysts were comparable in activity and selectivity to state-of-the-art platinum catalysts.
4.4 Other Materials Prepared

Several other avenues were explored for the preparation of active ORR catalysts, with limited success. This section contains descriptions of those studies and some of the results. These studies were not complete enough to merit publication in refereed journals, and should be thought of more as exploratory investigations into methods of producing more active materials. Attempts to grow nitrogen-doped fibers from alloy particles (Ni/Co and Fe/Cu) and ferrocene (both mentioned in the subsection ‘3.1.5 Unsupported Materials’) resulted in poor carbon yields, and were not investigated further, therefore, these materials are not discussed.

4.4.1 Phosphorus-doped carbon

In modeling work by Strelko et al., it was predicted that doping carbon with nitrogen would improve electron donation from the carbon [133]. Further, the researchers predicted that doping carbon with phosphorus within the carbon plane would have an even greater effect [133]. Therefore, several attempts were made at preparing phosphorus-doped carbon nanofibers. For these experiments Triphenyl Phosphine (TPP) was used as the phosphorus and carbon precursor. The TPP precursor, which is in the form of a solid, was placed in a quartz boat in the tube furnace, but near the outside entrance of the tube furnace. Two supports were examined for deposition, as received Vulcan Carbon XC-72, and 2-wt% Fe/VC. The support was placed in the center of the furnace, which was heated to 900°C under N₂ flowing at 150 sccm. Over the course of
several hours, while at 900°C, the tube was slid further into the furnace, in order to slowly evaporate the TPP, which has a boiling point of 377°C. The temperature at the outside edge of the furnace was measured to be about 300°C. For the treatment, 2 g of support, and about one gram of TPP were used. The evaporated TPP badly stained the inside of the tube.

Both supports underwent a significant weight gain during the treatments. The pure VC gained 21%, and the 2% Fe/VC gained 39%. The surface area of the VC support was slightly higher than that of the 2% Fe/VC, 98 m²/g versus 74 m²/g. There was not a significant improvement obtained in ORR activity, as measured with the RDE. The phosphorus treated VC sample had lower activity than pure VC. The Fe-doped sample had the ORR current peak at 235 mV vs. NHE. This is 200 mV more active than VC and about 70 mV more active than 2% Fe/VC treated with pure N₂. However, this is significantly less active the 2% Fe/VC treated with acetonitrile which peaked at 550 mV.

XPS characterization was carried out to determine if phosphorus found its way into the carbon. The binding energy of the phosphorus was around 132.1 eV in both samples, and the phosphorus compositions were similar, around 0.6% and 0.9% for VC and 2% Fe / VC respectively. It is not clear what form the phosphorus was in, but the binding energy indicates a form more oxidized than TPP [224]. Several publications have investigated the doping of carbon with phosphorus, however, generally, only the surface can be altered, not the interior of the carbon planes. The improvement in activity for the Fe-containing sample may therefore possibly be attributed to the presence of Fe.
A particular type of carbon that is of interest because of its high degree of edge plane exposure is stacked platelet carbon. Using a method described in the patent literature, stacked platelet carbon fibers were prepared from a gas feed of CO and H₂ using Fe:Cu 95:5 alloy particles [205, 225]. Several different studies were carried out with this material.

First, the effectiveness of this material as a support for platinum was compared to Vulcan Carbon and CNₓ prepared from Fe/Al₂O₃. Some reports in the literature indicated that stacked platelet carbon could function as a superior support for platinum or nickel particles [226, 227]. In these experiments, the three supports of interest (CNₓ, stacked platelets, and VC) were impregnated with 10-wt% chloroplatinic acid solution then reduced overnight at 200°C in 10% H₂ in helium. Next, the samples were tested for ORR activity, and were imaged by TEM to determine the degree of platinum dispersibility. The activity of the 10-wt% Pt/stacked platelets was 710 mV, compared to 700 mV for the 10-wt% Pt/CNx, and 600 mV for 10-wt% Pt/VC. The activities are slightly lower than the commercial 20-wt% Pt/VC, which peaked at 750 mV. The pure platelets and Vulcan Carbon both had no activity in their pure form (both peaked at 30 mV), while CNₓ peaked at 650 mV without any platinum. TEM images of the catalysts show that the stacked platelets were better at dispersing platinum particles than the other types of carbon (see Figure 94). Despite the lower surface area of the platelets (only 100 m²/g) the particles were much smaller and appeared to wet the surface.
In the second study with stacked platelet carbon, attempts were made to functionalize its surface. The objective was to add nitrogen groups, namely pyridinic nitrogen, in order to increase activity. First, the stacked platelets were washed for 4 hours in boiling nitric acid. This step dissolves metal particles and oxygenates the surface. This surface oxygenation allows carbon to be more easily functionalized by ammonia treatment, as other researchers have demonstrated. After the samples are washed and dried, treatment of 1 gram of platelets in 50% ammonia in helium flowing at 80 sccm is carried out at 600°C for 2 hours.

Electrochemical testing on the nitric acid treated fibers did not show good activity for the ORR, but another interesting trend is apparent. Figure 95 shows the testing results for this sample. A reversible redox reaction occurred on the surface of the sample that did not match the redox potential expected for Fe^{2+} to Fe^{3+} (see Figure and reference). In Figure 95b, the effect of adding O_2 to the electrolyte is apparent. The redox reaction is unaffected by the presence of O_2, and at very low voltages the ORR takes off. The activity matches the activity for Vulcan Carbon.

After the sample was treated with ammonia, activity improved slightly, and the reversible redox reaction was no longer apparent (see Figure 96). XPS analysis before and after the ammonia treatment showed that the ammonia removed oxygen groups from the surface and replaced them with nitrogen (see Table 20). The nitrogen content was rather low, and did not correspond to pyridinic nitrogen, and was possibly pyrrolic nitrogen. At this point the results from these experiments are still inconclusive considering the small changes in activity, and the low and questionable nitrogen content that was obtained.
Figure 94: TEM images of platinum particles on (a) Vulcan Carbon, (b) CN\textsubscript{x} stacked cups, and (c) stacked platelet carbon.
Figure 95: Cyclic voltammetry testing of stacked platelets (a) the argon background, and (b) effect of O$_2$ addition to the electrolyte.
Figure 96: Reductive sweeps for ammonia treated stacked platelets showing improved ORR activity and an absence of a redox reaction.

<table>
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<th>Region</th>
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<th>% Composition</th>
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Washed and NH₃ treated

<table>
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<tr>
<td>C1s</td>
<td>284.3</td>
<td>96.8%</td>
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Table 20: XPS analysis of stacked platelet carbon subjected to different treatments.
CHAPTER 5

CONCLUSIONS

Active catalysts for the ORR in a PEM fuel cell environment in the form of nitrogen-containing carbon were prepared from a variety materials. Catalysts with high activity (compared to pure carbon) were even prepared from starting materials with less than 1 ppm metal contamination. This is convincingly strong evidence that metal is not needed for the reduction of oxygen, but rather metal particles may be acting as catalysts for the formation of active sites during the high temperature pyrolysis of nitrogen/carbon precursors. The active site could not be proposed based on the work carried out to date. One way that metal particles could catalyze the formation of active sites is through the growth a nano-structures with a higher proportion of edge planes exposed, since the active site for oxygen reduction in non-noble metal catalysts is thought to be present on carbon edge planes.

The Fe-doped supports were the best precursors to active catalysts. These samples also had higher pyridinic-N content than Ni-doped and non-doped samples. There seems to be tremendous flexibility in the support that can be used for Fe during the pyrolysis of acetonitrile to form active ORR catalysts. The best materials prepared have activity, selectivity, conductivity, and surface area that are comparable to state-of-the-art
cathode catalysts. Based on these characteristics, it should be possible to prepare acceptable PEM fuel cells using cathode catalyst materials similar to the non-noble metal catalysts described once fuel cell preparation conditions are optimized.
CHAPTER 6

RECOMMENDATIONS

In the previous chapters, it has been shown that Fe is not part of the active site for oxygen reduction, but does act as a catalyst for the formation of nanostructures with more edge plane exposure and apparently more ORR activity. However, the exact nature of the active site is not yet clear. Furthering the understanding of the active site could lead to breakthroughs in catalyst development. For instance, if the active site is found to be a specific nitrogen group, then perhaps conductive polymers could be prepared with a high concentration of active sites. Advances in nanotechnology occurring nearly everyday could also lead to breakthroughs in ORR catalysts if the active site were better understood. Therefore, part of the objective of future work should focus on improving the understanding of the active site for oxygen reduction. A second objective is to demonstrate these materials could be a replacement for platinum by improving their activity and conductivity, and demonstrating there operation in a PEM fuel cell. Until this is accomplished, questions may remain as to their viability. This section overviews some final ideas for research that could be conducted on the materials described in the previous chapters. Some possible future directions include:
1.) Characterization and activity testing of materials grown from the unsupported metal particles. Using unsupported metal particles is an established technique for preparing nanofibers, so this approach could lead to different nanostructures from previous approaches. From a practical standpoint, such an approach produces easier to purify carbon, and thus the material may be easier to characterize.

2.) Selective armchair and zigzag blocking experiments. Park and Baker presented very interesting results on the effects that selectively blocking armchair and zigzag sites of the carbon edge plane had on the ability of carbon to support Ni [228]. Blocking of armchair sites can be accomplished with phosphorous, while zigzag sites can be capped with boron, as shown in Figure 97. Park and Baker described the procedure for the blocking treatments, which was taken from methods used to make carbon more resistant to oxidation. This procedure will be adapted to a nitrogen-containing carbon ORR catalyst to study the nature of the active site. First only armchair sites will be blocked for an active sample, then only zigzag sites, then both. The effects on activity will be studied to uncover clues to the nature of the active site.

Figure 97: Depiction of armchair and zigzag capping.
3.) Comparison of catalyst basicity to activity. Experiments should be carried out to
gauge the basicity of materials for comparison to the ORR activity, to see if there is a
correlation as van Dommele et al. [197] observed for their reaction. One simple
approach to quantify basic sites would be titration of the material in an aqueous
suspension. Adsorption techniques will also be reviewed since such experiments may
be more informative, and our research group possesses these capabilities.

4.) Considering the remarks recently made by an industry thought leader on the
viability of non-platinum catalysts [12], proving the performance of non-precious
metal catalysts is important to maintain life in this important area of research for
future generations of investigators. Several approaches could be carried out. First,
activity and selectivity testing could be done at 80°C in the half-cell set-up using a
ceramic RDE manufactured by Pine Instruments. This would eliminate the need to
rely on questionable extrapolations using assumed activation energies. Second, the
ultimate verification would be to demonstrate performance in an actual PEM fuel cell.
For this to be accomplished, the preparation procedures need to be optimized. A
possible route to improving conductivity in the cathode, that should be considered
during preparation optimization, is using a dual conducting polymer (rather than
Nafion) as the binding agent. Other polymers could provide both electrical and
proton conduction in the electrodes. The full PEM fuel cell testing conditions should
follow industry standards [12].
VOLUME II:

STEAM REFORMING OF METHANOL TO HYDROGEN OVER ZIRCONIA-CONTAINING Cu/ZnO-BASED CATALYSTS
ABSTRACT

The ability to produce hydrogen for fuel cells from renewable sources would be a great benefit to the next generation of energy conversion technology. Additionally, developing a means to safely store hydrogen would solve a major obstacle to fuel cell commercialization. Methanol can be produced from many sources, including renewable sources, and it allows hydrogen to be stored in the form of a higher energy density, less dangerous liquid. In this study zirconia-containing Cu/ZnO catalysts are examined for their use in the reaction of methanol with water to produce hydrogen. Catalyst samples with varying composition were prepared by means of a co-precipitation method, and the effect of different pre-treatment conditions was examined. The catalysts were characterized using BET surface area analysis, Cu surface area analysis, Temperature Programmed Reduction (TPR), Temperature Programmed Desorption (TPD), Thermo-Gravimetric Analysis with Differential Scanning Calorimetry (TGA-DSC), X-Ray Diffraction (XRD), and X-ray Photoelectron Spectroscopy (XPS). Characterization suggests that the most active steam reforming catalysts initially consist of CuO, ZnO, and a high surface area amorphous phase of zirconia that contains carbonates; however, partial reduction of surface copper during the reaction is apparent.
These catalysts were found to have varying activity depending on composition and pre-treatment conditions. The catalyst with a Cu:Zn:Zr mole ratio of 4:3:3 calcined at 350°C performed equally well with or without pre-reduction in hydrogen, while catalysts containing alumina or calcined at 550°C required pre-reduction with hydrogen for optimal activity. X-Ray Diffraction (XRD) and Thermo-Gravimetric Analysis (TGA) show that the bulk CuO phase of all the catalysts is reduced to Cu° when reduced with hydrogen, methanol, or methanol and water. Additionally, X-ray Photoelectron Spectroscopy (XPS) shows that the most active sample without pre-reduction suffers the least amount of Cu surface composition loss during reduction with the steam reforming reactants, although differences in Cu surface composition cannot completely account for activity differences. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) experiments show that catalysts in their most active form have uniquely different spectra from the less active samples. For steam reforming over unreduced Cu:Zn:Zr 4:3:3 calcined at 350°C, carbon dioxide bands eventually become the dominating feature, unlike the other catalysts. Consequently, this is the only sample that has a post reaction spectra that resembles the surface of its hydrogen-reduced counterpart. When steam reforming was carried out over the hydrogen-reduced surfaces, carbon dioxide is the dominating species observed for all samples, and the features that were apparent immediately after the hydrogen reduction remained intact. Several hypotheses are presented to explain these trends.
CHAPTER 7

INTRODUCTION

7.1 Hydrogen from Methanol

Methanol is potentially a good source of hydrogen for mobile fuel cells since it is a liquid at ambient conditions, has a high hydrogen to carbon ratio, and can be converted to hydrogen using either steam or oxygen at relatively low temperatures compared to other fuels. The Steam Reforming of Methanol (SRM) and the Partial Oxidation of Methanol (POM) reactions are shown here with heat of reactions at STP:

**SRM:**

\[
\text{CH}_3\text{OH} (l) + \text{H}_2\text{O} (l) \rightarrow \text{CO}_2 + 3 \text{ H}_2 \quad (\Delta H_{\text{rxn}} = 130.9 \text{ kJ/mol})
\]

**POM:**

\[
\text{CH}_3\text{OH} (l) + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{ H}_2 \quad (\Delta H_{\text{rxn}} = -154.9 \text{ kJ/mol})
\]

The SRM reaction produces three moles of hydrogen per mole of fuel, while the POM produces only two. However, the efficiency of the SRM reaction is hindered by its
endothermicity since heat must be provided for the reaction to run. Combining the two reactions for the Oxidative Steam Reforming of Methanol (OSRM) reaction is potentially the best option for mobile hydrogen production. The maximum theoretical efficiency based on the Lower Heating Value (LHV) of H₂ produced compared to the fuel consumed is obtained for the autothermal reaction in which enough oxygen is used to make the heat of reaction zero. Theoretically, methanol can be converted to hydrogen with better efficiency than any other hydrocarbon being considered for on-board hydrogen production [229]. The use of methanol to produce hydrogen is also attractive because of the relatively low selectivity to by-products such as carbon monoxide and methane compared to alkane or higher alcohol reforming.

7.2 Cu/ZnO-Based Catalysts

Cu-based catalysts are potentially useful for several reactions such as low temperature water gas shift [230-232], methanol synthesis [233-240], and the methanol reforming [241-247] and partial oxidation [248-251] to hydrogen. For these reactions, activity is generally proportional to Cu surface area and dispersion; therefore, the rate determining steps for the various reactions are generally assumed to occur on Cu or at a boundary between Cu and the support [234, 243, 244, 246, 249, 251-253]. Various oxides and mixtures of oxides can be used as supports for Cu, with the most common supports being ZnO, Al₂O₃, ZrO₂, and mixtures of these oxides. Additionally, other promoters [253-255] and novel support structures with favorable effects have been the focus of past research [256].
From an academic viewpoint Cu-based catalysts are interesting due to the multiple functions of the supports. Zinc oxide is known to both improve Cu dispersion and the reducibility of CuO, and the improved reducibility of CuO has been cited as a possible reason for the activity of Cu/ZnO catalysts if a Cu redox step occurs in the mechanism [245, 257]. However, it is also possible that adsorption improvements are a reason for better activity and that improved reducibility is a second-hand effect. The adsorption properties of the support could affect activity since spillover effects have been shown to play a role in reaction mechanisms for these catalysts. Hydrogen species are mobile over both phases of these catalysts and can be stored on the surface [235], while oxygen species have been shown to move from ZnO to Cu, most likely in the form of hydroxides [240].

Zirconia, similarly to ZnO, improves the reducibility of copper and aids Cu dispersion [243, 244, 247, 253]. Zirconia can also participate in spillover effects, as the build-up of hydrogen that has spilled over from Cu is possible on ZrO₂ as well [236, 258, 259]. For the methanol synthesis reaction, ZrO₂ is known to have the attractive property of being able to adsorb CO₂ where it can become hydrogenated [236, 260]. Likewise, for the steam reforming of methanol reaction, ZrO₂ can readily adsorb methanol [261]. Moreover, higher surface area catalysts can be prepared via co-precipitation methods when both Zn and Zr are used together. Therefore, we have observed that it is favorable to use both ZnO and ZrO₂ together as a support for CuO to form catalysts with higher activity [246].

Alumina is generally added to the catalysts to improve surface area, and prevent catalyst sintering [241, 249]. However, the presence of too much Al₂O₃ has been shown
to have an inhibiting effect on the SRM reaction in Cu/ZnO based catalysts [243, 246, 249]. Additionally, alumina does not improve the reducibility of CuO to the extent that ZnO or ZrO₂ does. The favorable effects of a small amount of alumina in reducing sintering generally outweighs the initial small loss of activity.

Limitations of these catalysts have been sited as being the need for pre-reaction reduction, pyrophoricity, and questionable long-term stability. In previous work we demonstrated that unreduced zirconium containing Cu/ZnO catalysts perform well for methanol reforming reactions even without pre-reaction reduction [246]. This is significant since pre-reduction with hydrogen would be particularly burdensome for steam reforming systems used in mobile applications. It was apparent that the Cu component of the catalysts was at least partially reduced by the reactants; however, some catalysts still performed better after reduction with hydrogen, such as alumina-containing samples and samples calcined at higher temperatures. Additionally, the deactivation extent of the samples depended on composition and pre-treatment conditions.
Cu/ZnO/Al$_2$O$_3$ catalysts have been extensively studied for the methanol synthesis reaction, the water gas shift reaction, steam reforming of methanol, and the partial oxidation of methanol [231-233, 235, 237, 248, 249, 251, 252, 262-268]. Cu is believed to be the active phase in these catalysts, since activity is typically proportional to Cu surface area. ZnO is known to improve the dispersion of copper and also its reducibility, which may be important if a redox reaction mechanism occurs [257]. Additionally, the importance of ZnO may be explained by spillover effects [239, 240]. The ability of ZnO to store hydrogen and transport species to the Cu phase has been demonstrated to have favorable consequences for many of the aforementioned reactions. The addition of Al$_2$O$_3$ improves the surface area and slows the sintering of the catalyst. Moreover, Al$_2$O$_3$ could contribute to advantageous spillover effects, although ZnO apparently has more advantageous effects with the Cu phase. Shortcomings of these catalysts have been noted as the need for a pre-reaction reduction to induce activity, low resistance to contaminants, and problems with long-term stability [231].

Copper supported by zirconia rather than zinc oxide or alumina has also shown good activity for the methanol synthesis reaction, the reverse of methanol reforming [234,
Similarly to ZnO, ZrO$_2$ improves the reducibility of CuO. Compared to alumina, zirconia has the advantage of possessing activity by itself or when used as a support for copper. Additionally, ZrO$_2$ is capable of adsorbing methanol making it an attractive support material for reforming catalysts [269].

More recently, zirconia-containing copper–based catalysts have shown promising activity for the SRM and the OSRM reactions [241, 243-245, 254, 266]. Breen and Ross studied the steam reforming of methanol using pre-reduced zirconia-containing Cu/ZnO/Al$_2$O$_3$ catalysts [241]. They found that using zirconia as a support for Cu and ZnO produces a more active catalyst than Cu/ZnO/Al$_2$O$_3$ for the SRM reaction. The stability of the catalyst was improved if a small amount of Al$_2$O$_3$ was added, most likely because the amorphous zirconia phase was stabilized. Velu et al. studied the OSRM reaction over pre-reduced zirconia containing Cu/ZnO/Al$_2$O$_3$ catalysts [243]. This group established that ZrO$_2$ is also a better support for OSRM. The better performance of zirconia containing catalysts was attributed to a higher Cu surface area, better Cu dispersion, and improved reducibility of Cu compared to Cu/ZnO/Al$_2$O$_3$ catalysts.

The pre-reduction of Cu/ZnO/Al$_2$O$_3$ catalysts is necessary to obtain maximum activity. This reduction must be carried out carefully in a diluted hydrogen stream with a slow heating rate in order to prevent catalyst sintering during the highly exothermic reduction of CuO to Cu$^0$. However, the previously studied reactions for these catalysts (i.e. the water gas shift and methanol synthesis reactions) are typically carried out in stationary large-scale operations where pre-reduction is not as much of a burden. In the following study we examine the activity of these catalysts without pre-reduction, since
this type of treatment would be inconvenient for mobile fuel cell systems. Only the SRM, the reforming reaction with the slowest kinetics, is examined in this study.

Other researchers have studied similar non-reduced Cu-based catalysts for methanol reforming reactions. Günter et al. examined the redox behavior of CuO/ZnO catalysts for methanol steam reforming using in situ XRD and XAS [270]. The work showed that the bulk CuO phase is reduced under steam reforming conditions to metallic Cu. Additionally, Cu/ZnO interactions had to be accounted for to explain activity observations. Specifically, increased disorder and micro-strain in Cu particles caused by interaction with Zn effected activity, not just Cu surface area. Likewise, for the partial oxidation of methanol Navarro et al. found that reduction of CuO occurred under reaction conditions and led to active catalysts for hydrogen production [250]. Idem and Bakhshi examined oxidized Cu catalysts promoted with various elements for methanol steam reforming [255]. They found that samples activated with the methanol and water reactant mixture were more active than samples reduced with hydrogen. The methanol/water-activated samples contained a higher ratio of Cu^{+1}/Cu^{0} on the surface, just as the more active samples (for the various promoters studied) contained a higher Cu^{+1}/Cu^{0} ratio in post-reaction analysis. This ratio was correlated to a stronger redox ability for Cu in these samples. Besides differences in Cu particle strain and redox ability (which may be related) differences in the Cu surface area after various additions of promoters and treatments could contribute to activity differences. Thermal sintering leading to a loss of Cu surface area is widely known to be the primary cause of deactivation in these catalysts [252, 271]. Varying promoters and pretreatments are also likely to affect Cu surface area via sintering differences.
CHAPTER 9

EXPERIMENTAL METHODS

9.1 Catalyst Preparation

The catalysts were prepared using a co-precipitation technique similar to the one described by Breen and Ross [241]. First, 1.25 M solutions of Cu, Zn, and ZrO nitrates were mixed and then precipitated using 0.25 M Na₂CO₃ added drop wise under vigorous stirring at room temperature, while the pH was maintained at 8.5. For some samples an alternative base was used to carry out the precipitation. After an additional 30 minutes of stirring the precipitate was then washed using suction filtration and 2 L of hot double distilled water to remove Na⁺ and any remaining soluble salts. The precursor was then dried overnight at 100°C, crushed to a fine powder, and calcined. Calcination was carried out in a tube furnace using air or N₂ flowing at 50 sccm. The temperature was ramped from 25°C to the maximum temperature at a rate of 5°C/min. The maximum calcination temperature varied between 350°C and 550°C for different samples and was held constant for 4 hours. If the catalyst was pre-reduced, it was done in situ at 250°C using 5% H₂ in N₂ flowing at 20 sccm for 3 hours before activity testing. Surface area was determined by N₂ physisorption using a Micromeritics ASAP 2010 adsorption instrument.
9.2 Cu Surface Area Measurements

The specific Cu surface area was measured for some selected catalysts by a N$_2$O passivation method, using an in-house constructed system described elsewhere [272]. First, samples were calcined in situ for one hour with 20% O$_2$ in He (50 sccm total flow) at the same calcination temperature used during catalyst preparation. Next, the catalysts were reduced with 5% H$_2$ in N$_2$ while ramping the temperature from 25$^\circ$C to 350$^\circ$C at 5$^\circ$C/min. H$_2$ consumption was monitored with a TCD, and was subsequently used to estimate the copper content of the catalyst by comparing to a pure CuO reference. The temperature was then lowered to 60$^\circ$C and pulses of N$_2$O diluted (< 20%) in He were passed over the sample. The decomposition of N$_2$O to N$_2$ was monitored with the online HP 5890 II GC-MS. The sample then underwent a second reduction up to 350$^\circ$C. The Cu surface area was calculated assuming that CuO was reduced to Cu$^0$ during the first reduction. Additionally, it is assumed that in the proceeding step surface Cu is oxidized to Cu$_2$O at a much faster rate than it is oxidized to CuO or than the subsurface is oxidized. This method must also assume 1.46x10$^{19}$ Cu atoms/m$^2$ to calculate Cu surface area from the amount of N$_2$O adsorbed. All of these assumptions are commonly used by researchers for measuring the Cu surface area of supported samples [273-275].
9.3 X-ray Diffraction

Powder X-ray diffraction patterns were obtained using a Bruker D8 X-ray diffractometer equipped with an HTK 1200 sample holder capable of controlling temperature and atmosphere. The X-ray source was Cu Kα radiation. Diffraction patterns were obtained for all samples after calcination. For selected samples, patterns were obtained during *in situ* calcination and reduction steps. In these experiments the temperature was ramped between measurements at a rate of 5°C/min with a 5-minute pause at each temperature before recording the pattern. Patterns for the pre-cursor to catalyst transition were recorded every 50°C while open to the atmosphere.

To obtain *in situ* H₂ reduction patterns a fresh sample was placed in the sample holder, then, using a vacuum pump, the atmosphere was replaced with 5% H₂ in N₂. The temperature was then ramped under 10 sccm of 5% H₂ in N₂ flow, up to 250°C at 5°C/min and held for 1 hour before taking the pattern. For *in situ* methanol reductions patterns, a fresh sample was placed in the holder, and the atmosphere was replaced with N₂ using a vacuum pump. The temperature was ramped to 250°C at 5°C/min under 10 sccm of N₂ flow. The temperature was held at 250°C for one hour, then a pattern was taken under N₂ flow. Next, 1% methanol flow in N₂ (10 sccm total) was initiated using a diffusion tube. Patterns were obtained after 1 and 2 hours of methanol flow, and for all the samples tested, these patterns were found to match each other. Water and methanol could not be sent to the instrument together because of the potential to produce an explosive mixture inside the instrument.
9.4 Temperature Programmed Desorption

Temperature programmed desorption studies were conducted using the previously described in-house built system with online GC-MS. The sample (100 mg, powder) was placed in a glass U-tube, sandwiched between plugs of silica wool for support. The sample was then cleaned by heating to the calcination temperature of the sample in He flowing at 30 sccm. For blank TPD experiments the temperature was increased from room temperature to 850°C at a rate of 10°C/min while using He as a carrier (flow = 20 sccm). Desorbing species were detected by the GC-MS.

9.5 TGA-DSC of Precursor Decomposition

Thermo-gravimetric analysis with differential scanning calorimetry experiments were conducted using a Setaram TG-DSC111 with the effluent gas connected to an online HP 5890II GC-MS. For the precursor decomposition experiments approximately 20 mg of washed and dried precursor was placed in a quartz crucible and loaded into the TGA-DSC. The temperature was then raised from 25°C to 800°C at a rate of 5°C/min under an approximate He flow of 40 sccm. Changes in weight and heat flow were detected with the TGA-DSC, while the major effluents produced (CO₂, H₂O, and O₂) were detected by the GC-MS.
9.6 TGA-DSC of Catalyst Reduction

Reduction of the catalysts with the reactants was examined using a Seteram TGA-DSC 111 connected to an on-line HP5890II GC/MS. For all tests the instrument was placed in corrosive gas mode, and approximately 20 mg of sample was loaded onto the balance in a quartz crucible. For H₂ reduction experiments, the temperature was raised to 250°C under He flow, and the balance was tared. Then 5% H₂ in N₂ was sent to the sample at 40 sccm while recording TGA and DSC signals for one hour. Next, the same sample was held at 250°C while purging with He flowing at 40 sccm for one hour. Finally, approximately 1% methanol and 1.5% water in He (40 sccm total) was sent to the sample using diffusion tubes for one hour to observe the effects of in situ steam reforming reaction with TGA, DSC, and MS signals. For non-reduced steam reforming experiments a fresh sample was loaded into the instrument, and the temperature was raised to 250°C under 40 sccm of He flow. Then 1% methanol and 1.5% water in He were sent to the sample while the TGA, DSC, and MS signals were recorded for 1 hour. For methanol reduction experiments a fresh sample was loaded into the instrument and the temperature was raised to 250°C under He flow, then 1% methanol in He (40 sccm total) was sent to the sample for one hour while recording TGA, DSC, and GC signals. The sample was then purged with He for one hour while holding at 250°C. Finally, the sample was reoxidized with 1.5% water in He flowing at 40 sccm for 18 hours at 250°C while performing TGA-DSC analysis. In all the experiments water was fed using a humidification bubbler and methanol was fed using a diffusion tube. After each experiment the flow was switched back to He to observe any changes in the baseline.
9.7 XPS Analysis

X-ray photoelectron spectra were recorded using an AXIS Ultra XPS with a Mg anode operating at 14 kV and 10 mA. The powder sample was supported by double-sided carbon tape. For post-reaction and post-reduction experiments the samples were sealed in He at the treatment temperature before being cooled, and loaded into the instrument without ever being exposed to the atmosphere by means of a glove box and a controlled atmosphere transfer chamber. Charge shift corrections were made by assuming a C 1s binding energy of 284.5 eV for the carbon tape.

9.8 Diffuse Reflectance Infrared Fourier Transform Spectroscopy

The surface intermediates formed during in situ reductions and reactions were observed with a Bruker 1600 IR, equipped with a controlled atmosphere sample holder. For all the experiments in which a fresh sample was used, the surface was first cleaned by heating the sample in situ to 250°C under He flow at 40 sccm for 1 hour, then a background spectra was taken at 250°C under He flow. For the H₂ reduced sample, 5% H₂ in N₂ was sent to the sample at 20 sccm while holding the temperature at 250°C for 1 hour, but the spectra in He before the reduction was still used as the background. The H₂ reduced samples were then subjected to a reaction mixture of approximately 1% methanol and 1.5% water (using the same feed system as in TGA experiments) in He flowing at 40 sccm. Spectra were taken every minute for 30 minutes, then every 5 minutes for the next 30 minutes. In one case additional spectra were taken every half
hour for 4 hours. After the reaction was complete, the sample was flushed with He for 30 minutes, then a final spectrum was taken at 250°C. For non-reduced steam reforming experiments, a fresh sample was loaded, and after taking a background, 1% methanol and 1.5% water in He with a total flow of 40 sccm was sent to the sample that was still at 250°C. Similarly to the pre-reduced sample, spectra were taken every minute for 30 minutes, then every 5 minutes for the next 30 minutes, and after 1 hour the sample was flushed with He for 30 minutes, and a final spectrum was taken at 250°C. Methanol reduction experiments were also performed by an identical procedure, with the only difference being 1% methanol in He was used rather than water and methanol.

9.9 Activity Testing

Activity testing was conducted in an in-house constructed reactor system with an on-line HP5890 GC equipped with a TCD and FID for determining product composition. The FID was equipped with a methanizer to allow detection of CO down to 10 ppm. For equal weight testing, 50 mg of the powder catalyst sample was loaded in a 5 mm I.D., 316 SS tube, while for equal surface area tests 4.4 m² of catalyst was used. The reactor tube was then encased in an in-house built furnace. A thermocouple measured the temperature at the bottom of the silica wool that supported the catalyst in the downward flow scheme. For all steam reforming tests the total flow rate was 100 sccm, with a composition of 15.5% methanol, 19.4% water, 36.9% N₂, and the balance Ar carrier. Both N₂ and Ar were bubbled through their respective controlled temperature saturation chamber containing water or methanol in order to achieve the desired feed composition.
Steady-state measurements were taken at least four hours after beginning flow to the reactor, at which point the product composition was stable. Data was taken at 200, 220, 250, and 300°C. Lower temperatures were recorded first, and at least four hours were given to reach steady state between temperature adjustments. For time on stream tests, 50 mg of catalyst was used and the temperature was held steady at 250°C. If the catalyst was pre-reduced it was done in situ at 250°C using 5% H\textsubscript{2} in N\textsubscript{2} flowing at 20 sccm immediately before beginning the reaction. Comparisons between catalysts are made with H\textsubscript{2} yield, defined as the percentage of theoretical H\textsubscript{2} produced based on all the methanol fed being converted to H\textsubscript{2} by the SRM.

9.10 Time-On-Stream Activity Testing

Activity testing was conducted in an in-house constructed reactor system with an on-line HP5890 GC equipped with a TCD and FID for determining product composition. The FID was equipped with a methanizer to allow detection of CO down to 10 ppm. For all deactivation tests 50 mg of the powder catalyst sample was loaded in a 5 mm I.D., 316 SS tube. The reactor tube was then encased in an in-house built furnace. A thermocouple measured the temperature at the bottom of the silica wool that supported the catalyst in the downward flow scheme. If the catalyst was pre-reduced, it was done in situ at 250°C using 5% H\textsubscript{2} in N\textsubscript{2} flowing at 20 sccm for 3 hours before activity testing. For all steam reforming tests the total flow rate was 100 sccm, with a composition of 15.5% methanol, 19.4% water, 36.9% N\textsubscript{2}, and the balance Ar carrier. Measurements of the product composition were taken for up to 48 hours time-on-stream.
CHAPTER 10

RESULTS AND DISCUSSION

10.1 Physical Properties of Catalysts Prepared

A list of the catalysts prepared and the respective preparation parameters and physical properties for each catalyst are reported in Table 21. Parameters that were varied during catalyst preparation included Cu content, Zn:Zr ratio, calcination temperature, base used for precipitation, and addition of aluminum. The addition of zirconia to Cu/Zn had an advantageous effect on surface area, and the addition of a small amount of Al₂O₃ improved surface area even more. These higher surface areas can be attributed to the presence of an amorphous zirconium phase. Aluminum could improve the surface area by stabilizing the amorphous zirconium and by preventing CuO and ZnO sintering during the calcination. Surface area was lost with increasing calcination temperature, while using an alternative base did not affect surface area as long as carbonates were present.
### Table 21: Catalyst naming scheme and preparation conditions for SRM catalysts.

<table>
<thead>
<tr>
<th>Catalyst name</th>
<th>Precursor (mol%)</th>
<th>Base used</th>
<th>Calcination T (°C)</th>
<th>BET S.A. (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Zn (350)</td>
<td>50.0 50.0</td>
<td>Na₂CO₃</td>
<td>350</td>
<td>22</td>
</tr>
<tr>
<td>Cu/Zr (350)</td>
<td>50.0 - 50.0</td>
<td>Na₂CO₃</td>
<td>350</td>
<td>86</td>
</tr>
<tr>
<td>Cu/Zr (550)</td>
<td>50.0 - 50.0</td>
<td>Na₂CO₃</td>
<td>550</td>
<td>43</td>
</tr>
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<td>CZZ-244 (350)</td>
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<td>Na₂CO₃</td>
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<td>75</td>
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<tr>
<td>CZZ-244 (450)</td>
<td>20.0 40.0 40.0</td>
<td>Na₂CO₃</td>
<td>450</td>
<td>66</td>
</tr>
<tr>
<td>CZZ-244 (550)</td>
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<td>Na₂CO₃</td>
<td>550</td>
<td>52</td>
</tr>
<tr>
<td>CZZ-424 (350)</td>
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<td>49</td>
</tr>
<tr>
<td>CZZ-442 (350)</td>
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<td>Na₂CO₃</td>
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<td>58</td>
</tr>
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<td>CZZ-433 (350)</td>
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<td>Na₂CO₃</td>
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<td>89</td>
</tr>
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<td>CZZ-433 KC (350)</td>
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<td>K₂CO₃</td>
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<td>91</td>
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<td>CZZ-433 AmC (350)</td>
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<td>(NH₄)₂CO₃</td>
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<td>88</td>
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<td>CZZ-433 AmOH (350)</td>
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<td>NH₄OH</td>
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<td>68</td>
</tr>
<tr>
<td>CZZ-433 (450)</td>
<td>40.0 30.0 30.0</td>
<td>Na₂CO₃</td>
<td>450</td>
<td>66</td>
</tr>
<tr>
<td>CZZ-433 (550)</td>
<td>40.0 30.0 30.0</td>
<td>Na₂CO₃</td>
<td>550</td>
<td>39</td>
</tr>
<tr>
<td>CZZA-433:0.5 (350)</td>
<td>38.1 28.6 28.6  4.8</td>
<td>Na₂CO₃</td>
<td>350</td>
<td>123</td>
</tr>
<tr>
<td>CZZA-433:1.5 (350)</td>
<td>34.8 26.1 26.1 13.0</td>
<td>Na₂CO₃</td>
<td>350</td>
<td>79</td>
</tr>
<tr>
<td>CZZ-811 (350)</td>
<td>80.0 10.0 10.0</td>
<td>Na₂CO₃</td>
<td>350</td>
<td>44</td>
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</tbody>
</table>

10.2 Reducibility and Cu Surface Area

The addition of ZnO or ZrO₂ lowered the reduction temperature of CuO pronouncedly compared to its pure form, as shown in Figure 98. The reduction peak for CZZ-433 (350) is much sharper and ends at a lower temperature than the other samples possibly because of the better Cu dispersion in this sample. A more detailed analysis of similar materials has been performed by other researchers [242, 257]. Only CuO phase is
reduced to its metallic form under the conditions of the TPR used here. The results of the Cu surface area measurements are shown in

Table 22. The amount of H₂ consumed during the initial reduction was used to determine the CuO weight % assuming that CuO was reduced to Cu⁰. These values were found to be very close to “as prepared” percentages. The measured Cu surface area was generally lower than expected based on the BET surface area and the Cu content of the catalysts. The values reported here are similar to other reports using the same technique [242, 249]. Interestingly, the aluminum containing catalyst had the highest Cu surface area. It is likely that sintering occurred during the initial reduction, thus decreasing the surface areas more for non-alumina catalysts. Sintering is known to be less drastic for samples containing alumina. Therefore, this method of measuring Cu surface area is biased towards samples that are more resistant to sintering during the reduction step, which reaches 350°C. However, since sintering is a major cause of deactivation in Cu catalysts, this is still an effective method for identifying active catalysts that will be more stable. The next highest Cu surface area was for CZZ-433 (350). It should be noted that during N₂O passivation experiments some of the samples, especially those with extremely low measured Cu surface areas, decomposed N₂O to N₂ at a steady rate even after N₂O consumption decreased and leveled out. This slower N₂O decomposition could possibly be attributed to one of three causes: subsurface oxidation, full oxidation to CuO, or oxidation of mass transfer limited regions. Regardless of its source, this decomposition was not used in the calculation of Cu surface area since none of these three causes would correlate to active Cu sites.
Figure 98: Comparison of CuO reducibility in supported and unsupported samples as seen in TPR profiles.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>As prepared CuO (wt%)</th>
<th>CuO (wt%) from TPR</th>
<th>Cu S.A. (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Zn (350)</td>
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<td>38</td>
<td>8.1</td>
</tr>
<tr>
<td>Cu/Zr (350)</td>
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<td>1.2</td>
</tr>
<tr>
<td>CZZ-244 (350)</td>
<td>16</td>
<td>18</td>
<td>5.6</td>
</tr>
<tr>
<td>CZZ-424 (350)</td>
<td>33</td>
<td>26</td>
<td>4.6</td>
</tr>
<tr>
<td>CZZ-433 (350)</td>
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<td>34</td>
<td>10.6</td>
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<td>CZZ-433 (550)</td>
<td>34</td>
<td>35</td>
<td>3.2</td>
</tr>
<tr>
<td>CZZA-433:0.5 (350)</td>
<td>33</td>
<td>27</td>
<td>16.9</td>
</tr>
<tr>
<td>CZZ-442 (350)</td>
<td>36</td>
<td>38</td>
<td>9.0</td>
</tr>
<tr>
<td>CZZ-811 (350)</td>
<td>76</td>
<td>69</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 22: Results from TPR and Cu surface area measurements.
10.3 XRD of Calcined Samples and \textit{in situ} H\textsubscript{2} Reduction

Diffraction patterns were taken during calcination of CZZ-433 (350) and CZZ-244 (350), and reduction of CZZ-433 (350), CZZ-433 (550), CZZ-811 (350) and CZZA-433:0.5 (350). The calcination of CZZ-433 precursor is shown in Figure 99. The corresponding d-spacings and hkl values for the diffraction lines identified using EVA software and the ICDD PDF database are given in Table 23. The diffraction pattern of the initial light blue precipitate was observed to consist mostly of the aurichalcite (Cu,Zn)$_5$(CO$_3$)$_2$(OH)$_6$ phase, along with hydrozincite Zn$_5$(CO$_3$)$_2$(OH)$_6$ and malachite Cu$_2$CO$_3$(OH)$_2$ crystal structures (Figure 99a). Since the most active catalyst was only calcined to 350$^\circ$C, it is interesting to note that the catalyst at this point was mostly amorphous with some crystallinity for the CuO and ZnO phases. This pattern matched the pattern of a sample subjected to a full 4 hours of calcination. As the temperature increased (Figure 99b), so did the crystallinity of CuO and ZnO, and at 500$^\circ$C crystalline ZrO$_2$ began to appear. Initially, ZrO$_2$ formed a possible rhombahedral phase at 500$^\circ$C, but eventually formed tetragonal ZrO$_2$ by 550$^\circ$C. The vertical lines in the figure help illustrate the shift occurring in the ZrO$_2$ pattern during the phase transition. The resulting post-calcined material was a dark brown color. As expected the only significant difference in the precursor to catalyst transition for CZZ-433 (350) and CZZ-244 (350) (not shown) was the intensity of the CuO peaks formed.

All of the post-calcined catalysts contained CuO and ZnO phases except the Cu/Zr samples, which do not contain ZnO. Samples calcined below 500$^\circ$C did not contain any detectable crystalline ZrO$_2$, while those calcined at 550$^\circ$C contained
tetragonal ZrO$_2$. The clearest differences between calcination temperatures are seen for Cu/Zr and Cu/Zr (550), as shown in Figure 100. After calcining at 550°C, Cu/Zr (550) contains tetragonal ZrO$_2$ and larger CuO crystals. Attempts were made to precipitate ZrO$_2$ by itself in order to better characterize the amorphous phase, however, a colloidal suspension formed which could not be washed by suction filtration, and upon drying at 100°C a white amorphous gel formed. TPD and TGA-DSC studies summarized in the next sections offer more insight into the nature of the amorphous zirconia phase in the catalysts calcined at lower temperatures.

Diffraction patterns taken in situ during the reduction process show that reduction of the samples only changes the CuO phase to Cu, with no effect on ZnO or the respective zirconia phase. However, the degree of copper sintering that occurs during the reduction is dependant upon the composition of the sample. Figure 101 and Figure 102 show a comparison of the in situ X-ray diffraction patterns taken during reduction of CZZA-433:0.5 (350), and CZZ-811 (350) respectively, the samples with the highest and lowest measured Cu surface areas, respectively. It is likely that the sintering of CZZ-811 (350) during the reduction is the cause of its low measured Cu surface area. The alumina containing material maintained its low crystallinity after the reduction; however, CZZ-811 (350) showed increased crystallinity with increasing temperatures. It is also interesting that for this sample adding a small amount of ZnO and ZrO$_2$ to CuO still improves reducibility as compared to pure CuO, but does not prevent sintering, showing the dual function of the supports in preventing sintering and improving reducibility of Cu. The reductions of CZZ-433 (350) and CZZ-433 (550) (not shown) were very similar to CZZA-433:0.5, except for the fact CZZ-433 (550) has a much sharper Cu$^+$ peak. This is
because CuO is much more crystalline after calcining at the higher temperature, as was seen during *in situ* XRD calcination. Consequently, because of the higher degree of sintering, CZZ-433 (550) has a much lower Cu surface area than CZZ-433 (350) or CZZA-433:0.5 (350).
Figure 99: In situ X-ray diffraction during calcination of CZZ-433 in air; (a) Precursor to catalyst transition (150–350 °C); (b) Catalyst crystallization (350–600 °C).
<table>
<thead>
<tr>
<th>Phase</th>
<th>d (Å)</th>
<th>2θ</th>
<th>h</th>
<th>k</th>
<th>l</th>
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<td>Monoclinic</td>
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<td>24.05</td>
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<tr>
<td>Zn$<em>3$Cu$</em>{2}$(OH)$_6$(CO$_3$)$_2$</td>
<td>3.262</td>
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<td>1</td>
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<td>Annalcite</td>
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<td>Monoclinic CuO copper oxide</td>
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Table 23: Major peaks in the XRD patterns of identified phases during *in situ* calcination of CZZ-433 precursor.
Figure 100: Comparison of XRD patterns of Cu/Zr samples calcined at different temperatures in air.
Figure 101: *In situ* XRD patterns taken during reduction in 5% H₂ in N₂ for CZZA-433:0.5 (350).
Figure 102: *In situ* XRD patterns taken during reduction in 5% H₂ in N₂ for CZZ-811 (350).
10.4 Temperature Programmed Desorption

Blank temperature programmed desorption experiments were carried out for calcined samples of Cu/Zn (350), Cu/Zr (350), and CZZ-433 (350). All of the samples containing the amorphous zirconia phase first released water over a broad range just above the calcination temperature of 350°C, followed by CO₂ evolution beginning around 500°C, which is approximately the same temperature crystalline ZrO₂ appears during \textit{in situ} calcination. These features are likely the products of the decomposition of carbonates. Cu/Zn (350) released only a small amount of CO₂ in this temperature range indicating that the CO₂ evolution is likely coming about from decomposition of the amorphous zirconia/zirconium carbonate in the zirconia-containing samples. A comparison of CO₂ evolution profiles for the samples is shown in Figure 103. All of the samples released O₂ at high temperatures as Cu oxide begins to decompose. All samples were red/orange in color after the temperature treatment, indicative of metallic copper.
10.5 TGA-DSC of Precursor Calcinations

More insight on the precursor to catalyst transition and the nature of the amorphous zirconia phase can be obtained from TGA-DSC experiments. The products released during an *in situ* calcination (in He) of CZZ-433 precursor are graphed together with the derivative of the weight change with respect to temperature in Figure 104a. Below 350°C, the peak positions for weight change, and CO₂ and H₂O released correlate nicely. The lower temperature peaks at 97°C and 175°C are most likely due to the loss of weakly adsorbed CO₂ and H₂O. Zirconia is known to release CO₂ and H₂O adsorbed
None of the Cu/Zn hydroxy-carbonate species detected by XRD are known to decompose in this low temperature range, however, desorption of H$_2$O and CO$_2$ from these species is also possible in this temperature range. It should be noted that no changes in the XRD pattern were observed below 200°C for a calcination in O$_2$. The peak at 245°C (which has a higher CO$_2$ to H$_2$O ratio) likely originates from decomposition of hydrozincite to ZnO [278, 279]. The large peaks at 333°C can be attributed to the decomposition of aurichalcite, the main phase present in the precursor as detected by XRD [278, 279]. DSC measurements presented in Figure 104b confirm that these decompositions are endothermic, as reported by other researchers [278-280]. Malachite is known to decompose to CuO at 303°C, so the shoulder preceding the aurichalcite peaks may be attributed to a small amount of malachite [278, 279].

Carbon dioxide is released endothermically at 463°C without water. Only one CO$_2$ peak was observed during blank TPD experiments, so this CO$_2$ release may take place at lower temperatures in the presence of O$_2$. All of the possible Cu and/or Zn carbonate containing phases are expected to decompose at lower temperatures [278-281], so this peak may be coming from a phase change in zirconia. The second smaller CO$_2$ peak begins just above 500°C, and reaches a maximum at 607°C. DSC shows a significant exothermic peak in the same region. This could be due to the release of heat from the exothermic crystallization of zirconia [277], but oxidation of carbonaceous species also is a possibility. At higher temperatures more heat is released presumably from sintering, showing how such sintering can be a self-perpetuating effect for these
catalysts. Similar to blank TPD results, O₂ is released near 800°C (not shown) from the reduction of CuO.
Figure 104: TGA-DSC analysis of CZZ-433 precursor decomposition in helium. (a) The derivative of weight change with respect to time and the amount of CO2 and H2O released as a function of temperature. (b) Weight change and heat flow as a function of temperature.
10.6 Steady-State Reaction Experiments

In the results of reaction testing H₂ yield is defined as the percentage of the theoretical H₂ produced based on methanol fed assuming one mole of methanol could react to form three moles of H₂. The SRM reactions were performed using an equal weight of catalyst in the reactor without a pre-reduction step. The amount of CO byproduct produced was always below the detectable limit for the TCD at these conditions, indicating that CO₂ selectivity was always greater than 99.8%. There was always CO detected by the FID using a methanizer, however, the concentrations were more of a function of methanol conversion rather than catalyst. Other researchers have reported trends in CO selectivity when methanol conversion was close to 100% for various catalyst compositions [245]. Methane product concentrations were always below 10 ppm and therefore undetectable. The FID with methanizer did detect small by-product concentrations of formaldehyde, formic acid, and methyl formate for all the samples; however, the concentration for any of these by-products was never more than 500 ppm.

The most active catalysts were prepared with 40-mol% of Cu precursors, and equal amounts of Zn and Zr precursors using a carbonate containing base. This configuration also yielded the highest Cu surface area among non-alumina containing samples. Using the alternative bases did not greatly affect the activity for steam reforming, however, when ammonium hydroxide was used, the resulting catalyst had slightly lower surface area and significantly lower activity (Figure 105a). It is possible that some Cu was lost during filtration due to the formation of the soluble copper amine complex; however, the catalyst prepared with ammonium carbonate still performed quite
well, suggesting that the low activity observed for the catalyst prepared with ammonium hydroxide was not simply due to the interaction of ammonia with copper. Although no Na or K was detected by XPS, it cannot be ruled out that these elements have a promoting effect considering their slightly higher activity. Ultimately, the formation of a hydroxy-carbonate precursor seems to be the key to preparing an active catalyst. It is known for copper-zinc based catalysts for the various reactions of interest that the decomposition of hydroxy-carbonate precipitates leads to high surface area active catalysts in which Cu is well dispersed. Likewise, the formation of such precipitates was observed to be important in this series of catalysts as well.

Varying other pre-treatment conditions had significant effects on activity. The effects of increasing copper content are observed when CZZ-244 (350), CZZ-433 (350), and CZZ-811 (350) are compared (Figure 105b). Likewise, the effect of Zn:Zr ratio is observed when comparing CZZ-433 (350), CZZ-442 (350), and CZZ-424 (350) (Figure 106a). The highest surface area and optimum activity by weight are obtained for CZZ-433 (350), which was also the sample with the highest measured Cu surface area of the group. The addition of aluminum decreased the activity of the sample. Even with its high BET and Cu surface areas, CZZA-433:0.5 (350) did not have better activity for the SRM reaction than CZZ-433 (350) (Figure 106b). Others have reported that Al₂O₃ has an inhibiting effect for the SRM in pre-reduced Cu/ZnO based catalysts [241, 243]. Increasing the calcination temperature decreased activity (Figure 107a) in addition to decreasing surface area and Cu surface area. Interestingly, samples calcined in the absence of oxygen still performed well, presumably because the hydroxy-carbonate precursors decompose to form metal oxides even in an inert atmosphere.
The next most active catalyst on an equal weight basis, after CZZ-433 (350) and its derivatives, was Cu/Zn (350) (Figure 107b), despite the fact that it had an extremely low surface area. Conversely, this catalyst had poor stability and lost activity when the reaction temperature was raised to 300°C. This was most likely due to sintering of the copper. In commercial Cu/ZnO/Al₂O₃ low temperature shift catalysts the addition of aluminum not only increases surface area, but also decreases the rate of such sintering. Copper supported by zirconia maintained a high surface area when calcined at 350°C and had good activity. Zirconia is known to be an effective support for copper for the methanol synthesis reaction, and steam reforming using pre-reduced catalysts, however, for steam reforming of methanol Cu/Zn (350) out performed the Cu/Zr catalysts. Increasing the calcination temperature resulted in a decrease in surface area, but no loss in activity for Cu/Zr (550).

Overall it appears that CZZ-433 (350) is the best catalyst for several reasons. It was prepared with a carbonate base, making the formation of a hydroxy-carbonate precursor possible, which is necessary for optimal activity since such a precipitate puts Cu and Zn in direct contact with one another. Additionally, this composition leads to the highest Cu surface area without the use of Al₂O₃, which would inhibit the reaction. Therefore, the high surface area with a large enough Cu content to yield a high Cu surface area, yet enough ZnO and ZrO₂ to prevent sintering makes for a good SRM catalyst that apparently does not require pre-reduction to obtain good activity.

SRM reaction experiments were also performed by keeping the catalyst surface area in the reactor constant. By normalizing surface area in the reactor, a better idea can be obtained of how catalysts perform on a molecular level. From Figure 108a it is
apparent that CuO mixed with ZnO is the most active catalyst on an equal surface area basis. Unfortunately, this catalyst has a low surface area to begin with, and suffers deactivation presumably due to sintering at increased temperatures, as was seen previously in equal weight measurements. Adding zirconia to Cu/ZnO, as in CZZ-433 (350), seems to provide better resistance to sintering. A comparison of catalysts with different compositions shows that CZZ-433 (350) is still the most active catalyst after Cu/Zn. It is interesting to note that on an equal surface area basis, the CZZ-433 catalysts calcined at different temperatures show the same activity (Figure 108b). Another interesting point about the equal surface area comparisons is that Cu/Zr catalysts become more active when calcined at 550 °C. Methanol synthesis work has shown that copper supported by either a zirconia aerogel or by crystalline zirconia is active for the reverse of the reforming reaction. In fact, Jung and Bell even showed that the level of activity was dependent on which crystalline phase of zirconia was used [236]. Therefore, it is possible that tetragonal ZrO₂ present in Cu/Zr (550) is a more effective support for Cu than amorphous Zr. This would explain why Cu/Zr (550) has the same activity as Cu/Zr (350) on an equal weight basis, despite having lower surface area.

Figure 109a and Figure 109b confirm that CZZ-433 (350) is the optimal composition even on an equal surface area basis, as would be expected by Cu surface area measurements. Intuitively, one may think higher Cu content samples would perform better on an equal surface area basis if Cu is the source of activity; however, characterization showed that CZZ-811 is extremely prone to sintering and has a low Cu surface area. Samples prepared from carbonate bases have approximately the same BET
surface area, and alumina containing samples have a higher surface area than CZZ-433 (350), therefore, equal surface area testing was not performed on these samples.
Figure 105: Steam reforming of methanol reaction testing for unreduced catalysts (catalyst weight = 50 mg) showing effects of: (a) base used for precipitation, and (b) Cu content.
Figure 106: Steam reforming of methanol reaction testing for unreduced catalysts (catalyst weight = 50 mg) showing effects of: (a) Zn:Zr ratio, and (b) addition of alumina.
Figure 107: Steam reforming of methanol reaction testing for unreduced catalysts (catalyst weight = 50 mg) showing effects of: (a) calcination conditions, and (b) composition.
Figure 108: Steam reforming of methanol reaction testing for unreduced catalysts (catalyst surface area = 4.4 m²) showing effects of: (a) composition, and (b) calcination temperature.
Figure 109: Steam reforming of methanol reaction testing for unreduced catalysts (catalyst surface area = 4.4m$^2$) showing effects of: (a) Zn:Zr ratio, and (b) Cu content.
10.7 Time-on-stream Activity Testing

CZZ-433 performed quite differently in time-on-stream tests depending on calcination temperature, pre-reduction with diluted H\textsubscript{2} at 250°C, or with the inclusion of alumina during preparation. When calcined at 350°C, CZZ-433(350) was the best performing SRM catalyst, and performed equally well with or without pre-reduction as shown in Figure 110a. Here, H\textsubscript{2} yield is defined as the moles of hydrogen produced divided by 3 times the moles of methanol fed, since the stoichiometry of the steam reforming reaction is 3 moles of hydrogen per mole of methanol. When calcined at 550°C, the zirconia phase changed from an amorphous carbonate-containing phase to tetragonal, accompanied by a loss in surface area. CZZ-433 (550) did not perform as well for the SRM reaction without pre-reduction as its 350°C counterpart did, but a temporary 2-fold increase could be obtained with a reduction in diluted hydrogen, as Figure 110b shows. This increased activity, however, did not last and after 20 hours on stream, the catalyst performance deteriorated to the same level that was observed for the sample that was not pre-reduced. Interestingly, when a small amount of alumina is added to CZZ-433 (350) a completely different trend is observed. Adding 5% alumina to the same ratio of components (named CZZA-433:0.5) resulted in a catalyst that required pre-reduction with H\textsubscript{2} to obtain an optimal activity that is retained over time. Figure 110c shows the trend seen for the alumina-containing catalyst. We have observed that this dependence on reduction with hydrogen for optimal activity is common for Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} commercial catalysts as well (data not shown).
Figure 110: Time-on-stream activity testing with and without pre-reduction by hydrogen for (a) CZZ-433(350), (b) CZZ-433(550), and (c) CZZA-433:0.5.
10.8 XRD of Reduction Treatments

For Cu-based catalysts using harsher reduction conditions, such as a faster ramp rate or more concentrated hydrogen, is unadvisable since this can decrease catalytic activity because of sintering and loss of Cu surface area. Therefore, we compared sintering effects of different reduction treatments by obtaining XRD patterns during *in situ* reductions. Interestingly, all of the samples had to be re-calcined before performing the experiments because of the apparent reactivity of CuO at atmospheric conditions. Several months after preparation it was observed that CuO peaks eventually vanish from the XRD patterns, while no new phase is apparent and the other metal oxides remain unaffected. A possible explanation of this could be the reaction of CuO with atmospheric water and carbon dioxide to form an amorphous hydroxy-carbonate, which was partially the form of the catalyst precursor. This process is known as the memory effect, and is commonly observed for calcined layered double hydroxides that have been exposed to water and carbon dioxide or aqueous carbonate solutions [282]. Recalcining the samples in oxygen returned them to their initial crystalline form. The three samples examined were CZZ-433(350), CZZ-433(550), and CZZA-433:0.5. Figure 111 shows the *in situ* XRD patterns of samples after calcination, after reduction in 5% H₂ in N₂ at 250°C, and after reduction in 1% methanol at 250°C. The samples all look similar, with the exception of the higher crystallinity and the presence of the tetragonal zirconia phase in the sample calcined at 550°C. Methanol, just like hydrogen, was able to reduce the bulk CuO to Cu° completely in all the samples. The higher intensity and the narrower width of the Cu° (111) diffraction line observed over the methanol-reduced samples clearly
shows that $\text{Cu}^\circ$ sinters more easily when reduced with methanol than with hydrogen. There are two possible explanations for the increased sintering caused by using methanol as a reductant. First, pure methanol could be causing a chemical effect, such as leading to the formation of Cu carbonyls species that facilitate faster sintering of the Cu. A second possibility is a thermal effect in which more heat is being released by using methanol as the reductant compared to hydrogen, as will be discussed in the TGA-DSC results section. It should be pointed out that the methanol was not sent to the sample until the temperature reached 250°C, while 5% $\text{H}_2$ in $\text{N}_2$ was sent to the sample during the temperature ramping. This was done to mimic the time-on-stream activity testing procedure and may have aided sintering during the reduction with methanol. However, for activity testing, a methanol concentration of 15% was used, not 1%, so the sintering may have been even worse for the non-reduced samples tested with time-on-stream, assuming the presence of water does not have a significant effect on the sintering process. Unfortunately, higher methanol concentrations and water together with methanol could not be sent to the XRD sample chamber because of safety concerns. Nonetheless, these experiments show that it is possible for methanol to completely reduce the bulk CuO phase, and to sinter the particles in the process even more so than hydrogen.
Figure 111: XRD patterns after various in situ treatments for (a) CZZ-433(550), (b) CZZ-433(350), and (c) CZZA-433:0.5.
Several experiments were carried out with the TGA-DSC set-up to better characterize the reduction process of the catalysts. All the catalysts showed similar trends, therefore, only the results for one of the catalysts, CZZ-433 (550), is presented in graphical form. This was the catalyst with the largest activity disparity for the non-reduced sample. Any observed differences between samples are noted in the discussion and also reported in Table 24.

In the first experiment, the catalysts were reduced with 5% H\textsubscript{2} in N\textsubscript{2} at 250\textdegree C. The Differential Scanning Calorimetry (DSC) signal shows that the reduction of CZZ-433(550) is fairly fast and exothermic (Figure 112). The total weight loss from the original weight during the reduction is 6.7%. If it is assumed that the only cause of weight change is the reduction of CuO to Cu, then based on the “as prepared” composition, a weight loss of 6.8% is expected, thus matching the measured value within the error of the measurement. The other samples tested, CZZ-433(350), and CZZA-433:0.5, had weight reductions of 7.2% and 6.7% respectively, as shown in Table 24. To obtain the heat released (heat of reduction) in Table 24 the exotherm was integrated and then divided by the amount of CuO in the sample. At 250\textdegree C and atmospheric pressure, the reduction of CuO with hydrogen is expected to be exothermic with a heat of reaction slightly more negative than the experimental values:

\[
\text{CuO} + \text{H}_2 \rightarrow \text{Cu}^0 + \text{H}_2\text{O} \quad \Delta H \text{ at } 250\textdegree C = -85 \text{ kJ/mol}
\]
The endothermic decomposition of hydroxy-carbonates during the reduction, as seen previously for the decomposition of the precursor [246], could account for the lower than expected heat of reduction seen in all the samples. These samples were calcined \textit{ex situ} to mimic the procedure used for activity testing, therefore, some hydroxy-carbonates that can form upon exposure to the atmosphere and decompose above 250°C could still be present. Carbon dioxide formation that was observed during the reduction of the catalysts with hydrogen lends further support to this possibility. This observation will be discussed further in the DRIFTS results section. Interestingly, CZZ-433(350) lost slightly more weight than the other samples and had the lowest heat release during reduction, suggesting that it might contain more hydroxy-carbonates than the other samples.

The reduction was also carried out for CZZ-433 (550) while ramping the temperature at 5°C/min from 25°C up to 300°C (data curves not shown). As shown in Table 24, the same amount of weight was lost, and only 1.5 kJ/mol less heat was released; however, in the ramping experiment it is more difficult to obtain a baseline for the DSC signal and therefore only constant temperature reductions were carried out for all the samples.

Next, the SRM reaction was carried out over the hydrogen-reduced catalysts. The reaction seemed to reach steady state very quickly for all catalysts, as Figure 113 shows for CZZ-433 (550). The reaction products and unreacted feed detected with the GC-MS reached a steady level after 5 minutes (not shown). The DSC signal dropped to an endothermic value for all samples due to the endothermic steam reforming reaction taking place on the sample. The weight of the samples only increased slightly (less than
0.5%) and remained steady for the duration of the hour-long experiment for all samples. This slight weight increase may be caused by intermediates present on the surface. After the reaction the sample was flushed with helium, and the DSC curve returned to the original baseline, while the weight remained slightly higher than the original baseline (about 0.1% for all samples). This could be due to partial reoxidation of the surface during SRM reaction or the presence of some intermediates still on the surface.

The steam reforming reaction was also carried out in the TGA-DSC system over the unreduced sample. The results of this experiment for CZZ-433 (550) are shown in Figure 114a, and the values for weight loss and heat released for all samples are reported in Table 24. The reduction of the bulk of the catalyst, that was seen through XRD when methanol alone was used as the reducing agent, occurs even in the presence of water. The TGA signal shows a loss of 6.4% of the catalyst weight, similar to the weight loss for the reduction with H₂. The DSC signal is also similar to the H₂ reduction signal, but falls to an endothermic baseline rather than to zero. This is because the endothermic steam reforming reaction begins to take place after CuO is reduced. Overall, this reduction occurred faster, but was less exothermic than hydrogen reduction. The other samples had the same trend and shape for the TGA and DSC signals. The products from the reaction, reported by the GC-MS analysis in Figure 114b, shows that more CO₂ and H₂O is being released when the sample is still losing mass, but the CO₂ and H₂O concentrations level out once the mass change subsides. Copper oxide is well known to catalyze the full oxidation of methanol to water and carbon dioxide [245, 265], with the reaction likely depleting the oxygen of the catalyst by the following reaction:
CuO + 1/3 CH₃OH → Cu⁺ + 1/3 CO₂ + 2/3 H₂O  \[\Delta H\] at 250°C = -60 kJ/mol

Per mole of CuO, this reaction is less exothermic than the reduction of CuO with hydrogen. The corresponding values from the integration of the DSC signal agree. However, sintering may cause some of the samples to have a higher heat of reduction, while carbonate/hydroxide decomposition could lower the heat of reduction. Coincidentally, the sample that is most active after reduction with the reactants, CZZ-433 (350), was the sample with the least amount of heat released during the reduction.

During reduction with methanol only, the reaction to CO₂ and H₂O is even more obvious. The DSC signal (shown in Figure 115a) is nearly the same as for steam reforming over a non-reduced sample, although the final baseline is less endothermic. Integration of the DSC curve indicates a more exothermic heat of reduction for the methanol reduction compared to the reduction where water is present as well. Figure 115b shows that CO₂ and H₂O are released only until the weight loss ceases. These trends held true for all three samples tested. With respect to the endothermic baseline, in time-on-stream activity testing the amount of CO produced was below 700 ppm, or a selectivity of CO₂ compared to CO greater than 99.8%. Even in preliminary reaction experiments where pure methanol was sent to a reduced catalyst, the conversion of methanol to CO was less than 1%, so it is unlikely the endothermic baseline is coming from the decomposition of methanol. It is difficult to detect such a small amount of CO with the MS considering the fact methanol, carbon dioxide, and even N₂ contamination have mass fragments at 28 AMU. The slightly endothermic baseline in this case may be coming, for the most part, from imperfect flow balance between the reference and sample.
side, rather than methanol decomposition. In the case where the steam reforming reaction can occur, the endothermic baseline (which is even lower) is likely coming from both the endothermic steam reforming reaction and partially from flow differences.

After one hour the methanol reduced sample was purged with He, then an attempt was made to reoxidize the samples with water vapor at 250°C (shown in Figure 116). Initially, the DSC signal indicated an exothermic spike, perhaps from leftover surface species reacting, although valve changes can cause experimental error in the signal. Then, the weight of the sample began to increase slowly over the next 18 hours. The final weight of the sample indicated it was about 50% reoxidized; however, examination of the sample upon removal from the instrument showed that the top layer was yellowish/green in color, while the layer in the bottom of the crucible was black, indicating the 50% oxidation may have been from uneven oxidation of the sample in the, not necessarily oxidation to Cu$^{+1}$. The weight of the other methanol-reduced samples slowly increased upon water addition in the same manner. It has been discussed in the literature that the oxidation of Cu$^0$ to Cu$^{+1}$ could be part of the reaction mechanism in steam reforming, water-gas shift, and methanol synthesis [255, 257, 270]. Evidently, from these experiments the re-oxidation of the bulk Cu with water is extremely slow compared to the reduction of CuO.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Reduction Atmosphere</th>
<th>Temperature (°C)</th>
<th>% Weight Lost</th>
<th>Heat Released (kJ/mol Cu)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>H₂</td>
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<td>72.8</td>
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<td>64.2</td>
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<td>73.7</td>
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<td>6.5%</td>
<td>63.5</td>
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</tbody>
</table>

**Table 24**: Overview of reduction experiments with TGA-DSC for SRM catalysts.
Figure 112: TGA-DSC signals for the reduction of CZZ-433(550) with 5% H₂ in N₂ at 250°C.

Figure 113: TGA-DSC signals for the *in situ* steam reforming of methanol over pre-reduced CZZ-433(550) at 250°C.
Figure 114: Steam reforming of methanol over non-reduced CZZ-433(550) at 250°C, (a) TGA-DSC signals for \textit{in situ} reaction, and (b) abundance of the products from the experiment detected with on-line mass spectrometer.
Figure 115: Reduction of CZZ-433(550) with methanol at 250°C, (a) TGA-DSC signals for in situ reduction, and (b) abundance of the products from the experiment detected with on-line mass spectrometer.
While XRD and TGA results agree that the bulk CuO phase of the catalysts is fully reduced, these techniques do not give any indication of the extent of reduction on the surface. Additionally, the same treatment conditions used for activity testing could not be used for these techniques because of instrument limitations. Therefore, XPS analysis was performed on all three catalysts after three different treatments. In the first treatment the catalysts were reduced with 5% H$_2$ in N$_2$ while ramping the temperature at 5°C/min up to 250°C, the second was with 15.5% methanol in He while holding at 250°C, and the third was with 15.5% methanol and 19.4% water in He at 250°C. These

Figure 116: TGA-DSC signals for the re-oxidation of methanol reduced CZZ-433(550) with water at 250°C.

10.10 XPS Analysis
conditions are identical to the conditions used for time-on-stream activity testing. The results of this analysis in terms of metal compositions on the surface and binding energies are presented in Table 25, with results from the calcined catalysts also shown for comparison. The trends seen in activity testing show some correlation to the copper surface concentration measured by XPS. When the catalysts are reduced carefully with H₂, the Cu surface area decreases slightly on a metal basis with the exception of the alumina-containing sample, which remains about the same. Alumina is well-known to reduce sintering of Cu during the reduction process because of strong interaction between Cu and surface Al [283]. However, the reduction of the catalysts in methanol cuts the Cu surface composition at least in half for all samples. Reduction of the catalysts with the water and methanol was not as harsh as methanol only, but the total Cu surface composition was still less than what was seen after hydrogen reduction. The catalyst calcined at 350°C seemed to fare the best after reduction with the reactants in terms of both Cu surface composition and activity. On the other hand, the differences in Cu surface composition between the various reduction methods for the samples alone do not appear to be extreme enough to account for the observed differences in activity.

The Cu 2p regions for samples that have been reduced by methanol, shown in Figure 117, and the for samples that have been reduced by the reaction mixture, shown in Figure 118, were both fit to a single peak. For all the samples the binding energy of this peak was close to, or slightly higher than, the binding energy for the corresponding sample reduced with hydrogen. It is possible to fit the peaks in Figure 117 and Figure 118 with a higher binding energy shoulder, as was done by Agrell et al. for similar samples after being exposed to a methanol and oxygen mixture. It is possible that there
are Cu⁺¹ species on the surface, since these species typically overlap the region where Cu⁰ species are present in Cu 2p XPS analysis. A detailed analysis of the Cu LMM region, which is not performed here, is necessary to differentiate between Cu⁰ and Cu⁺¹. Other researchers who have performed analysis of the Auger electron spectra have detected both oxidation states of Cu in reduced catalysts [284-286]. In their analysis of hydrogen reduced Cu/ZnO methanol synthesis catalysts, Okamoto et al. attributed the Cu⁰ phase to larger metallic Cu⁰ crystallites, and the Cu⁺¹ phase was assigned to a two dimensional Cu phase on ZnO that is derived from Cu dissolved in the ZnO lattice [284]. This may explain the slightly higher binding energies of some of the samples, and the possible higher binding energy shoulders. However, due to the absence of satellite peaks in the Cu 2p region, it can be definitively concluded that there are no Cu²⁺ species on the surface.

Generally, the surface coverage of Zn increased after reduction of CuO with any choice of reactant (see Table 25). Although the binding energies only changed slightly, they were consistently higher after reduction with the reactants. This trend holds true for post-reaction samples subjected to pre-reduction with hydrogen as well [246]. The Zn 2p region of CZZ-433 (550) after various treatments is shown in Figure 119, and in each case one peak provided a reasonable fit.

There was no consistent trend with regards to Zr surface composition of the catalysts. Interestingly though, the binding energy of the Zr 3d electron increased after reduction in any atmosphere for all the samples. Figure 120 shows the Zr 3d XPS spectra for CZZ-433(550). Others have used a two peak deconvolution to fit to the Zr 3d region in similar oxidized catalysts [287]. The reduced samples have spectra similar in shape to
the oxidized sample, however, the hydrogen reduced sample has the sharpest peaks. It is possible that various surface species are creating the broader spectra in the other samples. The adsorption of methanol and carbon dioxide on zirconia, as already discussed in the introduction, could lead to changes in the electron density surrounding Zr atoms.

For CZZA-433:0.5, a disproportionately large amount of alumina was found on the surface. A large enrichment of the surface with alumina has been reported for samples containing even less alumina as well [245, 283]. The alumina surface composition and binding energy decreased with reduction of CuO. There was no evidence of copper aluminate (in the Cu or Al spectra) from XPS, although others have detected this component by other means in similar catalysts [253, 283]. The Al 2p spectrum (not shown) is partially overlapped by the Cu 3p peak, therefore, deconvolution had to be used to get a rough quantitative measure of the alumina peak area.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Region</th>
<th>B.E. (eV)</th>
<th>Coverage</th>
<th>Surface Coverage</th>
</tr>
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<tbody>
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<td>CZZA-433 (550)</td>
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<td>Cu 2p&lt;sub&gt;3/2&lt;/sub&gt;</td>
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<td>18.1%</td>
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<td></td>
<td>Zn 2p&lt;sub&gt;3/2&lt;/sub&gt;</td>
<td>1022.2</td>
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<td>7.0%</td>
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<td>5.7%</td>
</tr>
<tr>
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<td>Cu 2p&lt;sub&gt;3/2&lt;/sub&gt;</td>
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<td>17.5%</td>
<td>6.5%</td>
</tr>
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<td>8.0%</td>
<td>3.9%</td>
</tr>
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<td>Al 2p</td>
<td>75.3</td>
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Table 25: Overview of post reduction XPS analysis for SRM catalysts.

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Figure 117: Cu 2p XPS spectra of samples after reduction with methanol.

Figure 118: Cu 2p XPS spectra of samples after reduction with the methanol and water reactant mixture.
Figure 119: XPS spectra of Zn 2p region for CZZ-433(550) after various pre-treatments.

Figure 120: XPS spectra of Zr 3d region for CZZ-433 (550) after various pre-treatments.
The surface reactions occurring over these catalysts during the reduction and reaction can be analyzed with diffuse reflectance FT-IR spectroscopy to uncover more details on the catalysts surface during various treatments. A limited amount of work has been performed to study the methanol reforming reactions using this technique [242, 263]; however, significant work has been carried out to study methanol synthesis on Cu-based catalysts [236, 259-261, 288-293]. This has helped the development of mechanistic models for steam reforming, the reverse of the methanol synthesis reaction. The experiments that were run on the samples while recording DRIFTS spectra mirrored the experiments run with the other characterization techniques in this study to allow for comparison of results.

In the first experiment, the catalysts were reduced with hydrogen to observe what changes occur in the IR spectrum of the surface. The results obtained after flushing with He are shown in Figure 121. The reduction caused broad valleys in the spectra near 1500 and 1379 cm\(^{-1}\). These valleys are likely from the loss of leftover carbonate species from the precipitation that were not removed during the calcination. It is also possible that such species formed from exposure to CO\(_2\) in the atmosphere. Monodentate carbonate is known to have bands consistent with the valleys observed, and has been reported to be a stable species on similar materials [269, 290, 293]. Although copper-oxygen bonds are expected to disappear during the reduction as well, these bands are not expected to be in this region [294]. Carbon dioxide peaks at 2359 cm\(^{-1}\) and 2327 cm\(^{-1}\) (not shown) were observed in the early stages of the reduction of the samples, evidence that a carbon
species was being reduced. Some loss of hydroxide species is also apparent in the spectra, with a consistent valley at 3656 cm\(^{-1}\). At higher wavenumbers, however, there is an apparent increase in intensity, which may indicate changes in the hydroxide region due to water formation.

Reduction with methanol was shown to have the same effect as hydrogen by XRD, TGA, and XPS, although methanol seemed to sinter the catalysts more. The DRIFTS spectra in Figure 122 show however, that the IR spectra of the methanol treated surfaces differ from the post-reduction with hydrogen spectra. The valleys at 3656, 1500 and 1379 cm\(^{-1}\) are still present, but leftover species from the reduction remained on the surface even after the He flushing. The bands for these species are labeled in Figure 122, and they match the bands for intermediate species often reported for the methanol synthesis and steam reforming reactions [242, 263]. Table 26 reports the identified stable intermediate species along with their band assignments. The first step in steam reforming is thought to be the adsorption of methanol to form a methoxy group. A plausible route for methoxy formation is the reaction of methanol with hydroxyl surface groups to form water and methoxy. The valleys in the hydroxyl region are consistent with this. Duprez et al. observed methanol adsorption on zirconia via this mechanism, and it is likely that other metal oxides could adsorb methanol in a similar manner [261]. It is also possible for methanol to adsorb onto Cu and Cu oxide surfaces, leading to the formation of methoxy groups [295-298]. Methoxy C-O stretching was observed at 1047 cm\(^{-1}\), and the C-H stretching bands were seen at 2821 cm\(^{-1}\) (symmetric), and 2926 cm\(^{-1}\) (asymmetric) on all the samples. Upon removal of a hydrogen atom, the methoxy species can form formaldehyde, which was possibly observed at 1148 cm\(^{-1}\). Some researchers believe this
band belongs to a bridging methoxy species, which is another possible assignment [299]. Furthermore, formaldehyde is not expected to be very strongly bonded to copper and generally reacts quickly at this temperature over Cu-based materials, whereas methoxy is known to be more stable [290, 292, 298]. However, several works have attributed this band as belonging to $\pi$-bonded formaldehyde [242, 293], and both possible species have C-H stretching bands reported to be near the methoxy C-H bands, so neither possibility can be positively ruled out. Before forming CO$_2$, the reactants are believed to pass through a formate intermediate. Formate bands were apparent at 1357 cm$^{-1}$, 1600 cm$^{-1}$, 2871 cm$^{-1}$, and 2961 cm$^{-1}$. The formate band at 1357 cm$^{-1}$ partially covers the valley believed to be from the removal of carbonates. Methanol synthesis work would suggest that these species are present on the zirconia or zinc oxide phases. However, since copper was oxidized prior to the introduction of methanol, these species could be present on Cu as well. In an earlier study by Wachs and Madix, it was shown that methanol adsorbs onto oxidized copper and decomposes to formaldehyde and formate while reducing Cu at the same time [298].

In the next series of experiments, methanol and water were sent to the oxidized catalysts at 250$^\circ$C. In this series of experiments there were significant differences between the samples, unlike the previous experiments. The same intermediate species that were leftover from methanol reduction can be seen on the samples during methanol steam reforming, with the methoxy species having a stronger presence during the steam reforming, as Figure 123a-c show. Additionally, gas phase or weakly adsorbed carbon dioxide bands are observed at 2327 cm$^{-1}$ and 2359 cm$^{-1}$. After flushing with helium the intermediate bands subside and the carbon dioxide bands disappear, although the
apparently more stable formate bands remain on the alumina containing sample, as shown in Figure 124. The post-reduction spectra also show that after reduction with the reactants, two of the catalysts do not have the large valley in the carbonate region. This could explain the oxidized Cu species observed in XPS when the samples were reduced with methanol and water, but not after the hydrogen or methanol-only reductions. However, the valley does look like it is starting to form for CZZ-433(350). Interestingly this catalyst also had an apparent abundance of hydroxides above the 3656 cm\(^{-1}\) valley that was not present for the other samples after reduction with methanol or methanol and water, but was present for all samples after reduction with hydrogen.

There are additional features in the FT-IR spectra that are worth noting when the sample is reduced with methanol and water (Figure 124). Interestingly, the alumina-containing sample has a unique band at 2095 cm\(^{-1}\), believed to belong to adsorbed carbon monoxide. However, the most interesting difference between the samples is the fact that the intermediates, with the exception of CO\(_2\), decline after half an hour on CZZ-433(350), while they remain steady on the other two samples. During actual reaction experiments the concentrations of methanol and water are higher, so these transitions likely occurred more quickly (before the first product sampling) in the activity experiments. It should again be pointed out that the CZZ-433(350) was also the only sample that performed equally with or without pre-reduction by hydrogen.

In the final series of experiments the samples were pre-reduced with hydrogen before the steam reforming reaction was initiated. On all the samples the intensities of the suggested intermediates were insignificant compared to the intensity of CO\(_2\), as Figure 125a-c shows. Taking into account the results just reported for non-reduced CZZ-
433(350) it is apparent that catalysts which give the best performance do not have a significant build up of the intermediate species (or maybe spectator species) observed on unreduced CZZA-433:0.5 and CZZ-433(550) samples. Additionally, the “activated” catalysts have a valley in the carbonate region, and a surplus of hydroxides above the 3656 cm⁻¹ valley. After several hours of treatment, CZZ-433(550) catalyst did not have any significant differences in the DRIFTS spectra (not shown) compared to the spectra after 30 minutes of reaction.

There are several possible explanations for these observations. First, more active samples form more CO₂ as a product, so the CO₂ peak would be expected to be more intense, although probably not to the extent observed. If this were the case then sintering effects could explain differences in Cu surface area and activity. Results from XPS after various treatments indicated a correlation between Cu surface area and activity. However, the differences were not as extreme as the activity differences. A second possibility is that different rate limiting steps could be controlling the reaction on different catalysts. The build-up of intermediate species would, in that case, be the result of a bottle-neck effect on the less active catalysts. If the mechanism proceeds through the spillover of a species this could explain why samples with better Cu dispersion might have a different rate controlling step. Third, despite the fact that the bulk CuO phase of all the catalysts can be reduced by methanol, it is possible that part of the surface is being left in an inactive state for some samples treated with the reaction mixture and that the assumed intermediates are just bystander species that are building up on these inactive sites. Finally, it is possible that multiple steady-states exist on these samples and the state reached depends on the surface species present when the reaction is initiated. In the case
of hydrogen reduced samples carbonates are cleaned from the sample and hydrogen is built up on the support creating the most active catalyst. Only the high Cu surface area CZZ-433(350) appears to be able reach this state with or without pre-reduction with hydrogen, perhaps because of differences in surface composition, while the other samples remain in a less active steady state unless pre-reduced with hydrogen.

**Figure 121**: DRIFTS spectra of samples after reduction with hydrogen at 250°C.
Figure 122: DRIFTS spectra of samples after reduction with methanol at 250°C.

Table 26: Surface species identified by DRIFTS.

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Vibration</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
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<td>M-OCH₃</td>
<td>ν(C-O)</td>
<td>1047</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>ν(C-H)ₘ</td>
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<td>bridging methoxy</td>
<td>M₂-OCH₃</td>
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<td>formaldehyde</td>
<td>π-bonded CH₂O</td>
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<tr>
<td></td>
<td></td>
<td>ν(C-H)</td>
<td>2961</td>
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</table>
Figure 123: DRIFTS spectra of *in situ* steam reforming of methanol over non-reduced samples (a) CZZ-433(550), (b) CZZ-433(350), and (c) CZZA-433:0.5.
Figure 124: DRIFTS spectra of samples after reduction with methanol and water at 250°C.
Figure 125: DRIFTS spectra of *in situ* steam reforming of methanol over hydrogen pre-reduced samples (a) CZZ-433(550), (b) CZZ-433(350), and (c) CZZA-433:0.5.
CHAPTER 11

CONCLUSIONS

Characterization of the zirconia-containing Cu/ZnO based catalysts showed that the catalysts calcined at 350°C consisted of CuO, ZnO, and a high surface area amorphous zirconia phase. This amorphous phase releases CO₂ upon its crystallization to a lower surface area tetragonal ZrO₂ phase at temperatures near 500°C.

Reaction testing showed that pre-reduction is not necessary to activate these catalysts and only provides temporary improved activity in the case of non-alumina samples. In accord with previous studies on pre-reduced zirconia-containing Cu/ZnO SRM catalysts, the most active non-reduced catalysts contained the high surface area amorphous zirconium phase and an optimal amount of CuO and ZnO to allow for high Cu surface area. From Cu surface area results it can be rationalized that this catalyst has good resistance to sintering compared to the poor performing samples. Although alumina increased Cu surface area, it had an apparently negative effect on SRM activity for non-reduced samples.

In general, characterization showed that the bulk CuO phase in all catalysts was reduced by the reactant mixture, similarly to a hydrogen reduction. However, reduction with methanol caused additional sintering and loss of Cu surface area compared to
reduction with hydrogen. If water was present in the feed, the exothermicity of the reduction and the loss of Cu surface area during the reduction was less significant for all samples.

Evidence suggests that hydroxide and carbonates are removed from the surface of the catalysts during reduction with hydrogen. The removal of these species appears to be essential for better activity. The only sample that had identical activity with or without pre-reduction was also the only sample in which hydroxide and carbonate species were removed during reduction with methanol and water as well as with hydrogen. Moreover, this sample had the least exothermic reduction, and the highest mass loss during different reduction treatments. Several possibilities were discussed to explain these observations. Overall, these insights will contribute to a better understanding and design of catalytic systems for mobile methanol steam reforming to hydrogen.


115. Faubert, G., Côté, R., Dodelet, J.P., Lefèvre, M., Bertrand, P., *Oxygen reduction catalysts for polymer electrolyte fuel cells from the pyrolysis of FeII acetate*


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APPENDIX

Sample Calculations
To measure the weight gain of a sample during pyrolysis, the weight loss that occurs during the initial temperature ramp was measured for each support. This was done in an inert atmosphere for each sample using a TGA, the value was recorded as “percentage of weight loss from TGA”. Then the following values were recorded before and after the pyrolysis:

1. Mass of empty boat = A
2. Mass of boat plus precursor/support = B
3. Mass of boat and sample after the pyrolysis = C

The weight gain was then calculated using the following equation:

\[
\% \text{ weight gain} = \frac{(C - B) + (\% \text{ lost from TGA} \times (B - A))}{C - A}
\]
To measure the conductivity of a sample, the powder sample is pressed between two copper plates creating a pellet of known dimensions. The voltage is swept from 0.0 to 0.1 V, and the final current is reported, measured by a potentiostat. The conductivity can then be calculated as follows:

\[
R_{\text{absolute}} = \left( \frac{0.1 \text{ V}}{\text{(final current in Amps)}} \right) - R_{\text{Cu plates}} \quad [\text{=}] \quad \text{Ohms}
\]

where \( R_{\text{Cu plates}} = 0.307 \text{ Ohms} \)

\[
R_{\text{intrinsic}} = R_{\text{absolute}} \times \text{Cross Sectional Area} / \text{Length} \quad [\text{=}] \quad \text{Ohms} \times \text{cm}
\]

Where:

\[\text{Cross Sectional Area} = \pi \times (0.325 \text{ cm})^2\]

\[\text{Length} = 0.015 \text{ cm}\]

\[
\text{Conductivity} = \frac{(100 \text{ cm} / 1 \text{ m})}{R_{\text{intrinsic}}} \quad [\text{=}] \quad \text{S} / \text{m}
\]