Synthesis, characterization, and performance of graphene nanoflakes as a non-noble metal catalyst in polymer electrolyte membrane fuel cells

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Abstract

One of the goals in catalyst research for proton exchange membrane fuel cells (PEMFCs) is to find a cost-efficient alternative to platinum. Due to sluggish kinetics, the major requirement of the platinum comes from the catalyst layer used for the oxygen reduction reaction (ORR). Functionalized carbon nanomaterials present themselves as good candidates for the replacement of platinum due to their low cost, excellent electrical conductivity, and chemical resistance to acidic and basic environments. In this work, graphene nanoflakes (GNFs), which are nanopowders consisting of stacked graphene sheets, were used to support atomic iron as a non-noble metal catalyst.

In the first stage of the study the iron-based catalyst was synthesized. Synthesis steps include the production of GNFs in methane plasma, adsorption of ferric acetate, and pyrolysis in ammonia-rich atmosphere. The catalyst structure was characterized at various stages throughout the synthesis steps and it was found that 0.28 atomic percent of iron could successfully be incorporated onto the surface. However, the synthesis method employed caused a general decrease to all calculated crystallinity parameters: purity decreased by 28%, crystallite size decreased by a factor of 2, and the average length of graphene plane decreased by a factor of 4. Characterization was also performed on the catalyst layer after it had been exposed to the PEMFC environment, revealing that the crystallinity parameters actually improved with respect to exposure time: after 100 hours purity increased by 32%, crystallite size increased by 25%, and the average length
of graphene plane increased by 107%. Exposure to the PEMFC environment repairs the damage done to the original GNFs during the synthesis steps.

The synthesized catalyst was used in the catalyst layer for the ORR of a PEMFC with a 1 cm$^2$ active surface. A current of 150 mA/cm$^2$ was observed at an applied voltage of 0.5 Volts with a catalyst loading of 1 mg. When the current is normalized with respect to the amount of metal present, the result of 11.8 A/mg of metal catalyst from the present catalyst out-performs most platinum-based catalysts being used in industry; current platinum catalyst have values ranging from 3 to 14 A/mg of platinum. In stability experiments, no losses were observed at the end of 100-hours long experiments performed at an applied voltage of 0.5 Volts. This represents a great improvement over comparable iron-based catalysts, which show a 45% loss under identical test conditions. The increased stability of the catalyst support structure demonstrates the advantage of the high crystallinity and large crystalline lengths of the GNFs in comparison to other commercial carbon blacks.
Abrégé

Un des objectifs de la recherche sur les catalyseurs pour les piles à combustible à membrane électrolyte polymérique (PCMEP) est de trouver une alternative moins coûteuse au platine. En raison d'une cinétique lente, le platine est surtout utilisé dans la couche de catalyseur au niveau de la cathode pour la réaction de réduction de l'oxygène (RRO). Les nanomatériaux de carbone fonctionnalisés se présentent comme de bons candidats pour le remplacement du platine en raison de leur faible coût, d'une excellente conductivité électrique et d'une résistance chimique aux milieux acides et basiques. Dans ce travail, les nanoflocons de graphène (NFG) constitués en moyenne d'une dixaine de plans de graphène empilées, ont été utilisés comme support aux atomes de fer pour créer un catalyseur métallique non noble.

Lors d'une première étape, le catalyseur à base de fer a été synthétisé. Les étapes de synthèse comprennent la production des NFG dans le plasma de méthane, l'adsorption de l'acétate ferrique, et la pyrolyse dans une atmosphère riche en ammoniac. La structure du catalyseur a été caractérisée tout au long des étapes de synthèse, et il a été constaté qu'un pourcentage de 0,28 % en atomes de fer ont été incorporé aux structures NFG. Cependant, la méthode de synthèse utilisée a provoqué une baisse générale de tous les paramètres cristallins calculés: la pureté a diminué de 28%, la taille des cristaux a diminué d'un facteur 2, et la taille moyenne des plans de graphène d'un facteur 4. La caractérisation a été également effectuée sur la couche de catalyseur après avoir été exposée à l'environnement PCMEP, révélant que les paramètres cristallins sont effectivement améliorés avec
la durée d'exposition. Au bout de 100 heures, la pureté a augmenté de 32%, la taille des cristallites de 25%, et la taille moyenne des plans de graphène de 107%.

L'exposition à l'environnement de PCMEP a réduit les dommages causés aux NFG pendant les étapes de synthèse.

Le catalyseur synthétisé a été utilisé pour la RRO dans un PCMEP avec une surface active de 1 cm². Un courant de 150 mA/cm² a été observé pour une tension appliquée de 0,5 volts et une masse de catalyseur de 1 mg. Lorsque le courant est normalisé par rapport à la quantité de métal présent, le résultat de 11,8 A/mg de métal surpasse les catalyseurs à base de platine les plus utilisés dans l'industrie. Les catalyseurs au platine ont des valeurs allant de 3 à 14 A/mg de platine. Dans les expériences de stabilité, pour une tension appliquée de 0,5 Volts, aucune perte de courant n'a été observée à la fin des 100 heures de l'expérience. Cela représente une grande amélioration par rapport aux autres catalyseurs à base de fer, qui montrent une perte de 45% dans des conditions expérimentales identiques. La stabilité accrue de la structure du catalyseur démontre l'avantage d'utiliser des NFG par rapport à d'autres nanomatériaux de carbone, grâce à leurs cristallinité élevée et leurs grandes longueurs cristallines.
1 Introduction

Energy production and consumption are vital to human existence. Most energy sources are non-renewable and lead to emissions harmful to the atmosphere. As society becomes more aware of its carbon footprint, more attention is being given to suitable clean energy technologies such as hydroelectricity, biomass, solar energy, wind energy, and fuel cells; this research project focuses on the latter of these sources and developing a catalyst to aid in the commercial development.

A polymer electrolyte membrane (also referred to as proton exchange membrane) fuel cell (PEMFC) is an energy conversion device with no moving parts that converts chemical energy to electricity. The PEMFC requires hydrogen and oxygen as gases. Relying on hydrogen as a fuel source is extremely advantageous since hydrogen is the most abundant element on the earth; hydrogen is most often found in nature to be combined with other elements and locked into compounds. The disadvantage to using hydrogen is low energy density. PEMFCs have high power densities and operate at relatively low temperatures (60°C to 80°C), making them a great choice for portable, stationary, and automotive applications. Currently, the catalyst used in PEMFCs is exclusively platinum, an expensive metal found in low abundance. Platinum and its alloys are the currently preferred catalyst material in industry due to their high catalytic activity and resistance towards corrosion in acidic media.

In order for PEMFCs to completely replace batteries and even the internal combustion engine, production costs must be significantly reduced. When
production is scaled-up, the majority of the production costs can be associated with the catalyst ink. One way to reduce production costs is to develop a corrosion resistant non-noble metal substitute to the platinum-based catalysts currently being used. Functionalized carbon nanomaterials, because of their excellent electrical conductivity and chemical resistance in acidic and basic media, have already been acknowledged as a potential alternative.

In the work published by Pristavita et al. in 2011, carbon black powders composed of layers of graphene sheets were produced. The powders, referred to as graphene nanoflakes (GNFs), were functionalized to achieve nitrogen sites that can be used to coordinate iron and form catalytic sites. The present research stems from that previous work and now focuses on the synthesis, characterization, and performance of an iron based non-noble metal catalyst from the graphene nanoflakes. The characterization seeks to determine the evolution of the catalyst over time, not only in the synthesis steps, but also after exposure to the PEMFC environment. The performance of the catalyst is observed through stability experiments in a PEMFC.
2 Background
2.1 Fuel cells

A fuel cell is an electrochemical galvanic cell that converts chemical energy into electrical energy. Although seen as a developing technology, the fuel cell has a long and rich history. In 1839, William Grove was contemplating the electrolysis process (separating hydrogen and oxygen atoms from water using electricity) when he had the idea to reverse the electrolytic process (combine oxygen and hydrogen) to generate electricity [1]. He was successful in creating a fuel cell, which he called a ‘gas battery’, by inserting two platinum electrodes in a sulphuric acid and water solution. In 1889, Ludwig Mond and Charles Langer elaborated on Grove’s work by implementing an additional clay barrier soaked in sulphuric acid. Mond and Langer are also credited with coining the term ‘fuel cell’ [1]. In 1937, Francis Bacon used nickel gauze electrodes for his fuel cell; this research was used in NASA’s Apollo space program [2]. Since the 1980s, fuel cell development has been growing steadily as they are seen as the future replacement of the internal combustion engine and batteries for portable power sources. Fuel cells have little to no emissions and are very quiet.

A fuel cell is classified by its electrolyte, the electrically conductive substance containing free ions. There are five generally accepted groups of fuel cells: alkaline fuel cells (AFCs), molten carbonate fuel cells (MCFCs), solid oxide fuel cells (SOFCs), phosphoric acid fuel cells (PAFCs), and polymer electrolyte membrane fuel cells (PEMFCs) [1-3]. Figure 2-1 shows a comparison of the different fuel cell types.
2.1.1 Alkaline fuel cells (AFCs)

The electrolyte in an AFC is potassium hydroxide, an aqueous alkaline solution, retained in an asbestos matrix. The electrocatalyst is sintered nickel electrodes with a platinum metal catalyst. For AFCs, there is a positive correlation between the operating temperature of the cell and the concentration of the electrolyte solution, i.e. a higher temperature requires a higher concentration. AFCs can run at room temperature and are the cheapest of the fuel cells to manufacture. When compared to other fuel cell types, AFCs have the highest voltage for a given current density and therefore, have the highest efficiency. The major drawback of AFCs is that the source of oxygen must be free of carbon dioxide because the
alkaline solution will react with this compound and be converted to potassium carbonate [3], thus damaging the fuel cell. This means that air cannot be used directly as a fuel without some pre-treatment to remove the carbon dioxide.

2.1.2 Molten carbonate fuel cells (MCFCs)

MCFCs rely on an electrolyte of alkali carbonates (lithium, sodium, or potassium) retained on a lithium aluminate matrix. The cathode material is usually nickel oxide and the anode is a nickel or aluminum alloy. They are classified as a high-temperature fuel cell with operating temperatures above 600°C [2]. The cost of the catalyst is less when compared to other fuel cell types since non-precious metals can be used. The overall cost is still high however, as high temperatures and high-pressures are needed to obtain high efficiencies, necessitating a complex gas delivery system. Contrary to AFCs, MCFCs have the ability to use carbon dioxide as a fuel source. MCFCs are finding applications in natural gas and coal-based power plants. The problem with MCFCs is that since they operate at such high temperatures, the breakdown of the fuel cell components is accelerated.

2.1.3 Solid oxide fuel cells (SOFCs)

The electrolyte in a SOFC is a layer of ceramic (usually a mixture of yttrium oxide and zirconium oxide) that can conduct oxygen ions, [3]. The cathode material is a praseodymium-zirconium dioxide/ tin oxide/ indium oxide alloy and the anode is made of yttria-stabilized zirconia material. Like MCFCs, SOFCs operate at high temperatures ranging from 500°C to 1000°C [2], implying that they too require inexpensive metals for catalysts. For SOFCs to be commercially
viable, progress must be made in reducing start-up time and lowering production costs. Because of the high temperatures needed for obtaining the conductivity of the solid electrolyte, the SOFC systems typically target stationary and medium power (typically 100kW and higher) applications.

2.1.4 Phosphoric acid fuel cells (PAFCs)

As the name implies, PAFCs have an immobilised liquid phosphoric acid electrolyte retained on a silicon carbide matrix. The electrocatalyst used is platinum on both the anode and cathode. PAFCs operate at temperatures of 150°C to 220°C [2]. The manufacturing costs of PAFCs are high due to the platinum catalyst cost. The disadvantages of this fuel cell type range from catalyst degradation to electrolyte migration and material corrosion. There is also a start-up problem because the melting point of phosphoric acid is 42.35°C, making PAFCs only useful for stationary applications such as electricity generators.

2.1.5 Polymer electrolyte membrane fuel cells (PEMFCs)

PEMFCs require an ion exchange membrane that conducts protons between the electrodes, but is an insulator for electrons while also preventing fuel gases from permeating through the membrane. The most common membrane used is perfluorosulfonated acid polymer (Nafion™) [5]. A platinum catalyst is used on both electrodes. The operating temperature for these fuels cells is from 50°C to 100°C [2]. This low temperature range in comparison to other fuel cells types, in addition to its smaller size, makes PEMFCs ideal for mobile applications and it’s being developed particularly for the automotive sector. The development of
PEMFCs has been hindered by its high production costs. Research is being done to decrease catalyst costs by finding a cost-efficient replacement for platinum. One of the leading candidates is a carbon-nitrogen-iron catalyst [6-14].

Direct methanol fuel cells (DMFCs) are considered a sub-category of PEMFCs, with the only difference being that they use methanol instead of hydrogen as a fuel. A polymer membrane acts as the electrolyte for a DMFC. The electrocatalyst used is platinum and ruthenium mixture. This type of fuel cell can operate in a temperature range of 60°C to 130°C [2]. Their efficiency is quite low and they release carbon dioxide as a by-product.
2.2 PEMFC anatomy

The PEMFC relies on the principle of reverse electrolysis with hydrogen and oxygen as fuels. A PEMFC is made up of the electrolyte membrane, catalyst layers, gas diffusion layers (GDLs), bipolar plates with fuel canals, current collectors, and end plates (Figure 2-2). The bipolar plates are conductive polymers, usually a carbon-filled composite, that act as the anode and cathode for the fuel cell stack.

As indicated earlier, the electrolyte membrane has high ionic conductivity and selectivity, is an electronic insulator, and also has mechanical, chemical, and heat...
stability. The thickness of the membrane is generally between 50-175 μm.[5]. The membrane is squeezed between the two catalyst layers, which are usually multicomponent metal composites based on platinum on a carbon support structure. The role of the catalyst layer is to catalyze hydrogen oxidation on the anode side and oxygen reduction on the cathode side. The catalyst layer must have high electrochemical activity, high poison tolerance, corrosion stability, and mechanical and heat stability. Another requirement of the catalyst is to have a large surface area per unit volume; catalyst nanoparticles are therefore used and fixed onto carbon substrate particles [6, 10, 11].

A structural objective for the catalyst layer is to maximize the surface area available for catalytic activity, while maintaining a uniform distribution on the carbon. This resulted in the use of nanostructured platinum and carbon supports, with attempts to reduce the agglomeration of the platinum particles that eventually decrease activity [8, 10, 11]. For every square centimetre of catalyst area, about 0.1 to 0.5 mg of platinum is needed. For the carbon support, carbon powders with high mesoporous areas are used. The following methods are used to deposit the catalyst onto the carbon support: decaling, electrophoretic deposition, evaporation, painting, screen printing, spraying, spreading, and sputtering [16].
2.3 PEMFC reaction pathway

At the anode, the platinum catalyst oxidizes hydrogen forming hydrogen ions and two electrons. The electrons leave the anode, travel through an external circuit (where they can be used to do electrical work), and then reach the cathode. Meanwhile, the hydrogen ions pass through the polymer electrolyte membrane. The incoming oxygen at the cathode reacts with the hydrogen ions and the two electrons from the external circuit and forms water. When referenced to the standard hydrogen electrode, the electrochemical reactions that take place (Equations 2-1 and 2-2) ideally generate 1.229 Volts of electric potential (open circuit voltage) per mole of hydrogen (Equation 2-3)[1].

\[ H_2 \rightarrow 2H^+ + 2e^- = 0 \text{ V} \]

**Equation 2-1. Anodic reaction**

\[ \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O = 1.229V \]

**Equation 2-2. Cathodic reaction**

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O = 1.229V \]

**Equation 2-3. Overall reaction**

Equation 2-2 shows the oxygen reduction reaction (ORR), which is the more problematic reaction. It has slow reaction kinetics and peroxide as an undesirable reactionary intermediate that degrades the electrode and lowers the cell voltage. The majority of the required platinum in a PEMFC stack therefore goes towards the cathode and the ORR, which is why it is targeted when developing new PEMFC catalysts.
2.4 PEMFC catalyst

2.4.1 Performance of platinum catalyst

As first mentioned in Section 2.1.5, the current catalyst for PEMFCs is platinum. The current benchmark for the cathode electrocatalysts is achieving performance losses that are less than 40% of the beginning-of-life activity for over 5000 hours of operation [17, 18]. The catalytic activities and platinum masses for some commercial platinum cathodes are presented in Table 2-1 [11, 12, 14, 19]. In this table, the values are normalized to the geometric surface area of the cathode-electrolyte-anode assembly carrying a current.

<table>
<thead>
<tr>
<th>Commercial Name</th>
<th>Catalyst Loading (mg Pt/cm²)</th>
<th>Current at 0.5 V (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 wt% Pt ELAT electrode from E-TEK</td>
<td>0.04 - 0.05</td>
<td>0.63</td>
</tr>
<tr>
<td>5 wt% Pt from E-TEK</td>
<td>0.1 - 0.12</td>
<td>0.93</td>
</tr>
<tr>
<td>Gore Primea MEA 5510 Cleo</td>
<td>0.3</td>
<td>&gt;1</td>
</tr>
<tr>
<td>Gore PRIMEA MEA 5510</td>
<td>0.4</td>
<td>&gt; 1.5</td>
</tr>
</tbody>
</table>

Table 2-1. Benchmark activities of commercial platinum cathodes

2.4.2 Cost of platinum catalyst

In a study conducted by Directed Technologies Inc., the manufacturing costs of PEMFCs at different production rates were examined [20]. The main categories that contribute to the stack component cost are: membranes, gas diffusion layers (GDLs), bipolar plates, catalyst ink, membrane electrode assembly (MEA) frame and gaskets, coolant and end gaskets, and endplates. The MEA is the stacking of the GDLs and the catalyst layers on either side of the membrane. The study concluded that at a production rate of 1,000 units, 72% of the cost could be attributed to the gas diffusion layer, the Nafion™ membrane, and the catalyst
(with the assumption that the catalyst was platinum on a carbon support). However, when a production rate of 500,000 units was considered, it was found that the costs of the diffusion layer and the membrane could be decreased with respect to the total cost, while the price of the catalyst could not because of the economics of platinum (Figure 2-3) [21]. This study, coupled with the generally increasing price of platinum (due to its limited availability), are indications that for PEMFCs to become commercially viable, a new catalyst material must be developed. This new material must have the required stability and activity to completely replace platinum as the PEMFC catalyst. Many possible candidates have been suggested over the years: transition metal oxides, transition metal carbides, cobalt, and iron.

![Figure 2-3. Stack component cost distribution](image)

2.4.3 Iron-based catalysts

The path to an iron-based catalyst started almost 50 years ago. In 1964, Jasinsky showed that cobalt phthalocyanine (Figure 2-4) displays a high activity for the oxygen reduction reaction (the cathodic reaction in a PEMFC) in alkaline
electrolytes [22]. Most recently, carbon black powder and iron acetate were pyrolyzed by Lefèvre et al. in an ammonia-rich atmosphere to produce a catalyst for the oxygen reduction reaction in a PEMFC [12]. The catalyst being considered in this work is based on these findings with the iron at the catalyst site being made available at the atomic level and the carbon support being a carbon nanopowder with nitrogen functionalization. This structure is discussed in Section 2.5.

![Figure 2-4. Cobalt phthalocyanine [23]](image-url)
2.5 Graphene nanoflakes (GNFs)

Graphene nanopowders are a great candidate for the catalyst support because of their electrical conductivity, chemical resistance in acidic and basic media, and high surface area. The active catalytic sites on graphene are iron atoms bounded to specific nitrogen atoms. From the work of Jaouen [9], it is known that the nitrogen bonding must be pyridinic for the iron to have the proper coordination with the nitrogen. This active site is very similar to heme (Figure 2-5), an iron porphryin structure found in the hemoglobin of blood. Ideally, the carbon nanopowder support should have a large amount of pyridinic nitrogen on the surface to promote the creation of catalytic sites.

![Heme structure](image)

**Figure 2-5. Heme structure [24]**

Graphene nanoflakes (GNFs) are a type of nanopowder that is compiled of graphene sheets. They can be produced by plasma decomposition of a carbon-containing feedstock, such as methane. By using a plasma process, pure graphene nanoflakes can be produced without generating carbon dioxide and while only generating trace amounts of impurities. Additionally, since the graphene is at high temperatures within the plasma system, it is possible to obtain a high degree of crystallinity, which is desirable for this application in relation to the stability.
requirements. The structure of the graphene nanoflakes has numerous edges that allow nitrogen functionalization. When graphene nanoflakes are functionalized with pure nitrogen gas, the result is nitrogen bonded to the surface of the graphene sheets. It was found that nitrogen incorporates itself, but does not affect the morphology of the GNFs. The graphene nanoflake production method developed by Pristavita [13] showed a limit as to how much nitrogen could be added; simply increasing the nitrogen flow rate or exposure time did not increase the amount of functionalized nitrogen. Obtaining more nitrogen sites on the graphene planes should yield an overall higher catalytic activity.

Nitrogen can bond to the surface in one of three ways: pyridinic bond, pyrrole bond, and the substituted quaternary bond. To obtain the active site, the nitrogen must be pyridinic. Knowing that graphene sheets can present one of two types of edges (an ‘armchair’ edge and a ‘zig-zag’ edge) and assuming that iron has a coordination number of 4, a hypothesis of potential active sites can be made (Figure 2-6). Having these hypothetical active site structures allows the calculation of the total maximum number of active sites that could be on the edge of the catalyst structure (refer to Appendix 1).
Graphene nanoflakes will be used because of their ability to attach pyridinic nitrogen to the surface and their high crystallinity, but that is not their most important characteristic. The main reason for their selection as the carbon support is because of the fact that they are composed uniquely of graphene sheets. Catalyst stability has already been linked to high crystallinity, but recent findings have also determined that the number of graphene sheets also plays a role [26]. The combination of a carbon support that has the highest reported degree of crystallinity in addition to a large number of graphene sheets is expected to produce a stable catalyst which also has a potential of enabling a larger number of atomically dispersed catalytic sites and thus enhancing catalytic activity.
3 Objectives

In order for PEMFCs to become commercially viable, a cost effective alternative to the platinum catalyst must be found. This alternative must be able to meet the current benchmarks of the platinum catalyst. The first objective of this work is to produce the nitrogen functionalized GNFs using the method developed by Pristavita and then incorporate the atomic iron to the nitrogen sites on the GNFs to form iron-nitrogen-GNF functionalized structures. This structure will then be dispersed on the gas diffusion electrode and applied to a standard PEMFC porous membrane support along with Nafton™ and integrated into a PEMFC stack.

The second objective is to characterize the iron-nitrogen-GNF structure at the different synthesis stages. The following will be investigated: number of graphene layers, sample morphology and particle size, graphitic content, and elemental surface composition.

The third objective is to evaluate the performance of this catalyst in a PEMFC environment. A fuel cell test bench must be built to perform fuel cell experiments. The activity (current generated at a specific PEMFC voltage) will be measured and the evolution in time of this activity will provide information on the catalyst stability in the PEMFC environment.

Finally, the fourth objective is to provide new knowledge on the evolution of the iron-nitrogen-GNF catalyst structure in time during PEMFC operation. This is similar to the second objective, with the structure here being the iron-nitrogen-
GNF structure coated in Nafion™ that has been exposed to the PEMFC environment.
4 Materials and methods
4.1 GNF growth with nitrogen functionalization

The procedure developed by R. Pristavita was used to produce functionalized carbon nanoflakes [27]. This method relies on plasma decomposition with methane as the carbon source and nitrogen as the functionalization gas. The equipment and procedures were already in place from R. Pristavita’s work: an inductively coupled thermal plasma (ICP) torch (TEKNA PL-35 model; 35kW power) and a radio frequency (RF) generator (Lepel; 60 kW power/2-5 MHz frequencies). The torch is attached to a custom built conical water-cooled reactor. The conical water-cooled reactor has a length of 50 cm and a full angle expansion of 14° (Figure 4-1). The conical reactor gives better results than a cylindrical reactor because the geometry allows a gradual gas expansion and minimizes recirculation areas while also providing a symmetrical flow pattern within the reactor chamber.

![Figure 4-1. Schematic of conical water-cooled reactor [25]](image-url)
As the name implies, an ICP torch relies on the principle of inductance to generate a plasma. A confinement tube in which the plasma is generated is wrapped on the inside of three to four turns of water-cooled copper coil. The RF magnetic field generated in the central gas induces currents that heat up a gas and creates a thermal plasma in the temperature range of 5,000 K to 12,000 K. There are three gas ports to the torch system: central, sheath, and injection. The injection probe is inserted into the torch so that the tip of the probe is just below the first copper coil turn; this ensures that injection occurs in the core of the plasma [27]. The methane and nitrogen are directed to the injection port, whereas argon is fed to the central, carrier, and sheath gas ports. The GNF structures are formed through homogenous nucleation of atomic carbon in a very specific temperature/flow filed within the reactor. Once formed, the presence of nitrogen ions and exited nitrogen species enable nitrogen functionalization to occur on the GNF structures during their transport to the collection sites [13, 25]. The GNF structures generated in this system have on average approximately 10 graphene layers with an observed range of 5 to 20 and sheet extensions between 50 to 100 nanometers [13, 25].

For the graphene nanoflakes used in this work, a 20 kW argon plasma was produced at a pressure of 8 psia. When the plasma was stable, methane and nitrogen were injected at flowrates of 1 and 0.1 standard litres per minute respectively. The injection time for these two gases varied from 15 to 25 minutes. The final graphene nanoflakes used for synthesis in the present work was a blend of three batches, all prepared under the same parameters (refer to Section 5.1).
4.2 Catalyst synthesis

The iron inclusion method established by Jaouen et al. [8] for carbon soot materials is applied here to add the iron to the nitrogen-GNF structure. This procedure is based on a series of mixing and thermal processed described in the rest of Section 4.2. An agreement to collaborate with the Institut National de la Recherche Scientifique (INRS) was reached at the beginning of this work which allowed the synthesis of the catalyst to be performed with the equipment at their facility.

4.2.1 Adsorption

Ferric acetate ($C_{14}H_{27}Fe_3O_{18}$) was chosen as an iron source. It is well known that the ligands on the iron centre of the salt can be substituted with other ligands (Figure 4-2). The ligand of interest for this work would be pyridine, or more specifically, the pyridinic nitrogen on the surface of the graphene nanoflakes. An adsorption step is used so that the graphene nanoflakes can take in the iron from the iron acetate salt.

In a beaker containing 75 mL of water and 25 mL of ethanol, 500 mg of phenanthroline ($C_{12}H_{18}N_2$), a heterocyclic compound made up of carbon and nitrogen, was added and mixed with a magnetic stir rod for 5 minutes. In the original work by Jaoeun et al., their starting carbon material did not have nitrogen so the phenanthroline (Figure 4-3) acted as the nitrogen source for their catalyst structure and was mixed in with the water-ethanol solvent before the adsorption step [8]. Since the GNFs in this work already had nitrogen functionalization, the
use of the phenanthroline was redundant, but was included nonetheless since the iron inclusion method was being precisely duplicated.

![Ferric acetate](image)

Figure 4-2. Ferric acetate [28]

![Phenanthroline](image)

Figure 4-3. Phenanthroline [29]

A 1% by weight proportion was chosen for the iron acetate, which equalled 32 mg. The solution was again mixed for 5 minutes. 500 mg of graphene nanoflakes, the same amount used for phenanthroline, was added to the solution. This solution was mixed for 2 hours. After mixing, the beaker was transferred to an oven and heated to 95°C for 24 hours. This was done so that all the liquid would evaporate and leave only a solid sample. The dried sample was then collected off the beaker walls.
4.2.2 Ball milling

Jaouen et al. originally performed a ball milling step because they believed that the key to forming iron active sites was to form a micro-sphere that would contain their original carbon soot, the nitrogen from the phenanthroline, and the iron from the ferric acetate [8]. Following with their method, a planetary ball mill with a grinding jar of approximately 100 mL attached to a rotating circular stand was used to ball mill the iron-nitrogen-GNF sample. The grinding jar rotates in one direction while the main stand rotates in the opposite direction at a different speed, thus mimicking a planetary system. In a nitrogen glove box (i.e. absence of oxygen) the grinding jar was filled with the carbon support sample collected at the end of the absorption step and 20 quarter-inch diameter chrome steel balls (the grinding medium). The sample was ball milled for 3 hours at 400 rpm.

4.2.3 Pyrolysis

Through pyrolysis, the chemical composition and physical phase of the graphene nanoflakes can be irreversibly changed to incorporate the atomic iron. Pyrolysis is essentially the thermochemical decomposition of organic material at elevated temperatures without the participation of oxygen. A two-stage pyrolysis was used for the synthesis of the catalyst.

Pyrolysis took place in a quartz tube installed in a hinged split tube furnace with a 40 cm long heating zone [9]. The powder sample was put in a test tube and placed inside the quartz tube so that it was outside the heating zone. A magnetic rod was also placed right before the test tube. The tube was purged with argon gas at 1
standard litre per minute (slpm) for 30 minutes, at which point the oven was set to a temperature of 1050°C for 2 hours. After this time, using another magnet, 3 equal movements (with 15-second pauses in between) were made to bring the sample to the center of the furnace. The sample was left in the center for 1 hour. Once complete, the furnace was turned off and the tube was left to cool naturally. This completed the first pyrolysis.

For the second pyrolysis, the sample was loaded differently. Instead of putting the sample in a test tube, the powder was now spread evenly and uniformly over a quartz boat (usually no more than 100 mg can be placed, which might necessitate several batches to complete what was prepared in just one batch in the first pyrolysis stage). Similar to the first pyrolysis, the quartz boat was placed in the quartz tube outside of the heating zone along with a magnetic rod manipulator and purged with argon gas at 1 slpm for 30 minutes. The furnace temperature for this second pyrolysis was set to a slightly lower value of 950°C. After 100 minutes, ammonia gas was introduced at a flow rate of 2 slpm for 20 minutes. Once 20 minutes had passed, the sample was brought to the center of the furnace using the same method as the first pyrolysis. The sample was left in the center with ammonia gas still flowing for 5 more minutes. Once complete, the gas flow and heating were shut off and the tube was left to cool naturally. This completed the second pyrolysis.

In summary, when considering only the time in which the sample is in the heating zone, the first pyrolysis is 1 hour of argon gas at 1050°C and the second pyrolysis is 5 minutes of ammonia gas at 950°C.
4.3 Catalyst ink preparation

The catalyst layer for the PEMFC was prepared as an ink and deposited onto a Teflon™ treated carbon cloth (ElectroChem, Inc.); Teflon™ is hydrophobic and helps for the water removal process following the cathodic reaction process, improving the catalyst structure availability for the ORR. The ink formulation contained the catalyst, water, ethanol, and Nafion™ 5 wt% solution; the 5% refers to the concentration in a mixture of lower aliphatic alcohols and water. Nafion™ is a perfluorosulfonated acid polymer that was developed by DuPont (Figure 4-4). It provides a good electrical path for the hydrogen ions from the nafion electrolyte to the catalyst. Nafion™ will also be used as the membrane in the fuel cell, to be described in more detail in Section 4.4.

![Figure 4-4. Nafion™ structure [30]](image)

The important factor in the ink formulation is the Nafion™-to-catalyst ratio. From previous findings by Proietti et al.[31], a ratio of 1.5 produced the best results and was chosen for the ink formulation. Using this ratio, a batch of 10 mg of catalyst required 344 μL of Nafion™ 5 wt% solution, 172 μL of ethanol, and 161 μL of water [12]. To assure perfect solubility, the solution goes through a 4-step
sequence of 30 minutes of ultrasonic mixing, 15 minutes of vortex mixing, 15
minutes of ultrasonic mixing, and finally 5 minutes of vortex mixing. To help the
mixing, 5-10 solid glass beads having 3 mm in diameter were added to the mixing
vials.

To achieve a cathode catalyst loading of 1 mg/cm$^2$, 67.7 $\mu$L of catalyst ink is
required for 1 cm$^2$ piece of carbon cloth. With a micropipette, the ink was
deposited on the carbon cloth that was being heated to 80°C on a hot plate. Once
deposited, the cloth was transferred to a vacuum oven and left to dry at 80°C for
an hour.
4.4 Membrane electrode assembly (MEA)

The membrane chosen was Nafion™ 117, which has a thickness of 183 μm. Nafion™ has high ionic conductivity, is an electronic insulator, and has mechanical, chemical, and heat stability. The membrane electrode assembly (MEA) is a stacking of components composed in sequence of the cathode gas diffusion layer, the cathode catalyst layer, the membrane, the anode catalyst layer, and the anode gas diffusion layer (see Figure 2.2). The ink deposited on the carbon cloth was used on the cathode side for the ORR reaction. For the anode, the catalyst used was a 1 mg/cm² platinum loading, 20 weight percent platinum/Vulcan XC-72 electrode (ElectroChem, Inc.).

Before preparing the MEAs, the Nafion™ membranes had to be cleaned and prepared. Cleaning the membranes require exposing them to three different solutions for 1 hour each. For each solution, 400 mL was prepared.

- Solution 1: Boiling Water plus 3 % peroxide solution.
  - This solution was prepared by mixing 21.8 mL of 50% peroxide solution with 378.2 mL of water. The solution was heated on a hot plate in a fume hood until boiling.

- Solution 2: Boiling Water plus 1.2 Mol sulfuric acid solution.
  - This solution was prepared by mixing 26.7 mL of 18 molar sulfuric acid with 373.3 mL of water. The solution was heated on a hot plate in a fume hood until boiling.

- Solution 3: Boiling Water
- 400 mL of water, heated on a hot plate until boiling. Membranes were left inside for 1 hour.

Once the membrane was cleaned, the MEA could be prepared by hot pressing the catalyst layers to either side of the membrane. A thin layer of the Nafion™ 5 wt% solution was applied to the anode and cathode sides that were to be in contact with the catalyst layers; this was done to help with bonding. The membrane and catalyst layers were then placed between 2 copper plates of 7 cm by 7 cm. The copper structure was placed in a hot press and the plate temperatures were set to 140°C; this temperature was chosen because it is 5°C above the glass transition temperature of Nafion™. The structure then experienced 3300 psi of pressure for 1 minute; these variables arise from experiments that determined what was needed to assure that the catalyst layers remained on the membrane.
4.5 Analysis techniques

4.5.1 Raman spectroscopy

Raman spectroscopy allows the identification of bond types by their molecular bond energies and orientation [32]. Monochromatic radiation is exposed to the sample and radiation is reflected or absorbed; a small fraction of the incident light scatters due to interactions with molecular bonds and excitation levels. The difference in energies between the incident radiation and the Raman scattering is referred to as the Raman shift and is directly related to the molecular bond energies [33]. By comparing the intensity of scattered light to the Raman shift, a Raman spectrum can be created and the bonds present in the sample can be determined. The Raman instrument used in the present project was an inVia Reflex confocal micro-Raman (Renishaw) with a laser emitting at a wavelength of 514.5 nm. All peak intensities and areas were measured using the Wire 2.0 software.

For carbon samples, three important peaks are investigated on the Raman spectra (Figure 4-5). To gain information on the graphitic content of the sample, the G peak, located in the 1500 cm\(^{-1}\) to 1600 cm\(^{-1}\) range, is observed [34, 35]. The D peak provides a measure for non-graphitized carbon (impurities, amorphous carbon, pentagon rings) and is found in the 1250 cm\(^{-1}\) to 1355 cm\(^{-1}\) range [34, 36]. The G’ peak is located in the 2650 cm\(^{-1}\) to 2750 cm\(^{-1}\) range and becomes sharper and intensifies as the number of graphene layers increases (Figure 4-6). This peak is typically important for the present graphene nanoflakes since these are
composed of 5 to 20 layers of highly crystalline graphene, a large number for graphene-based structures [37].

![Figure 4-5. Polarized Raman Spectra [35]](image)

Figure 4-5. Polarized Raman Spectra [35]

![Figure 4-6. Raman Spectra of G’ Peak [37]](image)

Figure 4-6. Raman Spectra of G’ Peak [37]

From the peaks on the Raman spectra, the overall intensity and the area under the peak can be measured. With these variables, certain graphitic indices can be calculated to help characterize the carbon material.

For a measure of the purity of the sample, the ratio of the intensity of the G peak with respect to the intensity of the D peak is observed. The intensity of the G peak
is an indication of the impurity content; low intensity of the G peak corresponds to low graphitization, in other words a less ordered structure as the amount of impurities increases [38, 39]. Another parameter that can obtained is the crystallite size, $L_a$, which is the in-plane dimension of uniform graphite structures [32, 34, 40-43] (Figure 4-7). The last parameter that was evaluated is the average length of the graphene plane (or crystallites) including distortions, $L_{eq}$ [44]. This last value is particularly important as the GNFs were shown to have an exceptionally high $L_{eq}$ value (up to approximately 40 nanometers) compared to all other carbon based nanoparticles, making it a special class of carbon material. The Raman parameters are summarized in Table 4-1.

![Figure 4-7. Schematic of distorted graphene plane [44]](image)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Indicator</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity</td>
<td>N/A</td>
<td>$\frac{I_G}{I_D}$</td>
</tr>
<tr>
<td>Crystallite Size</td>
<td>$L_a$</td>
<td>$4.44 \frac{A_G}{A_D}$</td>
</tr>
<tr>
<td>Average Length of Graphene Plane</td>
<td>$L_{eq}$</td>
<td>$8.8 \frac{A_{G'}}{A_D}$</td>
</tr>
</tbody>
</table>

Table 4-1. Characterization parameters for Raman spectroscopy [44]
4.5.2 X-ray photoelectron spectroscopy (XPS)

XPS is used to determine the elemental composition of surfaces up to 10 nm in depth, as well as identifying surface contaminants. The surface of the sample is exposed to a monochromatic x-ray under ultra-high vacuum and the kinetic energy and intensity of the emitted electrons are measured [32, 45-47]. By comparing the number of detected electrons to their kinetic energies, a XPS spectrum can be created. Since every element produces a unique spectrum, an analysis of the peak positions can determine the empirical formula and chemical structure of the sample.

The catalyst is primarily composed of carbon, nitrogen, oxygen, and iron. Each element is associated with an energy range on the spectrum; therefore a peak present within a given range is an indication of the presence of its corresponding element. The overall area under the peak is a measure of the atomic percent that element represents of all the surface elements. Each elemental peak is made up of specific bond types, so a de-convolution must be done. The peak position of these bond types can be found in the literature or from the National Institute of Standards and Technology (NIST) database.

When manipulating the XPS, the user determines the energy range and the number of scans needed. To begin analysis on an unknown sample, a general ‘survey spectrum’ is performed using a large beam energy (100 eV) over a large energy range of the photoelectrons (0-1200 eV); this scan rapidly shows which elements are present. Once the elements are determined, scans over smaller
energy ranges are performed at a smaller beam energy (20 eV). The number of 
scans needed for a particular range is reduced with stronger signals as the signal 
to noise ratio is higher.

All measurements were performed on an ESCALAB MKII at 300 W (20 mA and 
15 kV). The radiation source was Aluminum, which has an X-ray source energy 
of 1486.6 eV. The Avantage 3.7 software was used for spectra analysis with the 
peak widths determined by references specific to the instrument. Table 4–2 
summarizes the parameters used for the identification and de-convolution of the 
peaks.

<table>
<thead>
<tr>
<th>Element</th>
<th>Range (eV)</th>
<th>Peak Width (eV)</th>
<th>Number of Scans</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>275 – 305</td>
<td>1.6</td>
<td>~ 30</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>395 – 411</td>
<td>1.7</td>
<td>~ 80</td>
</tr>
<tr>
<td>Oxygen</td>
<td>525 – 545</td>
<td>1.8</td>
<td>~ 30</td>
</tr>
<tr>
<td>Iron</td>
<td>701 – 745</td>
<td>2.32 – 4</td>
<td>~ 200</td>
</tr>
<tr>
<td>Fluorine</td>
<td>678 – 698</td>
<td>1.73</td>
<td>~ 15</td>
</tr>
<tr>
<td>Sulfur</td>
<td>152 – 180</td>
<td>1.75</td>
<td>~ 100</td>
</tr>
</tbody>
</table>

Table 4-2. Summary of de-convolution parameters

4.5.3 Scanning electron microscopy (SEM)

SEM is a qualitative tool that provides high-resolution images allowing the 
observation of sample morphology and particle size [48]. A high-energy beam of 
electrons scans the sample surface in a raster scan pattern (scanning one line from 
left to right, and then jumping to the next scan line, similar to reading text). The 
interactions between the electrons and the sample surface provide signals. These 
signals are processed and allow images to be generated at the nanometre level. In
the analysis of the catalyst, SEM will be used to verify the possibility of structural changes of the GNFs throughout experimentation [13].

All SEM images were captured on a Hitachi S-4700 Field Emission Scanning Electron Microscope. The conditions used for all images were 5 kV accelerating voltage and 10 µA beam current.

4.5.4 Transmission electron microscopy (TEM)

In TEM as for SEM, magnetic lenses form a high voltage electron beam that is emitted by a cathode [48, 49]. The TEM beam however is transmitted through a very thin specimen; the result of this interaction for the electrons transmitted through the specimen provides a high-resolution image. TEM allows imaging at the atomic level, meaning dislocations, grain boundaries, and sub-nanoscale morphologies can be examined as well as nano-particle shapes and sizes. All TEM images in the present project were captured on a Philips CM200 equipped with a field emission gun (FEG-TEM).
4.6 Fuel cell test bench

A fuel cell test bench was constructed in the lab inside a fume hood. Gas cylinders containing hydrogen, oxygen, and nitrogen are attached to wall mounts outside of the fume hood. The gas delivery lines throughout the system are a combination of flexible stainless steel hoses and hollow stainless steel tubes. The exiting lines from the regulators of the gas cylinders are set up so that nitrogen can flow in either or both lines using switch valves; hydrogen and oxygen can only flow into their specific lines. Nitrogen is used in the start-up of experiments and when temperatures are reached, hydrogen and oxygen are introduced into the system.

The fuel cell test bench is controlled using a LabVIEW™ program; a schematic of the control scheme used during fuel cell operation is shown in Figure 4-8. The line leaving either the oxygen or hydrogen cylinder leads to a flow controller (F₁C and F₂C) with the set point entered into a LabVIEW™ program. On the exit of the hydrogen flow controller is a flame arrestor valve, put as a safety measure for the fuel gas. Each line then goes towards its individual humidity vessel. The humidity vessels are 14.5 cm tall with a 9 cm diameter with 5 in/out ports on the top. One port holds a stainless steel tube with a sparger at the end inside the vessel; the tube extends all the way to the bottom of the vessel. Other ports include a gas exit and a release valve (that also serves as an entry for water). The last two ports have thermocouples to measure the water temperature (T₆T and T₇T) and the exiting gas temperature (T₁T and T₂T).
Upon exiting from the humidity vessel, the gas is directed towards the fuel cell. The fuel cell is a 1 cm$^2$ PEMFC with a serpentine flow pattern, attached heaters, fittings, current collectors, and gaskets (ElectroChem, Inc.). The hydrogen enters on the anode side and the oxygen on the cathode side. The entrance to the electrode is the top port with the exit on the bottom port. A thermocouple is placed right before the entrance to the fuel cell to measure the temperature of the incoming gas ($T_3$ and $T_4$). As the gas exits the fuel cell, it passes through a back-pressure regulator and then a condenser. From the condenser, the gas goes to the exhaust of the fume hood.

The outside of the humidity vessel and the flexible stainless steel hose between the humidity vessel and the fuel cell are covered with heating tape. All temperatures are recorded with a data acquisition card that runs in conjunction with the LabVIEW™ program. The temperature setpoint maintains all gas temperatures at 80°C. Additionally, the fuel cell has built-in heating cartridges on each side and with the use of a thermocouple ($T_5$), the fuel cell can be kept at 80°C as well.
Figure 4-8. Control scheme for fuel cell test bench
4.7 Thermal shock treatment

To remove the catalyst layer from the membrane once it has been exposed to the fuel cell environment, a thermal shock treatment is used. The MEA from the fuel cell is inserted in a liquid dewar containing liquid nitrogen for five minutes; time experiments were conducted to determine a suitable exposure time. Differential thermal expansion allows a separation of the catalyst film from the membrane. The MEA is then removed and tweezers were used to peel and separate the catalyst layer off of the membrane.
5 Results and discussion

Section 5 is divided into four parts, beginning with the results showing the validity in mixing batches of graphene nanoflakes production in order to accumulate a large amount of sample for use in the catalyst synthesis route. The subsequent section shows the analyses of the catalyst structure at four different stages throughout the catalyst synthesis route: the analysis techniques used are XPS, Raman, SEM, and TEM. The fuel cell performance result, specifically the stability test of the catalyst on the cathode side of a PEMFC, follows. Lastly, the analyses of the cathodic carbon cloths retrieved from PEMFC tests are presented.

5.1 Graphene nanoflake batch mixing

In the method used to produce graphene nanoflakes, recall that the nitrogen injection time was limited to 15 - 25 minutes as it was found that longer injection times lead to more amorphous carbon depositing on the collecting surface [13, 25, 27]. With this time restriction, sample production usually yielded anywhere from 150 mg to 800 mg per batch depending on how much was lost during the manual collection of the sample. Thus multiple batches were combined in the present project to obtain a mixed “hybrid” sample of one gram needed for the catalyst preparation. In order to assess if the hybrid sample was similar to the individual samples obtained from the different batches, these were analyzed by XPS, Raman, and SEM.

The elemental surface composition of each sample was determined by XPS analysis. Each batch had a different nitrogen amount that ranged from 0.5 – 2.51
atomic percent. The batches with the highest nitrogen contents were used in proportions that enabled 1 gram of sample to be accumulated: 170 mg of batch A, 470 mg of batch B, 360 mg of batch C. This hybrid sample was then analyzed and compared to the individual batches (Table 5-1). The hybrid sample had 2.00 atomic percent of nitrogen, which represents a good average of the individual batches’ nitrogen content. This corroborates with Pristavita’s results [25], thus indicating a relatively stable plasma production process [25].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon (Atomic Percent)</th>
<th>Oxygen (Atomic Percent)</th>
<th>Nitrogen (Atomic Percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch A</td>
<td>95.13</td>
<td>2.37</td>
<td>2.51</td>
</tr>
<tr>
<td>Batch B</td>
<td>95.88</td>
<td>2.29</td>
<td>1.82</td>
</tr>
<tr>
<td>Batch C</td>
<td>95.87</td>
<td>2.56</td>
<td>1.56</td>
</tr>
<tr>
<td>Hybrid</td>
<td>95.72</td>
<td>2.28</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Table 5-1. XPS results of individual batches and hybrid sample

For further verification that the hybrid sample was an accurate representation of the original graphene nanoflakes, the Raman spectra (Figure 5-1) and SEM images (Figure 5-2) were compared. Figures 5-1 and 5-2 show only one individual batch and not all three since individual batches produce the same Raman spectra and morphology. No changes between the hybrid sample and an individual batch were identified.
Figure 5-1. Raman spectra of hybrid and individual batch
Figure 5-2. SEM image of (a) hybrid and (b) individual batch
5.2 Characterization during synthesis steps

5.2.1 XPS analysis on ball milling, first pyrolysis, and second pyrolysis

XPS was performed at different stages throughout the synthesis route. The catalyst surface was composed of carbon, nitrogen, oxygen, and iron. Carbon and oxygen were always present at over 90 atomic percent and 1.75-2.75 atomic percent respectively. The values of nitrogen and iron were closely monitored since they represent a measure of the number of catalytic sites. As seen in Figure 5-3, iron is present after the adsorption step and remains relatively unchanged throughout the pyrolysis stages. Furthermore, the value of nitrogen at the end of the second pyrolysis is only slightly less than the starting value.

![Graph showing nitrogen and iron contents (atomic percent) at the surface](image)

**Figure 5-3. Nitrogen and iron contents (atomic percent) at the surface**

Figures 5.4 to 5.7 show the XPS graphs achieved through a survey scan from 0 to 1200 eV (recall Table 4-2 in Section 4.5.2 to identify specific elements). The iron
signal, found in the range of 701 to 745 eV, is not present in Figure 5.4, but is present in Figures 5.5, 5.6, and 5.7. The signal is faint and is not immediately obvious when viewing the whole survey; further analysis on the signal showed that iron was initially present at 0.31 atomic percent (Figure 5.3). Table 5-2 shows the pyridinic, pyrrolic, and graphitic/quaternary nitrogen signals from the nitrogen peak in Figures 5.4 to Figure 5.7. A de-convolution of the nitrogen signal at the second pyrolysis stage shows that 39% of the peak (0.74 out of 1.88) is associated to pyridinic nitrogen, which is an increase over the original 26% pyridinic nitrogen (0.53 out of 2.00) before the pyrolysis treatment. The de-convolution of the iron peak did not provide any substantial information as the signal is close to the detection limit of the XPS instrument. The de-convolution peaks of the nitrogen signals used to produce the results in Table 5-2 can be found in Appendix 2.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>GNF</td>
<td>0.53</td>
<td>1.10</td>
<td>0.37</td>
<td>2.00</td>
</tr>
<tr>
<td>Ball Milling</td>
<td>3.45</td>
<td>1.18</td>
<td>0.00</td>
<td>4.63</td>
</tr>
<tr>
<td>First Pyrolysis</td>
<td>0.83</td>
<td>0.85</td>
<td>0.33</td>
<td>2.01</td>
</tr>
<tr>
<td>Second Pyrolysis</td>
<td>0.74</td>
<td>0.82</td>
<td>0.32</td>
<td>1.88</td>
</tr>
</tbody>
</table>

Table 5-2. Nitrogen species de-convolution at different stages of synthesis
Figure 5-4. XPS spectrum at GNF stage

Figure 5-5. XPS spectrum at ball milling stage
Figure 5-6. XPS spectrum at first pyrolysis stage

Figure 5-7. XPS spectrum at second pyrolysis stage
XPS analysis showed that iron can be successfully incorporated onto the GNF structure. The overall amount of iron present is very small at 0.31 atomic percent. This was expected as only a 1% by weight ratio of iron to GNF was used when adding iron acetate to the GNF sample during the adsorption step.

The amount of nitrogen on the surface more than doubled from 2.00 to 4.63 atomic percent after the adsorption and ball milling steps; this is also expected as the solvent used in the adsorption step is phenanthroline which contains pyridinic nitrogen. The use of a phenanthroline, which contains pyridinic nitrogen, explains why the overall amount of pyridinic nitrogen increased through the synthesis steps from 0.53 to 0.74 atomic percent, while the total amount of nitrogen decreased from 2.00 to 1.88 atomic percent. It is to be noted that the small relative amount of iron present in the sample is also the result of the relatively small number of the expected receptor sites formed by the pyridinic nitrogen. The effective number of active sites on the catalyst could not be evaluated, but the fact that iron and nitrogen are both present in very low amounts and that 4-6 neighboring pyridinic nitrogen atoms are needed for forming an iron-receptor site suggests a relatively low value of the number of catalytic sites in atomic percentage values; however the potential number of atomically dispersed catalytic sites is to be compared here with the number of catalyst nanoparticles used in conventional catalytic layers. The assumed active site would have iron coordinated with 4-6 pyridinic nitrogen neighbors, meaning that the ratio of pyridinic nitrogen to iron should be in the order of 4-6:1. The current ratio is
0.74:0.28 (or 2.64:1), this seems to suggest that only a fraction of the iron incorporated here in the structure can effectively be coordinated with pyridinic nitrogen.

5.2.2 Raman analysis on ball milling, first pyrolysis, and second pyrolysis

The parameters listed in Table 4-1 were measured at the 4 different stages (Figure 5-8) of the catalyst synthesis route and reported with 90% confidence intervals (Table 5-3). The purity of the catalyst structure characterized by the \( \frac{I_C}{I_D} \) ratio went down by 28% from the untreated GNFs to the GNFs after the second pyrolysis stage. By the end of the pyrolysis stages, the crystallite size \( (L_a) \) decreases by a factor of 2, while the average length of graphene plane \( (L_{eq}) \) decreases by a factor of 4 when compared to their starting values.

Figure 5-8. Raman spectra at the stages of synthesis
The overall trend observed indicates a decrease of crystallinity. The GNFs are generated in a one-step homogenous and high temperature nucleation process that creates a very pure sample. By performing the catalyst preparation steps on the GNFs, amorphous carbon and impurities are introduced into the structure and losses in crystallite size are observed. The inherent advantage of using GNFs was that the starting average length of graphene planes was very high, reaching values of $L_{eq}$ over 40, which corresponds to the highest value ever reported. The present iron-inclusion method is seen here to degrade many of the structural properties of the initial material.

5.2.3 Microscopy analysis on ball milling, first pyrolysis, and second pyrolysis

SEM and TEM were both performed at the different stages throughout the synthesis route. The major change noticed from SEM was that the structure no longer resembled the original nanoflakes because of the ball milling step; structures that will be described as “boulders” are now observed (Figure 5-9). The boulders at the ball milling stage had varying diameters in the range of 25 μm to 400 μm, with only a small proportion of the boulders being smaller than 100 μm. Additionally, the boulders at this stage had rounded edges. After the first
pyrolysis, the proportion of ‘small’ boulders increases dramatically and the boulders start to look more ‘jagged’. Having been exposed to a high temperature during the pyrolysis stage and with the additionally manipulation that comes with preparing the sample for the second pyrolysis stage (refer to Section 4.2.3), it is understandable that the boulders are now smaller and have a lower average diameter.
Figure 5-9. SEM image at (a) ball milling, (b) first pyrolysis, (c) second pyrolysis stage

TEM showed that the structure originally had around 12-15 graphene sheets and this range was maintained throughout the synthesis steps (Figure 5-10). The
planes do, however, get more distorted as more steps are performed. This is most noticeable in the image of the structure at the second pyrolysis stage, where an ‘S’ shape is detected.

Figure 5-10. TEM image at (a) ball milling, (b) first pyrolysis, (c) second pyrolysis stage
5.3 Fuel cell performance

5.3.1 Commissioning the fuel cell test bench

Preliminary testing was done to assess the performance of the in-house built fuel cell test bench. These tests showed oscillations of approximately ±20 mA (approximately 20% of the average 90 mA reading) in the current measurement, visible as spikes approximately every 20 minutes (Figure 5-11). The spikes correlate to the response of the control scheme used for the heating of all the elements within the fuel cell test bench; the small changes in temperature affected the humidity and temperature of the incoming gases. Further modifications and a tighter control on the heating system led to the overall fluctuations decreasing to about ±10 mA (approximately 11% of the average 90 mA reading), but the oscillations could not be completely eliminated and are thus found in all fuel cell results.

![Preliminary Testing](image)

**Figure 5-11. Measured current over time at an applied voltage of 500 mV**
5.3.2 Short-time experiments

Stability is a problem linked to degradation of the catalyst or poisoning when operating in the acidic environment of the fuel cell. Studying stability implies looking at the evolution of the catalyst structure in time within an active PEMFC. Since the present GNF material is very specific in terms of crystallinity and already well characterized, this forms a relatively unique opportunity to observe possible structural changes over time within an active PEMFC. The results of this study are the basis of Section 5.4, but in order to obtain samples of the catalyst at different exposure times, experiments of various time intervals were performed; 8-hour (Figure 5-12) and 12-hour (Figure 5-13) experiments were done. Both experiments produced essentially the same result; a stable current (with oscillations linked to the temperature control system) at an applied voltage of 500 mV with no systematic decrease. As mentioned in Section 2.4.1, stability is determined to be a decrease of less than 40% of the beginning-of-life activity for over 5000 hours. Compared to the 5000 hours used in industry, the time interval for these experiments is too small to declare the catalyst perfectly stable, but it is still an excellent result. Most non-platinum catalysts show an immediate decrease and lose anywhere from 20 to 60% of their activity within the first 100 hours [5, 12, 26] of operation, so the fact that this catalyst is still stable after 12 hours is a major achievement for a non-noble catalyst. The value of approximately 150 mA seen in Figures 5-12 and 5-13 also verifies the reproducibility of the catalyst’s performance as this is the value present during 100-hour experiments, to be discussed in Section 5.3.3.
5.3.3 Stability test

As mentioned in Section 5.3.2, non-noble catalysts typically show a decrease in activity very rapidly in the first few hours. The present iron-nitrogen-GNF
catalyst was shown to be stable over a time range of 12 hours, a new and important result. The activity evolution is evaluated in the present paragraph over an extended time scale of 100 hours, which is more in line with application requirements.

Figure 5-14 shows the measured current as a function of time for a catalyst layer having the characteristics reported in Section 5.2 (1.88 atomic percent of nitrogen with 0.28 atomic percent of iron). Although there are some fluctuations throughout the experiment, at the end of the 100-hour test the current generated by the PEMFC maintained its original starting value of approximately 150 mA at an applied voltage of 500 mV. The current fluctuations observed in Figure 5-14 correlate to fluctuations in the temperature control scheme applied on the PEMFC test bench.

![Stability Test](image)

**Figure 5-14. Measured current over time at an applied voltage of 500 mV**
The important result in Figure 5.14 is the complete stability of this catalyst over 100 hours of operation in a PEM fuel cell environment. This is a major breakthrough for non-noble metal catalysts as similar materials have shown a 45% decrease in current over the same time trials [31]. The stability observed can be attributed to the fact that we have a carbon material that is extremely crystalline and composed of stacked graphene sheets. In a paper published by Wu et al. [26] a cobalt-based catalyst showed stability in a PEMFC. Their work concluded that there is a strong link between the number of graphene sheets and the catalyst stability, with a high number of sheets being desirable. They reason that the graphene sheets enhance the electronic conductivity and corrosion resistance of the carbon-based catalysts [26, 50, 51].

Recall from Section 4.3 that a catalyst loading of 1 mg/cm² was used and the fuel cell had an exposed area of 1 cm², so the current can be written as a current density of 150 mA/cm². When comparing this result to the benchmarks in Table 2-1 at the same applied voltage of 500 mV, the current density of the present catalyst is 10% that of Gore PRIMEA MEA 5510 and 24% that of 2 wt% Pt ELAT electrode from E-TEK. This is just a direct comparison between values and does not take into account the relatively low amount of iron present in the catalyst structure. This result must be normalized with respect to the mass of iron.

Using the molar masses of the present elements, Avogadro’s number, and the XPS results of the atomic percents on the surface of the structure after the argon pyrolysis stage as a basis, an estimation of the mass fractions on the catalyst surface can be made (Table 5-4). This estimation produced a mass fraction of
1.27% for iron, meaning that with a catalyst loading of 1 mg, 0.0127 mg of iron is present. With this value, the present catalyst can be compared to the benchmarks in Table 2-1 on a normalized value of current per metal catalyst mass (Figure 5-15). From this figure, one can see that when considering the activity of the catalyst with respect to its’ very low non-noble metal content, it is performing well above most of the industry benchmarks.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Percent (%)</th>
<th>Moles</th>
<th>Molar Mass</th>
<th>Mass (g)</th>
<th>Mass Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>96.39</td>
<td>1.60E-22</td>
<td>12.0107</td>
<td>1.92E-21</td>
<td>94.34</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.88</td>
<td>3.12E-24</td>
<td>14.0067</td>
<td>4.37E-23</td>
<td>2.15</td>
</tr>
<tr>
<td>Iron</td>
<td>0.28</td>
<td>4.65E-25</td>
<td>55.8450</td>
<td>2.60E-23</td>
<td>1.27</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.72</td>
<td>2.86E-24</td>
<td>15.9994</td>
<td>4.57E-23</td>
<td>2.24</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>2.04E-21</td>
<td>2.04E-21</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-4. Estimate of mass fractions on the catalyst surface

![Figure 5-15. Comparison of catalyst on a current/metal catalyst mass basis](image)

58
Activity tests and electrochemical impedance spectroscopy tests were attempted, but the fluctuations in the system were even more present in these experiments because of the shorter time interval between data points. The fuel cell test bench needs to be improved for these experiments to be done correctly (refer to Section 7).
5.4 Characterization after exposure to fuel cell environment

5.4.1 XPS analysis on 8 hours, 12 hours, and 100 hours in PEMFC

XPS was performed on carbon cloths that had been used on the cathodic side of a PEMFC and exposed to the fuel environment for various times: 8 hours, 12 hours, and 100 hours. The catalyst structure was composed of carbon, fluorine, and oxygen. The fluorine, which was not present in the pre-fuel cell analysis, comes from the Nafion™ coating that is applied to the catalyst layer during the MEA step. A study on the nitrogen and iron amounts was not possible because of the high amount of fluorine on the surface of the catalyst. Furthermore, the signal for fluorine creates a doublet that shields the iron signal on the XPS spectrum, so obtaining an iron signal is not possible.

Figure 5-16 shows that 8 and 12 hour exposure times gave similar carbon and fluorine content (in atomic percent) whereas the 100 hour exposure time shows a complete reversal of atomic percentages. Carbon increased by 56% over its original starting value (38.84 atomic percent to 60.57 atomic percent) and fluorine lost 51% (56.97 atomic percent to 27.88 atomic percent). A de-convolution of the carbon peak further revealed a difference between the overall shape of the carbon signal (Figures 5-17 and 5-18). At 8 hours, the major peak in the carbon signal is at 296 eV, associated with fluorine-neighboring carbons. However, at 100 hours the major peak in the carbon signal is at 286eV, associated with graphitic carbon. By being exposed to the harsh fuel cell environment for a longer time, it appears that the catalyst structure is reverting back to its original graphitic state.
Figure 5-16. Carbon and fluorine atomic percents of surface composition

Figure 5-17. XPS carbon signal at 8 hours
5.4.2 Raman analysis on 8 hours, 12 hours, and 100 hours in PEMFC

The Raman spectra of Figure 5-19 and resulting parameters listed in Table 4-1 were measured at 3 different fuel cell exposure times and reported with 90% confidence interval (Table 5-5). A blank carbon cloth was used as a control to show if there is a difference between an unloaded carbon cloth and the samples coming from the fuel cell. This difference was a confirmation that the catalyst was present on the carbon cloth and the thermal shock treatment did indeed enable the recovery of the catalyst material after some active period in the PEMFC. From figure 5-19, it can be seen that the 100-hour curve resembles the initial carbon cloth curve (with the exception of the three major peaks); this may be the result of the more difficult recovery of the catalyst layer after a long exposure time, and/or...
a removal process that is now taking part of the cloth together with the catalyst.

From Table 5-5, the purity of the catalyst structure characterized by the I_G/I_D ratio increased by 35% from the 8-hour exposure time to the 100-hour exposure time. At the 100-hour exposure time, the crystallite size (L_a) increases by 25%, while the average length of graphene plane (L_eq) increases by 107% when compared to their values at the 8-hour exposure time.

![Figure 5-19. Raman spectra at different fuel cell environment exposure times](image)

<table>
<thead>
<tr>
<th>Time</th>
<th>I_G/I_D</th>
<th>L_a [nm]</th>
<th>L_eq [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Cloth</td>
<td>1.19 ± 0.03</td>
<td>5.61 ± 0.12</td>
<td>---</td>
</tr>
<tr>
<td>8 Hours</td>
<td>1.16 ± 0.11</td>
<td>5.60 ± 0.29</td>
<td>12.97 ± 1.54</td>
</tr>
<tr>
<td>12 Hours</td>
<td>1.19 ± 0.10</td>
<td>5.40 ± 0.17</td>
<td>16.10 ± 1.03</td>
</tr>
<tr>
<td>100 Hours</td>
<td>1.57 ± 0.09</td>
<td>7.02 ± 0.29</td>
<td>26.89 ± 1.83</td>
</tr>
</tbody>
</table>

Table 5-5. Crystallinity parameters at different fuel cell environment exposure times
The overall trends observed in all parameters indicate a reorganization of the carbon structure and an increase of crystallinity. The $L_{eq}$ has already surpassed the value observed after the ball milling stage in the synthesis route (24.51 nm). To understand this result, one needs to recall that the GNFs produced are very pure. The synthesis steps introduced impurities, but the exposure to the fuel cell’s harsh environment seems to be ‘cleaning’ the catalyst and reverting back to the structural properties of the initial material.

5.4.3 Microscopy analysis on 8 hours, 12 hours, and 100 hours in PEMFC

SEM and TEM were both performed at the three different fuel cell exposure times. Both techniques acted as a confirmation that the catalyst was still on the carbon cloth and that the thermal shock treatment was effective in removing the catalyst layer for analysis. Figure 5-20 shows that carbon deposits having diameters in the range of 10 μm to 200 μm are visible on the carbon fibres of the carbon cloth. The overall density of the deposition varied depending on the position, which would indicate that the deposition is not uniform throughout the active area. In Figure 5-21, the carbon deposition of the catalyst can be seen on the outside of the smooth carbon fibres of the carbon cloth. Since these are observations of a carbon material deposited on a different carbon material base structure, it was not possible to examine in detail the carbon deposition directly above the surface of the fibres because of the lack of contrast.
Figure 5-20. SEM image of (a) carbon cloth initially and after (b) 8-hour, (c) 12-hour, (d) 100-hour operation time in the PEMFC
Figure 5-21. TEM image of (a) carbon cloth initially and after (b) 8-hour, (c) 12-hour, (d) 100-hour operation time in the PEMFC
6 Conclusion
6.1 Catalyst structure

This work showed that nitrogen functionalized GNFs were able to incorporate atomic iron onto their surface. By using an adsorption step followed by ball milling and a two-stage pyrolysis, the amount of iron functionalized on the surface of GNFs with 2.00 atomic percent nitrogen is 0.28 atomic percent iron. The adsorption plus 2-stage pyrolysis method was used in this work because it produced good results in previous work where the starting material was a carbon nanopowder. The goal there was to create a micro-sphere that would ideally contain nitrogen from phenanthroline and iron from the iron acetate. This micro-sphere contains the needed material to form an active site. The difference between that work and this one is that the GNFs are already functionalized with nitrogen so the concept of creating a micro-sphere does not apply. A different method to incorporate iron that does not drastically change the average length of graphene planes must be used in the future.

The iron incorporation steps showed to decrease the crystallinity of the GNFs. However, it was found that the longer the catalyst was exposed to the harsh fuel cell environment, the more its crystallinity properties reverted back, as evidenced by the L_{eq} of 26.89 nm after 100 hours of exposure. The fact that the impurities could be diminished by being in the fuel cell environment might point to the impurities from the synthesis steps being superficial and not actually altering the original structure of the functionalized GNFs.
6.2 Catalyst performance

The catalyst proved to be stable when tested in a PEMFC for the ORR over 100 hours, which is a first for an iron-based catalyst. When comparing the activity level of the catalyst to industry benchmarks, the present catalyst was in the range of 10 to 24% of the typical performance of platinum on a mA/cm² basis at an applied voltage of 500 mV. However, when compared on a mA/mass of metal catalyst basis, the present catalyst outperformed all but one of the industry catalysts. This result verified the idea of iron potentially replacing platinum as a catalyst for the ORR of a PEMFC. Attention must now be given to incorporating more iron into the structure and creating a larger number of active sites. Two possible avenues to explore are: 1) to increase the total amount of nitrogen on the functionalized GNFs to promote iron incorporation and/or 2) implement a different method to introduce iron or use the same adsorption step but with a greater amount of iron.
7 Recommendations

The fuel cell test bench was adequate in performing baseline studies, but should not be used in its current condition for more advanced testing. The heating system and control scheme must be improved to eliminate oscillations in the temperature of incoming gases. Furthermore, the humidity control should be made with a continuously refilling water bath instead of a fixed amount. Additionally, the height of the boilers should be increased to allow the incoming gas more time to heat up and achieve the desired humidity. As well, the connections should be improved to eliminate breaks in the electronic measurement and allow for experiments of smaller time intervals to take place (i.e. activity and impedance measurements). Finally, the system should be completely automated to facilitate long-running experiments. With an improved system, different flow rates, voltages, pressures, humidity, and catalyst loading can easily be tested to completely optimize the catalyst’s performance. It is my recommendation that the entire fuel cell test bench be replaced by a more advanced system.
8 References


   


24. *Heme*. 2010 [cited 2012 December 2nd ]; Available from:


30. *Nafion NR50*. 2011 [cited 2011 Sepetmebr 1st ]; Available from: 


Appendix 1: Ideal active sites and atomic percent

‘Armchair configuration’

For the calculation of the ideal number of active sites, some assumptions are needed:

- Active sites are only found on the edges of the catalyst
- A nanoflake is 100 nm by 50 nm and contains 10 graphene sheets
- Nitrogen is perfectly positioned (no wasted spots)
- No oxygen present

For this configuration, a side view of the active site between 2 graphene sheets is shown in Figure A1-0-1.

Using 0.142 nm as the length of one side in the graphene structure, D can be calculated as 6 times this length, or 0.852 nm. Furthermore, with the geometry
specified, there are 117 and 58 possible active sites along each side of the nanoflake, so 350 possible sites when we consider the whole perimeter of the nanoflake. With the assumption of 10 graphene sheets, there would ideally be 5 possible interactions (1-2, 3-4, 5-6, 7-8, 9-10). This makes the final number of total possible active sites 1750.

With this ideal situation, we could also calculate the ideal atomic percents for the surface composition of the edge of the carbon nanoflake.

Carbon: \[(5 \times 117 + 1) \times 2 + (5 \times 58 + 1) \times 2\] \* 10 = 17540
Nitrogen: \[(2 \times 117) \times 2 + (2 \times 58) \times 2\] \* 10 = 7000
Iron: 1750
Total Atoms: 26290
Ideal Carbon Atomic Percent: 66.7 atomic percent
Ideal Nitrogen Atomic Percent: 26.6 atomic percent
Ideal Iron Atomic Percent: 6.7 atomic percent

‘Zig-zag configuration’

Using the same assumptions as in the ‘armchair’ configuration, a side view of the active site for this configuration is shown in Figure A1-0-2. Once again using 0.142 nm as the length of one side in the graphene structure, \(D\) can be calculated as 2 times this length, or 0.284 nm. With the geometry specified, there are 352 and 176 possible active sites along each side of the nanoflakes, so 1056 possible sites when we consider the whole perimeter of the nanoflake. Again assuming an
ideal 5 possible interactions, the final number of total possible active sites for this configuration is 5280.

![Diagram of active sites](image)

**Figure A1-0-2. Side view of active site for ‘zig-zag’ configuration**

Calculating the ideal atomic percents for the surface composition of the edge of the carbon nanoflake:

Carbon: \[(2 \times 352 + 1) \times 2 + (2 \times 176 + 1) \times 2\] \times 10 = 21160

Nitrogen: \[(2 \times 352) \times 2 + (2 \times 176) \times 2\] \times 10 = 21120

Iron: 5280

Total Atoms: 47560

Ideal Carbon Atomic Percent: **44.5 atomic percent**

Ideal Nitrogen Atomic Percent: **44.4 atomic percent**

Ideal Iron Atomic Percent: **11.1 atomic percent**
Appendix 2: De-convolution of nitrogen graphs

Figure A2-0-1. De-convolution of nitrogen signal of GNF sample

Figure A2-0-2. De-convolution of nitrogen signal of ball milling sample
Figure A2-0-3. De-convolution of nitrogen signal of first pyrolysis sample

Figure A2-0-4. De-convolution of nitrogen signal of second pyrolysis sample