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An applied investigation of Nafion membranes in PEM fuel cells: Durability issues

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AN APPLIED INVESTIGATION OF NAFION MEMBRANES IN PEM FUEL CELLS: DURABILITY ISSUES

A Project
Presented to the
Faculty of
California State University,
San Bernardino

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
in
Environmental Sciences

by
Amanda Rose Rodriguez
September 2010

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September 2010

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ABSTRACT

Proton exchange membranes used in fuel cell transportation applications have been identified as a major failing component of the system. The proton exchange membranes, Nafion 117 and 212, were used in chemical and radiation degradation studies for this project. Chemical degradation studies, carried out using Fenton's reactions, showed that the emission of fluoride ions from the membrane increased with time and were dependant on reaction conditions, such as temperature and reagent composition. The fluoride emission rate was observed to be greater for the Nafion 212 membrane as compared to 117; while the emission of sulfate appeared to be insignificant in both. The manufacturer of the membranes had reported the 212 membrane as having a greater chemical stability. The greatest emission rates of fluoride in 212 and 117 membranes were respectively 119 and 30 µmol F^-/gram of Nafion exposed-h. These rates corresponded to emission ratios of fluoride to sulfate (FER/SER). The ratios were 113 and 8, respectively.

Radiation exposure of proton exchange membranes, relative to operation in space flight, was performed with an X-ray Diffractometer. Exposed membrane solutions, analyzed by ion chromatography, showed that there was an increasing trend of sulfate evolution with time. The range of sulfate emission rates was 0.37 to 0.70 μmol SO_4^{-2}/gram of Nafion-hr exposed. In addition, sulfate to fluoride emission rates (SER/FER) were 1.6 and 138. This was pertinent to membrane degradation studies since the results conveyed that the well accepted unzipping mechanism could not be the dominant method of deterioration with greater sulfate loss as compared to fluoride.

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CHAPTER ONE

THE CONTRIBUTION OF FUEL CELLS TO ENERGY INDEPENDENCY

The Alleviation from Foreign Oil Suppliers

Growing interests in alternative energy sources have many researchers investigating new efficient and reliable means of generating electrical power worldwide. As many nations, including the United States, strive for economic independence from foreign oil supplies, a dependable and cost effective energy source needs to be developed. In addition to achieving energy independency for the nation, rising interests have also included the use of other sustainable energy sources and processes. The global green movement has developed more complex requirements for novel methods of energy development. Current research and development has indicated that fuel cell energy sources have a great potential to meet the upcoming energy needs of the nation and the world. On June 25, 2003, an agreement of cooperation was signed between the United States and the European community. The focus of this agreement was to develop hydrogen energetics and fuel cell systems. The communities found that hydrogen fuel cells were one of the most promising technologies in development that would prove a more secure energy supply system (1).

Dependency on foreign oil supplies have been a popular topic of discussion among many Americans today. The US Department of Energy has reported that major oil price shocks have disrupted world energy markets five times in the past 30 years (2). In November 2008, the International Energy Agency (IEA) predicted a $120 barrel of oil in 2030 due to demand (3). National statistics from 2006 conveyed that 8.9 million barrels of petroleum were used on a daily basis for transportation applications. The applications included light trucks and cars, but did not include medium and heavy trucks (4). The transportation sector had been reviewed as 97% dependent on petroleum fuels, and had thus accounted for 2/3 of the US petroleum demand (4). The US DOE has reported that there will be a shortage in the nation's oil reserves after 2020, and that shortage will exceed to 50 billion barrels by 2050 (5). As a result, it has been vital that an alternative energy source be developed for transportation use in order to wean our country off foreign oil suppliers.

Although the US has been known for its continuous efforts in focusing on practical ways to obtain a more efficient and dependable energy market, the rest of the world has also struggled in dealing with this issue. In 2003, the number of registered cars and trucks/buses were 590 and 224 million worldwide (5). Jun et al. (6) reported that between the years of 1993 and 2003, the numbers of cars and trucks had increased at a rate of 2.7 and 3.0% annually. The rates have been expected to increase even more with a rapidly expanding population and an increasing amount of industrialization taking place in developing countries. The rate of 3% would forecast that by the year 2010 the total number of vehicles worldwide would be almost 1 billion (5). Xie et al. (7) also noted that the global transportation sector utilized 58% of the total petroleum expenditure as compared to 67% consumed by the US the same year. Thus there is an increasing need by the global transportation market to develop new technologies to meet these energy needs. That technology should have the capability of becoming easily integrated into the already existing transportation infrastructure. Vehicles that obtain their power from fuel cells have been proposed to meet all of those expectations.

The Movement to "Go Green": The Role of Fuel Cells in Environmental Sustainability

There have been several drawbacks instilled upon the environment and people's everyday lives in regards to transportation technologies. Some of the disadvantages of these transportation technologies included air emissions, energy use, noise, accidents, congestion, water runoff and land use (8). Most people have concerned themselves with all of the drawbacks that technologies have incorporated with their production and utilization. Individuals have begun to focus on the need for awareness in regards to sustaining the environment, while also considering alternatives to materials and resources that have been used in their everyday lives. Generally, when consumers consider their use of technologically advanced systems, they generally do not think about all of the steps that it took to make those systems possible. However, people have begun to concern themselves with the need to sustain the environment not only for their own health, but for the future health of their children. In regards to the transportation sector, vehicle emissions have been a major concern. The typical internal combustion engines that have been used not only emit CO_2, but also emit other pollutants like nitrous oxides (NO_x), particulate matter (PM) and carbon monoxide (CO). The emissions have caused distress among the population since the drawbacks of greenhouse gases have become increasingly recognized; where greenhouse gases of concern are carbon dioxide (CO_2), methane (CH_4), oxides of nitrogen (NO_x) and ozone (O_3) (8).

Carbon dioxide, CO_2, is known to be a key contributor of the greenhouse warming effect. As a greenhouse gas, it absorbs radiation in the 710-530 cm^{-1} range, while completely blocking out the radiative flux between 670 and 630 cm^{-1} (9). The radiative flux that was absorbed by the atmosphere contributes to the greenhouse warming potential. The concern that increasing CO_2 levels have imparted on the greenhouse effect has involved the increasing amount of anthropogenic CO_2 contributions to the global carbon cycle. It has been well documented that the combustion of fossil fuels, by the burning of fossil fuels (such as coal and petroleum products), as well as the clearing of forests by slash burning, have significantly contributed to the increasing amount of CO_2 in the atmosphere (9). VanLoon and Duffy (9) have estimated that as much as 75% of anthropogenic carbon dioxide has been a result of fossil fuel combustion. Table 1 displays the estimated amount of

CO_2 released from fossil fuel based oils on a per gallon basis (10).

Table 1. Estimated Release of CO_2 with the Burning of Oil Based Fuels

Carbon Dioxide Emissions from a Gallon of Fuel			
	Grams	Kilograms	Pounds
	per gallon	Per gallon	per gallon
Gasoline	8,788	8.8	19.4
Diesel	10,084	10.1	22.2

Source: U.S. Environmental Protection Agency. Emission Facts: Average Carbon Dioxide Emissions Resulting from Gasoline and Diesel Fuel. www.epa.gov/OMS (accessed Feb. 2, 2009).

Reports of CO_2 residence time values have been highly variable among the literature, which was in part due to how calculations measured oceanic uptake of the gas. Therefore, it is imperative that a better understanding of the effects of anthropogenic carbon dioxide production, and its effects of the processes of thermal radiation, be examined and understood(9).

It has been estimated that transportation in the US has produced about 34% of nation's CO_2 emissions (4). The same report concluded that an improvement of 5 miles per gallon for vehicles would cut the CO_2 emissions by 239 million tons/year (decreasing it roughly by 20%) (4). Congress had set a goal to improve fuel economy standards by 40% by the year 2020. In the spring of 2009, President Obama had set forth a new vehicle mileage standard at 35.5 mpg for cars and trucks. The standard was mandated within 7 years of issuance. His aim was to reduce greenhouse gas emissions by 30% (11). On a worldwide scale, Maclean and Lave (12) reported that over 90% of automobiles have internal combustion engines (ICE). Therefore, if a cleaner and more technologically advanced form of energy was to become available, then it would greatly improve the environmental cost that motor vehicles exhibit around the world.

Although the environmental impact of vehicle power generation, like deforestation, has been more closely considered worldwide, it has not been the only negative aspect of concern. Many people have also carefully considered the need to sustain and improve the quality of air that we all breathe. The US annual health costs due to gasoline vehicle emissions have been estimated to be approximately \$20-50 billion (8). The Clean Air Acts of 1970, 1977 and 1990 regulated vehicle emissions in the

United States. The regulations were put into place so improvement in respiratory health could be made. The acts established regulations that promoted the use of cleaner fuels, more efficient energy vehicles, and required routine inspection and maintenance programs (12). The result of these Clean Air Acts was that vehicle pollutants were reduced by 77%, even though there was an increasing amount of vehicles and vehicle miles traveled (12).

Although vehicle emissions have been better controlled in the US, they have not been as closely regulated worldwide. The vehicle emissions from other parts of the world could possibly have an impact on the health of the US population. Therefore, a cleaner and reliable energy source, like fuel cells, needs to be developed so that total vehicle emissions decrease or become non-existent. For example, one important supplier of US oil has been the oil sands area of Alberta Canada. The US imports oil from Canada more than any other nation; approximately 19% of the foreign oil supply (3). However, the process of abstracting the oil from the sands has emitted more than 3 times the CO_2 that has been emitted by ground oil processes in Saudi Arabia (3).

Vehicle Efficiency and Emission Sources for Currently Used Systems

Only 20-25% of the energy in gasoline is actually used to propel the automobile (8). If the efficiency of vehicles were to improve to 80 mpg, then vehicles would have to achieve 40% thermal efficiency (8). To obtain this effectiveness a more efficient energy source would be helpful. One answer to an energy efficient vehicle system would be fuel cell technology.

Since an increasing amount of people own vehicles and have been commuting daily, there has also been an increased impact on the amount of emissions that have been released into the atmosphere. If people were to ignore the problem that an increased amount of cars owned has been equivalent to the increased amount of emissions in the air, then one would need to counteract the ignorance with a more efficient and less polluting vehicle. It would also be important to not only improve the impact of the vehicle's use, but to also consider the overall impact of the vehicle's design, development and production (13). The potential vehicle sources that could have a negative environmental impact have included material or extraction sources, the vehicle manufacturing processes, vehicle applications and the vehicle's lifetime. Vehicle applications have included the oil well to tank impact analysis, oil well to wheel (vehicle operation) analysis, amount of energy required for the vehicle, exhaust and emissions over duration of use, services and infrastructure (parking and roads), motor vehicle repair, and predetermined expenses (including insurance, license fees, vehicle depreciation, and loan finance charges) (13). The negative impacts that have involved after vehicle lifetime issues have included the emissions and energy use of the dismantling facility, the dismantling processes, the methods of fluid and metal recovery, vehicle shredding and the disposal of the shredder residue (13).

Fuel Cells: Their Potential as an Efficient Energy Source

Fuel cells have displayed their potential as a viable source of transportation electrical energy due to their relatively high electrochemical efficiency in comparison to internal combustion engines. A fuel cell's efficiency ranges from 40 to 65% (6). The efficiency is dependant upon the type of fuel used and the choice of electrolyte in the system. Although fuel cells have appeared to be a promising source of electrical energy for stationary applications, fuel cells have not yet been developed enough to convey their durability and affordability in the transportation market. Therefore, the motivation for this project was to develop a better understanding of fuel cell systems used in the transportation sector, and to discover what underlying conditions or components lead to their ultimate failure.

Kordesch and Simader (14) evaluated the impact of fuel cell technology in regards to meeting energy efficiency requirements. They found that there were both advantages and disadvantages for implementing fuel cell technology in the transportation market. The advantages included savings in fossil fuels, decreased heat transfer loss (more efficient energy conversion device), low pollution levels, and the production of water in H_2 and O_2 systems (to keep the membrane hydrated) (14). Fuel cells have also confirmed their value due to their small number of moving parts (ie. pumps, fans, blowers), low noise level (as compared to ICE engines), small amount of required maintenance (due to small number of moving parts) and their fast start up times at low temperatures (14). Fuel cells have also shown their potential to be regenerative hydrogen-oxygen systems and have also used low cost fuels with high temperature systems. The disadvantages of using fuel cell technology include the high initial cost of the system (ie. catalyst, membranes, accessories), high price of clean hydrogen (to avoid impurities) and the lack of hydrogen fueling stations (14). In addition to the previously listed downfalls, fuel cell technology has not been completely developed and therefore has not been well understood. The lifetime of the fuel cell systems have displayed declining power generation and researchers have been investigating the source of the problem. Furthermore, there have been electrolyte dehydration issues, which have shown a decrease in the function of the fuel cell system.

Purpose of the Study

Ex-situ tests were performed to observe the degradation behavior of PEM fuel cells in transportation applications. The particular component of the fuel cell that was under investigation was the electrolyte, also referred as the ionomer membrane. The electrolyte that was used was a proton exchange membrane (PEM) made of polyfluorinated sulfonic acid (PFSA), specifically Nafion membranes, which were originally manufactured and trademarked by DuPont. Ex-situ tests were performed for this investigation because they were less time consuming and cheaper than in-situ testing of the fuel cell. A review of the literature pointed out that suspected sources of membrane degradation in transportation applications included Fenton's reaction conditions and radiative exposure. The suspected sources were thus tested under varying exposure conditions (i.e. temperature, hydrogen peroxide concentration, metal concentrations and time).

The purpose of the study included the detection of membrane degradation products by two routes of membrane exposure (chemical and radiative). The detection of degradation products were used to relate their significance to the durability and stability of the Nafion polymer in fuel cell systems. The findings of the project were expected to contribute to a better understanding of the membrane degradation mechanisms in operation.

In addition, the research project aimed to find the critical concentration at which hydrogen peroxide (as well as metal contaminants) contributed to membrane degradation, and therefore hindered the functionality of the fuel cell. If it could be determined that a certain concentration of hydrogen peroxide was degrading to the membrane, then it would be pertinent to discover the amount of hydrogen peroxide produced by a poisoned catalyst. However, if the poisoned catalyst would still show that it could still produce power with a threshold concentration of hydrogen peroxide, then a better membrane needed to be produced for a viable transportation application. If the catalyst showed significantly reduced power generation had occurred before the membrane would display signs of degradation, then a better catalyst would be needed. Therefore, the purpose of the study was to determine the contribution of hydrogen peroxide generation to the lifetime of the membrane in fuel cell applications.

CHAPTER TWO

LITERATURE REVIEW OF FUEL CELLS AND THEIR DEGRADATION PATHWAYS

The Production of Electrical Power in Fuel Cell Systems

The source of creating the electrical energy within the fuel cell has involved the use of an electrolyte material. There have been many different types of fuel cells in use. The various types of fuel cells generally vary by the kind of fuel used, as well as the selection of electrolyte material. The most commonly used fuel cells include alkaline (AFC), proton exchange membrane (PEM), phosphoric acid (PAFC) (for stationary commercial sites), molten carbonate (MCFC) and solid oxide (SOFC) (15). This research project had addressed the role of platinum-catalyst PEM fuel cells operated in transportation applications.

In a PEM fuel cell, the electrolyte material is a polyfluorosulfonic acid (PFSA) membrane that is an efficient conductor of protons. The cell is an electrochemical device (galvanic cell) that utilizes proton exchange membranes to provide a high power density at a relatively low operating temperature (16). There are many different types of electrolyte membranes being developed, however none of the other materials have shown the same kind of chemical stability as PFSA membranes. In particular, Nafion membranes demonstrate immense stability characteristics. The general requirements for a durable fuel cell in commercial applications entails that it operates up to 6000 hours (17). However current fuel cell operations only last up to 1000 hours. A gradual decline in power output suggests that some type of deterioration is occurring during operation of the fuel cell system (18).

The basic components of the fuel cell include an ion conducting electrolyte, anode, cathode, fuel source (hydrogen), oxidant (typically atmospheric oxygen) and catalyst (platinum in this case). A basic fuel cell is depicted in Figure 1 of Appendix A. The electrolyte (PEM) is only permeable to positively charged ions and acts as a barricade to direct mixing of the fuel and oxidant, thus supporting the electrical potential difference or voltage of the cell. The PEM must stay hydrated in order to retain its conductivity (17). The function of the Pt catalyst is to be the facilitator between the reaction of hydrogen and oxygen. The most commonly used catalyst for PEM fuel cells is composed of platinum (Pt) nanoparticles. The Pt is thinly coated onto carbon paper or cloth. The typical loading of platinum onto the media ranges from 0.2 to 0.5 mg of Pt/cm^2 (19). The optimum amount of Nafion that is needed in a fuel cell unit has been measured to be 33 wt% of the catalyst (19). For an optimally running fuel cell, the catalyst (electrode) needs to be thin and porous. This allows a maximal amount of Pt surface area to be exposed to the hydrogen or oxygen. The catalyzed porous electrodes are separated by the ion conducting polymer (6). The platinum coated side faces the membrane. The significance of the electrode as a fuel cell component is that it is also the site where the reactions take place in the electrochemical cell.

An individual fuel cell can generally produce a current, at approximately 0.6 to 0.7 volts of electricity, which is about 200-500 mA/cm^2 (17). As a result, cells are generally lined up in the form of a stack so that a suitable amount of energy can be produced. The stack is connected in series by bipolar plates, which are utilized to assure the structural integrity of the cells (17). The electrochemical process that produces an electrical current across an external circuit is powered by the inner three layers of each cell. The inner three layers are commonly referred to as the membrane electrode assembly (MEA) (17).

The half-reactions that occur within the fuel cell to generate ions and electrical current are shown in Scheme I of Appendix B. The mechanism begins with the intake of hydrogen fuel at constant pressure on the anode side of the cell. The gas then spreads through the porous electrodes until it reaches the catalytic layer of the anode (6). Once the gas reaches this point, electrons from the hydrogen gas are released while also creating protons ($2H_2 \rightarrow 4H^+ + 4e^-$). The freed electrons are conducted through the anode and used in an external circuit. Concurrently the protons are transported across the electrolyte to the cathode (1). On the cathode side of the cell, there are etchings in the catalyst layer so that oxygen (generally air; the oxidant) can be evenly distributed on the surface of the catalyst. When the oxygen reaches the layer, it can then react with the electrons that are conducted back from the external circuit and the protons that were conducted through the electrolyte (6). The reaction of the combined elements forms water ($4H^+ + 4e^- + O_2 \rightarrow 2H_2O$). There are no chemical contaminants that are exhausted from the use of the fuel cell; only water, electrical energy and heat are produced.

Nafion Membrane Characteristics

Nafion membranes can be obtained from many different suppliers; however DuPont was the original creator of the polymer. Two types of Nafion membranes were utilized for this investigation (Nafion 117 and 212). Both membrane types were perfluorosulfonic acid/PTFE copolymers. More specifically, the Nafion 117 membranes were non-reinforced films in the acid form. The polymers are considered to be chemically resistant and durable. Nafion 117 membranes typically have a 183 micron thickness and their basis weight is 360 g/m^2 (20).

In comparison, Nafion 212 membranes were slightly different. The 212 membranes had also been chemically stabilized in the acid form (21), however 212 membranes were reported as displaying a substantially lower fluoride ion release. Both membranes had the same physical properties and shown some signs of similar chemical durability. The 212 membranes however were positioned between a backing film and a coversheet. The backing films were in place so that membranes could be better protected from air exposure and potential degradation prior to utilization. The typical thickness of Nafion 212 membranes is 50.8 micrometers and has a basis weight of 100 g/m^2 (21). Nafion's equivalent weight (EW) is 1100 g/eq (22).

Nafion (shown in Figure 2, Appendix A) is ideally chosen for fuel cell applications due to its ability to conduct protons. Its proton conductivity was in part due to its amphiphilic composition; the nanophase separation that occurred between the hydrophobic matrix and hydrophilic ionic domains during membrane hydration (23). The polymer backbone is a hydrophobic region and the acid sulfate group on the side chain is a hydrophilic domain (24). The polymer is a submicroheterogeneous system that contained sulfo groups in nanosize clusters that are connected by channels through which proton transportation occurred (1). In addition, Nafion's excellent resistance to oxidation and reduction demonstrates its stability (23). The elementary unit of the polymer and its chemical structure are what determines the membrane's thermal stability and resistance to oxidative conversions (1). Nafion membranes have displayed that they are stable in operating temperatures up to 80 °C.

Durability Issues for Nafion Membranes

Durability issues have been a key factor in assessing the lifetime of a fuel cell and its components. The literature has suggested that ion exchange membranes and catalysts used in fuel cells undergo degradation and may ultimately be the culprit hindering the long term functionality of the fuel cell (24). This project utilized accelerated ex-situ degradation studies of the polymer, Nafion. The accelerated studies were modeled after similar studies already published in the literature, so that a contribution could be made to better understand the underlying mechanisms in which Nafion membranes degrade during fuel cell operation. The degradation studies were modeled after two possible environmental conditions that fuel cells may become subject to in operation. The detection of any molecular fragments or ion loss from the membrane after exposure to either of these conditions would have indicated that membrane degradation had occurred with exposure. The indication of degradation would then further conclude that the membrane's integrity had been altered, and would allow one to suspect a decrease in the membrane's performance (24). The first condition that was investigated considered fuel cell transportation applications. The other exposure condition that was explored involved irradiation conditions that a fuel cell becomes subject to while used in space flight.

The use of proton exchange membranes in fuel cells has been previously investigated as a potential source of failure for the system. Tang et al. (25) mentioned that fuel cell failure has been credited to structural damage of the membrane, however this was not proven. The structural failure mechanisms of the membrane were suspected due to membrane cracking, tearing, puncturing, mechanical stress, inadequate humidification and reactant pressure in the cell (25). The structural damage of the membrane has been suspected to hinder the cell from working due to the vitality of its function. For this reason, one would be led to believe that it was imperative that the membrane be intact and in good working condition for the fuel cell to be efficient and reliable. It has also been essential that the membrane degradation routes be studied so that they can be improved upon. The routes of degradation that were carried out in the accelerated experiments had mimicked conditions that the membranes would undergo while in real-life operation. It was found that membrane degradation was suspected through the detection of fluoride and sulfate ion loss after experimentation (25). The emission of HF had also previously been observed in effluent fuel cell water (25). A study of the nanosize submicroheterogeneous distribution of sulfoacid groups and channels connecting these groups were found to be significant to membrane function (1). If there was a loss of these connecting groups within the membrane, then there was also a decreased amount of proton conduction through the membrane (26). This fact was key in trying to improve the working capacity of PEMs in fuel cells that operate at temperatures greater than 90 °C (1).

The literature conveys that suspected sources of membrane degradation were present due to the changing environment within the cell during operation. The changes that occurred included: strong oxidizing conditions, the presence of excess water, strong acidic conditions, high operating temperatures, high electrochemical potentials, the production of reactive intermediates, chemically reducing conditions at the anode, a high electric current and large potential gradients (18). Researchers wanted to determine how the membrane was broken down chemically so fuel cells could be further developed to increase their lifetime without also increasing their cost or performance loss (18). The goal of this project was to investigate the degradation pathways that involved the production of hydrogen peroxide in FC vehicles, and to investigate the potential exposure of fuel cells to irradiation during space flight.

Chemical Degradation of Nafion Membranes

In considering the realistic conditions that the membrane could undergo in a fuel cell, one should consider the fact that hydrogen peroxide (H_2O_2) has been found in the exhaust of fuel cell vehicles, as well as within the membranes of the fuel cells (27). The formation of H_2O_2 in the cathode region was suspected as a source of chemical degradation for the membrane (25). The production of H_2O_2 in the cell was not isolated to either the cathode or the anode side; therefore degradation of the membrane was suspected to occur on either side of the cell (27). Since H_2O_2 was not isolated to either side of the cell, the assessment of the chemical degradation pathways were even more complicated to evaluate. The formation of H_2O_2 itself was not considered to be the reason for degradation, but was believed to prompt a chemical reaction in the presence of metallic impurities in the fuel cell system (25). The metal impurities were a result of contamination from the end plates that were used in the system. The concentration of H_2O_2 that was produced in the fuel cell has not been well established, but has been estimated to be around 10-20 ppm (approximately 3-6 x 10^{-4} M) (24). The oxidizing conditions just mentioned were characteristic of a chemical reaction that has been used to degrade organic compounds in water treatment processes. The reagent that results from the combination of hydrogen peroxide and metal impurities (in this case iron) has been called a Fenton's reagent.

A Fenton's reagent has been defined as the iron-salt-dependent decomposition of hydrogen peroxide (28). The reaction has generated the highly reactive hydroxyl radical, which was believed to be formed through an oxoiron (IV) intermediate (28). The iron specific reaction was: $Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + \cdot OH + OH^-$ (27). However, the general Fenton's reaction that involves metal impurities is displayed by Scheme II of Appendix B.

Among the literature regarding fuel cell degradation pathways, two proposed mechanisms have been well supported. However, most of the literature regarding fuel cell chemical degradation pathways has confirmed that the most likely route has been through the unzipping mechanism of Nafion. The unzipping mechanism has been widely believed to become initiated by the presence of weak polymer end groups (the source of carboxylic acid end groups in the membrane) (7). The weak polymer end groups are not largely present in the membrane's final structure; however the manufacturing process results in producing an imperfect fluorinated polymer. The imperfection therefore results in the production of α hydrogens that are vulnerable to radical (hydroxyl) attack (17). Scheme III (Appendix B) displays the process by which carboxylic acid end groups have been produced by the membrane's reaction with hydroxyl radicals. The -Y in reaction YX denotes non-perfluorinated weak end groups.

In order to develop a more durable and economical fuel cell system, the membrane degradation pathways must be better understood. Therefore, continued research has been necessary in order to fully understand the degradation processes that occur in fuel cell operations. For example, Figure 3 (Appendix A) displays the chain end unzipping mechanism that coincided with the production of hydrofluoric acid (HF) and the loss of membrane integrity. The chemical reaction of how the unzipping mechanism was carried out was more descriptively displayed by the chemical reaction steps provided in Scheme IV of Appendix B. Xie and colleagues (7) proposed a kinetic model for the chemical degradation mechanisms of PFSA ionomers. The model was pertinent to the investigation of chemical degradation conditions, since the initiation mechanisms for the deterioration of the membranes have been crucial in the in-situ fuel cell environment. The model has been projected to quantitatively determine if and how degradation conditions affect the extent of side chain cleavage (7).

Scheme IV (Appendix B) displays that the unzipping mechanism resulted in each carboxylic acid end group reacting with 2 hydroxyl radicals. The reaction produced the loss of one CF_2 unit, with the formation of one CO_2 and two HF molecules (7). The literature had also supported the idea that once the unzipping reaction drew near the side chain connection, the side chain was cleaved from the polymer (17). The cleavage thus produced: $HOOC-CF(CF_3)-O-CF_2CF_2-SO_3H$. The production of this molecule, referred to as Molecule A, introduced the possibility for the continuation of the unzipping of the main chain (7). The formation of the products are displayed in Scheme V of

Appendix B. Molecule A was expected to be produced from Nafion (Equivalent Weight (EW) of 1100) at a rate of 1 molecule A per 15 carbons of Nafion's main chain. Xie and Hayden reported that Molecule A could persist in the unzipping reaction or it could diffuse out of the polymer membrane. If Molecule A had kept on unzipping, then the deterioration of the compound would produce CO_2, HF and sulfate ions (7).

The production of fluoride ions from the degradation mechanism was expected to occur with every degrading Molecule A, alongside the unzipping of Nafion's main chain backbone. Xie and Hayden reported that the amount of fluoride ions that were released were mainly due to the unzipping of the main chain. The proposed ratio of fluoride ions released by the unzipping of Molecule A to Nafion's main chain was 8:31, which was about 20% of the maximum amount of fluoride atoms present in the polymer (7). However, the researchers believed that the majority of fluoride atoms in Molecule A did not end up as emitted fluoride ions. Therefore, Molecule A's contribution to the fluoride emission rate was negligible.

The researchers suggested that Molecule A's contribution to the emission rate was subdued by the escape of the molecule's degradation products by diffusion. The detection of products from Molecule A (besides ion release) would be difficult to assess. The ensuing molecules such as HOOC-CF_2-SO_3H and CF_3COOH were so small that they could effortlessly flee the fuel cell system or they could also evaporate due to their relatively low boiling points (7). For example the molecule, CF_3COOH, has a boiling point of 78 °C, which was often lower than temperature of the accelerated degradation test conditions (80-100 °C) and operating temperatures of the fuel cell system. Xie and Hayden (7) reported that the presence of CF_3COOH was verified by its detection in effluent fuel cell water.

Table 2 displays several literature sources that had investigated the use of a Fenton's reagent to chemically break down Nafion membranes. The table shows the conditions that were used for the chemical reactions. Some reactions were held at approximate operating fuel cell temperatures (around 80 °C) and others were held at temperatures reaching up to 100 °C. The reported emission rates for the detection of fluoride by some type of instrumental method varied.

Table 2. Fenton's Experiments Performed in the Literature

Type of Nafion Used	Concen. Fe^{2+}(ppm)	Concen. H_2O_2 (%)	Volume Of Fenton's Reagent (mL)	Exposure time (hours)	Temp (°C)	F^- Emiss. Rate Reported[a]	Ref (#)
111	20	30	100	Up to 96	100	0.15mg/h	29
111	12.3	30	Not specif.	Up to 96	80-90	0.15mg/h	25
117	0.1 $mol \cdot d/m^3$	30	10	12	80	1% after 5.5 days	30

[a] Some studies had mentioned sulfate detection; however none of the literature had reported values of an emission rate for it. In addition, the emission rates are assumed to be per gram of Nafion exposed.

Tang et al. (25) investigated how the reaction of H_2O_2 and metal impurities could cause chemical decomposition of the membrane. They used 30% H_2O_2 and 12.3 ppm Fe^{2+} to create a Fenton's reagent that could mimic realistic fuel cell conditions (at an amplified pace). The study was run in an 80-90 °C oil bath and used Nafion 111 membranes. Samples were taken every 30 minutes, replenished and then analyzed. The researchers also took polymer fragments out of the solution at 48, 72, and 96 hours to determine decomposition of the membrane with FTIR analysis. The investigation found that $-SO_3^{3-}$ and -COOH groups were present among the decomposed fragments collected from the Fenton's solutions. The fluoride emission rate (FER) from the membrane was determined by the use of atomic absorption spectroscopy. The reported FER was 0.15 mg/h, which was equated to 0.036 wt% of fluoride released from the membrane per hour. It was proposed that the fluoride content of the membrane was about 15% by weight. The literature has stated that PEM fuel cell tests had found fluoride ions, and low molecular weight organic compounds in the drain of exhaust gases (from vehicles) (27).

In a very similar study performed by Wang et al. (29) the researchers chemically decomposed Nafion 111 membranes. The membranes were 10 x 10 cm^2 in size and were degraded with 30% H_2O_2 and 20 ppm Fe^{2+} at 100 °C. The reaction was refreshed at every 30 minute interval and the solution was replaced to keep the H_2O_2 concentration constant (29). Samples were collected at 48, 72 and 96 hours to analyze by various parameters. FTIR analysis was performed to evaluate the result of chemical exposure for different lengths of time. FTIR analysis confirmed membrane mass loss of CF_2 groups from the reduction of C-F symmetric stretching bands that appeared in their results, which also indicated that F^- was released from the membrane. The FER was found to be

0.15 mg/h and was correlated to 0.024 wt% of fluoride released per hour. The release rate from the Wang experiment was relatively close to the calculated 0.036 wt% loss reported for the Tang et al. study. Interestingly the calculated release weight for Tang was more than the Wang experiment since their chemical reaction was held at a lower temperature. This was alarming because higher temperatures have been suspected as a contributing factor to increased membrane degradation. In addition, the Tang et al. study used less iron in their experimental procedure.

The experiment by Wang et al. (29) found that proton conductivity decreased with increasing exposure time to Fenton's reagent. The decrease in conductivity was indicative of degradation to the grafted sulfonic acid moieties of the membrane.

Kinumoto et al. (30) investigated the chemical degradation of Nafion 117 membranes in a Fenton's reagent. The investigation was performed using 30% H_2O_2 and 0.1 mol·d/m^3 Fe (d= days) at 80 °C for 12 hour intervals. Refreshment stages were performed at 12 hours with the replacement of the entire allotment of 30% H_2O_2 solution. The process was repeated for 5-9 days. The researchers found that fluoride and sulfate ions were present in their reaction solution. They also noted that the presence of iron (Fe^{+2}) significantly enhanced the rate of ion loss from the membrane. The decomposition ratios of the membrane in the presence of iron demonstrated that the C-F bond reached 68% and the sulfonic acid groups reached 33%. The decomposition ratios were in reference to percent composition of the analytes in Nafion. The ratios were taken after 9 days of repeated exposure. It was not stated as to what was done with the membranes while they were not immersed in the reagent. Kinumoto (30) also shared that the surface area and thickness of the Fenton's exposed membranes were significantly different after treatment. The total membrane weight loss was reported as approximately 40% after 5 days. Figure 4 in Appendix A displays the weight loss trend found after 12 hours of Fenton's exposure each day. Kinumoto (30) concluded that membrane deterioration was due to direct attack of both the main chain and side chain at similar rates.

In regards to the membrane staying physically intact, surface scanning electron microscope (SEM) results verified that the Fenton's treated membranes had many small bubbles present on their surfaces (25). Tang et al. conveyed that the small bubbles later became pinholes in the membrane, in which both cases allowed an increase in gas crossover of the membrane. SEM micrographs were also used in the study performed by Wang and colleagues. SEM technology was used to investigate the morphological damage done to the surface of the membranes. Their study found that after the membranes were exposed to Fenton's reagent, several small bubbles were found on its surface (29). Furthermore, Wang and his colleagues also verified that the small bubbles increased in the chemical decomposition process. In addition, the bubbles had also been observed to become pinholes. It was determined that the appearance of deterioration to the membrane's surface was due to the decomposition to the polymer's repeating units (29). The deterioration observed by SEM technology is shown in Figure 5 of Appendix A.

The Effect of Radiation Exposure on Nafion Membranes

The radiation experiments performed for this study were motivated by the utilization of fuel cells in space. The fuel cells that were used on the Gemini mission in the 1960s were polymer exchange membrane, PFSA fuel cells. The 1kW unit PEM fuel cells that were utilized contained Nafion type membranes (31). The function of the fuel cell in space was to provide not only energy for space vehicles, but to also provide drinking water for individuals (26). Space flight missions generally expose the membranes to severe conditions during their operation, so irradiation studies intend to mimic the harsh conditions imposed upon the membrane during this time. During space flight, Nafion membranes become subject to open, non-equilibrium thermodynamic systems. At lower Earth orbits, the spacecraft materials could become simultaneously exposed to deep vacuum, solar radiation, thermal cycling, protons, molecular flux of residual atmosphere particles and other environmental factors present in space. The irradiation from space could therefore be the reason for structural damage that the membrane exhibits after flight.

The fundamental concept of radiation damage in regards to organic polymers can be referenced back to the radiolysis of water. The radiolysis of water was considered in this study since Nafion membranes must be hydrated in order to properly function. Nafion membranes were also known as being able to absorb a rather large amount of water at room temperature (Nafion EW 1200 absorbs at 28%) (22). The radiolysis of water had been found to produce damage to organic materials that were in the presence of water. The basic process by which radiolysis occurs is due to the presence of ionizing radiation and the organic material. The chemical reaction resulting from irradiation causes the production of a hydrogen atom (reducing species) and the hydroxyl free radical (oxidizing species). Zimbrick displayed the proposed mechanism of the radiolysis process in Scheme VI of Appendix B. One of the resulting products from the reaction mechanism was hydrogen peroxide, which was identified as a potentially degrading solution in the presence of metal impurities in an operating fuel cell. Laboratory experiments had consequently supported that the radiation of a hydrated membrane could be the reason for the formation of peroxide deep within the polymer phase (22).

In radiation chemistry, researchers have developed the idea of the radiative chemical yield of a substance (31). The radiation chemical yield, or G value, is based upon the number of product moles formed for every 100 eV of radiation energy deposited. The concept is widely used by radiation chemists today, since it conveys a method of quantifying product yields with respect to an absorbed dosage (31). The measurement units are in μmol/joule. In relation to the radiation experiments performed for our study, we assumed that with the increasing amount of membrane exposure to radiation, there would also be an increased amount of radiation energy deposited. The deposited energy would thus be the cause of chemical damage to the membrane through the formation of hydrogen peroxide and the presence of metal impurities in the fuel cell system (if in use). However, the membranes that we irradiated were only suspended in water after exposure to X-rays. Therefore, if damage had occurred, it was due to decomposition of the membrane's structural properties. The structural damage was theorized to be due to backbone breakage and physical decomposition mechanisms within the membrane.

If the emission of ions was detected after membrane irradiation, then it would be verification of structural damage that had occurred. In this experiment, the detection of fluoride and sulfate ions in membrane solution were analyzed for their correlation to the amount of exposure time the membranes underwent. If sulfate ions were present, then it would be indicative of decomposition of the sulfonic acid moieties present in Nafion membranes. If fluoride was detected in membrane water then it was a marker of the removal of side groups after C-F bond rupture. The literature supported that the dominant mechanism of membrane degradation was suspected to be due to ionizing radiation and through the mechanism of simple chain cleavage. It was also stated that the larger and short-chain products can be gathered and qualitatively measured (22).

CHAPTER THREE

THE UTILITY OF FUEL CELLS IN TRANSPORTATION APPLICATIONS

The Role of Platinum in Fuel Cell Systems and The Reason to Reduce its Use

One hurdle that research and development (R&D) teams must overcome in order to make fuel cell technology more cost effective has been to lower the amount of platinum used as a system catalyst. Platinum has been favored to be used as the catalyst because it effectively scavenges the hydrogen peroxide and/or hydroxyl radicals that were produced in the fuel cell during operation. The catalyst has also been preferred since it can decelerate the decomposition of Nafion by decomposing H_2O_2 without producing hydroxide radicals (27).

In 2007, the Energy Information Administration (EIA) reported that 1.7 ounces of platinum was used for an 80kW fuel cell system. Since the infiltration of fuel cell vehicles into the economy would projectively increase the demand for platinum in the global market, it has been an imperative goal for research and development teams to decrease the amount of platinum needed in fuel cell vehicles. The US Government has given its R&D groups a goal of reducing the amount of platinum needed for an 80kW system to 0.56 ounces by 2015 (32). That reduction would be approximately 33% of its use in 2007 fuel cell systems. The 2015 goal was set out to estimate that if fuel cell vehicles were to penetrate the market at a rate of 500,000 units/yr, then the amount of platinum catalyst required would be an additional 8 tons of Pt to be produced (32). If the increased demand for platinum would increase the market prices significantly, then a feasible fuel cell vehicle would be a greater feat to accomplish. Essentially, researchers would have to investigate the use of other catalysts that have been more plentiful, while also low in cost. Catalysts must be able to achieve a 50% market share of light duty vehicles (LDVs) (32). The EIA has also stated that even if the use of internal combustion-LDVs decreased, the decreased demand for catalytic converters will only marginally reduce the demand for platinum that would be needed for fuel cell vehicles. The EIA also projected that if fuel cell vehicles were to achieve 50% infiltration in the US transportation system, then that would be approximately 148 million fuel cell vehicles in the market. It would take about 160 tons of platinum to equip the first 10 million fuel cell vehicles, assuming the 2015 goal had been met. This would also mean that a 50% market share of fuel cell vehicles would demand 2400 tons of platinum (32).

Hydrogen: A Cleaner Fuel Source

The most significant challenge facing fuel cell integration has been the need for a different fuel infrastructure (13). Hydrogen fuel cell vehicles can utilize various sources in the production of hydrogen (shown in Figure 6). Efficiencies of hydrogen production range from 23 to 57% (13). The most common source of hydrogen production has been through the process of steam methane reformation (5). The steam methane reformation process could emit a small amount of CO_2 in the process, as well as hydrogen gas and carbon monoxide (5). The drawback in regards to CO_2 however is minimal in comparison to the extraction of fossil fuels from their natural resources. Natural gas has been thought of as the most readily available natural fuel source to transition to since the technology and pipeline infrastructure already exists. The technology of hydrogen production from natural gas has also been rapidly advancing (33). The US Department of Energy

(DOE) estimated that if fuel cell vehicles used hydrogen produced by natural gas methods, then greenhouse gas emissions would reduce by about 60%. However the DOE has also estimated that since our natural gas resources are limited, unfortunately, the US would transition its dependence from foreign oils to foreign gas. The US DOE has also reported that if the transition to a hydrogen infrastructure was successful, then hydrogen would be available un-taxed at $2-3 per gasoline gallon equivalent (33). The equivalency has indicated that the successful transition would cost the consumer the same out of pocket expenditure on a cost-per-mile-driven basis as the existing internal combustion engine or hybrid.

Although there were rapidly developing and existing processes to convert natural gas to hydrogen, there have also been other routes of hydrogen production that could be more sustainable. Renewable energy sources such as solar, wind and biomasses have all been thought of as possible sources of hydrogen production (as seen in Figure 6 of Appendix A)(34). The route of hydrogen production that ultimately gets chosen to energize fuel cells, would not only depend on the cost-effective production strategy, but would also include the utility of the gas itself. For instance, if an individual were to extract hydrogen by gasification, then their resulting product would contain impurities. Generally, the generation of hydrogen from natural gas and coal, will result in the production of carbon monoxide (CO), ammonia (NH_3), hydrogen sulfide (H_2S) and hydrocarbons (34). The impurities that are potentially present in the hydrogen gas could ultimately affect the power output of the fuel cell by poisoning various components (34). The effected components have been identified as the catalyst, electrolyte, and/or ionomer membrane (34). Those components could potentially be permanently or reversibly affected. The importance of catalyst (platinum) poisoning in regards to the focus of this paper was due to the fact that the catalyst surface was affected. The hindrance would reduce or eliminate the Pt in its function, and thus blocks chemical reaction sites that were crucial to maintaining the integrity of the membrane (34).

Since the production of hydrogen is unlimited, the implementation of a hydrogen infrastructure would not be hindered by the lack of an available fuel. In 2003, President Bush announced a Hydrogen Fuel Initiative (HFI) that intended to develop hydrogen, fuel cell and transportation technologies to make fuel cell vehicles a realistic goal by 2020. However, the initial cost of implementing the infrastructure (as well as purchasing the vehicle) was what impeded most from agreeing to the fuel cell vehicle transition. As most recently as February of 2009, the US DOE had released hydrogen production figures for the world and the US (35). The DOE stated that worldwide, the total production of hydrogen was 13 trillion standard cubic feet per year, and for the US it was 8.2 trillion standard cubic feet per year. The DOE also reported that 90% of the small merchant delivery loads in the US were by liquid tanker, with carriage of hydrogen as a compressed gas tube trailer at 7%. The other 3% was movement of hydrogen by a compressed gas cylinder (35). The DOE's remarks conveyed that current technology existed for hydrogen transportation, however the methods may still need further development in regards to the successful transition to a hydrogen-based infrastructure. Since hydrogen has not been commonly used as a fuel there may be non-transparent problems that may exist in the use, implementation, and commercialization of hydrogen fueling stations. In fact, as of January 2009, there were only 58 hydrogen fueling stations in the US (35). The stations mainly existed in large urban areas and were placed so that hydrogen fueled cars could travel between them. However, the replacement of the gasoline fuel station infrastructure with hydrogen fueling stations has been estimated to cost half a trillion US dollars (35).

The US DOE Hydrogen Resource Center reported that in order to provide the same amount of energy as 1 kg of hydrogen, it would take 1.014 gallons of reformed gasoline. In comparison to diesel fuels, it would take 0.896 gallons of diesel to equal the energy. In order to fully appreciate the potential of hydrogen's higher energy value, one must consider that 10.7 million metric tons of US hydrogen would produce an equivalent amount of energy as 660 thousand barrels of crude oil or 1.4 trillion cubic feet of natural gas (18).

The Role of the Membrane in a Hydrogen Fuel Cell Vehicle: The Cost Analysis

The EIA has estimated from 2003 hydrogen fuel cell vehicle data that the average fuel cell vehicle price in 2001 was around $81,000. The vehicle miles per gallon were around 52.9 and had a range of mileage around 450. The US Department of Energy reports that for an 80 kW direct hydrogen fuel cell automotive system in 2007, the estimated stack cost would be broken down as follows:

- Membrane 8%
- Electrode/Catalyst 57%
- Final assembly 11%
- Seal 6%
- Gas Diffusion Layer 6%
- Bipolar plate 9%
- Other Components 3%

In 2005, the National Renewable Energy Laboratory determined that the fuel cell stack was about 83% of the vehicle's cost (36). The number would decrease with a smaller amount of platinum used in the cell and the increased development of its components. However, the cost of the fuel cell will only decrease slightly until a more durable membrane and cost effective catalyst could be found.

Necessary Changes for Fuel Cell Vehicle Integration

A life cycle assessment needs to be carried out for transportation applications before their distribution among the market. A vehicle would be evaluated on its environmental and economical impact before it can be integrated among existing technology. The level of impact has been based upon the unit's contribution to emissions (i.e. manufacturing process, operation and maintenance), fuel combustion efficiency, unit disposal, and infrastructure construction (including its costs). In regards to fuel cell vehicles, a life cycle analysis would not only include the previously mentioned ideas, but would also include the weight of additional factors that are specific to a fuel cell unit. The factors include the electrode durability, system costs, hydrogen consumption and the influence of the bipolar plate material on the cell performance (34).

In this project we investigated how the function of one cell component effects the lifetime of the entire system. The component that was chosen, a proton exchange membrane, was understood to be a significant factor in the system's ability to operate. The component facilitates the electrical current produced within the cell, which was necessary to produce the power that operates the fuel cell. The deterioration or destruction of any functioning part of the membrane would play a critical role on the system's lifetime. It has been shown in the literature that the degradation of the membrane has not been well understood. It is also not known how a degraded membrane, in a functional fuel cell, affects the unit's lifetime. If the role of the membrane was better understood, then its lifetime in the fuel cell could be better evaluated.

New membranes must be stable in the fuel cell working environment. The membrane should accordingly be an efficient ion conductor and a stable redox media (which includes stability in cases of elevated temperatures) (1). In addition, the membrane must be non-selective for catalyst types (ie. to reduce the reliance on platinum) and must have a low permeability to the fuel used or its components (hydrogen, methanol, oxygen) (1). Since membranes are known to be exploited in the hydrated state for up to 30,000 hours, then they must also be able to preserve their strength during long exposure times. In addition, the membranes should be able to retain water under working conditions in order to function properly (1). Although there are many requirements for durable membranes, the membranes must remain feasible in meeting most, if not all, these expectations (1). It has therefore been imperative that fuel cell transportation technology and its components be better developed. A well prepared product would have a better chance of successful integration throughout the world.

CHAPTER FOUR

MATERIALS AND METHODS

The chemical degradation methods were modeled after various literature sources that investigated the chemical decomposition of proton exchange membranes in fuel cells. Studies have explored the concept of destructive oxidation pathways that potentially occur while the fuel cell has been in operation. Since it has been observed that hydrogen peroxide was generated during the operation of the cell, many studies have utilized its presence in degradation studies. It has also been found that trace metals were present as a result of bipolar plate decomposition. The combination of metals and hydrogen peroxide has been known to be reactive, therefore the combination of their presence had become suspected as potentially destructive sources within the cell. The reaction of hydrogen peroxide and trace metals has been known to be a highly oxidative and damaging solution. The reaction has been referenced as a Fenton's type of reaction. In a Fenton's reaction, a metal catalyst will react in the presence of hydrogen peroxide to destroy organic compounds. Since the concentration of hydrogen peroxide in the operating fuel cell has not yet been confirmed, then the exploration of the membrane's oxidative breakdown cannot also be validated. Accelerated chemical degradation studies have investigated an array of chemical conditions involving the concentrations of hydrogen peroxide and metal catalysts. The methods in this study were constructed to model very high concentrations of hydrogen peroxide production and high operating temperatures within the fuel cell. The high values were used to ensure membrane destruction so that the conditions could then be varied to find the limits of membrane structural damage.

Experimental Method of Chemical Degradation of Nafion Membranes (2009-A Method)

Nafion 117 and 212 membranes were studied. For each reaction four membranes were cut into 1.0 cm x 3.0 cm strips while keeping the protective coatings on the Nafion 212. Before starting a pre-conditioning process on the membranes, the protective layers were peeled off Nafion 212 and initial dry weights were obtained.

Next, pre-conditioning steps were carried out in 15 mL volumes and at 80 °C for 30 minutes each. The first step was to place the membranes in 5% (wt) H_2O_2, the second was to place them in distilled water, followed by a soak in 8% (wt) HCl and again placement in distilled water. Most of the reactions that were carried out by the Fenton's procedure were not weighed after this conditioning process and were immediately placed into a Fenton's reaction vessel. Some membranes were weighed after this procedure to investigate whether or not a noticeable difference was observed in membrane weight.

The Fenton's reaction was performed at a constant volume of 15 mL and a temperature of 100 °C. A water bath was used in order to keep the glass reaction at 100 °C during the experiment. Overall, the Fenton's reagent consisted of 15 mL of 30% (wt) H_2O_2 and 20 ppm Fe^{+2}. A mass of 1.1 mg of $FeCl_2 \cdot 4H_2O$ was used to provide the 20 ppm Fe^{+2} concentration. The Fenton's reaction was initiated by first heating up the hydrogen peroxide to 100 °C, and then the membranes and iron were added to start the reaction.

The Fenton's reaction was carried out for 5 to 6 hours and 5 mL samples were taken every 30 minutes to assess if membrane components were in the solution. The samples that were taken were replaced with refreshments of hydrogen peroxide and iron (II) (in proportion to the approximated amounts removed in the sampling procedure). For example, every 5 mL sample removed 1/3 of the reaction volume and therefore 1/3 had to be replaced to keep the proportion of membrane to Fenton's solution constant. Each refreshment thus consisted of 5 mL of 30% H_2O_2 and 0.3-0.4 mg of $FeCl_2 \cdot 4H_2O$.

After 5-6 hours of Fenton's reaction, the membranes were removed from the reaction vessel and the final solution was collected. The Fenton's treated membranes were immediately placed in 15 mL of 8% (wt) HCl to remove the iron from the membranes. This step was repeated multiple times to ensure that none of the iron was left behind. Subsequent washings with highly purified distilled water were also performed to ensure the removal of residual chloride from the acid. The final dry weights were then determined for membrane weight loss comparison.

Experimental Method of Chemical Degradation of Nafion Membranes with Iron Loading Step (2009-B Method)

Nafion 117 membranes were studied. For each reaction membranes were cut into 1.0 cm x 3.0 cm strips. Four membrane strips were used in each reaction. Before starting the reaction period, the membranes underwent a pre-conditioning process. The pre-conditioning steps were carried out in 15 mL volumes and at 80 °C for 30 minutes each. The first step was to place the membranes in 5% (wt) H_2O_2, the second was to place them in distilled water, followed by a soak in 8% (wt) HCl and again placement in distilled water. The two reactions that were carried out were not weighed after the conditioning process and were immediately placed into a Fenton's reaction vessel.

The 2009-B method was established to load the Nafion 117 membranes with the same concentration of iron that was previously used in the 2009-A Method. The loading of iron onto Nafion membranes involved soaking 4 membrane strips in 20 ppm of iron (II) solution for at least 24 hours. The 20ppm Fe^{2+} solution was prepared with 15 mL of water and $FeCl_2 \cdot 4H_2O$. The loading procedure resulted in having 0.00537 mmol of iron loaded onto the membranes, which was roughly 2.6% of the membrane loaded with iron. This step was used in only a few reactions to date. The reactions were carried out for 2 and 5 hours at 100 °C. The refreshment stages of the method were performed by replenishing only the 5 mL of 30% H_2O_2 that was taken out for each sample. The membranes were removed after the allotted reaction time and placed again in acid to remove the iron from them. They were subsequently rinsed with distilled water at least 5-8 times and dried to obtain their final weights.

Flame Atomic Absorption (AA) Spectroscopy

The Flame AA method was used to determine how much of the iron from the soaking solution was actually being loaded onto the membrane. The same procedure and calculations were used to find out how much iron was present in the resulting acid soaks. The calculations to determine the successful loading (% capacity) of the membranes are outlined in Appendix C.

Flame Atomic Absorption analysis was performed with a Perkin Elmer AAnalyst 100 spectrophotometer. The wavelength that was used in the iron detection process was 305.9 nm. Standards of iron were made up to 150 ppm to determine the linear calibration curve needed to assess the sample's iron content.

Experimental Method of Chemical Degradation of Nafion Membranes with Iron Loading Step (2009-C Method)

There were two methods of loading membranes used throughout the research project. One route of membrane loading was outlined in the Fenton's 2009-B Method. The

2009-C Method differed in its loading procedure in that the membrane would be considerably loaded with iron before its addition to the reaction vessel. A different amount of iron was used in an effort to find an optimal iron concentration for the most successful Fenton's reactions. An optimal Fe^{+2}:H_2O_2 ratio was based on the review of literature from successful remediation procedures using Fenton's reactions for water contaminants. Equation 1 of Appendix C demonstrates how to calculate the molar equivalent of Nafion used in a given reaction.

After determining the equivalent weight of Nafion used in a reaction, another calculation was used to determine the amount of iron necessary to load the membrane. The calculation was shown by Equation 2 of Appendix C. Equation 3 (Appendix C) illustrates the amount of $FeCl_2 \cdot 4H_2O$ that was required to load the membrane. The amount used was then increased by a factor of 2-3 to ensure full loading of the membrane. The excess solution that was used to soak the membrane was set aside for Flame AA analysis to verify the amount loaded onto the membrane and then it was discarded. Equation 2 (Appendix C) shows that 0.21 mmol of Fe was pre-loaded onto the membrane before reaction. Within a 15 mL

Fenton's reaction volume, this corresponds to an equivalent concentration of 780 ppm iron.

The reaction used 15 mL of 10% H_2O_2 heated to 70 °C. The membranes were dropped into the solution once it reached the correct temperature. Refreshment of hydrogen peroxide and iron was performed every 30 minutes for up to 5 hours. The refreshment consisted of the equivalent amount of iron and hydrogen peroxide that was taken for sampling for every 30 minute interval. Table 3 is a summary of all the Fenton's methods performed in this study.

Table 3. Fenton's Reactions Performed for Chemical Degradation Studies

Method Name	Membrane Type[a]	Temp (°C)	% Wt. of H_2O_2	Amount of Iron Added to Solution
2009-A	117 and 212	100	30	20 ppm in solution (membrane not pre-loaded)
2009-B	117	100	30	20 ppm pre-loaded in membrane relative to solution (2.6% loaded)
2009-C	117 and 212	70	10	780 ppm pre-loaded in membrane relative to solution (100% loaded)

[a] NafionEW. 1100g/mol

Chemical Analysis of Fenton's Reaction Samples

Ion Chromatography (IC) Method

The IC method was conducted with a Metrohm 761 Compact IC with a 15 x 0.5 cm quarternary amine polyvinyl alcohol column. The sample method included ion suppressed conductivity detection. The eluent was 1.8 mM Na_2CO_3 + 0.7 mM $NaHCO_3$, and the injection volume was 20 µL. The samples were generally ran for a duration of up to 20 minutes, since retention times of the ions were never seen past the 20 minute mark (found by previous analyses). The flow rate of the instrument was set at 0.70 mL/min.

From each 5 mL sample taken during the Fenton's procedure, 2 mL was used for ion chromatography analysis. Each 2 mL was pipetted into its own clean centrifuge tube and NaOH was added until the solution reached a pH of approximately 8 to 9. The tubes were then centrifuged for 20 minutes to remove $Fe(OH)_3$ from solution. To remove evolving gas from the solutions, the tubes were agitated by sonnication for 5 hours to remove evolving gases from solution. Once the bubble evolution had ceased, the samples were filtered with a 0.45 µm filter into a clean sample vial. A blank was also prepared for each reaction to check for signs of contamination during this process (distilled water, NaOH, filtration and placement in a clean vial). Each vial was capped and then analyzed by ion chromatography to detect anion evolution from the Nafion membranes. The fluoride and sulfate peaks were identified in each sample chromatogram and their respective concentration values were recorded. Calibration was performed with solutions that contained 0.1, 1.0 and 10.0 ppm of both fluoride and sulfate ions. Calibration curves were determined before each day's analysis to ensure accurate calculation of sample ion concentrations.

Gas Chromatography/ Mass Spectrometry (GC/MS) Method

The method was performed with a Varian CP-3800 GC coupled to a Varian Saturn 2000 MS. The parameters of the MS included a 29 minute run period, a low mass (m/z) ratio of 40, a high mass (m/z) ratio of 650, and EI and CI Auto programs. The GC parameters were set for a front injector type 1177, injector temperature of 280 °C, a column flow rate of 1.0 mL/min at a constant flow rate. The column oven temperature program was set at the conditions outlined in Table 4.

Table 4. Gas Chromatography/Mass Spectrometry Parameters used for Electron Ionization and Chemical Ionization Auto Programs

Step	Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
1	40	---	2	2
2	140	10.0	0	12
3	280	20.0	10	29

The final 3 mL of the 5 mL samples taken during the Fenton's procedure were reserved for GC/MS analysis. The solution was acidified with 1 drop of 12 M HCl. The 3 mL solutions were extracted with an equal amount of solvent, methylene chloride (CH_2Cl_2). The extraction was done in a two step process. The first step was done by adding the first 1.5 mL and then the organic layer was removed. The second half of the methylene chloride addition was then added and the subsequent extraction was performed. This step was done so that any eluted organics that were derived from the membrane could be collected. The collected organic layers from the extractions were each placed in their own GC sample vial and capped. The samples were then ready for analysis by chemical ionization (CI) and electron ionization (EI) methods by GC/MS. Any peaks that were not present in the solvent blank, however were seen consistently between reaction comparisons (ie. for time exposed and similar exposure conditions), were suspected as being organic decomposition fragments of the membrane.

The Production of Methylene Blue Test Strips to Verify the Presence of Hydroxyl Radicals in Reaction Solution

Hydroxyl radicals in the Fenton's reaction were verified with methylene blue test strips prepared in house using the procedure of Satoh et al. (37). Visual bleaching occurred on the strip if hydroxyl was present. The procedure of producing the strips began by the preparation of a stock solution of 10 mM methylene blue dye with methanol. The solution was prepared by adding 0.3739 grams of methyl thionine chloride to a 100 mL volumetric flask, and diluting up to 100 mL with methanol. The stock solution was then used to prepare a second diluted solution of 1.0 mM methylene blue dye from ultra pure water. Next, grade 1 qualitative filter paper was cut into rectangular test strips. The strips were cut down to 2 cm x 6 cm. A black, fine point, permanent marker was then used to draw horizontal lines on both sides of the test strips. The lines were place 1.5 cm from the bottom of the strip. The lines were dried before proceeding to the next step. Subsequently, the strips were dipped in the 1.0 mM methylene blue dye about 10 times. The strips were only dipped up to the mark that was drawn by the permanent marker. The strips were then dried on a clean, flat surface and allowed to dry. The reference stated that the strips should be allowed to dry for at least 24 hours before using them.

Experimental Method for Radiative Degradation Of Nafion Membranes

X-ray Exposure of Membranes

Nafion 212 membranes were used for X-ray exposure testing. The membranes were first cut into 1.0 cm x 3.0 cm strips and their weights were determined. Next, a preparation procedure was carried out at 70 °C. The first step was a 1 hour, 5 mL soak of membranes in 1.5% H_2O_2. Next, the membranes were incubated in 5 mL of deionized water (Barnstead Nanopure, 18.2 MOhm-cm), followed by a 5 mL soak of 1M HCl (both for one hour). The last preparation step required soaking the membrane in 10 mL of deionized water (Barnstead Nanopure, 18.2 MOhm-cm) for one hour. Subsequent washings with deionized water were often needed to ensure residual chloride from the acid was not present after the preparation steps (last step was performed multiple times).

The Nafion was dried flat in a vacuum oven at approximately 70 °C for 2 hours. The dried membranes were then taken out of the oven and placed in a dessicator and re-weighed. The prepared membranes were then placed between Kimwipes, and stored in a plastic Ziploc bag at room temperature until X-ray exposure. The prepared membranes were kept up to 2 weeks before exposure.

Nafion membranes were exposed to radiation with a Philips X'Pert X-ray diffractomer. The instrument's parameters were controlled for by the X'Pert Data Collector PANalytical software; Version 2.2a. The method of irradiating the membranes in the X-ray diffractometer (XRD) was conducted by warming the X-ray tube until the current reached 50 mA. The tension parameter was set at 40 kV. The membrane that was to be exposed was taken out of the Ziploc bag by Teflon coated tweezers, and placed on the center stage of the XRD. The exposure of the membrane was set at a 90° angle so that the maximum amount of membrane area could be exposed during the time frame (not all of the membrane was exposed in the procedure). A high end estimate of membrane radiation exposure was approximated to be 400 Grays per hour by our adjoining physics team.

The radiation exposure of membranes was recorded from 0 to 48 hours. After irradiation, the membranes were taken out of the XRD and placed in a 4 mL deionized water extraction. The soak was done in a tested (by IC), clean glass jar. The jar was tested for cleanliness since effluent degradation levels were expected to be in the low ppm range. The water extraction of membranes was conducted for 24 hours, followed by the removal and rinsing of the membranes with 1 mL of deionized water (collected in the same 4 mL soak), so that the final collecting solution was 5 mL. The membranes were then placed in 5 mL of 1 M HCl to bring them back to an acidic state. The soaking was done for at least one hour and was followed by subsequent rinses of deionized water. The membranes were then dried and re-weighed for final weights to see if weight loss occurred after exposure. The final membranes were placed between Kimwipes and stored in Ziploc bags.

Chemical Analysis of Irradiated Nafion Samples

Ion Chromatography (IC) Method

The IC method for analyzing radiated membrane extractions was the same as the method for Fenton's treated membranes. A Metrohm 761 Compact IC with a 15 x 0.5 cm quarternary amine polyvinyl alcohol column was used. The instrumental analysis was performed with ion suppressed conductivity detection. The eluent was 1.8 mM Na_2CO_3 and 0.7 mM $NaHCO_3$. The injection volume used was 20 µL. The sample runs were performed up to 30 minutes to allow for the detection of larger fragmented ions.

Since no metal catalysts were used in the radiation procedure, we omitted the centrifuge, NaOH addition and sonnication steps. IC analysis was directly performed on water extraction solutions, with the exception of samples that that were exposed for longer than 24 hours. Samples exposed longer than 24 hours were filtered with a 0.45μm filter before analysis. This was done to prevent large floating fragments of the membrane from clogging the IC instrument. Of the 5 mL samples taken, 2 mL was designated for the IC analysis procedure; 3 mL was set aside for GC/MS analysis. Fluoride and sulfate peaks were detected in the sample chromatograms by retention times around 4 and 16 minutes respectively. The concentrations of detected anions were determined daily by a calibration curve. Any other pertinent information was collected from the chromatograms as well (ie. presence of unexpected peaks).

Gas Chromatography/ Mass Spectrometry (GC/MS) Method

The GC/MS preparation stage for radiated samples was performed using similar methods to the chemical degradation experiments. The method was performed with a Varian CP-3800 GC coupled to a Varian Saturn 2000 MS. The parameters of the MS included a 29 minute run period, a low mass (m/z) ratio of 40, a high mass (m/z) ratio of 650, and EI and CI Auto programs. The GC parameters were set for a front injector type 1177, injector temperature of 280 °C, and a column flow rate of 1.0 mL/min at a constant flow rate. The column oven temperature program was set as outlined in Table 4.

From the 5 mL samples that were taken, 3 mL were saved for GC/MS extraction. The 3mL were extracted with 3 mL of CH_2Cl_2, and the resulting organic layers were collected in their own GC vials. Any peaks that were not present in the solvent blank, but were persistent in similar sample times and conditions, were accounted for as fragments of membrane degradation products.

CHAPTER FIVE

RESULTS OF DEGRADATION EXPERIMENTS

Iron Loaded Nafion Membranes Exposed to Fenton's Reagent [2009-C Method]

The method of determining the correct ratio of Fe^{+2} to H_2O_2 for the Fenton's reaction procedure was not successful in the degradation of the membrane. The results indicated that at 70 °C and 10% H_2O_2, the reaction performed minimal damage to the membrane's integrity.

Membrane loading experiments using this method displayed that 100% of the membrane's capacity was loaded. The calculations displayed in Equation 2 and 6 of Appendix C show how to determine the iron capacity and concentration of iron loaded onto the membranes. The iron concentration data was obtained by Atomic Absorption (AA) analysis. Equation 3 (Appendix C) displays how to calculate the amount of $FeCl_2 \cdot 4H_2O$ required to load the membrane. Equation 4 of Appendix C then illustrates the amount of iron that was placed into solution with membrane after a 24 hour soaking period. The method utilized a higher concentration of Fe than other literature sources outlined in Table 2. The 100% load of the membrane therefore displayed that it was less successful in membrane degradation than the 2.6% load used in the 2009-B Method (described below).

Iron Loaded Nafion Membranes Exposed to Fenton's Reagent (2009-B) Method

In these experiments, the membranes were pre-loaded with 20 ppm $FeCl_2 \cdot 4H_2O$ in an overnight soaking solution. The solution volumes were 15 mL and prepared with ultra pure water. The reaction conditions followed the 2009-A Fenton's Method pre-conditioning steps and the reaction refreshment stages. The reactions utilized 30% H_2O_2 and were run at 100°C. The reactions were carried out at 2 and 5 hours; where 5 mL samples were removed every 30 minutes followed by replenishments of fresh solution. The two hour reaction was the result of a broken reaction vessel after the removal of the 2nd hour sample. The rest of the solution fell into the water bath and was therefore discarded. The five hour reaction followed the 30 minute refreshment scheme, however between the 2.5 and 3.5 hours, the removal of sample was missed, and the rest of the reaction was carried out as if it was not. Two refreshment conditions for this experiment were only conducted with the replenishment of hydrogen peroxide. Iron was left out of the refreshment procedure. The idea was to investigate the role of iron in membrane degradation conditions, and if fresh iron was needed for continued degradation. If iron was not needed, the reaction would continue to degrade the membrane due to the existing reactants.

The results of the study displayed that the reaction continued to emit fluoride anions in an increasing manner, and that the reaction did not lag or subside without iron addition. This result infers that membrane degradation does not require much iron metal contamination to be present (2.6% loaded membrane), and that the concentration of available Fe^{+2} does not need to be replenished. The results also confirm that maybe an excess amount of iron (even a 100% load; 2009-C Method) may sequester the reaction. Due to the time constraints of this paper, only two reactions were carried out. As a result more testing is needed to verify if the results can be reproduced.

Figures 8 and 9 of Appendix D show the results of the 2009-B reactions 21 and 22. In Figure 8, data obtained from ion chromatography analysis indicated that the two reactions also had increasing trends with respect to fluoride evolution. Reaction 21 of Figure 8 displayed a greater increase (slope) of fluoride evolution with increasing reaction time (with respect to all other Fenton's degradation methods). The emission rate of fluoride evolution was shown in Table 5. The emission rates were calculated using Equation 7 of Appendix C. The fluoride emission rate for reaction 21 was 25 μmol F^{-}/gram of Nafion-hr, which was larger than the results of other Fenton's methods (Methods A and C). Reaction 22 of Figure 8 displayed the same increasing trend that the fluoride evolution in Method A had shown. The similarity inferred that Method B was at least as successful, in membrane deterioration, as Method A.

Figure 9 displays the sulfate evolution with time for Method 2009-B. The result was that the emission of sulfate was increasing (just on a much smaller scale than fluoride). In fact, reaction 21 had a greater sulfate evolution rate than reaction 22. The emission rates for the reactions (determined by Equation 7) are displayed in Table 5. The table shows that the evolution of sulfate for reaction 21 was 0.44 μmol SO_4^{-2}/gram of Nafion-hr, while the emission for reaction 22 it was 0.09 μmol SO_4^{-2}/gram of Nafion-hr. In addition, the FER/SER and SER/FER ratios presented in Table 5 illustrate the magnitude of fluoride evolution, which was 50 to 80 times greater than sulfate. For example, the FER/SER for reaction 21 was 57, while the SER/FER for the same reaction was 0.02. The ratios obviously affirm that fluoride was emitted more readily than sulfate.

Table 5. Emission Data for Method 2009-B[1,2]

Reaction #	F^- Emission Rate(FER)(µmol F^-/gram of Nafion-hr)	SO_4^{-2} Emission Rate (SER)(µmol SO_4^{-2}/gram of Nafion-hr)	FER/SER	SER/FER
21	24.74	0.4369	56.63	0.0177
22	7.777	0.0943	82.47	0.0121

[1] References Figures 8 and 9 of Appendix D
[2] FER and SER calculated using Equation 7 of Appendix C

Nafion Membranes Exposed to Fenton's Reagent (2009-A Method)

Figure 10 of Appendix D is the graphical representation of fluoride emission data obtained by Ion Chromatography analysis. The figure displays the data for Nafion 117 membranes exposed to Fenton's reagent at 100 °C for up to six hours. The reactions were numbered 13 through 20, and all were included in the graph except for reactions 16 and 18. Reactions 16 and 18 were omitted from the graph due to the analyst's failure to carry out all the outlined reaction conditions.

The emission rates obtained by IC analysis varied, however most of the experiments displayed an increasing trend of fluoride emission. The emission rates are detailed in Table 6. The range of fluoride emission for Nafion 117 was 0.08 to 30 µmol F^-/gram of Nafion-hr. The sulfate emission range for 117 membranes was 0.1 to 3.9 µmol SO_4^{-2}/gram of Nafion-hr. One experiment performed for Nafion 117 had refreshment stages at intervals of 40 minutes instead of 30 minutes. An increasing trend was found, however the emission rate was not as great as those reactions that had 30 minute refreshment intervals.

Table 6. Emission Data for Nafion 117 Membranes Degraded by Method 2009-A[1,2]

Reaction #	F^- Emission Rate (FER) (µmol F^- /gram of Nafion-hr)	SO_4^{-2} Emission Rate (SER) (µmol SO_4^{-2}/gram of Nafion-hr)	FER/SER	SER/FER
13	30.35	3.917	7.748	0.1291
14	16.76	0.9788	17.12	0.0584
15	24.00	0.1322	181.6	0.0055
17	0.0789	0.1112	0.7095	1.409
19	8.552	0.1445	59.18	0.0169
20	4.145	0.1484	27.93	0.0358

[1] References Figures 10 and 11 of Appendix D
[2] FER and SER calculated using Equation 7 of Appendix C

Figure 10, of Appendix A, displays the sulfate emission for Nafion 117 Fenton's experiments, which were performed at 100 °C for up to six hours. The graph displays the results of experiments 13 through 20, and excludes reactions 16 and 18. The figure shows that sulfate emission levels were 7 to 180 fold less than that of fluoride. For instance, reaction 15 had an FER/SER of 182 and a SER/FER of 0.006. Figure 10 also illustrates that the sulfate emission levels were inconsistent between experimental runs.

Nafion 212 degradation results were distinguished by Figures 12, 13 and 14 of Appendix D. Figure 12 shows the fluoride evolution from the membrane after exposure to Fenton's reaction. Fluoride appears to be released from the 212 membrane with an increasing trend in respect to exposure time. In this figure, reaction 18 was not refreshed as the 2009-A Method outlined. The last two refreshments occurred at 1 and 1.67 hours instead of thirty minute intervals. The result of the variation in refreshment time for fluoride emission was not as great as other refreshment stages performed in other methods. Most of the reactions that were performed coincided with Nafion 117 fluoride emission results; there was an increasing trend of fluoride loss. However, the fluoride loss appeared to occur at a greater rate for Nafion 212 membranes as compared to Nafion 117 membranes.

The emission rates for both fluoride and sulfate are displayed in Table 7. The range of fluoride and sulfate emitted from the membrane was 17-119 μmol F^-/gram of Nafion-hr and 0.02-1.9 μmol SO_4^{-2}/gram of Nafion-hr respectively.

Table 7. Emission Data for Nafion 212 Membranes Degraded by Method 2009-A[1,2]

Reaction #	F^- Emission Rate (FER) (mg/gram of Nafion-hr)	SO_4^{-2} Emission Rate (SER) (mg/gram of Nafion-hr)	FER/SER	SER/FER
13	47.31	1.857	25.48	0.0393
14	60.50	0.3975	152.2	0.0066
16	18.98	0.0218	870.6	0.0011
17	25.84	0.4708	54.89	0.0182
18	33.48	-20.49[2]	-1.634[3]	-0.6120[3]
19	17.03	0.3850	44.23	0.0226
20	119.1	1.059	112.5	0.0089

[1] References Figures 12 and 14 of Appendix D
[2] FER and SER calculated using Equation 7 of Appendix C
[3] Negative since considers first outlying data point (refer to Figure 13)

Figure 13 displays the results of a reaction performed at 80 °C using the Fenton's 2009 method conditions. The amount of fluoride emitted from the membrane was far less in comparison to reactions performed at 100 °C. More specifically, the emission levels for fluoride at 80 °C were about 30 times less than those at 100 °C. The sulfate emission levels at 80 °C were below the detection limit and therefore were not graphed.

Figure 14 (Appendix D) and Table 7 present the emission of sulfate for Nafion 212 membranes. Figure 14 displays that sulfate emission levels were 20 to 800 orders of magnitude lower than fluoride emission levels and were non-increasing with time. Table 7 illustrates the difference in the fluoride and sulfate emission rates.

Figure 15 of Appendix D is the graphical comparison of fluoride emission for Nafion 212 & 117 Fenton's treated membranes. The results show that there was a greater loss of fluoride from Nafion 212 than Nafion 117 membranes. Tables 6 and 7 show the contrast between the FER/SER rates. The largest FER/SER ratios for 212 membranes were 871 and 152. In comparison, the largest 117 membrane FER/SER ratios were 182 and 59.

In contrast, Figure 16 of Appendix D shows that Nafion 212 & 117 membranes have similar cases of stability in regards to the emission of sulfate. The consistency between membrane stability was shown for reactions held up to 6 hours of exposure to Fenton's reagent.

Degradation of Nafion Membranes by X-ray Radiation

The results of Nafion 212 X-ray radiation experiments graphically represented in Figures 18 and 19 of Appendix D. Figure 18 shows the fluoride emission levels and Figure 19 displays sulfate emission levels. Figure 18 conveys that the data obtained for replicate runs was not always accurate. The imprecision therefore inhibited the ability to conclude that fluoride was leaving the membrane in an increasing trend. It first appeared that there was an increasing fluoride loss, which was comparable to earlier data. However, additional experiments must be performed to confirm whether this holds true. Table 8 below shows the emission rates obtained for Figure 18. The fluoride emission rates determined for both data sets varied. The fluoride emission rates were 0.24 and 0.005 µmol/gram of Nafion-hr.

Table 8. Emission Data for Nafion 212 Membranes Degraded by X-ray Radiation[1,2]

Data Year	F^- Emission Rate (FER) (µmol/gram of Nafion-hr)	SO_4^{-2} Emission Rate(SER)(µmol /gram of Nafion-hr)	FER/SER	SER/FER
2008	0.2366	0.3729	0.6345	1.576
2009	0.0051	0.7042	0.0072	138.1

[1]References Figures 18 and 19 of Appendix D
[2]FER and SER calculations displayed in Equation 7 of Appendix C

Sulfate emission levels were depicted in Figure 19 of Appendix D (also shown in Table 8). The data obtained for sulfate was much more consistent than the data obtained for fluoride. An increasing trend of sulfate loss was demonstrated with increased radiation time for Nafion 212 membranes. The two sulfate emission rates were 0.37 and 0.70 μmol/gram of Nafion-hr.

A comparison of FER/SER and SER/FER ratios in Table 8 illustrated that there was a difference between degradation mechanisms for Fenton's treated and irradiated membranes. The SER/FER ratios that were obtained for radiation experiments were much higher than other SER/FER ratios displayed in Tables 5-7. In fact, the radiation data obtained in 2009 had a SER/FER value of 138. The value was much greater than any of the other emission rate ratios obtained.

Figure 20 (Appendix D) illustrates a sample chromatogram obtained from ion chromatography analysis. The detection of fluoride and sulfate were confirmed with the presence of peaks around 3 and 11 minutes respectively. The peak that occurred at 28 minutes was an unknown ion that was only detected in the Nafion irradiation experiments. The unknown peak area increased with increasing exposure time, which suggested that the peak's identity was a result of membrane deterioration.

Methylene Blue Test Strips to Verify the Presence of Hydroxyl Radicals in Reaction Solution

The use of in house prepared, methylene blue test strips was performed during all experimental methods. The result of using the strips was that it verified hydroxyl radicals were produced at various points throughout the time of reaction. Bleaching of the blue portion of the strip verified the presence of hydroxyl radicals. Testing was routinely performed before the beginning of reaction, once the reaction began, and after every refreshment period.

CHAPTER SIX

DISCUSSION OF EXPERIMENTAL RESULTS

Accelerated Degradation of Nafion Membranes

The detection of anions in membrane solution was found to be indicative of degradation processes that had occurred upon vital membrane components. The loss of anions therefore coincides with the integrity of the membrane's performance in the fuel cell system. Our research focused on investigating the degree by which the ion or fragment loss from the membrane may be the origin of failure for a fuel cell system. The following discussion sections describe the contribution of various factors to membrane degradation mechanisms.

Weight Loss Observed in Degraded Nafion Membranes

Weight loss detection, in both chemically treated and irradiated Nafion membranes, has been inconsistent. The theoretically expected loss of weight from these degradation routes have been calculated to the fourth decimal point. Therefore, since the sensitivity of our balances was only to the fourth decimal place, we encountered standard error problems with weight loss detection. For example, if 100 μmol of fluoride were lost per gram of Nafion exposed, then the respective weight loss would be 0.0056 grams. In addition, if 20 μmol of sulfate were lost per gram of Nafion exposed, then the observed weight loss would be 0.0019 grams. An error in the figure in the ten-thousandths place could significantly hinder the quality of the data collected. If weight loss was discovered, then there was never any relation to increased membrane exposure times in regards to reagent exposure or irradiation. In the kinetic model study, regarding chemical degradation of PFSA membranes, it suggested that Fenton's exposed ionomers were expected to have an insignificant weight loss (7). The researchers reported that this was due to the fact that the Fenton's degraded membranes only had a fluorine loss of 3%. The findings were verified by ion chromatography (7). Figure 4 displayed the results of the Kinumoto study that described their detection of weight loss for the Nafion membranes. The figure shows that after 5 days of membrane exposure to Fenton's reagent for 12 hours each day, there was a reported weight loss of 40%. The present study was not able to carry out degradation reactions and weight loss experiments of the Nafion membranes at such long intervals of time. Therefore, the damage that resulted after chemical decomposition may not have been extensive enough to detect. If the emission curve in Figure 4 was utilized as a standard reference, then at 6 hours the expected weight loss would be less than 5% of the original membrane weight. Figure 4 coincides with the findings of other literature sources and experimental results obtained for this research project.

In addition, Nafion has been known to readily absorb water at room temperature. Therefore the obtainment of our initial and final membrane weights could have been performed in a more carefully controlled environment to minimize water absorption. Perhaps a room with better controlled humidity and temperature levels could have been utilized to obtain more accurate measurements. The everyday fluctuations of humidity in the atmosphere could have affected our ability to observe the very small difference in membrane weights after their exposure. Furthermore, a likely source of error in membrane weight obtainment could have been due to the iron that gets left behind in the membrane after the reaction period. The residual iron could overcome the weight loss if it occurred.

It is pertinent to investigate whether or not membrane weight loss had occurred after degradation studies since the occurrence of weight loss coincides with an increase in the membrane's proton conductivity. The increase in conductivity also increases the membrane's water absorption (another source of concealing weight) and gas permeability, which ultimately causes the deterioration of the membrane's mechanical properties (38).

Effect of Temperature on Nafion Membrane Degradation

It is well understood that temperature plays a key role in the ability of a fuel cell to function during transportation applications. At temperatures greater than 80 °C, fuel cells exhibit system failure. The failure has most often been attributed to the effects that high temperatures may have on the composition of the membrane. The literature has shown that accelerated degradation studies of the membrane with temperatures ranging from 80 to 100 °C convey deterioration of the membrane. In the experiments described here, the results displayed an observable increase in the amount of degradation products was detected with increased temperature.

The reactions that were performed at 80 °C, did not display that the data was following any increasing or decreasing trend. The data was scattered for fluoride emission (shown in Figure 13), while the sulfate emission data was so minute, it was too close to the lower detection limits to report. It has been reported that there were observable trends of degradation at 80 °C (25); however those reactions used longer time intervals greater than 5-6 hours. The importance of longer reaction times was relevant to longer operating hours, where the temperature was an influential factor in membrane degradation. However, since our study used smaller hours of exposure, the goal was to contribute factors that may express how the initial degradation of the membrane takes place. If the initiation of membrane degradation becomes better understood, then the development of a more stable material can come about from that knowledge. The following sections outline the significance of chemical degradation conditions, like temperature and iron concentration, as well as the influence of radiative damage to membrane exposure.

(2009-C Method) Membrane Loading Condition Followed by Fenton's Degradation

The method of utilizing an optimal iron concentration to hydrogen peroxide ratio in the determination of the most chemically degrading Fenton's procedure was unsuccessful for this project. The reaction scheme involved the use of 10% H_2O_2 at 70 °C. Both the temperature and concentration of hydrogen peroxide may have had an effect on the unsuccessful outcome of chemical degradation on the membrane. The emission results obtained after exposure to the Fenton's reagent were minimal and did not convey an increasing trend. The temperature may have not reached a reaction potential that was inherent for the Fenton's procedure to undergo an activated oxidation state. It was also possible that the concentration of hydrogen peroxide was not great enough to meet the lowest degrading conditions required. The reaction temperature of 70 °C was chosen since it was relative to the average temperatures experienced for fuel cells in transportation applications.

The concentration of hydrogen peroxide generated in the fuel cell has been estimated to be 10 to 20 ppm. The 10% concentration of hydrogen peroxide that was used for these experiments however was four orders of magnitude greater than what was expected to be generated in the cell. It was therefore expected that degradation would be observed for the conditions similar to those present in an operating fuel cell. As a result, since degradation was not detected after the reaction, it was confounding to determine why the expected results were not obtained. Further research would be necessary in order to verify which operating cell temperatures, hydrogen peroxide concentrations, and loaded membrane ratios, could meet the degradation mechanism's minimal requirements. It would also be pertinent to discover the rate law of Fenton's degradation reactions, which would help further develop the membranes used in fuel cell systems.

It was suspected that the ratio of loading the membrane played a key role in the failure to observe degradation products. It was observed that the addition of $FeCl_2 \cdot 4H_2O$ to the reaction vessel initially caused an excessive amount of bubble formation upon the membrane. However, the bubble formation ceased after 5 minutes and with some later additions of the $FeCl_2 \cdot 4H_2O$ and hydrogen peroxide, the reaction was not as vigorous. The development of the experimental method had focused on trying to investigate whether or not too much of the $FeCl_2 \cdot 4H_2O$ was present (relative to an optimal ratio), and therefore the reaction had become quenched with iron.

Iron Loaded Nafion Membranes Exposed to Fenton's Reagent (2009-B Method)

Nafion 117 membranes were utilized for this experiment. Due to the time constraints of this project, an insufficient amount of data had been collected to verify the results. However, the preliminary findings appear to be successfully degrading (there was an increasing trend). The first two reactions utilized a 2 hour conditioning procedure with iron loading for 24 hours (at 20 ppm) and Fenton's conditions at 100 °C and 30% H_2O_2 (15 mL). The reactions were only replenished with fresh solutions of hydrogen peroxide (5 mL). The replenishments that were previously performed in other current Fenton's methods replaced not only the hydrogen peroxide, but the theoretical amount of iron was removed as well. Therefore, a significant finding was that only fresh hydrogen peroxide solution was necessary to continue the membrane deterioration mechanism. Since fuel cell operations continually generate H_2O_2 (30), a supporting degradation environment would be present throughout the cell's lifetime.

It may be important to continue testing with the 2009-B Method since the reaction mechanisms could be affected by how close the reactants are localized on the surface of the polymers. It was observed that in other methods, iron additions to the Fenton's bath resulted in the appearance of white spots on the membrane. The white spots would appear only in regions where the iron was dropped directly onto the polymer. The rest of the membrane would still appear to produce bubbles in solution; however the membranes appeared to be more transparent if not in contact with iron additions directly. After continued reaction time, the membranes took on a more opaque appearance similar to the membrane shown in Figure 17 of Appendix D. It was observed that at lower reaction times, the membranes that were loaded with 20 ppm Fe^{+2} turned opaque and white. This result occurred much later in time in regards to reactions where membrane loading was not present. Again, more research is needed to support these findings; however the preliminary results show that membrane deterioration is present and increasing when fresh hydrogen peroxide solution is added periodically.

The emission data for the 2009-B Method is displayed in Table 5. The data shows that the FER/SER was greater than the SER/FER; which confirms that the fluoride evolution was greater than sulfate. It was interesting to see that in Figure 8, the emission of fluoride did not display any slow reaction step, which was present in the beginning hours of reaction 21. Meaning, an increasing slope of fluoride evolution began after the initiation of reaction. There was not a lag in time present before the emission rate began to take off. The result supports the idea that perhaps the localization of reactants upon the polymer was a pertinent factor in beginning the degradation process at a quicker rate. Reaction 21 had a fluoride emission rate of 0.47 mg F^-/gram of Nafion-hr. In contrast to reaction 21, reaction 22 was similar to the fluoride emission results obtained using the 2009-A method. Reaction 22 had a fluoride emission rate of 0.15 mg F^-/gram of Nafion-hr. For that reason, further investigation is necessary to see if the outcome of reaction 21 could be reproduced. If reaction 21 is reproducible, it would support the idea that the membrane loading and localization of reactants is a crucial aspect of membrane degradation.

Fenton's Reagent Exposure of Nafion Membranes at 100 °C (2009-A Method)

The Fenton's reactions carried out in this study conveyed that both fluoride and sulfate were detected in membrane solutions. The detection of both ions differed in that fluoride displayed an increasing trend of emission but sulfate did not. The emission of ions from both types of Nafion membranes were similar, however it was observed that the 212 membranes had emitted more fluoride ions than the 117 membranes (Figure 15). The variation was notable since the manufacturer of the membranes claimed that 212 membranes were more chemically stable than the 117 polymers.

The reason that the fluoride emission rate may have been greater for 212 membranes could have been based on the idea that the membranes were thinner and therefore may have had a larger available specific surface area exposed to the chemically degrading solution. This might have resulted in increased penetration of H_2O_2 throughout the membrane volume making it more susceptible to chemical attack. The increased chemical attack would verify that the Fenton's reaction was dependant on the localization of reactants to membrane.

In contrast, the two membranes that were used in this study conveyed that there was some similarity in the mechanism of deterioration that occurred after Fenton's reagent exposure. The two membranes exhibited a slow start up time before the emission of fluoride increased (shown in Figure 15). The results conveyed that perhaps the degradation products became greater after 1.5 hours when the emission of fluoride occurred. For this reason, it is proposed that there may be some underlying reaction kinetics that are not completely understood during the initial hours of exposure to Fenton's reagent. The activation energy of the reactions may not be reached until after the 1.5 to 2.0 hour mark, and once reached, fluoride emission drastically increases.

Literature sources (Table 2) have provided estimated emission rates for fluoride; however none of these studies discuss the idea of a slow decomposition rate at start up hours. Therefore the investigation of the degradation mechanisms at lower exposure hours has been vital to the discovery of the initiation of the mechanism that inherently degrades the membrane in operation. Figure 7, extracted from the Wang et al. study (29), illustrated the inverse relationship that decomposition products of the membrane have with the conductivity of the membrane. The study conveyed that as more decomposition products were detected with increasing exposure time to the Fenton's reagent, the conductivity of the membrane also increased. The increase in conductivity ultimately had a negative effect on the continued function of the membrane with increased hydration and gas permeability; it degraded Nafion's mechanical properties.

The analysis performed by GC/MS for the Fenton's 2009-A method, was not successful in detecting organic compounds emitted from the membranes. The inability to detect any molecular fragments may have been due to the low boiling points of the compounds. Their low boiling points would thus allow them to escape into in the atmosphere during the reaction time or immediately after. All deterioration products may have therefore not been present during the collection of the sample solutions, as some of the ultimate products are CO_2 and HF. Besides the possible escape of compounds, several hours had elapsed before the samples were analyzed, and further reaction of molecular fragments could have occurred. The GC/MS portion of methods 2009-A, B and C need to be developed further to accommodate for these losses.

The chemical degradation studies performed with 2009-A and 2009-B methods both resulted in having noticeably degraded membranes. It was physically apparent that the membrane composition was altered and bubble formation upon the membrane had taken place. In some instances there were also small pinholes or tears in the membranes. The Tang et al. (25) study reported that they were also able to visually witness the physical results of the Fenton's reaction conditions. The Wang et al. (29) study further investigated the extent of membrane deterioration by physically identifying it with SEM technology (shown in Figure 5). The resulting image confirmed that pinholes and bubble formation was present throughout the entire span of the membrane. I would suspect that similar scans of our chemically treated membranes would confirm the same results.

Irradiation of Nafion Membranes

The research conducted by Balko et al. (22) confirms that HF is released from the membrane during radiation experiments. They reported that the emission of fluoride primarily due to the exposure to β radiation. The slope for the 1100 EW Nafion materials was found to be 8.8×10^{-7}

moles of fluoride/M-rad·g of dry resin (22). Due to our sample collection method, we may not have seen the total amount of nonvolatile product that was formed after irradiation exposure of our membranes. The Balko study collected colorless grease from the membrane by Soxhlet extraction with chloroform. The extraction was performed after drying the membrane at 110°C. They used IR analysis to verify the constituents of the grease that they collected. The IR results verified the presence of newly formed carboxylic acid groups, which may be indicative of membrane degradation (22). The study also verified the presence of volatile radiolysis products in the gas space of the sample bags used during their irradiation experiments. The GC/MS method also found several nonvolatile products confirming degradation of the membrane had occurred.

GC/MS methods were used for the analysis of radiated membranes (in this experiment) in order to investigate whether or not organic compounds may be present in sample solution. This method was chosen since larger unknown anions were detected in sample solution by ion chromatography analysis. Sample chromatograms displayed an unknown ion peak at retention times around 28 to 30 minutes (shown in Figure 19) for all the varying exposure hours. Since unknown anion peaks were observed in X-ray experiments (and not Fenton's), then the results suggested that side chain cleavage could more readily occur with radiation damage. The damage would thus produce organic fragments upon membrane exposure. However, despite our enthusiasm to detect organic compounds with GC/MS analysis, our results did not meet expectations. We were unable to detect any fragment peaks that did not coincide with our solvent blank. After numerous reactions and sample extractions, the result was that a different extraction method was needed in order to collect the degradation products that Balko and other researchers have been able to detect after experimentation.

Additionally, the radiation experiments performed for this project confirmed that the durability of Nafion was affected by X-ray radiation. The degradation that resulted from irradiation was correlated to the amount of time that the membrane was exposed to X-rays. It was observed that as time increased, both the fluoride and sulfate emission levels also increased in the membrane sample water. The sulfate emission levels were also found to increase more rapidly than the release of fluoride. Since most of the literature mentions the observance of sulfate emission and does not quantify those levels, then our study focused on reporting an emission rate for the anion. The amount of sulfate detected ranged from 0 to 70 ppm in solution. The 70 ppm level was an extreme finding among the other data points collected for X-ray studies. The next largest detection of sulfate within the linear emission range was around 35 ppm. The calculated emission rates for sulfate ranged from 0.37 to 0.70 μmol SO_4^{-2}/gram of Nafion-hr.

Table 8 illustrated that there was a greater value for SER/FER than FER/SER. This finding was significant in that it verified membrane radiation effects were greater upon sulfonic acid moiety scission than carbon-fluorine breakage along the main chain. The SER/FER values were 2 to 138 times greater than the FER/SER. The difference indicates that the radiolysis of water within the membrane and subsequent degradation processes were not the major mechanism behind the polymer's deterioration. The proposed hydroxyl radical formation would thus not be important in the deterioration mechanism, and the unzipping mechanism would not be dominant. This assumption was based on the fact that in the unzipping mechanism, the fluoride evolution is greater in comparison to sulfate. The conclusion was affirmed by Balko in his findings (22) when he reported that he found the radiolysis of water was not the mechanism by which irradiated membranes degraded. The results from this project displayed that there must be an entirely different degradation mechanism that directly attacks sulfonic acid moieties.

The presence of sulfate ions indicated that with X-ray irradiation, there was considerable carbon-sulfur bond breakage occurring. The breakage of carbon-sulfur bonds is significant to the working conditions of the membrane in the fuel cell. The sulfonic acid groups that are affected by the bond breakage are viable to the transport of protons within the membrane. The disruption of proton movement in the membrane would thus impede the performance of proton conductivity, and as a consequence, decrease the condition of efficient electrical power generation.

Limitations of the Study

Due to the time constraints of the project, the study was limited by the lack of replicate samples obtained. It would have been better to accumulate numerous amounts of runs for each reaction condition to verify any apparent trends or correlating factors. It is more statistically sound if experimental data could be reproduced many times so that an accurate way of assessing the data could be performed. It would have also been statistically sound to show that the results had a low standard deviation among the various times of exposure (in relation to emission rates).

In addition, the reproducibility of both radiation and Fenton's reaction experiments were not acceptable enough to conclude reliable emission rates. The graphs conveyed that there were trends in some of the data (i.e. the shape of the curve or a linear progression); however some of the experiments that were repeated did not coincide with another. The deviation from run to run was sometimes large. Again, this could have been more easily avoided with a vast amount of experiments having been done.

The Fenton's reaction investigation was also restrained by the researcher's ability to carry out reactions at longer exposure times (i.e. longer than 6 hours). The literature had shown that most reactions were carried out for days, weeks or even by multiple person shifts. It was therefore difficult to assess if the emission rates that the results were conveying were comparable to the longer hours of literature findings. The comparison was hard to accomplish for Fenton's reactions due possibly to the presence of some underlying activation energy for the reaction mechanism and or the reproducibility among sample sets. Since the reaction took some time to take off, usually around 1.5 to 2 hours, the experiment was generally done right when the degradation would appear to begin.

Lastly, the project was limited by the escape of molecular fragments that evaporated into the atmosphere. The reaction vessels and methods did not provide a means to entrap any effluent compounds. Perhaps a better experimental setup would find a way to radiate the membranes while kept in an enclosed water solution. Additionally, the Fenton's reactions could become better housed while the reaction is taking place, so that effluent gas and molecular compounds could become entrapped before potential loss to the environment.

CHAPTER SEVEN

CONCLUSIONS

Significance of the Results

The result of exposing the membranes to Fenton's reagent displays that Nafion 212 membranes have a greater tendency to be broken down chemically than 117 membranes. DuPont, however, had described their 212 membranes as being more chemically stable than their 111 and 117 products. The Fenton's degradation experiments that were performed on Nafion 117 and 212 membranes displayed dissimilar emission rates for fluoride. The greatest amount of fluoride detection from Nafion 212 membranes was approximately 119 μmol F^-/gram of Nafion exposed; in contrast the greatest amount of fluoride detected from Nafion 117 degradation studies was approximately 30 μmol F^-/gram of Nafion. There was a four-fold difference between the emission rates of both membranes under the same reaction conditions.

In addition, the literature has consistently reported that the emission rate of Nafion membranes was 0.15 mg F^- per hour of exposure to Fenton's reagent (as shown in Table 2). Since previous experiments (Table 2) did not convey that the rate was in reference to a per gram exposure basis of the Nafion membranes, it was assumed to be on a per gram basis for the purpose of comparing our degradation experiments. Since the findings of this project found greater than reported emission rates, it was hypothesized that the Nafion 117 and 212 membranes were less chemically stable than the membranes investigated in the literature (111 models). Studies using Nafion 117 and 212 membranes were not found so a direct comparison between emission rates could not be performed.

Another significant finding that resulted from the Fenton's experiments was that there was an initial lag in the fluoride emission of the membrane. The emission trend conveyed that there was an activation mechanism that had to be overcome for the Fenton's reaction to effectively begin. If the conditions critical to overcoming this step were better understood, then perhaps the conditions that initiate membrane degradation can be better controlled for during operation or membrane manufacturing. The development of the membrane and essentially the fuel cell are reliant upon understanding all the factors of degradation mechanisms.

For Fenton's reactions performed on Nafion membranes it was hypothesized that degradation would be greater under membrane loading conditions since the hydroxyl radical would be generated in a position more closely located to the membrane. It may be an important factor for the hydroxyl radicals to be more closely located to the membrane if a maximal amount of damage was to occur. Further experimentation would be needed to support this hypothesis.

After analyzing the results pertaining to the radiative exposure of Nafion 212 membranes to X-rays, it was concluded that the sulfate emission was greater than the fluoride emission after exposure. This finding was significant since it alluded to the idea that sulfate groups were being cleaved directly from the membrane, and that in fact, the predominant degradation mechanism due to X-ray exposure was not an unzipping mechanism. If an unzipping mechanism was present, then the ratio of fluoride to sulfate would be greater. This finding was vastly different from the results obtained from Fenton's exposure experiments. In those experiments, an unzipping mechanism was more likely the cause of membrane degradation due to the amount of fluoride being detected in samples taken from the reaction vessel. A greater amount of fluoride was produced for the unzipping mechanism since the deterioration of the membrane would primarily occur at $-CF_2$ units and result in the loss of one CO_2 and two HF molecules per unit. However, our radiation studies were distinguished by the levels of sulfate detected. The levels indicated that there was greater direct attack and cleavage of the membrane's sulfonic acid moieties than cleavage of CF_2 units.

In addition, the sulfate emission findings were noteworthy because the literature had never mentioned the quantification of sulfate emission levels. The emission rate range for the Nafion 212 membrane experiments performed for this project were 0.0051 to 0.2366 µmol SO_4^{2-} per gram of Nafion exposed-hr (displayed in Figure 19). Assuming an X-ray dose rate of 400 Gy/h, this corresponds to an emission rate of $2x10^{-5}$ µmol/g·Gy.

The results from the Fenton's experiments showed that although extreme reaction conditions were used, like temperatures higher than operating fuel cells and larger concentrations of H_2O_2, the membranes displayed stability against degradation experiments. More specifically, the membrane weight loss was insignificant and was difficult to detect. This meant that the loss of membrane components was minute and therefore it had allowed the membrane to retain some of its structural integrity. If even the most extreme reaction conditions cannot display that significant membrane deterioration had occurred, then the membrane must in fact be fairly resistant to chemical and radiative attack. With the exception of membranes irradiated for more than 24 hours (began to break apart), the membranes appeared to maintain their structural integrity throughout both degradation processes. It would therefore appear that less severe, and realistic fuel cell conditions, may not be as damaging to the membrane as suspected. If there was minimal damage to the membrane after many, even thousands, of hours of operation, then perhaps the membranes were not the initial cause of failure of the entire fuel cell system.

The Logic of Integrating Fuel Cells as an Efficient Energy Source

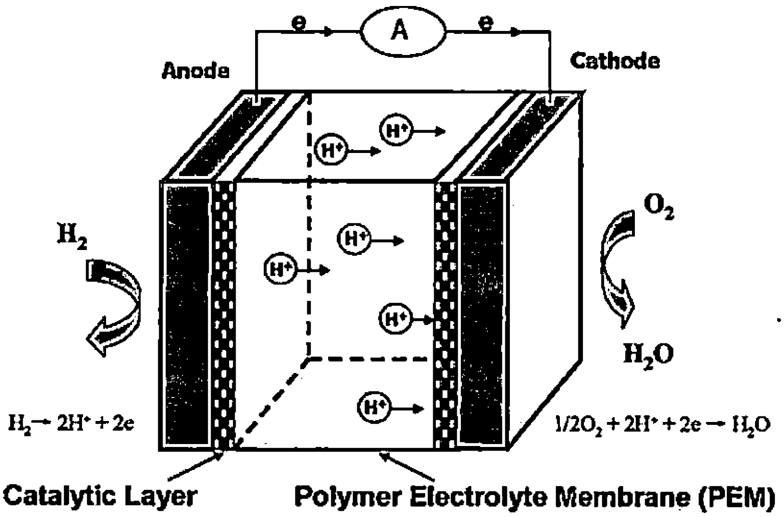
Although further research and development in fuel cell technology is needed before they can be operated at extended hours and at high temperatures, they are still one of the most promising sources of electrical power generation. Since energy independence is a major concern among today's society, there will continue to be an interest in the development of promising technologies that will promote economic and social independence from other nations. The integration of a fuel cell system cannot come into play until a more cost effective and reliable system exists. The initial cost of implementing a society that is dependant upon hydrogen technology will be quite expensive at first; however all the advantages of using that technology will be greater than the expense. Fuel cell systems offer savings in fossil fuels, low pollution levels, quieter engines, a small amount of required maintenance and inexpensive fuel options (14). In addition, the development of fuel cells will allow many nations to wean themselves from the oil based economies that they all rely upon. The discontinued use of oil will allow those markets to become independent of collapsing oil prices.

In regards to the environmental drawbacks that are associated with vehicle use and energy extraction processes, the amount of emissions released in the atmosphere will not be as great as currently used systems. The utilization of fuel cells will decrease overall emissions that include extraction sources, associated manufacturing processes, operations of energy technologies and recovery of those sources. The use of fuel cell systems will also contribute to a more controlled anthropogenic carbon footprint. The decreased emissions of CO_2 and other greenhouse gases will also decrease the use of emission control technologies and their associated expenses. The reduction of emissions will not only have a profound effect on the environment, but will also contribute to improving the overall respiratory health of individuals everywhere (39). The diminished amount of contaminants in the air will ultimately decrease the associated healthcare expenses (38).

APPENDIX A

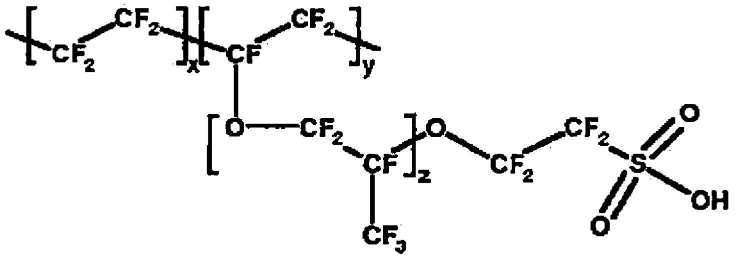
FIGURES FOR FUEL CELL BACKGROUND

Figure 1. How a Proton Exchange Membrane Creates an Electrical Current



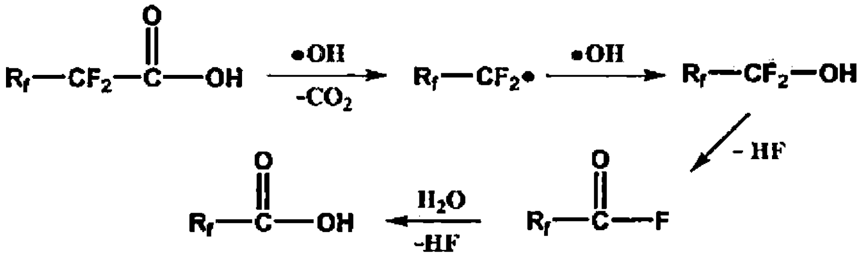
(40)Clarkson University. Camp Annual Report 2007-2008.

Figure 2. Nafion Membrane Structure



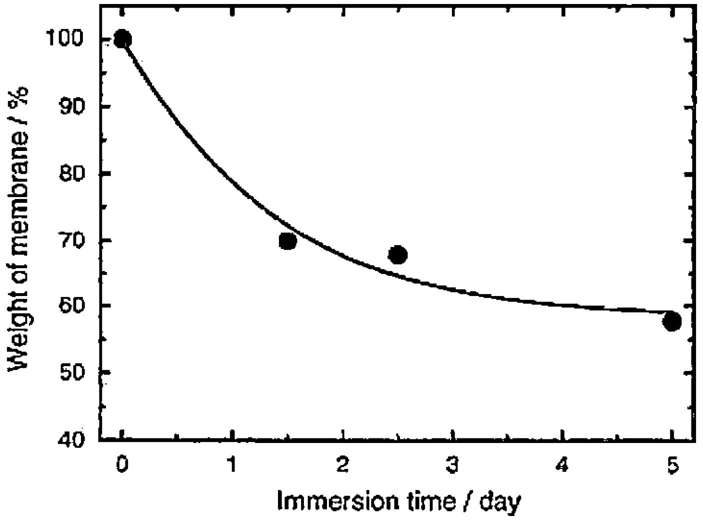
(13)Ivanchev, S.S. Fluorinated Proton-Conduction Nafion-Type Membranes, the Past and the Future. *Russ. J. Appl. Chem.* 2008, 81, 569-584.

Figure 3. Chain End Unzipping Mechanism



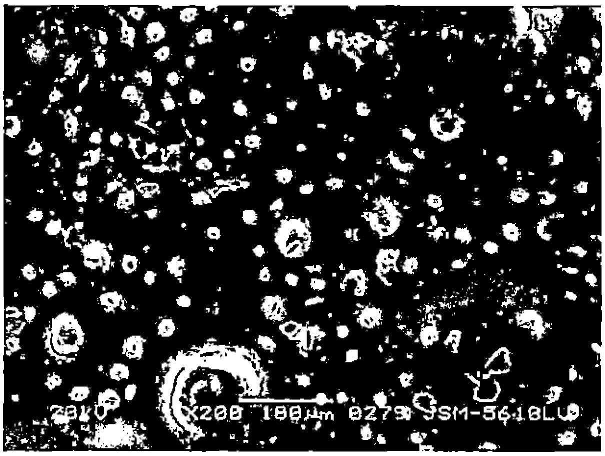
(26)Bosnjakovic et al. Nafion Perfluorinated Membranes Treated in Fenton Media: Radical Species Detected by ESR Spectroscopy. *J. Phys. Chem.* 2004, 108, 4332-4337.

Figure 4. Reported Loss of Membrane Weight after Fenton's Exposure



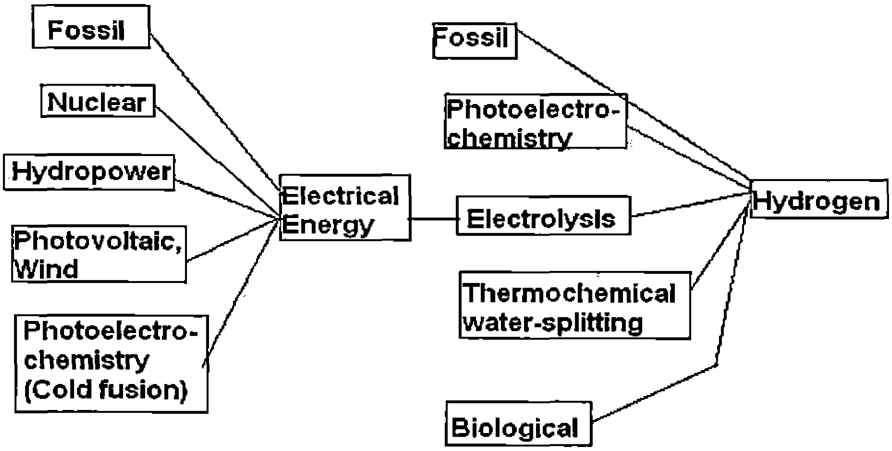
(30)Kinumoto, T. et al. Durability of perfluorinated ionomer membrane against hydrogen peroxide. *J. Power Sources* 2006,158,1222-1228.

Figure 5. A SEM Micrograph of Nafion after Fenton's Exposure for 48 Hours



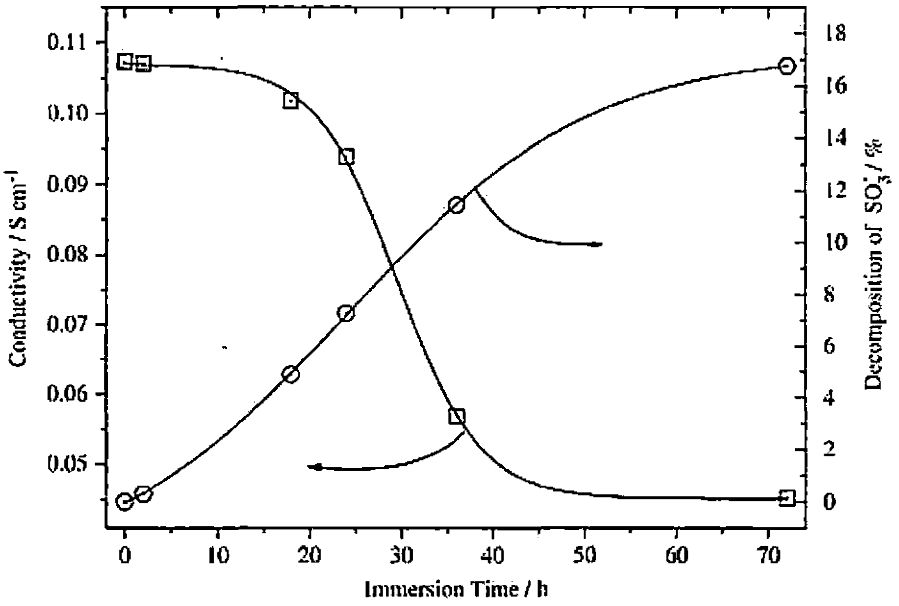
(29)Wang, F.; Tang, H.; Pan, M. and Li, D. Ex situ investigation of the proton exchange membrane chemical decomposition. *Int. J. Hydrogen Energy* 2008,33,2283-2288.

Figure 6. Different Ways Hydrogen Fuel Can be Produced



(14)Kordesch, K.V. and Simader, G.R. Environmental Impact of Fuel Cell Technology. *Chem. Rev.* 1995, 95, 191-207.

Figure 7. Relationship between Membrane Conductivity and Decomposition



(29)Wang, F.; Tang, H.; Pan, M. and Li, D. Ex situ investigation of the proton exchange membrane chemical decomposition. *Int. J. Hydrogen Energy* 2008,33,2283-2288.

APPENDIX B

SCHEMES FOR FUEL CELL REACTIONS

Scheme I. Half Reactions that Occur in the Fuel Cell

Rx. X Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Rx. Y Cathode: $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$

Rx. XY Net reaction: $2H_2 + O_2 \rightarrow 2H_2O$ + heat + electrical energy

Scheme II. General Fenton's Reaction

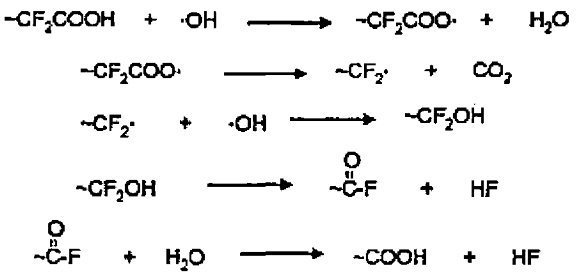
Rx. XX $M^{+2} + H_2O_2 \rightarrow M^{+3} + \cdot OH + OH^-$

Rx. YY $M^{+3} + H_2O_2 \rightarrow M^{+2} + \cdot OOH + H^+$

Scheme III. The Production of Carboxylic Acid End Groups

Rx. YX $\sim CF_2CF_2\text{-}Y + \cdot OH \rightarrow \sim CF_2COOH$ + others

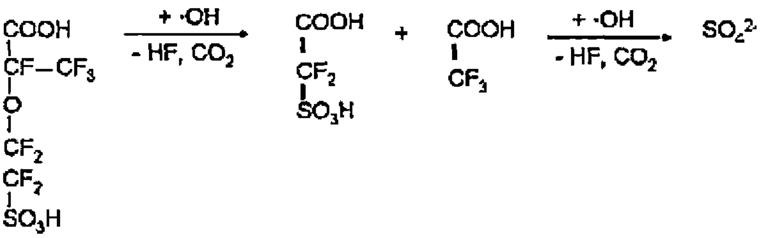
Scheme IV. Proposed Degradation of Nafion Membranes-Unzipping Mechanism



$$\sim CF_2COOH + \cdot OH \longrightarrow \sim CF_2COO\cdot + H_2O$$
$$\sim CF_2COO\cdot \longrightarrow \sim CF_2\cdot + CO_2$$
$$\sim CF_2\cdot + \cdot OH \longrightarrow \sim CF_2OH$$
$$\sim CF_2OH \longrightarrow \sim \overset{O}{\overset{\|}{C}}\text{-}F + HF$$
$$\sim \overset{O}{\overset{\|}{C}}\text{-}F + H_2O \longrightarrow \sim COOH + HF$$

(7)Xie, T. and Hayden, C.A. A kinetic model for the chemical degradation of perfluorinated sulfonic acid ionomers: Weak end groups versus side chain cleavage. *Polymer* 2007, 48, 5497-5506.

Scheme V. The Complete Degradation of Molecule A and its Products[1]



(7)Xie, T. and Hayden, C.A. A kinetic model for the chemical degradation of perfluorinated sulfonic acid ionomers: Weak end groups versus side chain cleavage. *Polymer* 2007, 48, 5497-5506.

[1] Double bond is missing between CF_2 and CF_2 in first molecule shown.

Scheme VI. The Radiolysis of Water

Rx. XXX $H_2O \rightarrow H_2O^+ + e^-$

Rx. XXY $e^- + H_2O \rightarrow H^\bullet + OH^-$

Rx. XYY $H_2O^+ \rightarrow OH^\bullet + H^+$

Rx. YXX $H^+ + OH^- \rightarrow H_2O$

Rx. YYX $H^+ + H^\bullet \rightarrow H_2^+$

Rx. YXY $H_2 + OH^\bullet \rightarrow H_2O + H^\bullet$

Rx. XYX $OH^\bullet + OH^\bullet \rightarrow H_2O_2$

(31)Zimbrick, J.D. Radiation Chemistry and the Radiation Research Society: A History from the Beginning. *Radiat. Res.* 2002, 158, 127-140.

APPENDIX C

CALCULATIONS FOR METHODS AND RESULTS

Equation 1. Determination of Nafion Equivalents Used

$$(1100\ \mathrm{g/eq})^{-1}(1000\ \mathrm{meq/eq}) = 0.909\frac{\mathrm{meq}}{\mathrm{g}}$$

$$(0.909\ \mathrm{meq/g})(\text{mass Nafion}) = \text{meq Nafion in reaction}$$

Equation 2. Amount of Iron Necessary to Load a Membrane

Example: A membrane sample that weighed 0.4628 grams

$$0.909\frac{\mathrm{m\cdot eq}}{\mathrm{g}} \bullet (0.4628\mathrm{g\ Nafion})\left(\frac{1\mathrm{mmolFe}}{2\mathrm{meqFe}}\right) = 0.210\ \text{mmol Fe required}$$

Equation 3. Amount of $FeCl_2 \cdot 4H_2O$ required to load membrane

$$0.210\ \mathrm{mmol\ Fe}\left(\frac{1\mathrm{molFeCl_2 \cdot 4H_2O}}{1\mathrm{molFe}}\right)\left(\frac{198.81\mathrm{gFeCl_2 \cdot 4H_2O}}{1\mathrm{molFeCl_2 \cdot 4H_2O}}\right) = 41.8\mathrm{mg}\ \ FeCl_2 \bullet 4H_2O$$

required

Equation 4. Amount of Fe^{+2} Placed into Solution with the Membrane for a 24 Hour Soaking Period

If a reaction used 0.1137g $FeCl_2 \cdot 4H_2O$ in the soaking solution (2-3 times excess to ensure 100% load), then the amount of iron used was:

$$0.1137\mathrm{g\ FeCl_2 \cdot 4H_2O}\left(\frac{1\mathrm{mol\ FeCl_2 \cdot 4H_2O}}{198.81\mathrm{g\ FeCl_2 \cdot 4H_2O}}\right)\left(\frac{1\mathrm{mol\ Fe}}{1\mathrm{mol\ FeCl_2 \cdot 4H_2O}}\right) = 5.718\mathrm{x}10^{-4}\mathrm{mol\ Fe}$$

Equation 5. The Amount of Iron left in Soaking Solution

If Flame AA analysis results show that 1340 mg/L Fe was detected in the solution then:

$$1340\frac{\text{mg}}{\text{L}}\,\text{Fe}\left(0.015\,\text{L}\right)\left(\frac{1\,\text{mmol Fe}}{55.85\,\text{mg Fe}}\right)\left(\frac{1\,\text{mol Fe}}{1000\,\text{mmol Fe}}\right)=3.60\text{x}10^{-4}\,\text{mol Fe}$$

Equation 6. Iron concentration loaded onto the membrane at 100% theoretical capacity

The difference between Equation 4 and Equation 5 is the amount loaded onto the membrane:

(0.57 - 0.36) mmol = 0.21 mmol= theoretical capacity for iron calculated in Equation 2. Therefore the membrane is 100% loaded, and the reaction contains 0.21 mmol Fe, or 780 ppm Fe relative to 15 mL reaction volume.

Equation 7. The Determination of Emission Rates for Fluoride and Sulfate Detected by Ion Chromatography*

The raw data obtained by ion chromatography analysis was in ppm units. Each individual data set for each reaction was then calculated to give units µmoles of either sulfate or fluoride. The data was also divided by each membrane's mass for each reaction to give the amount of anions emitted on a per gram of Nafion basis. The data was plotted in respect to reaction time. The graphical representation of data was performed with trendlines. From the trendlines the slope was acquired. The slope was the emission rate for each individual reaction, and was equal to µmol/gram of Nafion exposed·hr. An example of the raw data conversion to µmol units is displayed below.

$$\left(\frac{(\frac{mg}{L})\cdot(L)\cdot(1000)}{\frac{g}{mol}}\right)+\left(\frac{\frac{mg}{L}\bullet 0.01\bullet 1000}{\frac{g}{mol}}\right)=X \text{ µmoles of anion emitted}$$

X/grams of Nafion weighed= µmol/gram of Nafion

APPENDIX D

FIGURES FOR MEMBRANE DEGRADATION RESULTS

Figure 8. IC Analysis of Fluoride Emission after Membrane Loading at 20 ppm Fe^{+2} Before Exposure to Fenton's Reagent (2009-B) Method

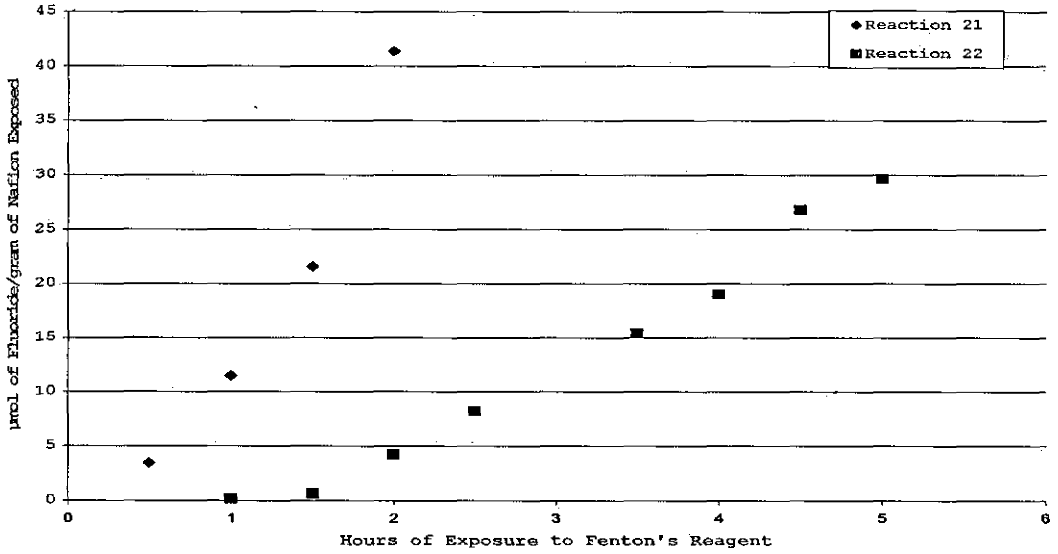


Figure 9. IC Analysis of Sulfate Emission after Membrane Loading at 20 ppm Fe^{+2} Before Exposure to Fenton's Reagent (2009-B) Method

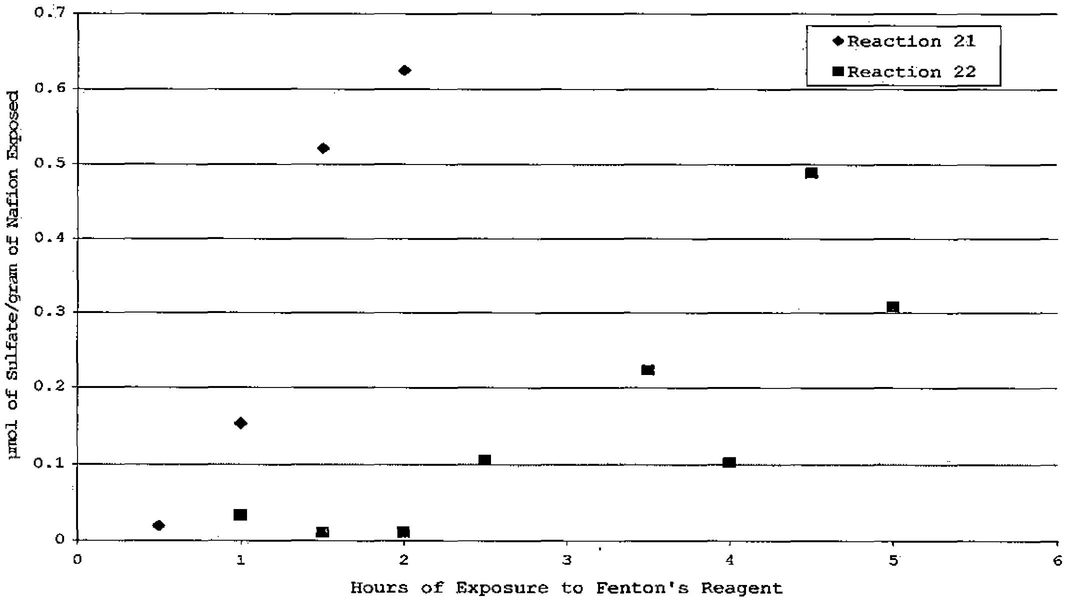


Figure 10. IC Analysis of Fluoride Emission from Nafion 117 after Fenton's Treatment (2009-A Method) at 100°C

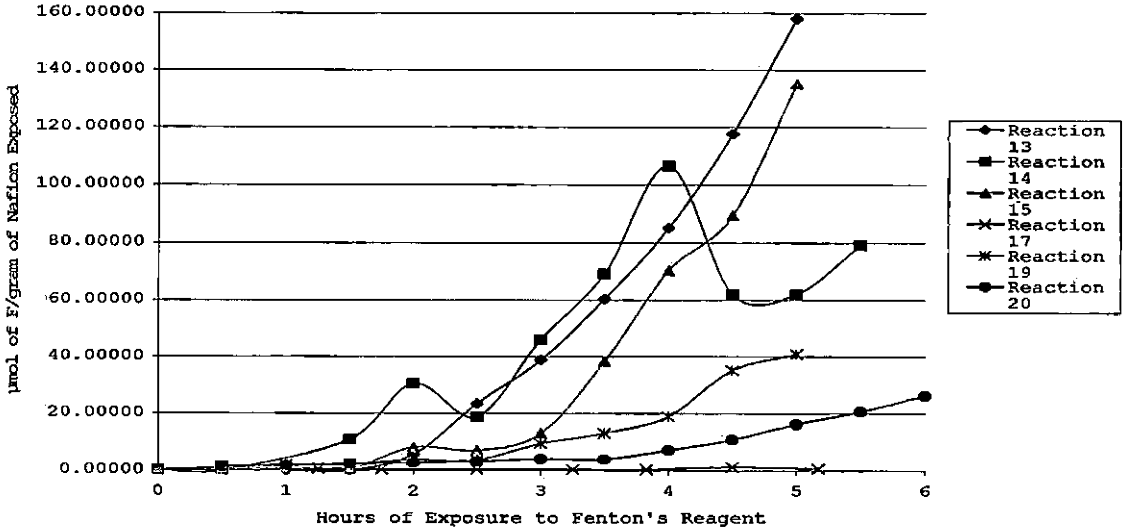


Figure 11. IC Analysis of Sulfate Emission from Nafion 117 after Fenton's Reaction (2009-A Method) at 100°C

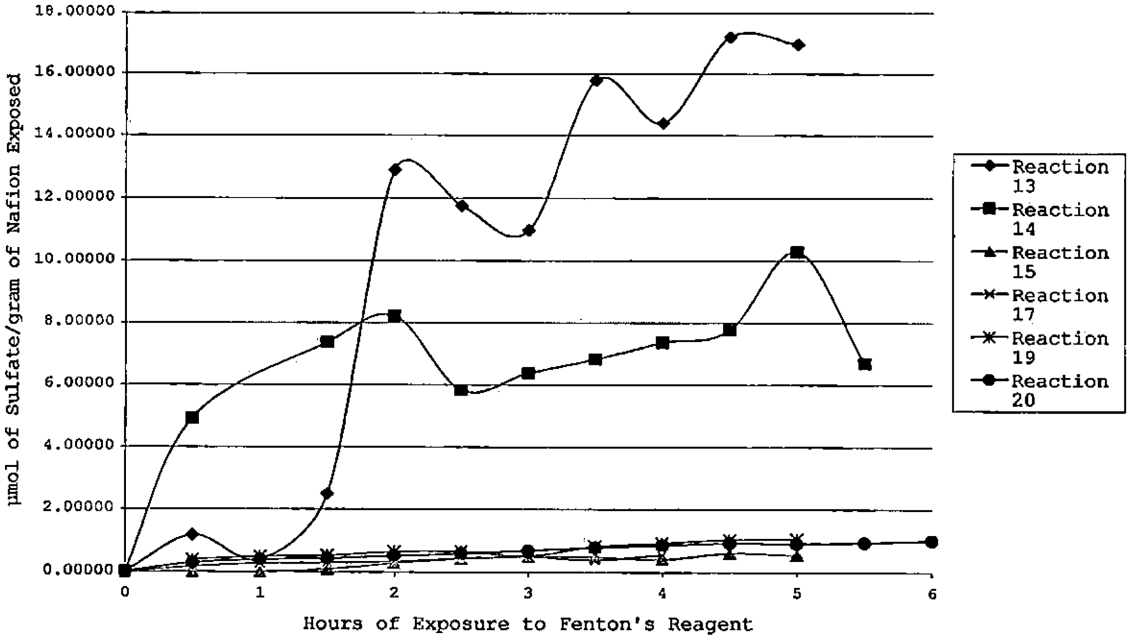


Figure 12. IC Analysis of Fluoride Emission from Nafion 212 after Fenton's Degradation (2009-A Method) at 100°C

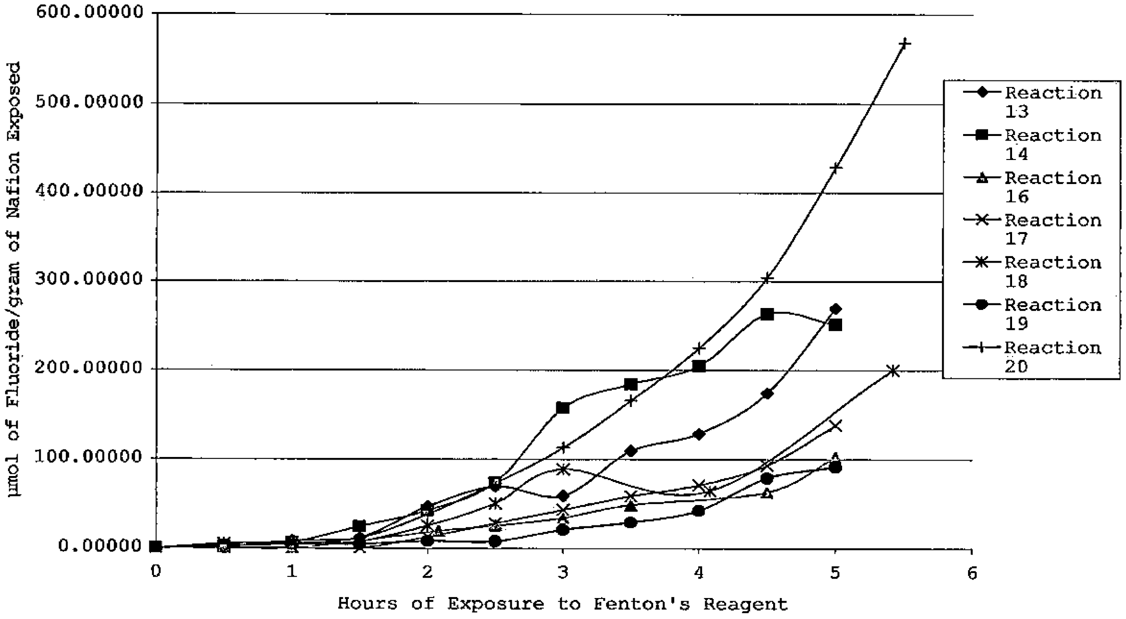


Figure 13. IC Analysis of Fluoride Emission from Nafion 212 after Fenton's Degradation (2009-A Method) at 80°C

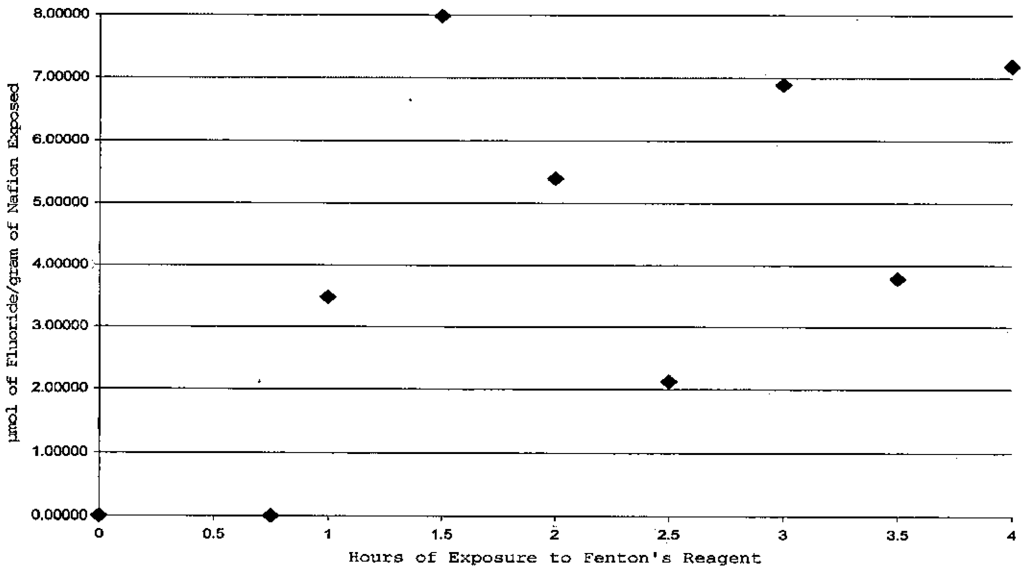


Figure 14. IC Analysis of Sulfate Emission from Nafion 212 after Fenton's Degradation at 100°C (2009-A Method)

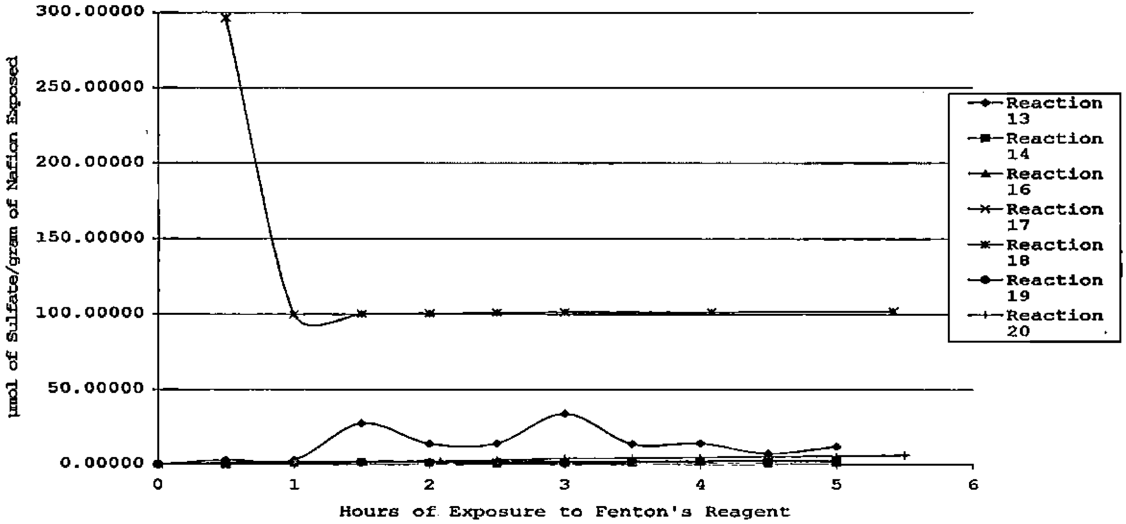
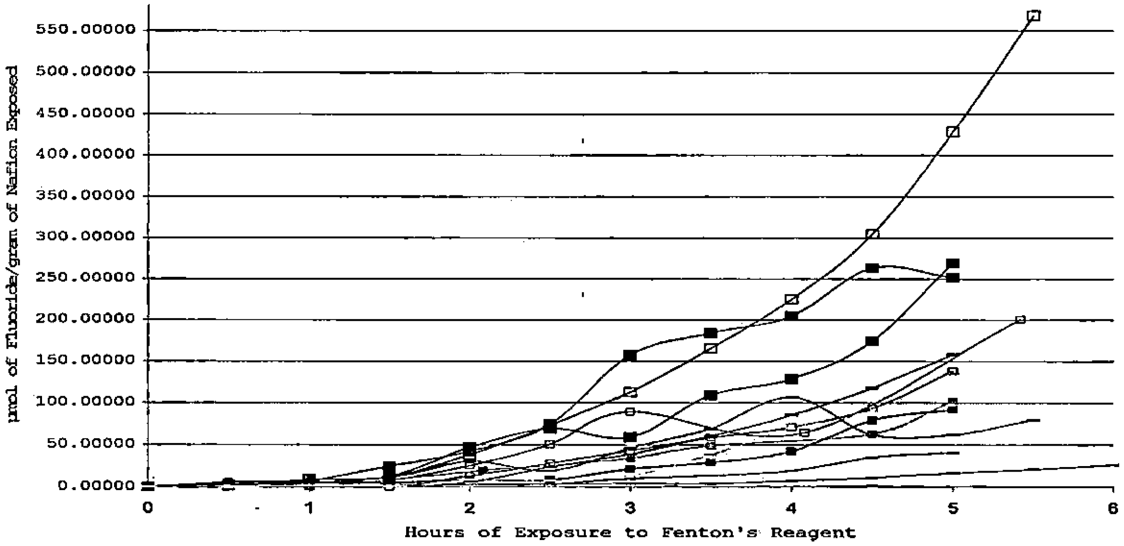
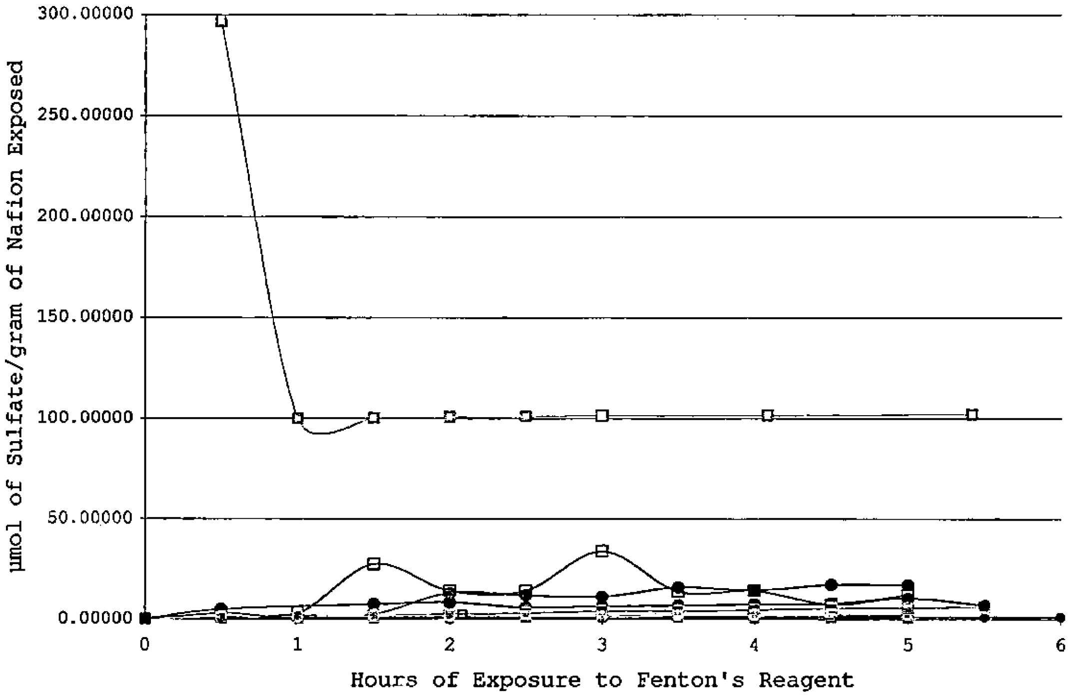


Figure 15. IC Analysis of Fluoride Emission for both Nafion 212 & 117 Membranes after Fenton's Degradation at 100°C*



*Nafion 117 data was shown by dashes. Nafion 212 data was displayed by squares (figure shows comparison between the two membranes for 2009-A Method).

Figure 16. IC Analysis for both Nafion 212 & 117 Sulfate Emission after Fenton's Degradation at 100°C*



*Nafion 117 was displayed by circles and Nafion 212 was shown by squares (figure shows comparison between the two membranes for 2009-A Method).

Figure 17. Visual Confirmation of Membrane Degradation after Exposure to Fenton's Reaction (2009-A Method)

Figure 18. IC Analysis of Fluoride Emission for Nafion 212 after Radiation Experiments

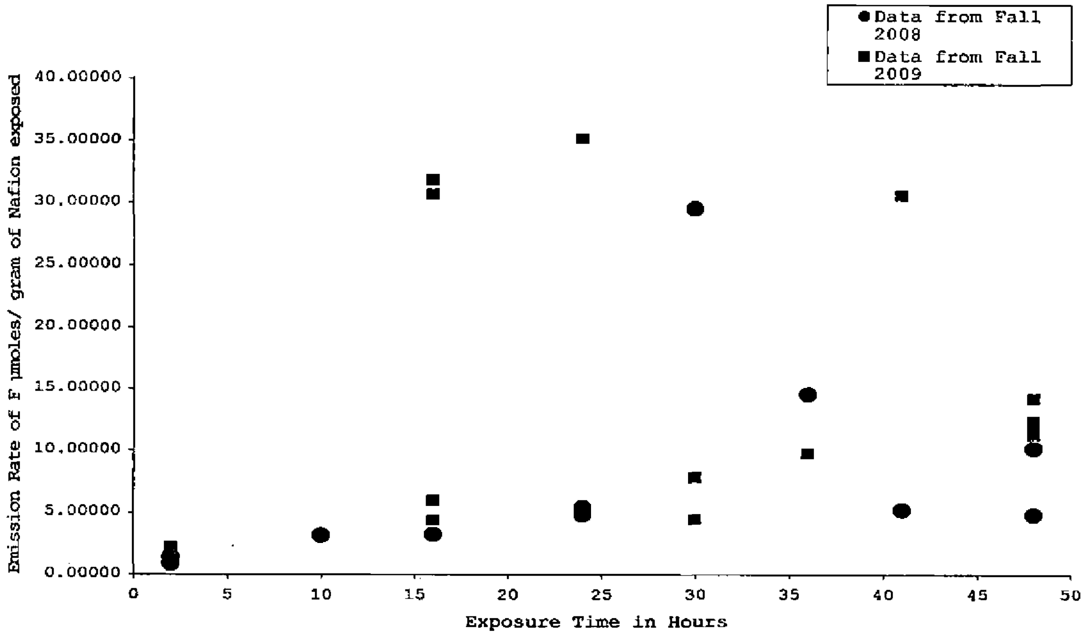


Figure 19. IC Analysis of Sulfate Emission for Nafion 212 after Radiation Experiments

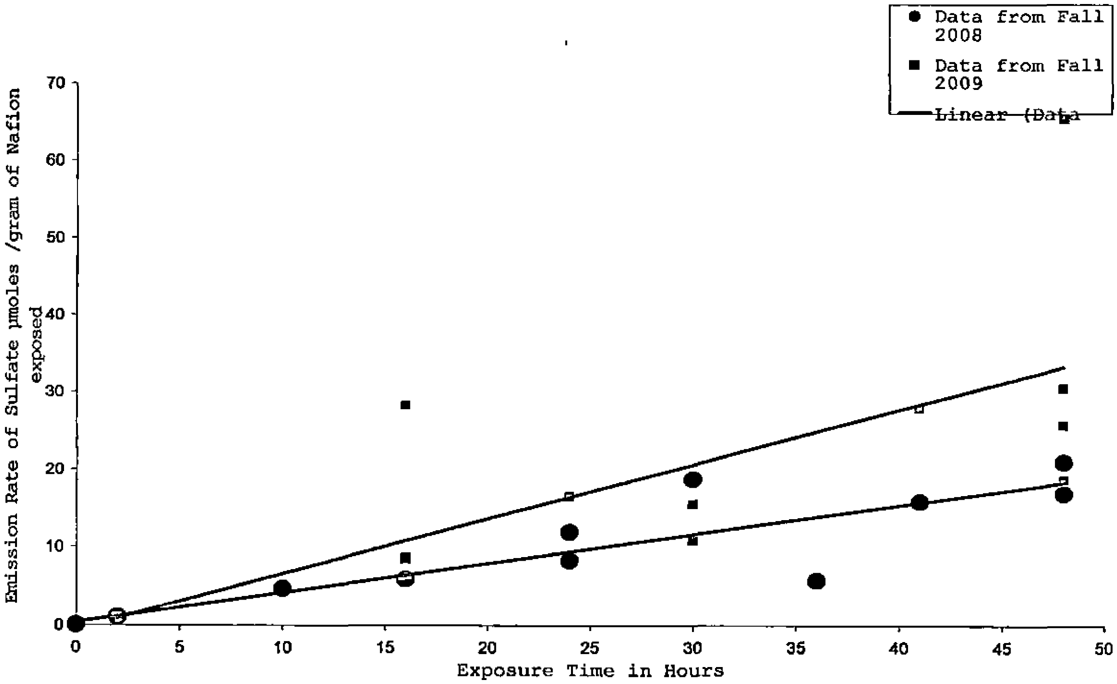
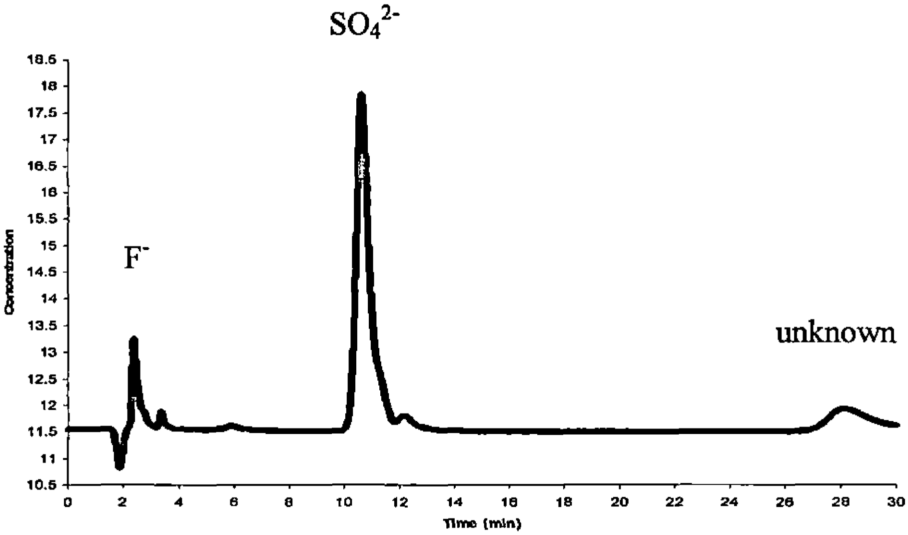


Figure 20. Example of a Chromatogram for a Nafion 212 Irradiated Membrane after 41 Hours of Exposure



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