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The feasibility of proton exchange membrane fuel cells

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The Feasibility of Proton Exchange Membrane Fuel Cells

By

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A project
presented to Ryerson University
in partial fulfillment of the requirements for the degree of
Master of Engineering
in the Program of Mechanical Engineering

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Abstract

Proton exchange membrane (PEM) fuel cells' main components are the anode, cathode and the membrane. A conventional membrane used in today's PEM fuel cells is the Nafion 117 membrane. In this project, the Nafion 117 membrane is discussed in detail to demonstrate its ability to absorb water and the capability to operate in a specific range of temperatures. In addition, an extensive simulation using CATIA V5 is used to determine the highest stress distribution on the membrane for various boundary conditions. Other membranes materials were also considered in this report. They include the Dias membrane, the bacterial cellulose membrane to expand the selection of candidate membranes that can be used in PEM fuel cells for future research.

Optimization methods were utilized to maximize the performance of the PEM fuel cells. The Genetic Algorithm is used to solve optimization problems by implementing powerful search techniques to find an optimal solution within a large set of solutions. In this project, the Genetic Algorithm is used to show the impact of the stack positions in order to optimize voltage output. In addition, the Nafion content and platinum loading are adjusted to optimize the performance of the current density within PEM fuel cells.

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Nomenclature

Alphabets

A	Tafel slope [v]
G	Modulus of elasticity in shear
T_g	Transition temperature
S	Entropy
P	Pressure
P_i	Partial pressure of species i [atm]
P_o	Reference pressure
X_i	Molar fraction
T	Temperature
B	Concentration loss constant [v]
F	Faraday constant [96,485 col/sec]
R	Gas constant [8.314 J/mol K]
U	Heat transfer coefficient [W/cm ² K]
V	Voltage [volt]
N	Number of electrons
E	Cell potential
E_t	Theoretical cell potential
A_s	Active area
Z	Number of connected series cells in stack
V_o	Electrode potential [V]
ΔH	Enthalpy of overall reaction [J/mol]
ΔG	Gibbs energy change
V_s	Stack voltage
E_o	Open circuit voltage
E^o	Standard Potential
E_m	Equivalent membrane weight
C_{H_2}	Hydrogen bulk concentration
C_{O_2}	Oxygen bulk concentration

$C_{O_2}^S$	Oxygen electrode surface concentration
$C_{H_2}^S$	Hydrogen electrode surface concentration
t	Membrane thickness
f	Swelling coefficient
s	Conductivity
i_L	Limiting current density
I	Current density [amp/cm ²]
i_o	Exchange current density [amp/cm ²]
m_{pt}	Catalyst mass loading [g/cm ²]
z	Charge number of the electrochemical reaction
r	Specific Area Resistance [kΩcm ²]

Greek Symbols

α	Charge transfer coefficient
ε_N	Volume fraction of Nafion in the catalyst layer
ε_S	Volume fraction of solid catalyst particles in the catalyst layer
ε_V	Volume fraction of void space in the catalyst layer
η	Efficiency
ρ	Solid density [gr/cm ³]
ρ_N	Mass density of Nafion [g/cm ³]
ρ_{Pt}	Mass density of the platinum [g/cm ³]
ρ_C	Mass density of the carbon black [g/cm ³]
σ	Membrane conductivity
σ_x	Principle Stress in x-direction
σ_y	Principle Stress in y-direction
σ_z	Principle Stress in z-direction
λ_R	Relaxation Time
η_s	Coefficient of viscosity in shear
ρ_m^{dry}	Dry membrane density
ν	Poisson Ratio

γ_E	Elastic strain
γ_v	Viscous strain
τ_{xy}	Shear stress
η_d	Osmotic drag
λ	Hydration index

Abbreviations

PEM	Proton Exchange Membrane
MEA	Membrane Electrode Assembly
NASA	National Aeronautics and Space Administration
SMR	Steam Methane Reformer
LLNL	Lawrence Livermore National Laboratory
ORR	Oxygen Reduction Reaction
EMF	Electromotive Force
HHV	Higher Heating Value
LHV	Lower Heating Value
NTP	Normal Temperature and Pressure
RH	Relative Humidity
PTFE	Polytetrafluoroethylene
EW	Equivalent Weight
DOE	Department of Energy

Superscripts

o	standard
s	surface

Subscripts

g	glass
o	reference or standard
t	theatrical
oc	open circuit
s	stack, solid
o	open
m	membrane

eff	efficiency
pt	platinum
L	limiting
N	Nafion
v	volume, viscous
c	carbon
E	elastic
d	drag

CHAPTER 1 - Introduction to PEM Fuel Cells

1.1 History of Fuel Cells

In recent years, the demand for environmentally effective alternatives to the traditional combustion power has significantly grown. As a result, many scientists have spent considerable amount of time in finding and implementing new methods of energy conversion systems. Energy can now be provided by the newest method known as fuel cells. A fuel cell is a simple static device that converts chemical energy into electrical energy [1]. As quoted by Brain Cook “Whereas the 19th century was the century of the steam engine and the 20th century was the century of the internal combustion engine, it is likely that the 21st century will be the century of the fuel cell”[2].

Figure 1: Grove's first fuel cell developed in 1839 [2]

The invention of the fuel cell began with the work conducted by Sir William Grove, who was a Welsh judge and amateur scientist. In the 1830's, he discovered that

mixing hydrogen and oxygen in the presence of an electrolyte produced electricity and water. Grove was able to develop a fuel cell with a maximum output of 1 V.

The term “fuel cell” came about in the 1880’s by L. Mond and C. Langer, who attempted to develop a fuel cell that used industrial coal gas and air. Their effort had no practical value until the 1930’s, when Francis T. Bacon began his groundbreaking research. T. Bacon applied the platinum catalysts employed by Mond and Langer in a hydrogen-oxygen fuel cell that used less corrosive alkaline electrolyte and nickel electrodes. It took Bacon years to overcome technical challenges, and it was not until 1959 that he and his co-workers were able to demonstrate a practical five-kilowatt fuel cell stack.

In addition, the National Aeronautics and Space Administration (NASA) were interested in this new technology for its high efficiency. They used fuel cells in the 1950’s when they decided to supply power during space flight for their manned space missions. When the missions were a success, fuel cells were proven a breakthrough in delivering “clean” energy. NASA initiated funds for over 200 research projects on fuel cell technology and, consequently, fuel cells have provided on-board electricity and water to the Gemini, Apollo and space shuttle missions.

1.2 Types of Fuel Cells

There are five types of fuel cells: alkaline fuel cells, molten carbonate fuel cells, solid oxide fuel cells, phosphoric acid fuel cells and proton exchange membrane fuel cells. However, both solid oxide and molten carbonate fuel cells have high operating temperatures in the range of (600-1000 °C) [3] not making it adequate for the use in automobiles. Alkaline fuel cells have been used in the space program since the 1960’s.

The downfall associated with alkaline fuel cells is that they are highly susceptible to contamination. Since they require only pure hydrogen and oxygen, the cost of eliminating contamination is impractical for consumer markets. The phosphoric acid fuel cell runs at lower operating temperatures and consumes a reasonably small volume. However, it must be warmed up in order to operate properly. This warm up time removes its practicality to use in automobiles due to the fast-paced consumer world. It is, however, a useful stationary power system. The proton exchange membrane (PEM) fuel cells have the highest power density compared to other fuel cells. In addition, according to P.S. Combe [4], the PEM fuel cells are able to operate under low temperatures, ideally under 100 °C. This temperature allows PEM fuel cells to be especially appealing for automobiles. The U.S Department of Energy [5] suggests that low temperature operation allows PEM fuel cells to start quickly (less warm-up time) and result in less thermal stress on system components. Table 1 below summarizes some facts about various types of fuel cells.

	AFC	MCFC	PAFC	PEMFC	SOFC
Electrolyte	KOH solution	Molten carbonate salt	Liquid phosphoric acid	Ion exchange membrane	Solid metal oxide
Operating Temp °C	70-90	600-1000	150-200	60-100	600-1000
Efficiency (LHV) %	55-60	45-60	35-50	35-50	45-60
Max Power Output	100KW	2MW	1 MW	250 KW	220 KW
Oxidant	O ₂ /Air	CO ₂ /O ₂ /Air	O ₂ /Air	O ₂ /Air	O ₂ /Air

Table 1: Selected specifications for the five types of fuel cells [3]

1.3 A Look at the PEM Fuel Cells

The process of PEM fuel cells is categorized into four different stages. First, hydrogen fuel is fed through a field flow plate to the anode on one side of the fuel cell. Oxygen from the air is channeled to the cathode on the other side of the cell. At the

anode side, a catalyst causes the hydrogen to split into positive hydrogen ions, known as protons, as well as negatively charged electrons. Next, the electrolyte membrane allows only the positively charged ions to pass through to the cathode. The negatively charged electrons are forced to travel through an external circuit to the cathode where electricity is being extracted for useful work. Finally, the proton H^+ meets with the oxygen ion from the air to produce water as the byproduct [1]. This process is depicted in Figure 2. Note that the byproduct water from PEM fuel cells is pure the astronauts from the Gemini and Apollo used it as drinking water.

Figure 2: PEM fuel cell showing ion flow

The reaction that occurs at the PEM fuel cells consists of the following half reactions [5]:

The above two half-reaction makes up the cell's full reaction:

1.4 Cost and Storage of Hydrogen Gas Used in PEM Fuel Cells

Although fuel cell technology is efficient and provides a clean energy source, it is also very expensive. The main challenge of PEM fuel cells is to reduce the overall cost of operation. One aspect of the challenge faced by developers is to reduce the associated cost of producing hydrogen which is the main fuel type used in PEM fuel cells. Hydrogen is usually produced from hydrogen rich materials such as natural gas or coal [6]. This process can be completed by the reformation of natural gas to release the hydrogen stored. In addition, after hydrogen is produced, it must be compressed, purified and finally stored for dispensing. Hence, these processes increase the cost considerably. As of 2003, the cost to produce hydrogen by steam reforming is \$5.0/kg [7]. However, it is expected that the cost will be reduced to \$1.5/kg in 2010. This target cost of hydrogen for 2010 makes fuel cell technology a feasible energy conversion system.

Figure 3: Breakdown process contributing to the cost of hydrogen [7]

To meet the targeted cost of \$1.5/kg in 2010, researchers are making efforts towards improving the performance of the fuel processor. To enhance this stage of the design, a better performing catalyst, new reactor designs and better integration of the various fuel-processing components will be required. Aaron T. M. from Praxair Inc [8] suggests the use of existing steam methane reformer (SMR) and purification process technologies to lower the cost of hydrogen production. The improvement of the reformer process is half of the challenge. The other half of the challenge is the catalyst addition to the rich hydrogen materials. J. P. Kopasz [9] suggested that tests on the fuel blends indicate that fuels that are high in naphthenic catalyst produced by Merichem Co. provide good hydrogen yields. However, naphthenic catalyst produces a high yield of hydrogen at a small operating range. This limitation of small operating window creates difficulties when working with naphthenic catalyst in the process. The reforming process to extract hydrogen is a practical method and is practiced today across the U.S and around the world.

The next challenge for the development of a PEM fuel cells system is an adequate storage space for hydrogen, in view of the fact that there is limited space in a vehicle. N. Sirosh from Quantum Technology achieved "World Record" hydrogen storage mass efficiency. His record was 11.3-weight percentage on a prototype 5,000-psi tank, with Lawrence Livermore National Laboratory (LLNL) and Thiokol Propulsion [10]. He also developed and demonstrated 7.5-weight percentage and 8.5-weight percentage Type IV composite hydrogen storage tanks of specified sizes.

Figure 4: Hydrogen storage tank by Quantum [10]

The challenge with hydrogen storage not only relies on mass efficiency but also on the size and the weight of the tank. A. Weisberg *et. al.* [11] suggested that structural improvements can deliver slight volume reduction. In addition, storage volume can be dramatically improved by increasing stored hydrogen pressure and decreasing temperature. Nevertheless, these improvements reach diminishing returns above roughly 15,000 psi. Hydrogen storage tanks with this pressure capability have not yet been developed. Continual structural innovations will be required to withstand these higher pressures with affordable mass and cost.

1.5 Project Outline

The first chapter gives a brief introduction about the PEM fuel cell technology. In addition, it gives a brief history to how the technology evolved. The second chapter focuses on the fundamentals of fuel cells to give an insight on this new technology. The discussion of the PEM fuel cells' efficiency is introduced under different operating conditions. In addition, the open circuit voltage of PEM fuel cells is shown by the Nernst equation.

The third chapter of the project focuses on the electrodes in PEM fuel cells. In principle, there are three types of overpotentials: the activation overpotential, ohmic overpotential and concentration polarization overpotential. All three types of overpotentials are discussed in fair detail to understand how they affect PEM fuel cells.

The fourth and fifth chapters of the project mainly concentrate on evaluating the Nafion 117 membrane. This type of membrane is of great importance due to its ability to absorb water. It is one of the most used membranes in PEM fuel cells. Nafion 117, being a polymer material, has an impact on its operational behavior. One important characteristic, which is fully considered, is the effect of physical aging of this polymer membrane. A simulation was produced for the Nafion 117 membrane to evaluate the stress distribution and to determine the fracture point of the membrane. The CATIA V5 software package was used to input the boundary conditions. The parameters input in this simulation were obtained from an experiment conducted by University of Duke [29]. In addition, other membranes are briefly discussed to introduce the diversity of other feasible membranes in use today.

The sixth chapter highlights the use of the optimization methods utilized in the operation of PEM fuel cells. The Genetic Algorithms is used to configure the stack positioning within PEM fuel cells to yield maximum voltage output. The Nafion content along with the platinum loading are adjusted to optimize the performance of current density. This chapter of the project is of great importance to validate the applicability of fuel cells technology for the near future.

CHAPTER 2- Fundamentals of PEM Fuel Cell Technology

2.1 Efficiency

The efficiency of a fuel cell is determined by the Gibbs free energy, ΔG , and the enthalpy ΔH . The enthalpy is the value given to the heat that would be produced by burning the fuel. Hence, the efficiency of a fuel cell is given by:

$$\eta = \frac{\Delta G}{\Delta H} \quad (2.1)$$

Equation (2.1) represents the ideal work delivered over the energy supplied into the fuel.

The theoretical efficiency for PEM fuel cells at 25 °C is 83% (Table 2). However, this is not accounting for losses such as the activation, ohmic losses and mass transport limitations that will lower the theoretical efficiency value.

Form of water product	Temp	Efficiency
Liquid	25	83%
Liquid	80	80%
Gas	100	79%
Gas	200	77%
Gas	400	74%
Gas	600	70%
Gas	800	66%
Gas	1000	62%

Table 2: Efficiency for various temperatures [42]

Fuel cells are more efficient at lower temperatures; on the other hand, in higher temperature fuel cells the voltage losses are much less. Therefore, it is more advantageous to operate fuel cells at a higher temperature to achieve higher operating voltages.

2.2 Open Circuit Voltage

The reversible standard potential E^0 of an electrochemical reaction is defined as:

$$E^0 = \frac{\Delta G^0}{zF} \quad (2.2)$$

Where ΔG^0 is the Gibbs energy change for the reaction under normal temperature and pressure (NTP) condition, z is the reaction charge number and F is the Faraday constant. The reaction takes place at essentially constant temperature and pressure, and the Gibbs free energy relation gives the free energy change:

$$\Delta G = \Delta H - T\Delta S \quad (2.3)$$

Where ΔH is the reaction enthalpy change, T is the temperature, and ΔS is the reaction entropy change. Note, from the Gibbs free energy relation $\Delta G = \Delta H$ if $\Delta S = 0$.

Form of water product	Temp [C]	ΔG [KJ/mole]	E^0 [V]
Liquid	25	237.3	1.23
Liquid	80	228.2	1.18
Gas	100	225.3	1.17
Gas	200	220.4	1.14
Gas	400	210.3	1.09
Gas	600	199.6	1.04
Gas	800	188.6	0.98
Gas	1000	177.4	0.92

Table 3: Gibbs free energy for various temperature and states [42]

Substituting the standard conditions values for hydrogen and oxygen [36] into Equations (2.2) and (2.3) gives:

$$E_{H_2/O_2}^0 = \frac{237.3 \text{ KJmol}^{-1}}{(2)(96,487) \text{ Cmol}^{-1}} = 1.23 \text{ V}$$

The theoretical potential E_t for an electrochemical reaction can be expressed by the Nernst equation [40]

$$E_t = E^0 - \frac{RT}{zF} \ln \left[\prod_i a_i^{v_i} \right] \quad (2.4)$$

Where R is the gas constant, T is the temperature, a_i is the activity of the species i , and v_i is the Stoichiometric coefficient of species i , z charge number of the electrochemical reaction. E^0 is defined in Equation (2.2) which is a function of temperature and pressure.

Assuming that gases can be taken as ideal, meaning that the activities of the gases are equal to their partial pressures, then Equation (2.4) gives:

$$E_t = E^0 - \frac{RT}{zF} \ln \left[\prod_i \left(\frac{P_i}{P_o} \right)^{v_i} \right] \quad (2.5)$$

Where p_i is the partial pressure of species i and p_o is the reference pressure. For ideal gases, partial pressure of species i , P_i can be expressed as a product of total pressure P and molar fraction x_i of the species:

$$P_i = x_i P \quad (2.6)$$

For example, if a hydrogen-air fuel cell is operating on dry gases, Equations (2.5) and (2.6) give:

$$E_t = E^0 - \frac{RT}{zF} \ln \left[\frac{P_o^{3/2}}{P_{H_2} (0.21 P_{air})^{1/2}} \right] \quad (2.7)$$

At standard temperature and pressure, the theoretical potential of hydrogen-air fuel cell can be calculated as:

$$E_{t,H_2/air} = 1.23 - \frac{8.314 \times 298.15}{(2) \times (96,487)} \ln \left[\frac{1}{(0.21)^{1/2}} \right] = 1.2199$$

When calculating the ideal potentials for various types of fuel cells, it is proven that PEM fuel cells provide the highest cell potential. This is one of the main reasons PEM fuel cells are a very attractive application for automobiles. Table 4 shows the cell potential calculations provided for various fuel cells at their operating temperatures.

Cell Type	Temp [K]	Ideal Potential [V]
Ideal	298.15	1.2199
PEMFC	353	1.17
PAFC	478	1.14
MCFC	923	1.03
SOFC	1373	0.91

Table 4: Ideal potential for various types of fuel cells

CHAPTER 3 - Electrodes

All electrochemical reactions take place on the electrode surface. Catalysts are always placed on the electrode to speed up cell reactions. Most catalyst particles are always platinum or an alloy of platinum. Since PEM fuel cells operate under low temperature and low pH it makes the use of catalysts necessary [34]. In the absence of catalyst, the oxygen reduction reaction (ORR) on the cathode becomes a slow process.

The electrodes are usually made of a porous mixture of carbon supported platinum. In order to be able to catalyze reactions, catalyst particles must have contact with both protonic and electronic conductors. Furthermore, there must be pathways for reactants to reach the catalyst sites and for reaction products to exit. The contacting point of the reactants, catalyst and electrolyte is conventionally referred to as the three-phase interface.

In order to achieve acceptable reaction rates, the effective area of active catalyst sites must be several times larger than the geometrical areas of the electrodes. Therefore, the electrodes are made porous to form a three-dimensional network in which the three-phase interfaces are located. Nowadays, most PEM fuel cells developers have chosen the thin-film approach, in which the electrodes are manufactured directly on the membrane surface. The benefits of thin-film electrodes include lower price, better utilization of catalyst and improved mass transport. The thickness of a thin-film electrode is typically 5-15 μm and the catalyst loading is between 0.1 to 0.3 mg/cm^2 [35].

In the electrodes, the overall cell voltage drops due to various irreversible loss mechanisms. The loss, which is often called overpotential η , is defined as the difference between the theoretical potential E_t from the actual cell potential E .

$$\eta = E_t - E \quad (3.1)$$

In a fuel cell, overpotentials originate from three sources:

1. Activation arises from the kinetics of charge transfer reactions.
2. Ohmic losses arise from component resistances.
3. Diffusion arises from the limited rate of mass transfer.

3.1 Activation Overpotential

Activation overpotential arises from the kinetics of charge transfer reaction across the electrode-electrolyte interface. In other words, a portion of the electrode potential is lost in driving the electron transfer reaction. Activation overpotential is directly related to the nature of the electrochemical reactions, which is represented by the magnitude of activation energy when the reaction propagates at the rate demanded by the current.

In PEM fuel cells, the contribution of anode activation overpotential is relatively small, since the oxygen reduction on the cathode is significantly slower than the hydrogen oxidation on the anode [36]. The activation overpotential decreases as the potential shifts to the negative direction. This makes the activation overpotential significant only at low current densities.

Expressions for the activation overpotentials can be derived from the Butler-Volmer equation. The anode activation overpotential increases with current density and can be expressed as:

$$\eta_{act,a} = \frac{RTi}{Fi_{0,a}} \quad (3.2)$$

Where i is the current density, $i_{0,a}$ is the anode reactions exchange current density, F is Faraday constant, T is temperature, and R is the gas constant. Exchange current density represents the reaction rate. The equation for cathode activation overpotential is:

$$\eta_{act,c} = -\frac{RT}{\alpha nF} \ln \left(\frac{i}{i_{0,c}} \right) \quad (3.3)$$

From the logarithmic rule, Equation (3.3) can be rewritten as:

$$\eta_{act,c} = \frac{RT}{\alpha nF} \ln i_{0,c} - \frac{RT}{\alpha nF} \ln i \quad (3.4)$$

Where α is the charge transfer coefficient and $i_{0,c}$ is the cathode reaction exchange current density, n is the viscosity overpotential. Equation (3.4) can be expressed as:

$$\eta_{act,c} = a + b \ln i \quad (3.5)$$

Where:

$$a = (-2.3RT / \alpha nF) \log_{10} i_o$$

$$b = 2.3RT / \alpha nF$$

Figure 5: Example of Tafel plot [36]

Equation (3.5) is known as the Tafel equation. An example of an experimental Tafel plots is presented in Figure 5. Tafel plots are used to determine i_0 and b to solve Equation (3.5). The exchange current for the anode reaction in fuel cell conditions is between 0.1 and 100 mA/cm². The cathode exchange current is about 10⁻⁵ times smaller [34, 37].

3.2 Ohmic Overpotential or IR-losses

Resistance to the flow of ions in the electrolyte and resistance to the flow of electrons through the electrode cause ohmic overpotential (IR-loss). These resistances can be practically found in all fuel cell components: ionic resistance in the membrane, ionic and electronic resistance in the electrodes, electronic resistance in the gas diffusion backings and electronic resistance in the terminal connections. However, the dominant contribution to the ohmic overpotential arises from the electrolyte membrane [38]. The ohmic overpotential η_{ohmic} is expressed as:

$$\eta_{ohmic} = IR \quad (3.6)$$

Where, I is the current and R is the total cell resistance. R , is the resistance between the electrolyte and the electrodes. This resistance is a dominant contributor to the overpotential loss and research in this area should be aimed at decreasing electrode separation to enhance ionic conductivity.

3.3 Concentration Polarization or Diffusion Overpotential

Concentration polarization is caused by slow rate of mass transfer of the reactants near the electrodes. Electrode reactions require a constant supply of reactants in order to sustain the current flow. When the concentration polarization or diffusion limitations reduce the availability of a reactant, part of the available reaction energy is used to drive

the mass transfer, thus creating a corresponding loss in output voltage. Similar problems can develop if a reaction product accumulates near the electrode surface and obstructs the diffusion path or dilutes the reactants. The PEM fuel cell diffusion overpotential can be expressed as:

$$\eta_d = \frac{RT}{zF} \ln \frac{C_{O_2}^S C_{H_2}}{C_{O_2} C_{H_2}^S} = \frac{RT}{zF} \left(\ln \frac{C_{O_2}^S}{C_{O_2}} - \ln \frac{C_{H_2}^S}{C_{H_2}} \right) \quad (3.7)$$

Where C_{H_2} and C_{O_2} are the hydrogen and oxygen bulk concentrations, and $C_{H_2}^S$ and $C_{O_2}^S$ are the hydrogen and oxygen electrode surface concentrations, respectively [37]. If the concentration profile between the flow channel and the electrode surface is assumed linear (Nernst diffusion layer model), the relation between the current density and the concentration can be solved using Fick's and Faraday's law. As a result, the diffusion overpotential can be expressed as:

$$\eta_d = \frac{RT}{zF} \left[\ln \left(1 - \frac{i}{i_{l,c}} \right) - \ln \left(1 - \frac{i}{i_{l,a}} \right) \right] \quad (3.8)$$

Where $i_{l,a}$ and $i_{l,c}$ are the anode and cathode limiting currents, respectively.

The main source for diffusion overpotential is considered by the diffusion of oxygen through the partially flooded gas diffusion backing on the cathode side [39]. Using pure oxygen removes the diffusion problems related to reactant availability, but the mass transfer can still be affected by obstruction of diffusion paths and reactant dilution. Diffusion overpotential is much smaller on the anode than on the cathode, since the diffusion of hydrogen is much faster than that of oxygen. Expressions for anode and

cathode potentials can be derived from the Equation (3.1) and overpotential Equations (3.3) to (3.8). The anode potential is expressed as:

$$E_a = E_{t,a} + \eta_{act,a} + \eta_{d,a} = \frac{RT}{F} \frac{i}{i_{0,a}} + \frac{RT}{zF} \ln \frac{C_{H_2}^S}{C_{H_2}} \quad (3.9)$$

For the cathode potential, it is expressed as:

$$E_c = E_{t,c} + \eta_{act,c} + \eta_{d,c} = E_{t,c} - \frac{RT}{\alpha n F} \ln \left(\frac{i}{i_{0,c}} \right) + \frac{RT}{zF} \ln \frac{C_{O_2}^S}{C_{O_2}} \quad (3.10)$$

The potential of an electrochemical cell is defined as the potential difference between the cathode and the anode. Using Equations (3.9) and (3.10), and taking in account ohmic losses Equation (3.6), the fuel cell voltage can be expressed as a function of current density:

$$E = E_{t,c} - \frac{RT}{F} \left[\frac{\ln(i/i_{0,c})}{1-\alpha} + \frac{i}{i_{0,a}} \right] + \frac{RT}{zF} \ln \frac{C_{O_2}^S C_{H_2}}{C_{O_2} C_{H_2}^S} - IR \quad (3.11)$$

Concentrations in Equation (3.11) can be expressed as functions of current density using the Nernst diffusion layer model and Equation (3.8).

$$E = E_{t,c} - \frac{RT}{F} \left[\frac{\ln(i/i_{0,c})}{1-\alpha} + \frac{i}{i_{0,a}} \right] + \frac{RT}{zF} \left[\ln \left(1 - \frac{i}{i_{l,c}} \right) - \ln \left(1 - \frac{i}{i_{l,a}} \right) \right] - IR \quad (3.12)$$

As it can be observed from the Nernst Equation (3.12), there are many variables when considering the electromotive field (EMF) of a fuel cell, which makes them very complex in analyzing and optimizing.

A characteristic of typical PEM fuel cells' current-voltage curve is presented in Figure 6. The curve can be divided into three regions, which are governed by the different overpotentials. Activation overpotential dominates at low current densities in region 1. Region 2 is governed by the ohmic losses or IR-losses. At high current densities, the concentration polarization takes place and this is represented in region 3.

The middle region in Figure 6 is nearly linear and is governed by IR-losses. The ionomer conductivity depends on the humidification level, and thus drying out of the MEA increases total cell resistance, making the voltage drop more rapidly.

Figure 6: Different types of overpotential Loss

Diffusion overpotential is the dominating loss mechanism at higher current densities, which is identified at region 3, where the mass transfer limits the reaction rate. Water management is of key importance in controlling the diffusion overpotentials. Excess water in the gas diffusion backing or on the electrode obstructs the reactants diffusion to the active area. Diffusion overpotentials bend polarization curves down at

high current densities. Future research is required to develop an efficient electrode, which will aid in reducing the overpotentials.

CHAPTER 4 - Membranes of PEM Fuel Cells

PEM fuel cells have three major components: the electrodes, the membrane and the catalyst. The catalyst splits the hydrogen atoms into electrons and hydrogen ions (H^+), the membrane allows for proton movement only, and the electrodes direct the flow of current. Although the electrodes, the membrane, and the catalyst are the main components of a PEM fuel cells there are still other components remaining to make up a complete system of PEM fuel cells. Figure 7 depicts all the components within a PEM fuel cell.

Figure 7: Breakdown of a single proton exchange membrane fuel cell [25]

4.1 Introduction to the Membrane of PEM Fuel Cells

The electrolyte membrane allows protons to pass through to the cathode side, but separates hydrogen and oxygen molecules and therefore prevents direct combustion. The membrane also acts as an electronic insulator between the bipolar plates. The proton conducting membrane usually consists of a polytetrafluoroethylene (PTFE) based polymer backbone, to which sulfonic acid groups are attached. The acid molecules are fixed to the polymer preventing any leakage, but the protons on these acid molecules are free to migrate within the polymer. The most common membrane material in PEM fuel cells prototypes is Nafion, which is manufactured by DuPont.

Every product ever developed was constructed using the engineering fundamentals that are applied to develop new materials. Materials play an important factor in the development of new and powerful products. Without the familiarity of the behavior of materials, there would be no development. Materials play an essential role in the environment, research and development. In this chapter, the investigation of the Nafion 117 material is conducted to examine its suitability for the PEM fuel cells.

Aside from the conventional Nafion 117 membrane there are also other materials used to construct the membrane of PEM fuel cells. Some examples are the Dais from Dias-Analytic Corporation, Aciplex by Asahi Chemical Company, Flemion from Asahi Glass Company [12-14]. The study of other candidate materials to construct the membranes for PEM fuel cells is still under development and has not yet been fully commercialized.

4.2 Overview of the Nafion 117 Membrane

Nafion is a trade name of a perfluorosulfonate ionomer from DuPont. It is used frequently as an ion exchange membrane in electrochemical applications, such as fuel cells, water electrolyzers and as polymer-modified electrodes [15-17]. Nafion membrane consists of a PTFE backbone. These structures offer a high ionic conductivity, high mechanical, thermal and chemical stability. The properties of Nafion are strongly influenced by the equivalent weight (EW), water content, nature of solvent, exchanged cations and temperature. Nafion is readily available and can be purchased from different suppliers. Its molecular structure is represented in Figure 8. Usually the molecular structure of the material plays an important role in their behavior under certain conditions. The length of the polymer chain has an important effect on properties. A long chain can form more secondary bonds with neighboring chains than a short chain [19].

Figure 8: Nafion membrane molecular structure

Nafion is currently one of the leading choices for PEM that took the attention of many researchers. The purpose of a membrane in the PEM fuel cells is to:

- To separate the anode and cathode
- To prevent mixing of the fuel and oxidant

- To provide a conductive pathway for protons

A material for a membrane for PEM fuel cells is determined on many factors. Some of the factors that affect the choice of the membrane are as follows:

- High ionic conductivity under cell operating conditions
- Long-term chemical and mechanical stability at elevated temperatures
- Good mechanical strength, with resistance to swelling
- Low oxidant and fuel cross-over and pinhole free
- Interfacial compatibility with catalyst layers
- Long term stability

The tendency for Nafion 117 membrane to conduct ions across it is high. This process allows power to be generated. Nafion mechanical property, which can be found in Table 5, can also predict the behavior of the membrane under different boundary conditions. In the Simulation chapter, this is shown in detail.

Mechanical Properties	Typical Values
Tensile Modulus [MPa]	249 Mpa
Tensile Strength [MPa]	34 Mpa
Elongation [%]	200
Density [g/cm ³]	2
Thermal Conductivity [W.m ⁻¹ . K ⁻¹]	0.1
Poisson Ratio	0.48

Table 5: Mechanical properties of Nafion membrane [20]

4.3 The Ability of Nafion Membrane to Absorb Water

Water transport and water content in a membrane plays an important role in the conductivity of protons and gas permeability. As the water content increases in the membrane, the conductivity of protons through it will also increase, hence increasing the efficiency of the fuel cells. This process will achieve higher generation of electricity

within PEM fuel cells. However, large water content in the Nafion membrane could cause flooding of the cathode, which will reduce the overall efficiency of the fuel cells. Therefore, it is extremely important to remain at a state of equilibrium when it comes to the water content inside Nafion membranes. The water flux in a membrane can be expressed by the following equation:

$$WaterFlux : F = \frac{t \cdot M_{water}}{T \cdot A_s} \quad (4.1)$$

Where M_{water} is the mass of water collected from the cathode exhaust, in grams, T is the duration of the test in hours, t is the membrane thickness in cm and finally A_s is the active area, in cm^2 [21].

A study conducted by Cao and Djilali [22] successfully models the water transports across the Nafion 117 membrane. This is illustrated using the osmotic drag coefficient and water content in the membrane:

$$n_d = \frac{2.5}{22} \lambda \quad (4.2)$$

Where λ is the hydration index, which is defined as the number of moles of water per equivalent sulfonic acid group SO_3^- , in the membrane. The hydration index can be expressed as follows:

$$\lambda = \frac{c_w}{e - f c_w} \quad (4.3)$$

Where f is the experimentally determined swelling coefficient for the membrane, c_w is the molar concentration of water and e is expressed as:

$$e = \frac{\rho_m^{dry}}{E_m} \quad (4.4)$$

Where ρ_m^{dry} the dry membrane density and E_m is the equivalent membrane weight.

In addition, c_w can be expressed as:

$$c_w = \frac{e\lambda}{f\lambda + 1} \quad (4.5)$$

Therefore, for the Nafion 117 membrane the electro-osmotic drag coefficient n_d can be finally expressed as:

$$n_d = \frac{2.5}{22} \frac{c_w}{e - fc_w} \quad (4.6)$$

Equation (4.6) illustrates that each proton ion H^+ that is transported across the Nafion 117 membrane drags 2.5/22 molecules of water along with it. Equation (4.6) shows the capacity of water content 11% being able to pass across the Nafion membrane via the osmotic drag coefficient.

Nafion water uptake depends on the drying method before an experiment can be conducted. Samples that have been dried at room temperature achieved higher water content compared to samples boiled at temperatures of 105 °C. It was found that the destruction of the cluster took place when the Nafion membrane was exposed to high temperatures. This resulted in the lower uptake of water content in the Nafion membrane. Lower uptake of water content through the membrane reduces the ionic conductivity, therefore, lowering the efficiency of the operation [23]. Table 6 compares the conductivity of protons in Nafion 117 samples. The results from [23-25] show that Nafion samples that are heated to temperatures <80 °C perform better than samples that are boiled in water at 105 °C for 1 hours.

Membrane	H ₂ O/SO ₃	Cation	Comments
Nafion 120	16.5	H ⁺	Room Temp
Nafion 120	22.3	H ⁺	T=180°C
Nafion 117	21	H ⁺	27<T<80
Nafion 117	11	H ⁺	Boiled at 105°C for 1 hr
Nafion 117	80	Na ⁺	Pre-swollen in glycerol at 225°C

Table 6: Effect of water uptake at various temperatures [23-25]

4.4 Physical Aging of Nafion 117 Membrane

The ability to account for the effects of physical aging is critical to the design of engineering structures involving advanced polymers and polymer composites [26]. After reviewing different literatures it was determined, that Nafion membrane exhibits a distinct material property, i.e., it is viscoelastic. Viscoelastic is referred to as a mechanical property that is time-dependent, which can change the material's physical structure. The Maxwell model best illustrates the viscoelastic mechanical property. The Maxwell element model is represented by a simple spring and dashpot in series. The total shear strain is the sum of the elastic and viscous-strain components [19].

$$\gamma = \gamma_E + \gamma_v \quad (4.7)$$

$$\frac{d\gamma}{dt} = \frac{1}{G} \frac{d\tau}{dt} + \frac{\tau}{\eta} \quad (4.8)$$

$$\tau = \eta_s \frac{d\gamma}{dt} - \left(\frac{\eta_s}{G} \right) \frac{d\tau}{dt} \quad (4.9)$$

Where η_s is the coefficient of viscosity in shear, G is the modulus of elasticity in shear and $\lambda_R = \eta_s/G$ is the relaxation time.

One of the important parameters in the Maxwell element model is the relaxation time term. This term can predict the mechanical behavior of the Nafion 117 membrane with time. The relaxation term in the Equation (4.9), implies that as the membrane is allowed to age the structure will become closely packed together, in other words, contract. In addition, the relaxation term predicts the behavior of the viscous flow. For example, with quicker time values of λ_R , the Nafion 117 membrane will become softer, and with longer time values of λ_R , the Nafion 117 membrane will exhibit solid characteristics. The Maxwell element model implies that if the Nafion 117 membrane is exposed to viscous shear, depending on the relaxation time, it can alter the behavior of the membrane i.e., becoming softer or harder. This model can predict the conductivity of the membrane if subjected to continuous viscous shear stress.

Physical aging of polymers can also be explained by considering the free volume theory, which states that, in order for molecular motion to occur, free volume must be present between polymeric chain segments [26]. As time progresses, the polymer will shrink and that is referred to as the physical aging process. Both the free volume theory and the Maxwell element model are proven consistent in predicting the physical aging process. Physical aging can be reversed if a polymer is heated above a particular temperature, i.e., T_g and if left constant for some time the physical aging of the polymer can disappear. Figure 9 below shows the aging of a polymer as time progresses. The volume increases since the molecules are closely being packed together.

Figure 9: Shows the effect of Physical aging of polymer's volume [26]

It was determined that, as Nafion was allowed to undergo physical aging, the structure became closely packed together. This process may hinder the ability of the membrane to pass protons through them. The ability of a membrane to pass protons through them is directly related to the amount of free volume in the structure. If the free volume increases, the ionic transport (membrane allowing proton to pass through it) will increase. Therefore, the increase of free volume in a polymer will increase the diffusion coefficient of a membrane.

4.5 The Role of Temperature on the Nafion Membrane

It is necessary to understand how the properties of a Nafion 117 membrane vary over a wide range of temperature. The property most convenient to monitor is specific volume. Since the Nafion membrane is a polymer material, it is stated that when a polymer reaches the melting point T_m a sharp drop will occur in specific volume.

In addition, polymer materials below the T_g known as the glass transition temperature will be in the stage of amorphous solid. When the Nafion membrane is in

the amorphous stage, it will be highly ductile. Nafion 117 being in this stage will result in the molecule motion to slow down. In the amorphous stage if the membrane is exposed to water content it will swell. Having the membrane to be swollen means that the membrane is capable of carrying high water content which in result will increase the conductivity of proton across the membrane.

However, if the temperature is allowed to go above the T_g temperature, the Nafion 117 membrane will act as a flexible rubbery material. At this condition, the Nafion 117 will have sliding segments of the polymer chain that can cause fracture [19]. This will increase the internal energy resulting in an increase in thermal expansion. This can be shown by the first law of thermodynamics:

$$dU = TdS - pdV + PdL \quad (4.10)$$

Where S the entropy of the system at temperature T , pdV the work done in changing the volume at pressure P , PdL the work done by a tensile force P in changing the length of the system. The above equation can be rearranged to yield:

$$\left(\frac{\partial L}{\partial T}\right)_{P,V} = \frac{1}{P}\left(\frac{\partial U}{\partial T}\right)_{P,V} - \frac{T}{P}\left(\frac{\partial S}{\partial T}\right)_{P,V} \quad (4.11)$$

All factors in the entropy term in Equation (4.11) are positive, which shows that an increase in temperature results in a decrease in length. In a rubbery state, the entropy term predominates, so that an increase in temperature results in a contraction in length [19].

It is important to avoid the Nafion 117 membrane from reaching the T_g since it will rapidly reduce the modulus. These characteristics can greatly affect the Nafion 117

membrane performance in the fuel cells. Figure 10 defines the amorphous stage as it approaches T_g temperature.

Figure 10: Polymer change of state with respect to temperature

Figure 11 shows that with increasing temperature the conductivity across the membrane nearly diminishes. On the contrary, Nafion membranes can safely operate over a wide range of temperature yielding reasonable stability.

Figure 11: Nafion 117 proton conductivity vs. temperature [27]

Each material has its advantages and disadvantages. The Nafion 117 tends to decrease its conductivity with increasing temperature as shown in Figure 11. Nafion 117 operating over 100 °C will not have a long life cycle and will fracture. Now R&D efforts are focused on finding a new class of membrane materials that are able to withstand elevated temperatures without causing it to fracture.

Many studies have been conducted to examine Nafion membranes. The continuous research will allow developers to make Nafion membranes widely commercialized for many applications. Besides temperature affects on the membrane other tests were conducted by P. D. Beattie *et. al.* Table 7 shows Nafion membrane under different pressure to observe the diffusion of oxygen in to the membrane, the solubility and finally the permeability of gas [28].

Pressure	Diffusion [$\text{cm}^2 \text{s}^{-1}$]	Solubility [mol.cm^{-3}]	Permeability [$\text{mol.cm}^{-1}.\text{s}^{-1}$]
2.0	5.24	6.36	33.40
2.5	5.46	7.89	43.10
3.0	5.48	9.35	51.20
3.5	5.47	10.93	59.80
4.0	5.71	11.93	67.50
4.5	6.71	12.10	81.20
5.0	7.07	12.52	88.50

Table 7: Diffusion coefficients, solubility and permeability data for O₂ in Nafion 117 Membrane [28]

4.6 Other Membrane Materials

Aside from the Nafion 117 membrane researchers have had some attempts with materials such as; bacterial cellulose. *Gluconoacetobacter* sp. bacteria produce bacterial cellulose during growth on carbohydrate sources. Nascent cellulose strands, synthesized

by the bacteria, are secreted and form layers at the air-liquid interface [16]. Figure 12 is a micrograph of dried bacterial cellulose.

Figure 12: Micrograph of freeze-dried bacterial cellulose [16]

This network of cellulose fibrils is spongy looking, which is referred to as pellicule. After removing the cellular debris, the pellicule typically contains greater than 99% H₂O, the remainder being cellulose. On drying the pellicules to remove water, the layers of cellulose collapse on top of each other to produce a very thin membrane (< 50 μ m thick). The US Department of Energy (DOE) efforts are focused on the development of thermo-stable membranes. This will facilitate the transfer of protons from the anode to the cathode during the operation of a PEM fuel cell at high temperatures roughly greater than 120 °C.

Bacterial cellulose has several unique properties that potentially make it a valuable material for the development in PEM fuel cells:

- It is an inexpensive and non-toxic natural resource
- It has good chemical and mechanical stability
- It is very hydrophilic
- It does not re-swell after drying

Additionally, its thermal stability and gas crossover characteristics are superior to Nafion 117, a material widely used as a proton conductive membrane in PEM fuel cells.

However, further testing is required since this is a new class of material that can potentially be used as an operable membrane for PEM fuel cells in the near future.

From Table 8 it shows that bacterial cellulose can operate at much higher temperature without critical damage. In the same time, it has higher tendency of the ion exchange capacity. It is also seen that bacterial cellulose has superior mechanical stability when compared to the conventional Nafion 117 membrane. Bacterial cellulose is able to withstand rough acid conditions up to 39%, which is very crucial under standard operation.

Types of Stabilities	Membrane Characteristics	Bacterial Cellulose	Nafion 117
Physical Properties	Dry membrane thickness (mm)	0.023	0.199
	Wet membrane thickness (mm)	0.081	0.225
	H ₂ O content /g	3.16	0.31
	Thermal Stability (°C)	245	<90
	Ion exchange capacity (mequiv/g)	1.3	0.9
	H ₂ crossover (nmol.mil/h.cm ² .atm) ²	267.2	2039.4
Mechanical Stability	Resistance to crack being dry	No	Yes
	Resistance to crack being hydrated	Yes	Yes
	Resistance to tearing being dry	No	Yes
	Resistance to tearing being hydrated	Yes	Yes
	Resistance to gas pressure (dry)	30 psi	>50 psi
Chemical Stability	Acid Stability (% weight loss)	39	2.5

Table 8: Comparison of bacterial cellulose to the conventional Nafion 117 [16]

Another type of membrane used in fuel cells is the Dais membrane. It was created to “fill in the gap”, since Nafion 117 is expensive and might not be cost effective for use in home and small business applications. The Dias membrane unlike the bacterial cellulose has a very low operational temperature ranging from 35 °C to 70 °C, which is lower than that for Nafion. This material is considerably cheaper and as result, offers an affordable alternative for lower cost room temperature use. Dais membrane is focused on

PEM fuel cells that will help power portable electronics and other low power applications. The molecular structure of the Dias material is shown in Figure 13. It consists of CH₂ with SO₃H group.

The reason Dias is chosen for fuel cell applications, is its ability to selectively pass positively charged particles, a distinctive characteristic made possible because of its structure. While these materials have different backbones, they have one important feature in common with Nafion 117 membrane, i.e., they both have sulfonic acid side groups. This is a key role in ion transport, which makes it possible for PEM fuel cells to provide energy.

Figure 13: Molecular structure of the Dias Membrane

4.7 Summary of PEM Membranes

In this chapter, it is shown that an increase in water content will help proton conductivity across the membrane. The osmotic drag coefficient was obtained to help understand the relationship between the water content and the behavior of the Nafion 117 membrane. In addition, the physical aging of the membrane was discussed. It was observed through the Maxwell element model that with increasing time the molecules will tend to come together as closely packed as possible. This process will hinder the ability of the membrane to allow proton ions to pass through it. However, by bringing up

the temperature to $\sim T_g$ the process of physical aging can be reversed and completely disappear. T_g is an important parameter in the behavior of the Nafion 117 membrane. If the membrane is allowed to go below the T_g temperature it will be in an amorphous stage, which will help preserve the water content in the membrane. In this stage the membrane can pre-swell, therefore, increase the proton conductivity through it. On the other hand, if the membrane is operating above the T_g temperature it will be in the rubbery state. At this state, the membrane may fracture and the PEM fuel cells' efficiency will nearly diminish. It is important to keep the PEM fuel cells in isothermal operation ideal to the Nafion 117 membrane. An ideal temperature that the Nafion 117 membrane can operate under is 80 °C. This chapter examined the different scenarios that the Nafion 117 membrane can encounter during operation.

CHAPTER 5 - Simulation for Evaluation of Membrane Performance

5.1 Steps Prior to Simulation

Using the software CATIA V5 [44] package, simulation was conducted to evaluate the behavior of Nafion 117 membrane under various temperatures. The generative capability of CATIA V5 analysis solution provides fast analysis iteration for any type of design. Moreover, because of the CATIA V5 architecture, it is easy to drive product optimization based on analysis specifications and results.

The process began by defining the mechanical property of the Nafion 117 membrane. Some of the properties include Young Modulus, Poisson ratio, density of material, thermal expansion and the materials yield strength. These mechanical properties were manually inputted into the software package.

The next step is to design the Nafion membrane into the software package based on the mechanical properties chosen. The Nafion that was constructed had a dimension of, length ~25 mm, width ~6 mm and thickness of 0.178 mm, which is displayed in Figure 14. These values were chosen to mimic the exact sample that was used by University of Duke to conduct their research on the Nafion membrane sample.

Figure 14: Dimension of the Nafion membrane model

Prior to executing the simulation, the boundary conditions on the design are required. The purpose for this simulation is to test the membrane with varying temperatures and a tensile force at a uniform rate until the membrane fractures. This will show the maximum stress points on the material, which will enable in determining whether the membrane is capable of operating under these temperatures. The set of boundary conditions used is a preloaded force of 0.005 N; an isothermal at 333 K, 363 K and 393 K and an upper tensile force of 18 N [29] which are displayed on Figure 15.

Figure 15: Layout of boundary condition on membrane

The symbol T in the design is the value of the temperatures that the membrane will encounter. The arrows on Figure 15 indicate the preloaded forces. In addition, the design was clamped to eliminate any movement or vibration that could deviate from obtaining accurate results upon completion.

The CATIA V5 software package examines the design before the simulation. Then it automatically generates the structural data based on the design. The structural computations generated include the number of nodes, elements and the degree of freedom associated with each element. The structural data for this design is displayed in Table 9.

Number of nodes	170
Number of elements	384
Number of D.O.F	510
Linear tetrahedron	384

Table 9: Structural data used in computation

The CATIA V5 software is an attractive simulation package for its ability to automatically generate representative data of the design prior to conducting simulations. One important factor is the ability of the software to mesh the design to perform the analysis. Table 10 shows the representative data that is defined automatically by the CATIA V5 software based on the design. It also displays the method of mesh used and the matrix size generated for the design.

Number of connected nodes	170
Nodal maximum front width	11
Nodal maximum band width	28
Method	SPARSE
Number of super nodes	119
Number of coefficients	11577

Table 10: Representative data used in computation

Another unique feature the software provides its ability to evaluate each single element in the design. After designing the Nafion membrane, it was found that it took 384 elements to complete the design. Prior to conducting the simulation, the design must be validated to ensure that all elements are linked properly to minimize any error on the stress distribution results. The software rates, the elements of the design based on the different criterion being skewness, stretch, etc. Table 11 displays the element quality for this design.

Criterion	Good	Poor	Bad
Skewness	61 (15.89%)	323 (84.11%)	0 (0.00%)
Stretch	384 (100.00%)	0 (0.00%)	0 (0.00%)
Min. Length	384 (100.00%)	0 (0.00%)	0 (0.00%)
Max. Length	384 (100.00%)	0 (0.00%)	0 (0.00%)
Shape Factor	384 (100.00%)	0 (0.00%)	0 (0.00%)
Length Ratio	384 (100.00%)	0 (0.00%)	0 (0.00%)

Table 11: Element quality of Nafion membrane under different temperatures

5.2 Simulation Results for Varying Temperatures

5.2.1 Static Case with 333 K Applied Constant Temperature

Based on the tensile force and the temperature applied to the design, the software calculates the forces and moments experienced by the membrane in 3D. These results are displayed in Table 12. The results of these forces is used in explaining the distinct mechanical property (viscoelastic) of Nafion 117, but will not be used further.

Components	Applied Forces	Reactions	Residual	Relative Magnitude Error
F_x (N)	3.90E-14	-5.97E-13	-5.58E-13	3.85E-15
F_y (N)	-2.10E-06	2.10E-06	4.47E-12	3.08E-14
F_z (N)	-8.69E-15	3.86E-14	2.99E-14	2.06E-16
M_x (N.m)	-5.25E-09	5.25E-09	2.77E-15	1.27E-15
M_y (N.m)	-3.89E-16	5.38E-15	4.99E-15	2.29E-15
M_z (N.m)	-1.72E-09	1.72E-09	-8.04E-15	3.69E-15

Table 12: Resultant forces under 333 K temperatures

After the simulation has been executed, the Nafion membrane deformed due to the force and temperature applied. The membrane also experienced strain energy of 3.325×10^{-2} J. The result of the deformed mesh is shown below in Figure 16.

Figure 16: Static case solution under 333 K constant temperature

The most important result from this simulation is to show the stress distribution on the Nafion membrane and its fracture point. In addition, it will show whether the Nafion membrane will reach its ultimate yield stress and hence fracture. It will also underline the maximum range of temperature in which the membrane can operate. To evaluate the stress distribution on the Nafion membrane the Von Mises Stress criteria was used:

$$\sigma_o = \sqrt{\frac{(\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2 + 6(\tau_{xy}^2 + \tau_{yz}^2 + \tau_{xz}^2)}{2}} \quad (5.1)$$

Where σ_x , σ_y , σ_z are the principle stresses in the x, y, z directions. Figure 17 shows the stress distribution on the Nafion membrane. The design was solved using the boundary conditions defined prior to executing the simulation.

Figure 17: Nodal solution for 333 K temperature, using Von-Mises stress criteria

The results from Figure 17 show that the maximum stress tensor was calculated to be $1.12 \times 10^7 \text{ N/m}^2$ with a minimum stress tensor of $1.33 \times 10^6 \text{ N/m}^2$. The result for the first case, which is exposed to 333 K of temperature, showed that the Nafion membrane is operating under normal conditions since most of the membrane is experiencing low stress tensor. In addition, the highest stress tensor experienced by the Nafion membrane is much lower than the yield stress of the actual material. This indicates that there is no fracture under these boundary conditions.

5.2.2 Static Case with 363 K Applied Constant Temperature

The temperature exposed on the Nafion membrane to determine its stability is increased by 30 K for this second case, while the tensile force stayed the same, varying only the temperature. Based on the tensile force with an applied constant temperature the software calculates the forces and moments experienced by the Nafion membrane. The results from Table 13 will assist in determining the behavior of the membrane to give an insight on the mechanical property of the membrane such as the viscoelastic property.

Components	Applied Forces	Reactions	Residual	Relative Magnitude Error
$F_x \text{ (N)}$	1.4527E-015	-1.1921E-012	-1.1906E-012	4.8257E-015
$F_y \text{ (N)}$	-2.1000E-006	2.1000E-006	2.8422E-012	1.1519E-014
$F_z \text{ (N)}$	-5.8520E-015	3.8192E-014	3.2340E-014	1.3107E-016
$M_x \text{ (N.m)}$	-5.2500E-009	5.2500E-009	2.6818E-015	7.2462E-016
$M_y \text{ (N.m)}$	-1.3028E-016	8.9859E-015	8.8556E-015	2.3928E-015
$M_z \text{ (N.m)}$	-1.72178E-009	1.7177E-009	-1.3845E-014	3.7410E-015

Table 13: Resultant forces under 363 K temperatures

Comparing results from Table 13 to Table 12, the Nafion membrane seems to damp the forces and moments on the design. This can be explained by the viscoelastic property of the material. Since Nafion membrane is developed from polymer material, it

exhibits viscoelastic characteristic. This characteristic tends to absorb some of the force applied on the design, hence explaining why the design shows lower reaction forces with increased temperature.

After the simulation has been executed for the second case, the Nafion membrane deformed further due to the force and increased temperature applied. The membrane experienced strain energy of 9.612×10^{-2} J.

Figure 18: Nodal solution for 363 K temperature, using Von-Mises stress criteria

Again, the Von Mises criterion was used to demonstrate the stress distribution for this second case with the elevated temperature. The result from Figure 18 indicates that the maximum stress tensor increased to 1.91×10^7 N/m² with a minimum stress tensor of 2.26×10^6 N/m². This shows that the Nafion membrane developed an increased stress level. However, the Nafion membrane is still operating under normal conditions since most of the design is experiencing low stress tensor. In addition, the highest stress tensor experience by the membrane is still under the ultimate yield stress of the actual material.

This indicates that there is no fracture under these boundary conditions, also leaving an adequate factor of safety. It is recommended that a safety factor of 1.5 should be used for materials such as polymers [18].

5.2.3 Static Case with 393 K Applied Constant Temperature

In the third simulation, the temperature exposed on the Nafion membrane to determine its stability is further increased by 30 K to reach 393 K, while the tensile force stayed the same. Based on the preloaded forces applied the software calculated the forces and moments experienced by the Nafion membrane in 3D.

Comparing the new results from Table 14 with Table 13, the Nafion membrane seems to damp the forces and moments even further. Restriction to this behavior is due to the nature of the material exhibiting viscoelastic property. This characteristic tends to absorb some of the force applied on the design, hence explaining why it shows lower reaction forces with increased temperature.

Components	Applied Forces	Reactions	Residual	Relative Magnitude Error
F_x (N)	1.0561E-013	-1.4964E-012	-1.6020E-012	4.5987E-015
F_y (N)	-2.10000E-006	2.1000E-006	5.5849E-012	1.6032E-014
F_z (N)	-6.8435E-016	-2.3093E-014	-2.37770E-014	6.8256E-017
M_x (N.m)	-5.2500E-009	5.2500E-009	1.5536E-014	2.9733E-015
M_y (N.m)	-4.2806E-018	1.1618E-014	1.1622E-014	2.2242E-015
M_z (N.m)	-1.72178E-009	1.7177E-009	-1.5992E-014	3.0604E-015

Table 14: Resultant forces under 393 K temperatures

The membrane experienced a further increase in its strain energy of 1.916×10^{-1} J. The Von Mises criterion was used to demonstrate the stress distribution for this last case with further elevated temperature. The results from Figure 19 show that the maximum stress tensor was 2.7×10^7 N/m² with a minimum stress tensor of 3.2×10^6 N/m². The

increased stress tensor indicates that the Nafion membrane is now operating in undesired conditions and that this temperature is not recommended for safe operation.

Figure 19: Nodal Solution for 393 K temperature, using Von-Mises stress criteria

Since the recommended factor of safety is 1.5 for polymer materials, thus the maximum stress tensor $2.7 \times 10^7 \text{ N/m}^2$ will exceed the actual yield strength of the Nafion membrane $3.4 \times 10^7 \text{ N/m}^2$. This indicates that temperatures of 393 K and higher will have a high tendency to fracture the Nafion 117 membrane. This simulation proves the same results obtained experimentally from University of Duke [29]. The need for a new class of material to design the membrane is required. This will widen the feasibility of the technology.

CHAPTER 6 - Optimization Methods for PEM Fuel Cell

Design

The purpose of this chapter is to focus on optimization methods to improve the performance of PEM fuel cells. The Genetic Algorithm is a search method that solves optimization problems by implementing powerful search techniques to find an optimal solution within a large set of solutions. Research was conducted to demonstrate how this could be accomplished. Particularly, the stack arrangements within PEM fuel cells are optimized to deliver maximum voltage output. Hence, the Genetic Algorithm is a powerful tool that is utilized to converge to an optimal solution for any engineering application.

The adjustments of the Nafion content within the membrane and the platinum loading are used to optimize the current density within PEM fuel cells. The Nafion content is adjusted in the membrane, while the platinum loading is adjusted in the electrodes. The Membrane Electrode Assembly (MEA) concept will be considered since the two parameters adjusted belong to the MEA setup. In addition, the variability of the MEA arrangements is used to increase other performance such as the water retention and proton conduction at high temperatures. It could also be used to increase the voltage output of the fuel cell and to increase the efficiency of the fuel consumption. In general, MEA consists of five basic components: anode, cathode, catalysts, ion exchange polymer membrane, anode and cathode gas diffusion layers. The functions of these basic components are intimately related in optimizing the current density of PEM fuel cells.

6.1 Genetic Algorithms

The fuel cell stack has to be configured so that it delivers the maximum output power at the load's operating voltage. This part of the chapter will focus on how the

Genetic Algorithm technique is applied to optimize fuel cell stack design. This is accomplished by searching for the best configuration of cell numbers and cell surface area.

Genetic Algorithm works by generating a large set of possible solutions to a given problem. It then evaluates each of these solutions and decides on a “fitness level” that is closer to the optimal solution [45] and it then breeds new solutions. The parent solutions that are a better fit will more likely reproduce, while those that are less fit will not. Genetic Algorithm operators are crossover and mutation, which achieve the reproduction of solutions [46].

Crossover combines the features of two parent chromosomes (solutions) to form two new similar children (new solutions) by swapping corresponding segments of parents. Mutation randomly changes one or more genes (parameters within a solution) with a probability equal to the mutation rate. Crossover is aimed at exchanging information between different potential solutions, while mutation is aimed at introducing some extra variability into the population [48].

I. Mohamed [47] focused on three design parameters within the PEM fuel cell stack. The three parameters used in the Genetic Algorithm method are number of stack cells in series, number of stack cells in parallel and in cell’s surface area. First, he started with a set of criteria to setup the size of this Genetic Algorithm method. The following criteria are presented in Table 15.

Parameter	Value
Number of generations	200
Population size	20
Number of parameters	3
Crossover rate	90%
Mutation rate	10%

Table 15: Setup of genetic algorithms parameters [47]

In order for the Genetic Algorithm to work, the upper and lower limits are defined. The designer starts with generating solutions by randomly selecting values for the design parameters between the upper and lower limits. Usually the designer has an idea in selecting those limits; however, they are nowhere close to the optimal solutions. The three design parameters are listed in Table 16 with their upper and lower limits defined by I. Mohamed [47].

Parameter	Lower Limit	Upper Limit
Number of stack cells in series	1	50
Number of stack cells in parallel	1	50
Cell's area (cm ²)	10	400

Table 16: Upper and lower limits of possible solutions [47]

The fitness function evaluates these solutions based on the fuel cell mathematical model derived from [43]. The fitness function consists of the overpotentials that take place in the PEM fuel cell. This single Equation (6.1) is a combination of all the overpotentials. It is then used in the Genetic Algorithm method to find the optimal result within the upper and lower limits. The fitness function equation is given by:

$$V_s = Z \left[E_o - A \ln \left(\frac{i + i_n}{i_o} \right) - r(i + i_n) + B \ln \left(1 - \frac{i + i_n}{i_L} \right) \right] \quad (6.1)$$

Where V_s is the stack voltage, Z the number of series connected cell in stack, E_o open circuit voltage, A the Tafel slope, i_o the exchange current density, r the specific area resistance, B the concentration loss constant given in volts, i_L the limiting current density.

Figure 20 : Flow chart to approach optimal solution [47]

Figure 20 shows the penalty approach [48] to penalize solutions not producing the desired output power. Those that do so, are ranked using a linear rank selection technique [46] according to the nearness of stack operating voltage at the maximum power point. Then, a stochastic universal sampling method [48] was used to select some of the good solutions to form a new population of solutions. Crossover and mutation are then applied as defined in Table 15 to the selected solutions to produce new off springs. This process continues until the specified number of generations is reached. The designer knows the solution has converged to the optimal, when the difference between the last two solutions is small. The optimal solutions resulting from the Genetic Algorithm method are shown in Table 17.

Parameter	Optimal Value
Number of stack cells in series	21
Number of stack cells in parallel	1
Cell's area (cm ²)	12.5 X 12.5

Table 17: Optimal solutions resulting from the genetic algorithm method [47]

Table 17 shows PEM fuel cells with 21 stack cells in series and 1 stack cell in parallel having a cell's surface area of 12.5 by 12.5 cm will yield the highest voltage performance.

6.2 Parameters Adjustments for Optimized Current Density

MEA, the central element of a fuel cell consists of electrodes and a polymer electrolyte membrane. The fuel cell reaction takes place in the three-phase zone in electrodes (anode and cathode), the membrane and the gas phases. Altering the parameters of the MEA can result in optimizing the performance of the PEM fuel cell. In order to achieve optimal condition a numerical model will be discussed based on some literature survey [49, 50].

The following four design variables are used: Nafion volume fraction ε_N , void space volume fraction ε_V , Pt loading m_{Pt} and catalyst layer thickness L . Since PEM fuel cells usually operate in a specific voltage range, the objective of this optimization problem is to maximize the current density at a given voltage. Denoting the current density generated in the catalyst layer as I_0 at a given electrode potential V_0 , the general optimization problem can be stated as Maximize I_0 with respect to ε_N , ε_V , L and m_{Pt} .

Subject to:

- $0 < \varepsilon_N < 1, 0 < \varepsilon_W < 1, 0 < \varepsilon_S < 1$
- $\varepsilon_N + \varepsilon_W + \varepsilon_S = 1$

Where ε_s is given by:

$$\varepsilon_s = \left(\frac{1}{\rho_{pt}} + \frac{1 - \%Pt}{\%Pt \rho_{pc}} \right) \frac{m_{pt}}{L} \quad (6.2)$$

The weight percentage of Nafion to the sum of Nafion and solid particles denoted by $\%N$ is usually used to measure the Nafion content in the electrode and can be calculated from the volume fraction as:

$$\%N = \frac{\rho_N \varepsilon_N}{\rho_N \varepsilon_N + (1/\%pt)(m_{pt}/L)} \quad (6.3)$$

Where ρ_N is the mass density of Nafion in liquid water. The MEA arrangements shows that by varying the Nafion content in the membrane to 0.32%, the current density at electrode potential $V_0 = 0.6V$ reaches its maximum of 0.93583 A/cm², which is presented Figure 21.

Figure 21: Nafion Content vs. Current density from the optimized model [51]

The next result from Figure 22 shows the fitting current density curve as a function of platinum loading. The highest current density is 0.71492 A/cm^2 when the platinum loading is 0.21032 mg/cm^2 , which is very close to D. Song, *et. al* [51] who achieved an optimum platinum loading of 0.20 mg/cm^2 .

Figure 22: Platinum loading Vs. Current density from optimized model [51]

The design optimization problems for cathode catalyst layer are discussed numerically by taking one or two of the four design parameters (ε_N , ε_V , m_{Pt} and L) as the corresponding optimization parameter(s). Numerical analysis shows that when one of the four design parameters is taken as the optimization parameter, the corresponding one-parameter optimization always has an optimal solution. The catalyst layer performance is much more sensitive to the thickness than to the other three parameters. Additional, attention should be paid to a thinner catalyst layer design in order to avoid a large drop in current density. If two of the four design parameters are taken together as the optimization parameters, the corresponding two-parameter optimization also has a global optimal solution. Numerical analysis shows that by changing the thickness and Pt loading the catalyst layer can reach its best performance compared with changing other pairs of

parameters. The accuracy of the optimization problem highly depends on the accuracy of the catalyst layer model [49], that is, the mathematical description of the phenomena in the catalyst layer.

CHAPTER 7 - Conclusion

There are still other aspects of research to be extended for the development of PEM fuel cells. For instance, the operation of PEM under high temperature conditions [52]. Developing PEM fuel cells that can operate under high temperatures requires many alterations to the existing designs. First, by increasing the temperature, the polymer electrolyte membrane is in a particular need to be improved to withstand the elevated temperatures. Some of the materials that are used today to construct the ion exchange membrane are Dais from Dias-Analytic Corporation, Nafion from DuPont Manufacturer, Aciplex by Asahi chemical company and Flemion from Asahi Glass Company [12-14, 20]. Conversely, most of the materials listed above are deficient in terms of ionic conductivity above 100 °C and at low relative humidity (RH %). Such conditions tend to dry out the membrane and thus drastically reduce membrane proton conductivity. Furthermore, the loss of water causes the membrane to become brittle, resulting in membrane cracking, reactant cross-leakage and poor electrode-membrane contact [53]. Hence, a more effective membrane with good proton conductivity that is less sensitive to high temperatures is required.

PEM fuel cells operating at high temperatures provide many advantages. C. Yuh *et. al.* [53] proposes that operating the PEM fuel cells at higher temperatures helps mitigate the CO poisoning. Many other advantages can also be recognized, such as faster electrode kinetics, lower voltage loss, cathode flooding mitigation. At the beginning of fuel cell technology, researchers believed that voltage loss was caused by an increase in temperature. However, the majority of the voltage loss is due to the increase in cathode polarization. In order to achieve high temperature in PEM fuel cells, the cathode

performance is essential. In addition, the development of a new class of material for a suitable membrane is required. Based on the literature survey, no membranes reported so far can achieve all the above-required goals.

The challenges with high temperature PEM fuel cells are evident and have not yet been fully reached. However, researchers are striving for a new class of materials that offers high performance, low cost membranes for PEM fuel cells. H. Neil [16] proposes the use of bacterial cellulose as a potential membrane. Bacterial cellulose has several unique properties that can potentially make it a valuable material for the development of PEM fuel cells. It is an inexpensive and non-toxic natural resource, it has good chemical and mechanical stability, it is very hydrophilic and it does not re-swell after drying. Additionally, its thermal stability and gas crossover characteristics are superior to materials that have been mentioned, such as Nafion 117, Dias, Aciplex and Flemion, which have currently been widely used as a proton conductive membrane in PEM fuel cells.

To improve the effectiveness of the overall performance of PEM fuel cells optimization methods are introduced. Optimization methods have proven to be a powerful tool that can maximize the desired parameters, such as efficiency of a system, while minimizing undesired parameters, such as fuel consumption and material usage. In this report, Genetic Algorithm was used to maximize the current and voltage distribution across the PEM fuel cell. In addition, the Membrane Exchange Assembly, known as MEA, is utilized to evaluate the behavior of Nafion percentage (being the membrane) and platinum percentage to optimize the current density of the fuel cell.

The optimization of the PEM fuel cell is essential to the survival of the new technology. At this present time, this technology is feasible; however, comes at a high

price. One way to lower the cost is by reducing the usage of platinum within the electrodes. In addition, thin film electrode will reduce the price and would enhance the utilization of catalyst. Also, there should be new class of materials used for the construction of the membrane. The membrane material should be thermally and mechanically stable and comes at a low price. Another aspect that drives the price of PEM technology even higher is the production of hydrogen. The production of hydrogen undergoes many steps to become in its purest form; this increases the cost even further. In order for the PEM fuel cells technology to be a feasible conversion device, it must come at a low cost. In the future, researchers need to focus on driving the cost of hydrogen down and on the other hand find low cost materials to construct PEM fuel cells so they can become an attractive alternative to powering future applications.

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