DESIGN AND FABRICATION OF A PASSIVE
DIRECT METHANOL FUEL CELL

A MAJOR QUALIFYING PROJECT SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE

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Approved by ____________________________________________________

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ABSTRACT

In this project a PDMFC was fabricated using a previously recommended design. The cells were then tested using this design, and experiments were run using pure methanol and methanol gel. The main focus of this research was to successfully build the optimized design that was suggested in the previous work by Lugo and Rivera, and then successfully draw voltage from the finalized product. The experimental results show that the PDFMC can run on pure liquid methanol. Mathematical models were designed to illustrate the mass transfer in the Passive Direct Methanol Fuel Cell. Although the stack was successful, a new design is recommended.

Keywords: Passive Direct Methanol Fuel Cell, PDFMC, DMFC, Methanol Fuel
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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G^\circ$</td>
<td>Gibbs free energy (standard)</td>
</tr>
<tr>
<td>$\Delta H^\circ$</td>
<td>enthalpy (standard)</td>
</tr>
<tr>
<td>$V^\circ 0$</td>
<td>Standard thermodynamic potential</td>
</tr>
<tr>
<td>$V^\circ_{\text{max}}$</td>
<td>Standard maximum potential</td>
</tr>
<tr>
<td>$\rho_{\text{Pt}}$</td>
<td>Platinum Density</td>
</tr>
<tr>
<td>$\rho_{\text{Ru}}$</td>
<td>Ruthenium Density</td>
</tr>
<tr>
<td>$d_{M,A}$</td>
<td>Anode catalyst metal crystalline diameter</td>
</tr>
<tr>
<td>$d_{M,C}$</td>
<td>Cathode catalyst metal crystalline diameter</td>
</tr>
<tr>
<td>$\phi_I$</td>
<td>available metal surface involved in electrocatalysis in contact with ionomer</td>
</tr>
<tr>
<td>$i * A, 0,\text{ref}$</td>
<td>exchange current density, anode, reference</td>
</tr>
<tr>
<td>$i * C, 0,\text{ref}$</td>
<td>exchange current density, cathode, reference</td>
</tr>
<tr>
<td>$C_{\text{Me,ref}}$</td>
<td>concentration of methanol, reference (Standard)</td>
</tr>
<tr>
<td>$C_w$</td>
<td>concentration of water diluted methanol solutions</td>
</tr>
<tr>
<td>$T_{\text{ref}}$</td>
<td>temperature, reference</td>
</tr>
<tr>
<td>$p_{0_2,0,\text{ref}}$</td>
<td>partial pressure of oxygen, reference</td>
</tr>
<tr>
<td>$\alpha A$</td>
<td>transfer coefficient, cathode</td>
</tr>
<tr>
<td>$\nu A e -$</td>
<td>electron stoichiometric number, anode</td>
</tr>
<tr>
<td>$\alpha C$</td>
<td>transfer coefficient, anode</td>
</tr>
<tr>
<td>$\nu C e -$</td>
<td>electron stoichiometric number, cathode</td>
</tr>
<tr>
<td>$\nu A e -$</td>
<td>stoichiometric coefficient of electrons in MOR</td>
</tr>
<tr>
<td>$\nu A Me$</td>
<td>stoichiometric coefficient of methanol in MOR</td>
</tr>
<tr>
<td>$E_{A, \varphi 0}$</td>
<td>effective activation energy for MOR</td>
</tr>
<tr>
<td>$E_{C, \varphi 0}$</td>
<td>effective activation energy for ORR</td>
</tr>
<tr>
<td>$K_{\text{Me}}$</td>
<td>equilibrium constant</td>
</tr>
<tr>
<td>$L_D$</td>
<td>anode gas diffusion layer thickness</td>
</tr>
<tr>
<td>$L_B$</td>
<td>Nafion® 117 membrane thickness</td>
</tr>
</tbody>
</table>
\( L_E \)  
\( \varepsilon_E \) cathode gas diffusion layer thickness  
\( \varepsilon_D \) void fraction of gas diffusion layer, cathode (porosity)  
\( \varepsilon_D \) void fraction of gas diffusion layer, anode (porosity)  
\( \kappa_{O_2} \) partition coefficient of oxygen  
\( \kappa_{Me,D} \) partition coefficient of methanol through ADL  
\( \kappa_{Me,B} \) partition coefficient of methanol through CDL  
\( \xi \) electro-osmotic drag coefficient of water  
\( E_\mu \) activation energy for water viscosity  
\( \lambda \) water molecules per sulfonic group in Naftion®  
\( \delta \) ratio of mutual to matrix diffusion coefficients  
\( q_W \) volume fraction of water formation at cathode  
\( D_{Me,W} \) diffusion of methanol in water  
\( D_{Me,D} \) diffusion of methanol in anode GDL  
\( D_{O_2,W} \) diffusion of oxygen in water  
\( D_{O_2,E} \) diffusion of oxygen  
\( p_w \) water vapor pressure in cathode  
\( R_l \) MEA interfacial resistance  
\( F \) Faraday's constant  
\( R \) gas constant  
\( \mu \) Viscosity of Water  
\( V \) Cell Voltage  
\( V_0 \) DMFC Cell Potential theoretical  
\( \eta_A \) overpotential, anode  
\( \eta_B \) Ohmic overpotential  
\( \eta_C \) overpotential, cathode  
\( \eta_I \) Interfacial resistance  
\( x_{Me,b} \) mole fraction of methanol in PEM  
\( \kappa_{W,B} \) partition coefficient of methanol through CDL  
\( i_{A,0} \) exchange current density, anode  
\( i_{AL} \) limiting exchange current density, anode
\( i_{c,0} \) exchange current density, cathode
\( i_{c,l} \) limiting exchange current density, cathode
\( i_{X,O_2} \) crossover current density, oxygen
\( i_{X,Me} \) crossover current density, methanol
\( i_{X,Me,L} \) limiting crossover current density
\( \gamma_{MA} \) electrocatalyst roughness, anode
\( \gamma_{MC} \) electrocatalyst roughness, cathode
\( \rho_{MA} \) Pt-Ru Alloy density
\( k * Me, D \) rate constant for reaction
\( C_{O_{2,0,ref}} \) concentration of oxygen, reference
\( C_{Me,0} \) initial concentration of methanol
\( C_{O_{2,0}} \) concentration in CCL under equilib
\( C_{Me,b} \) concentration of methanol in PEM
\( C_{W,b} \) concentration of water in PEM
\( C_{O_{2,b}} \) concentration of oxygen in PEM
\( m_{M,A} \) catalyst leading
\( m_{M,C} \) catalyst leading
\( \omega_{Ru} \) mass fraction of RU
\( \theta_{COS} \) adsorbed carbon monoxide sites
\( \theta_{COS,ref} \) adsorbed carbon monoxide sites, reference
\( C_{Me,A(a)} \) Concentration Profile
\( D_{e_{O_{2,E}}} \) diffusion of oxygen in cathode
\( D_{e_{Me,b}} \) diffusion of methanol in PEM
\( D_{e_{O_{2,B}}} \) diffusion of oxygen in PEM
\( P_{e_{Me,D}} \) Effective Methanol Permeance
\( P_{e_{O_{2,E}}} \) Effective Oxygen Permeance
\( P_{O_{2,E}} \) Oxygen permeance
\( \varepsilon_{B} \) void fraction of gas diffusion layer, anode (porosity)
\( K_{a} \) dissociation equilibrium constant for acid sites
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{B_0}$</td>
<td>percolation threshold</td>
</tr>
<tr>
<td>$\sigma_B$</td>
<td>effective PEM conductivity</td>
</tr>
<tr>
<td>$\beta$</td>
<td>degree of dissociation</td>
</tr>
</tbody>
</table>
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We would like to thank Professor Ravindra Datta for his great advice and guidance throughout the project, and for allowing us to take on the task of building this fuel cell. We would also like to thank Jack Ferraro, Doug White, and Kevin Arruda who helped us to manufacture and fabricate the individual pieces for our final product. We would like to thank Jason Hopkins for assistance with AutoCAD drawings.

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CHAPTER 1: INTRODUCTION

Passive direct methanol fuel cells (PDMFC) are currently being researched, with new developments and improving efficiencies noticed over time. The main issue with the direct methanol fuel cell (DMFC) technology is the portability and storage of the fuel. The consumer does not want a bulky and dangerous cell in order to power a lamp or laptop. The conventional DMFC and their extra equipment are simply too large to feasibly power small appliances. The following research conducted is concerned with the improvement and fabrication of passive direct methanol fuel cells (PDMFC).

These cells do not need balance of plant equipment to feed fuel into the fuel cell, which passively diffuses into the cells, or to remove products or heat. The design of a PDFMC comprises mainly of a chamber in which to store the fuel, which allows the fuel to passively diffuse into each cell, and ultimately the membrane electrode assembly (MEA) in the stack. The design of the entire stack affects the portability and performance. The fuel type, whether it is pure or diluted methanol or even a methanol gel, affects the performance as well, which must be taken into consideration when designing the PDMFC.

The next chapter provides a thorough background on the history of the development of the DMFC and the PDMFC, leading up to the most recent designs and applications. The fabrication of the PDFMC in this research is described in the third chapter, along with the assembly of the stacks. Many studies have been done on different MEAs and current collectors, resulting in varying opinions on the construction of an ideal PDMFC. Using considerations from past research, the goal of this research was to improve the performance of PDMFC’s using recommended hardware and assembly methods. Chapter 3 provides details of the PDMFC design and experimental methodology, while Chapter 4 provides theoretical considerations. Chapter 5
describes the experimental performance results obtained. Finally, Chapter 6 provides conclusions of this study, and recommendations for future work.

As is the case with any new technology, there are is abundance of issues that must be looked at when a PDMFC is tested. These issues can be caused by the hardware used to build the stack along with any leakage allowed by the design of the stack. The most important issue is to keep the cells airtight, preventing fuel from escaping and also preventing air and contaminants to leak into the fuel compartment and decrease the performance of the stack. A lot of attention must be paid to the fabrication and design of each individual piece of the cells and overall stack. The starvation of individual cells due to the physical placement of the cells can also be a major issue. The current stack has 8 cells with 4 on each half of the stack all equally spaced from each other. It has been found that methanol diffuses upwards, starving the bottom cells and this must be taken into consideration. The fuel chamber in the latest PDFMC can be fitted with an absorbent pad, which can soak neat methanol fuel and distribute it more equally to each of the cells. This, of course, does not address the methanol crossover and performance issues that are fully explained in Chapter 2.

Methanol as a fuel is inexpensive and readily available as a liquid or gel. This is an advantage due to the volatile nature and decreased portability of other fuels such as hydrogen. The passive nature of the PDMFC construction allows for a longer durability and a high efficiency, as no energy is used in fans, pumps, or exchangers that may be required in other fuel cells or engines. PDMFC’s are completely silent and can continuously produce energy as long as fuel is fed to the chamber. Costs of PDMFC’s can be high due to the expensive nature of catalyst and Nafion membranes employed.
In today’s market where sustainability is a major consideration, a passive direct methanol fuel cell provides a viable option for powering small appliances with minimal waste and high efficiency. The current research hopes to provide results toward the development of a practical PDMFC to power portable devices, while cutting down on cost and maximizing the performance.
CHAPTER 2: BACKGROUND

This chapter provides the necessary background along with a review of the relevant literature.

2.1 Direct Methanol Fuel Cells

2.1.1 Conventional Direct Methanol Fuel Cells

A Direct Methanol Fuel Cell (DMFC) is composed of several layers. There is an anode bipolar plate, a cathode bipolar plate, a membrane electrode assembly (MEA) that consists of an anode and a cathode gas diffusion layer (GDL), and a proton exchange membrane (PEM). These layers can be seen in Figure 1.

![DMFC Schematic](image)

The MEA has a positive and negative side, which are, respectively, the cathode and anode. The methanol oxidation reaction (MOR) and the oxygen reduction reaction (ORR) take place on these electrodes. The MOR produces electrons, while the ORR consumes electrons. This production and consumption of electrons creates a current that is collected through the two bipolar plates. They are usually constructed from a conductive material, like graphite to
maximize the flow of electrons. The plates sheath the MEA and feed methanol at the anode and O\textsubscript{2} at the cathode. They simultaneously remove any products, such as CO\textsubscript{2} bubbles. The bipolar plates are constructed with a unique flow pattern, which assists in the uniform spread of the methanol and oxygen across the anode and cathode. The shapes of the fuel flow channels in the plates are important, as an optimal design can enhance mass transfer, and eliminate kinetic and electric limitations. The predominant flow pattern used is a serpentine channel, although other paths are used with limited success. In a passive fuel cell these paths are usually omitted, due to the lack of pumps and compressors to move the fuel. The bipolar plates separate the gases between the cells, as well as providing a conductive medium between the anode and the cathode. The plates provide a solid structure as well as transfer heat out of the cell.

Bipolar plates are required to be impermeable to gases and must have a good electrical conductivity. The plates must have a good balance between conductivity, strength, size and weight, since the fuel cell must be portable and durable. These plates must have a good resistance to corrosion and must be easily manufactured in a large quantity to reduce overall cost.

The GDL is a porous and conductive material that allows the flow of O\textsubscript{2} in and expels CO\textsubscript{2} and H\textsubscript{2}O. The GDL is composed of a conductive carbon paper or carbon cloth that distributes fuel and products to and from the anode and cathode. A very useful quality of the GDL is that it helps disperse the heat generated by the reactions and electrical currents in the fuel cell. The layer can be treated with polytetrafluoroethylene in order to wet proof it, as well as treating it with a hydrophilic anode backing layer [2]. This treatment would improve the life of the cell and the overall performance. A sample GDL is shown in Figure 2.
The catalyst, which is necessary to promote both half-cell reactions, is comprised primarily of platinum (Pt) and ruthenium (Ru) alloy at the anode and just platinum at the cathode. [4] Increasing the loading of the catalyst improves the DMFC performance, but also increases the cost of the MEA and the fuel cell as a whole. At the anode, a pure metal catalyst is not capable of activating methanol because the CO generated by the MOR, as an intermediate, binds to the catalyst blocking the sites the methanol needs to react. The ruthenium is used to create hydroxide (OH) plus another proton and electron by the decomposition of water. The CO then reacts with the hydroxide to produce carbon dioxide, as well as, another proton and electron. The reactions at both the anode and cathode are shown in Table 1.
Table 1: Chemical Equations

<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td><strong>oxidation</strong></td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6 \text{H}^+ + 6 \text{e}^- + \text{CO}_2$</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td>$\frac{3}{2} \text{O}_2 + 3 \text{H}_2\text{O} + 6 \text{e}^- \rightarrow 6 \text{OH}^-$</td>
</tr>
<tr>
<td><strong>Overall reaction</strong></td>
<td>$\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{CO}_2$</td>
</tr>
</tbody>
</table>

The final component in a conventional direct methanol fuel cell is the membrane that separates the cathode from the anode. This membrane is made out of a nafion, which is a sulfonated tetrafluoroethylene polymer. The role of the nafion membrane is to allow the flow of water and protons from the anode to the cathode without allowing oxygen or methanol through. The protons that are created in the oxidation reaction pass through the nafion membrane by moving from one sulfonic acid group to another within the nafion structure. The reason nafion has been chosen as the primary PEM is because it’s high conductivity to cations along with having a high mechanical and thermal stability. One of the main drawbacks to the nafion membrane is its high permeability to water [5]. Even though the membrane is supposed to allow the flow of water, methanol is able to dissolve in the water and travel through the nafion membrane. Once at the cathode this methanol undergoes the oxidation reaction just as it would at the anode catalyst, which causes over potentials. These problems seen in the nafion membrane has led to more research into different types of membranes used for direct methanol fuel cells.
2.1.2 Alkaline Anion Exchange Membrane Direct Methanol Fuel Cell

In conventional direct methanol fuel cells the MEA is usually made up of a proton exchange membrane. In an alkaline anion exchange membrane DMFC the MEA is made up of an alkali anion exchange membrane (AAEM). This is a semipermeable membrane made from ionomer that is impermeable to gases but allows the conduction of anions. The AAEM still plays the same role as the PEM does in a conventional DMFC, but it has different features [6].

One of the biggest improvements seen with these membranes is the kinetics of the ORR and MOR are faster. The kinetics for the reactions occurs at a higher rate because the intermediates formed at the electrolytes have much weaker bonds to the catalytic sites. Weaker bonding of intermediates to these sites allows for more methanol and oxygen to reach the sites where the reaction occurs. With weaker bonding of intermediates and faster kinetics the catalyst loading used in an AAEM MEA is lower than that of a PEM MEA. Using less catalyst greatly reduces the total cost of the cell because the platinum used is very expensive [6].

Also the environment in the AAEM MEA is less corrosive that its PEM counterpart. In a less corrosive environment it is possible to use catalyst other than Pt and Ru. Not only could this lower the total cost of the cell, but it also introduces the possibility of finding catalysts that are more selective. Having a catalyst that is more selective would reduce the risk of methanol and oxygen cross over. This would be accomplished by having a catalyst on the anode side that only reacts with the methanol, while the cathode side would only react with oxygen. These more reactive catalysts could end up in the development of mixed fuel sources [7]. A mixed fuel source cells would not need bipolar plates because the oxygen and fuel could be both placed in the fuel chamber as a mixture. The advantages of not needing the bipolar plates would be a reduction in cost and a reduction in size. The size reduction is very appealing because fuel cells
are poised to replace batteries. So size is one of the factors hindering fuel cells from replacing batteries [8].

Another advantage AAEM’s may have over PEM’s is the decrease in methanol crossover. Even though AAEMs are still a young technology early signs have shown better resistance to methanol crossover. In this fuel cell the membrane that is used is made up of polyvinylidene fluoride-polystyrene sulfonic acid. Using this membrane the elector-osmotic flow for water is from cathode to anode. There is more resistance to crossover because the electro-osmotic flux flowing from the cathode to the anode hinders the flow of methanol to the cathode. Even though a decrease in methanol crossover should allow the AAEM’s to perform better than the PEM’s that is not the case [7].

One of the biggest problems plaguing the AAEM is the fact that their performance drops at higher current densities. Figure 3 below shows the polarization curve for both a PEM cell and a AAEM cell operating at the same conditions. At higher current densities CO$_2$ is produced more rapidly in the AAEM. These CO$_2$ molecules react with the OH molecules to form bicarbonates. When these OH molecules react with the CO$_2$ rather than the MeOH the conductivity of the cell is reduced. This reduction in conductivity can be seen as a drop in performance at higher current densities for the AAEM. One way found to reduce this effect is to use aqueous potassium hydroxide (KOH) to allow OH molecules to be efficiently supplied to the anode instead of reacting with CO$_2$ [7].
2.1.3 Anionic-Cationic Bi-Cell Direct Methanol Fuel Cell

In an anionic-cationic bi-cell an anion exchange membrane (AEM) and a PEM are connected in series and share the same fuel tank. In order to connect these two MEAs in series the cathode at the anionic cell had to be connected to the acidic cell’s anode. The reason two different MEA’s are used in this type of fuel cell is because the two electrodes are at nearly the same potential resulting in little to no current loss. Figure 4 shows a schematic drawing of the bi-cell [9].
Figure 4: Schematic Drawing of an AEM-PEM bi-cell[9]

In the schematic above the PEM and the AEM work together to produce a voltage. The combination of a, b, and c is the PEM part of the cell and the combination of d, e, and f is the AEM cell. The AEM reaction at the anode produces both OH\(^{-}\) and \(\text{H}_2\text{O}\) molecules. The OH\(^{-}\) molecules pass through the AEM membrane and react at the AEM cathode. The water that is produced is allowed to pass through the methanol fuel chamber to then be consumed at the PEM anode. This combination of membranes helps with the water management of the cell because it is produced at one end and consumed at the other [9].

In a PEM-PEM bi-cell there is a current flow of around 4\(\mu\)A between the anode and the cathode. In the AEM-PEM bi-cell there is no current flow from the anode to the cathode. Having the two electrodes at the same potential and no current flow lowers the chance of shorting the circuiting in the bi-cell. Figure 5 compares the polarization curve of both the PEM and AEM
under the same conditions. It can be seen that the AEM passive cathode has a similar potential as the PEM anode [9].

![Figure 5: Polarization curves of PEM and AEM [9]](image)

Similar potentials between the anode and cathode are not the only advantage seen when using an AEM-PEM bi-cell. Another big advantage is the water management seen in the bi-cell stack. Water is produced at both the cathode and the anode of the AEM, but it is also consumed at the cathode of the AEM and the anode of the PEM. This consumption and generation of water makes the bi-cell self-sufficient in water management [9].

2.1.4 Micro Direct Methanol Fuel Cell

One new focus is on reducing the size of the DMFC stack for use in portable applications. A micro DMFC is composed of two distributors, an anode monopolar plate, three one-side bipolar plate, and four pairs of electrodes. The anode side uses an n-inlet and an n-outlet (NINO) flow fields to properly distribute the methanol fuel. The NINO flow fields are able to improve the transport efficiency of the fuel to the anode by improving the transport of CO\textsubscript{2} away from the anode. Figure 6 shows a schematic of the micro DMFC. [10]
One of the biggest improvements for performance in the micro DMFC is the use of the NINO flow fields instead of conventional parallel flow fields. Figure 7 shows that the conventional flow fields are out performed by the NINO flow fields. One of the main reasons this occurs is because the conventional flow fields result in non-equal distribution of the fuel. At higher pressures, as seen with the NINO, the velocity of the methanol from the flow channels to the GDL is increased. Increased pressure also decreases the size of CO₂ bubbles that form in the flow fields. Decreasing the size of these bubbles reduces the amount of methanol that is blocked from the anode reaction sites [10].
2.1.5 DMFC Performance

Direct Methanol Fuel Cells (DMFC) are one of the only competitors to H₂-O₂ polymer electrolyte membrane fuel cells for low temperature cells. DMFC’s are able to run under temperatures of 100° C, which greatly reduces the cost of these cells [11]. The first performance advantage seen in the DMFC is the fact that the fuel is methanol instead of hydrogen. Methanol has a theoretical energy density of 6100 W h/kg [12]. The advantages of using methanol instead of hydrogen do not stop there. It is also easier to store and transport methanol than it is for hydrogen. Hydrogen is costly and difficult to compress and is very dangerous to transport because of its high pressure [11].

DMFC’s are made up of anode and cathode ends with a Membrane Electrode Assembly (MEA) that contains that GDL, the catalysts, and the Proton-Exchange Membrane [11]. At the anode side of the cell, the partial methanol oxidation reaction (MOR) occurs as shown below:
The CO is adsorbed on the Pt catalyst sites, which block the methanol from undergoing the oxidation reaction. From the equation above, it appears that the methanol at the anode side has only reacted to produce 4 protons and 4 electrons. When looking at the overall equations, at the anode side it can be seen that methanol reacts to form a total of 6 protons and 6 electrons. This is accomplished by adding ruthenium to the platinum catalysts. The function of the ruthenium in the catalyst is to decompose the water at the anode in to hydroxide radicals (OH). The OH radicals formed are then able to react with the CO intermediate to generate CO\(_2\) plus 2 more protons and electrons. [2]. The equations for the intermediate steps can be seen below:

\[
\text{H}_2\text{O} \rightarrow \text{OH}_{\text{ad}} + \text{H}^+ + \text{e}^- \\
\text{CO}_{\text{ad}} + \text{OH}_{\text{ad}} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- 
\]

At 25°C and 1 atm, the reversible potential available in the methanol oxidation reaction is 1.18V [13]. However, this maximum voltage is never actually obtained in a DMFC because of different polarization losses. Polarization is the drop in performance from OCV when an electric current is applied to the fuel cell. This drop in voltage is the result of different mass and current transports that lead to overpotentials. Below Figure 8 shows a typical polarization curve for a fuel cell:
Region I from the figure above gets its shape from the activation overpotential of the DMFC. This activation overpotential is present because of the kinetics of the reactions at the anode as well as at the cathode. The activation overpotential at the cathode for the ORR is also extremely large, in addition to the overpotential for the MOR, which is substantial because of CO adsorption and water dissociation. The drop in region II is a lot slower than the rapid drop in region I and has more of a pseudolinear shape. In this region the pseudolinear shape is a result of ohmic overpotentials due to the resistance of different fuel cell components, especially in the PEM. These internal resistances slow the flow of electrons, and the flow of ions through the electrolyte membrane. The final region, region III, is a result of mass transfer limited overpotentials. Since the mass transfer rates are slow within a DMFC at higher current densities this slow rate begins to limit reactant supply. At slow reactant rates the electrodes have less material to react, which decreases the voltage [14].
2.1.6 DMFC Issues

Even though DMFC’s could offer a promising future in the field of energy, as of now there are too many issues that they encounter that prevent them from being widely used. The biggest problem found in DMFC’s is methanol crossover. Methanol crossover occurs when the methanol absorbs through the MEA and travels from the anode to the cathode. Once at the cathode the methanol begins to react as it would at the anode side [11]. However, when the MOR occurs at the cathode side, this causes mixed potential and an overall reduction in the cells voltage, in addition to loss of fuel and faradaic efficiency. The cells voltage comes from the difference between the potentials at the anode and cathodes. The theoretical potential at the anode side is 0 volts (V), while the theoretical potential is 1.2V for the cathode. This should give the cell a total voltage of 1.2 V, but this is not the case. When mixed potentials occur at the cathode side the potential is decreased, which in turn lowers the voltage of the cell [15]. Even though the Nafion membrane should ideally block the flow of fuel from the fuel chamber, methanol solubility in water allows it to be absorbed through the MEA.

Methanol crossover is reduced in a cell by many different ways. The first method to limiting methanol crossover is to use a very low feed concentration of methanol between about 1-2 M. Lower concentrations of methanol limits the mass transfer of methanol, which limits the amount of crossover [11]. However, this also results in an increase in size of the overall cell stack.

Another way to decrease the methanol crossover is by changing the thickness of the membrane. An increase in membrane thickness will increase the resistance causing lower methanol to crossover. The only trade off with increasing the thickness is that it also decreases the transport of protons, which limits the performance at high current densities. In the graph
below, Figure 9, it can be seen that increasing the membrane thickness decreases the voltage efficiency of the cell. However, there is a large increase in fuel utilization at higher thickness, which is able increase the overall efficiency of the cell [16]

![Figure 9: Effect of membrane size on efficiency [16]](image)

A second major issue for DMFC is the fact that by-products are formed in the MOR and ORR that negatively affect the cell. As stated before, the MOR produces CO, which is then oxidized further to produce CO$_2$. If this CO is not oxidized further to produce CO$_2$ it can easily poison the catalyst [2]. Though there is still a trade off when oxidizing CO byproducts to CO$_2$ because the CO$_2$ may not poison the cell but it still has adverse effect on the performance. This happens because the CO$_2$ formed can block off channels and reaction sites that lead to the
catalysts. Blocking these channels slows the transfer of methanol and oxygen to the reaction sites. This effect is seen at higher current densities because not enough fuel is able to reach the catalysts reducing the overall voltage [11].

2.2 Passive Direct Methanol Fuel Cells

2.2.1 Conventional Passive Direct Methanol Fuel Cells

In a passive direct methanol fuel cell (PDMFC), there are no pumps, fans, or extra equipment to accelerate fuel input and flow. The lack of this equipment makes the passive cell less costly and enhances its portability. However the performance of the PDMFC is lower than a DMFC due to a slower fuel flow inside the cell, as well as transport limitations of oxygen passive diffusion at the cathode.

The catalyst used in the MEA to promote the half-cells reactions is usually made of platinum and ruthenium alloy at the anode and platinum at the cathode. There is a certain amount of improvement that can come from adding more catalyst; however this reaches a maximum where performance begins to level off.

2.2.2 Passive Direct Methanol Fuel Cell with Porous Carbon Plate

In the design of a PDMFC using porous carbon plates (PCP) it was found that methanol concentrations up to 100% could be used. Usually at these high concentrations the performance of the cell is dramatically reduced by anode kinetics as well as by methanol crossover from the anode to the cathode. This is why the PCP used in the PDMFC must have a high bubble point pressure and resistance to fluid flow to reduce the effect of crossover [17]. Figure 10 shows the structure of a single cell with PCP:
Not only does the PCP help in reducing methanol crossover it also helps lower the effect of CO$_2$ poisoning on the cell. Since the PCP is positioned between the reservoir and the anode current collector the methanol has to pass through the PCP. The PCP allows the methanol vapor to diffuse through the CO$_2$ bubbles that have built up on the anode flow channels. This increase in methanol vapor passing the CO$_2$ bubbles increase the performance and fuel efficiency of the cell [17].
In single cell test the power density was found to be greater than that of the full 8 cell stack test. These results are shown below in Figure 11. For the single cell test the power density was found to be low at first because of the low vapor pressure of methanol in the PCP. Over time the power density increased as the nitrogen, from the air, in the PCP was replaced by methanol. The reason behind the single cell testing better was the increase in temperature seen in the stack testing. This temperature increase was seen because the stack design had relatively low heat dissipation, which caused the PEMs to become dehydrated [17].

2.2.3 Tubular Shaped Passive Direct Methanol Fuel Cell

Tubular shaped PDMFC resemble modern day batteries in shape in size. This shape gives the cell one of its biggest advantages. As fuel cell technology gets better and batteries are phased out these types of fuel cells will make it easier to transition from batteries to fuel cells. With its small shape and size the tubular cell uses fewer materials to construct reducing the total cost of the cell. Figure 12 shows a schematic of the tubular cell [18].
When compared to planar-shaped PDMFC, tubular PDMFC have many advantages other than its size and shape. Tubular PDMFC have greater instantaneous power density than planar-shaped cells. This higher total energy is a result of a larger active area for the fuels to react. Another big advantage is the fact that tubular cells can be operated without depending on orientation. In planar stack designs usually can only operate at one orientation and even then some cells face starving. Being able to operate at any orientation is useful for portable devices. These devices are usually run at multiple orientations, which give the tubular cells a large advantage over their planar counterpart [18].
2.2.4 PDMFC Performance

The DMFC described in the sections before depends on different added equipment, such as pumps and heat exchangers, to increase the flow rates of the methanol and operating temperature of the cell. However, these different pieces of equipment raise the energy usage, bulk, and cost of these cells. In a passive direct methanol fuel cell (PDMFC), there are no added pumps or exchangers to change the operating temperature or flow. PDMFC’s run using ambient conditions of the surrounding temperature and the natural diffusion rate of methanol and air. As a result, PDMFC’s usually have a large drop in performance when compared to DMFC’s. On average, the drop in performance from a DMFC to a PDMFC is found to be almost 70%, with a maximum drop from 45 mW/cm$^2$ to 13 mW/cm$^2$ [11]. This drop in performance is due to PDMFC not having a continuous and active flow of fuel and having an operating temperature that depends on the exothermic reactions and the surrounding temperature only. Figure 13 shows the average drop in performance between a DMFC and a PDMFC.
In the graphs above, it can be seen that the highest open circuit voltage (OCV), voltage when no load is applied, and the highest power density is from the DMFC and the lowest from the PDMFC. Also shown in the graph is the change of one side, anode or cathode, to passive
while keeping the other side active. The anode side shows higher power density and OCV when it is passive and the cathode is active. These result shows that the air flow of oxygen to the cathode side being higher and the flow of methanol slower because of diffusion only increased the performance of the cell. This increase in performance might be due to when the anode side is kept active more methanol crossover occurs when the flow rate of methanol is increased [19].

It can also be seen that active DMFC can operate at much higher current densities then PDMFC. At high current densities there is a high flow of charge leaving the fuel cell. In a passive cell at high current density the passive flow of methanol is not quick enough to supply fuel to the cell at the rate it is being consumed. The reason active cells can operate at these high currents is that new fuel is constantly being supplied to the cell. Another issue in passive cells at higher current densities is the formation of CO₂ molecules. These molecules block the sites where the methanol would react and with no flow of CO₂ away from the cell the performance drops [19].

Since PDMFC’s rely only on diffusion of methanol to reach the anode, the concentration of methanol used in PDMFC’s tends to be much higher than the concentration for DMFC’s. In many studies done by Liu et al., they have found that as the methanol concentration was increased so did the maximum power density. However, just as in the DMFC the concentration could not be increased forever, there was a point at which the concentration became too high and crossover began to decrease the performance. The optimal concentration was found to be 5.0 M, with a maximum power density of 20 mW/cm² [11].

For a while it was believed that the higher concentration of methanol increased performance because of improved methanol mass transfer. Liu et al. found that it wasn’t the
increased mass transfer that improved the cell, but actually a rise in temperature of the cell. Shown below in Figure 14 is increase in temperature seen when the concentration of methanol is increased. Temperature increases in the cell because the ORR at the cathode side of the cell is exothermic. When the temperature of the cell increases the electrokinetics at the MOR and ORR is increased as well as a decrease in the cell’s internal resistance [12].

![Figure 14: Temperature Increase with Concentration (Room Temp=23°C) [12]](image)

Liu et al. were able to prove their results by testing different concentrations with and without the presence of cooling water in the cell. The cell was able to run at 4.0 M and 2.0 M at ambient conditions at first without any water to measure the maximum power density and then with cooling water to see the difference in power density [12]. The results are shown in Figure 15:
2.2.5 PDMFC Issues

PDMFC’s suffer from most of the same issues as DMFC’s, such as catalyst poisoning and crossover. The biggest problem in PDMFC, just as for the DMFC, is methanol crossover from the anode to the cathode. This performance drop from crossover is seen more in PDMFC because passive cells use a higher concentration of methanol coupled with diffusion limitations of oxygen at the cathode, which as stated before increases the rate of methanol crossover. The reason crossover occurs is because the concentration for methanol is very low on the cathode side, as it should be, and very high at the anode side. At start-up the methanol is only consumed at the anode. As the operating time increases the methanol dissolves in water and is able to transfer through the MEA and react at the cathode. As the methanol reacts it decreases the potential of the cathode and at the same time increases the temperature of the cell. As time goes on, the methanol begins to be consumed, which starts to decrease the methanol in the reservoir. As the total methanol decreases, the concentration gradient between the cathode and anode reduces, causing less methanol crossover [20].
Changing the phase of methanol has been found to decrease the rate at which methanol crosses from the anode to the cathode. The solution to this problem was found to be soaking the methanol in hydrogels instead of methanol liquid. The reason methanol was soaked in hydrogels was because this gel was able to decrease the diffusion rate of the methanol, which lowered the amount of methanol crossover. Using hydrogels the performance of the cell was increased from around 16 mW/cm$^2$ to 22 mW/cm$^2$ [2].

A big problem that is unique to PDMFC’s is the starving of particular cells in the fuel cell system. Starving of cells occurs when the methanol vapor from the reservoir does not reach certain cells. Since the cells of the fuel cell system are all wired in series the cells that have no methanol to react are forced to use something else to produce a reaction. These cells are forced to consume the carbon that is present in the catalysts. The longer these cells are starved the more carbon reacts and eventually the catalyst has to be replaced. Starving of cells was found to be reduced when different orientations of the fuel cell system were used [11].
In DMFC’s there is a heat source that is able to cool or heat the fuel cell to an optimum operating temperature. Without heat exchangers another problem unique to PDMFC’s arises, which is heat management [11]. Also as discussed in the performance section for PDMFC’s, the increase in temperature of the cell is directly related to the performance of the cell. So not only does the PDMFC have a drop in performance because of heat loss, but also there is a drop in performance due to the lack of heat in the fuel cell system.

Just as with the DMFC’s, transport limitations due to CO₂ and H₂O poisoning at the anodes and cathode, respectfully, is a major performance loss. The CO₂ and H₂O lower the performance of the cell by blocking the catalytic sites. When these sites become blocked less MeOH and O₂ is able to react decreasing the total voltage of the cell [21]. Figure 17 shows how voltage is affected by catalytic poisoning.

![Figure 17: Polarization Plot of PDMFC with one Refueling](image)
At time 0, an initial amount of MeOH fuel was placed in the reservoir (the one at the end of paragraph). The initial spike in voltage is the OCV and after 30-40 minutes the voltage is reduced to half the initial value [21]. The increase in temperature is also due to methanol crossing over to the cathode where the anodic oxidation of methanol reduces to heat and water. At time 180, a second amount of MeOH, equaling the initial amount, was added to the PDMFC. From the graph it can be seen that the initial jump in voltage is not as high as when the initial amount of MeOH was added. This drop in voltage is seen as methanol crosses over to the cathode. Without any ancillary equipment to increase the flow of oxygen and to facilitate the flow of water away from the cell, the water blocks the catalytic sites, which decreases the voltage of the fuel cell [21]
CHAPTER 3: DESIGN AND EXPERIMENTAL

3.1 Stack Design and Fabrication

The construction of a passive direct methanol fuel cell stack is simpler than that of an active stack because of the absence of additional equipment. However, without the active components that facilitate flow to and from the cells it is important that the stack is sealed airtight. If air was able to leak and react at the anode, the performance of the cell is dramatically decreased. Allowing air to react at the anode causes overpotential just as methanol does when it reacts at the cathode side. The fuel chamber of the stack must also be sealed to prevent the methanol stored inside from diffusing out of the stack without reacting. This does not decrease the voltage of the cell but effects the fuel utilization of the stack and efficiency.

The design of the stack started with a prefabricated polycarbonate base with eight cutouts for the passive cells. The base had two sides that each held 4 of the individual cells and was fastened together using large metal screws. This allowed for the stack to be easily separated so that different fuels could be loaded into the fuel chamber. Once the base was obtained, we needed to build each of the eight cells that each had a total area of 45 cm² and an active area of 25 cm². The construction of the individual cells started by buying 8 MEA’s from IRD Fuel Cells Company. These MEA’s contained both the Nafion membrane and also the catalysts for the reactions. Located between the anode current collector and the MEA was a carbon cloth gas diffusion layer that was used to evenly distribute the methanol to the catalyst. The carbon cloth had a total area of 25 cm² and was positioned right up against the MEA.

The current collectors that were fabricated used both perforated steel and porous stainless steel. The stainless steel was used as the anode current collector and a combination of perforated steel and porous stainless steel was used as the cathode current collector. The reason a
combination of the steels were used was because the porous steel was very malleable, so the perforated stainless steel plates added structural stability. The perforated steel had to be cut to the dimensions of 7x7 cm with a hole for the screws in the middle of each side. The manufacturing of the stainless steel was more complex than the perforated steel because flow channels had to be cut into the stainless steel to allow for the diffusion of fuel to the cell. These channels were cut into the active area of the steel using AutoCAD and the machinery in Higgins.

Figure 18: Porous Steel and Perforated Stainless Steel

Once all of the components of the cell were fabricated, each cell was attached to the polycarbonate base using IsoPlast screws that were made out of a non-conductive plastic. Since the stack and cells had to be airtight, different gaskets and sealants were used to achieve this goal. For each individual cell, 2 foam gaskets were used to seal around the Nafion membrane and the catalysts. These gaskets were used to prevent any mixing of fuels and to prevent air from leaking in through the screw holes. To seal the two sides of the stack, and also the individual
cells to the base, red rubber sealant was used. In addition to the red rubber, vacuum gel was used to make sure the seal between the rubber and the base was airtight.

To insure that the maximum voltage could be obtained from the stack, each cell was wired in series from cathode to anode. The cells were wired in series to ensure that the voltage of each cell was added together, while keeping the current on each cell the same. To wire each cell, slits were cut into the current collectors. Copper wires were then cold soldered into the slits using a pure silver conductive epoxy. The pure silver epoxy was used because it had a very high conductivity with a low electrical resistance, while also being easy to apply as a cold solder. The stack could be used to power different appliances by the addition of 2 alligator clips attached to the cathode current collector of one cell and the anode current collector of another to create a closed circuit. Figure 19 shows an AutoCAD design of the complete stack.
3.2 Experimental Setup

The collection of data while testing utilized the computer program FuelCell 7. The cell was connected to the load box testing station using alligator clips to create a closed circuit that runs through the load box. The load box had a wide range of possible experiments through the control of fuel flow, temperature, humidity, and load. However, the stack was passive so fuel flow, temperature, and humidity did not play a role and were disregarded when testing. Different tests were set up using the FuelCell 7 computer program. The program already had setups that could be used to run various tests. These setups allowed the user to change different aspects of the experiment to collect many different types of data. While the program was testing the data was stored in a excel file, which made analysis easier. Figure 20 shows the interface of the program.

Figure 20: Interface of FuelCell 7
3.2.1 Open Circuit Voltage Setup

The first setup used was an experiment that measured the voltage of the stack operating without the addition of a load for an extended period of time. The OCV test was used to show the maximum voltage of the stack. The test was run until all of the fuel inside the stack was exhausted because of crossover. Figure 21 shows the setup used for this test.

![Figure 21: OCV Test Setup](image)

3.2.2 Current Scan Setup

In addition to OCV testing the stack was also tested at different current densities. The current scan setup started collecting voltage and power density reading at a current of 0 amps. The current was then increased by a set value periodically until the voltage of the stack dropped below 0.1 volts. To ensure that the voltage was at equilibrium at each current density, there was a
time interval of 3 minutes between each current increase. Figure 22 shows the setup used for this test.

Figure 22: Current Scan Setup
CHAPTER 4: MODELING AND THEORY

In addition to collecting data using experimental methods it is also beneficial to develop equations that can determine the performance of the cell under different conditions. The math modeling described below is an adaption to Rosenthal et al [23] model that was made to determine the performance of an active cell. The main difference between these two models is the mass transfer equations used for the flow of fuel. Since this model is for a passive cell the flow of fuel to the cathode and anode are only due to diffusion.

4.1 Overall Equations

The equations used to model these cells use many different parameters and behaviors to determine the overall voltage of the cell under different operating conditions. These parameters are thermodynamic, transfer equations, and reaction kinetics. The overall voltage of the cell is determined by the difference in potential between the different components in the cell. This equation is shown as Equation 1:

\[ V = V_0 - \eta_A - \eta_C + \eta_B + \eta_I \]  

In the equation the overpotentials at the anode, PEM, cathode, and interface are given as \( \eta_A, \eta_B, \eta_C, \) and \( \eta_I \) respectively, while \( V_0 \) is the thermodynamically calculated value for voltage. The max voltage that can be obtained in theory is given by the thermodynamic value, but due to crossover and catalyst poisoning this value is much higher than the actual voltage seen. The thermodynamic voltage is shown below in Equation 2:

\[ V_0 = 1.214 - 1.4 \times 10^{-4} (T - 298) + \frac{RT}{6F} \ln \left\{ \frac{a_{Me}}{a_{H_2O}} \left( \frac{P_{O_2}^{3/2}}{P_{CO_2}} \right) \right\} \]
The overpotential values for the anode and cathode depend on limiting factors that include crossover of fuels, and current densities. These limiting factors impact the anode overpotential because of methanol and oxygen crossover, but are not included in the cathode due to the assumption of negligible oxygen crossover. Equation 3 is the overpotential for the anode, while Equation 4 is for the cathode. Also shown below are the overpotentials due to the PEM and Interface given by Equation 5 and Equation 6, respectively:

\[
\eta_A = \frac{RT}{\alpha_A^* v_{A,e}^* F} \sinh^{-1} \left[ \frac{1}{2} \left( \frac{(i + i_{X,O_2})/i_{A,0}}{1 - (i + i_{X,O_2})/i_{A,L}} \right) \left( 1 + \frac{1}{i_{A,L}} \left( i_{X,Me,L} + 3 \frac{\kappa_{Me,B}}{\kappa_{W, B}} x_{Me,b} \tilde{e} \right) \right) \right] \tag{3}
\]

\[
\eta_C = \frac{RT}{\alpha_C^* v_{C,e}^* F} \sinh^{-1} \left[ \frac{1}{2} \left( \frac{(i + i_{X,Me})/i_{C,0}}{1 - (i + i_{X,Me})/i_{C,L}} \right) \right] \tag{4}
\]

\[
\eta_B = \left( \frac{L_B}{\sigma_B} \right) i \tag{5}
\]

\[
\eta_t = i R_i \tag{6}
\]

The power of the cell can be easily calculated by multiplying the voltage calculated above by the current density applied to the cell. Equation 7 shows this:

\[
P = i V_0 - \frac{iRT}{\alpha_A^* v_{A,e}^* F} \sinh^{-1} \left[ \frac{1}{2} \left( \frac{(i + i_{X,O_2})/i_{A,0}}{1 - (i + i_{X,O_2})/i_{A,L}} \right) \left( 1 + \frac{1}{i_{A,L}} \left( i_{X,Me,L} + 3 \frac{\kappa_{Me,B}}{\kappa_{W, B}} x_{Me,b} \tilde{e} \right) \right) \right]
+ \frac{iRT}{\alpha_C^* v_{C,e}^* F} \sinh^{-1} \left[ \frac{1}{2} \left( \frac{(i + i_{X,Me})/i_{C,0}}{1 - (i + i_{X,Me})/i_{C,L}} \right) \right] \frac{\tilde{F} L_B}{\sigma_B} - \tilde{F} (R_i) \tag{7}
\]
4.2 Catalyst Loading

Since catalyst poisoning is one of the main performance determinants in PDMFC it is important to determine how this effect performance. At both the cathode and anode the catalyst is a mixture of platinum and ruthenium the density of the catalyst is a combination of the density of the two elements. Equation 8 shows this calculation:

$$\rho_{M,A} = (1 - \omega_{Ru})\rho_{Pt} + \omega_{Ru}\rho_{Ru}$$  \hspace{1cm} (8)

The calculated density from above is then used to determine the electrocatalyst surface roughness of the catalyst. The roughness is the surface area of the catalyst on each side of the catalyst and is given in Equation 9:

$$\gamma_M = \varphi_I m_M \frac{6}{\rho_M d_M}$$  \hspace{1cm} (9)

Once roughness is known it is used to determine the exchange current density. The amount of carbon monoxide that is blocking the reaction site of the catalyst is shown by Equation 10 shows this calculation:

$$\theta_{CO^S} = \frac{K_{Me}c_{Me,0}}{1 + K_{Me}c_{Me,0}}$$  \hspace{1cm} (10)

Where the adsorption constant for CO on the catalyst at equilibrium as given by Equation 11:

$$K_{Me} = \frac{1.41 \times 10^{-8} \exp \left(\frac{130,000 \text{ J mol}^{-1}}{RT}\right)}{1}$$  \hspace{1cm} (11)
4.3 Transport Parameters

This section of the math model is the main difference between the model that was determined by Rosenthal et al. These equations are similar once the fuel reaches the anode, but differ in the concentration of fuel that reaches the anode. Once methanol diffuses to the anode it is dissolved in water present at the anode side. The diffusivity of methanol is given in Equation 12:

\[
D_{Me,W} = 2.1 \times 10^{-5} \exp\left\{-\frac{20.460}{R} \left(\frac{1}{T} - \frac{1}{313}\right)\right\}
\]  

(12)

Since oxygen has a low solubility in water the bulk of the oxygen at the cathode side is mainly in the gas phase. The diffusion of oxygen to the cathode is given in Equation 13:

\[
D_{O_2,E}^i = d_E^{\frac{1}{2}} (1 - q_W)^{\frac{1}{2}} D_{O_2,E}
\]

(13)

Just as above, the diffusion of methanol to the anode is shows in Equation 14. This equation is a simplified version that does not take into consideration the gas partition of methanol and the poisoning of CO₂.

\[
D_{Me,D}^i = 9.75 \times 10^{-1} \exp\left(-\frac{30.975}{RT}\right)
\]

(14)

Due to methanol’s solubility in water it is able to pass through the PEM and react at the cathode side of the cell. The diffusion of methanol through the PEM is given in Equation 15:

\[
D_{Me,P}^i = \varepsilon_B^{\frac{1}{2}} D_{Me,W}
\]

(15)
In an active cell there are pumps that facilitate the flow of methanol and oxygen to the catalyst. In a passive cell the fuel sources must rely on diffusion to the anode as the transport equation. Shown in Equation 16 and 17, are the equations for the mass transfer coefficients.

\[ k_i = 2.696 \frac{D_i}{d} \left(1 + 0.139 \frac{d^2}{R_i} \right)^{0.81} \]  
\[ k_i = 0.5 \left( \frac{D_i}{d} \right) \]  

Also used in the modeling for a passive cell were different assumed concentrations of methanol at the anode side for different fuel sources. When using methanol gel the effective concentration at the anode was assumed to be anywhere between 1-3 molar concentrations. However when using pure liquid methanol the concentration could react upwards of 10 molar due to the high concentration of methanol used.

### 4.4 PEM Resistances

The resistance of ions and water in the PEM is directly related to the thickness and conductivity of the membrane. These resistances can help the overall voltage of the cell by inhibiting the flow of methanol across, but can decrease the overall voltage with a high resistance for ion flow. Equation 18 gives a simplified calculation for the conductivity of the PEM:

\[ \sigma = \left(\frac{349.8}{1+\delta}\right)^{1.3} \exp \left[ -\frac{E_{\mu}}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \right] \left( \frac{1}{18\lambda} \right) \beta \]  

The equation for \( \beta \) and the dissociation equilibrium equation is given below in Equation 19 and 20, respectively:
4.5 Characteristic Current Densities

To accurately measure the overpotentials at the different components of the cell it is necessary to derive an equation to relate the crossover current to the measured current and temperature. Driving these equations for the two electrodes uses the exchange current and limiting current. The limiting current is the crossover current density when the cell is operating at OCV. This current density is the maximum crossover possible. Equation 21 derives the equation for the limiting current density, which is then used in Equation 22 that calculates the methanol crossover current.
The limiting crossover for the GDL at the anode side is given by Equation 23 and Equation 24 is given for the oxygen crossover current. Also the anode and cathode exchange current density is given in Equation 25 and 26, respectively.

\[
i_{\text{A,2}} = \left( \frac{V_{\text{A,2}}}{e} \right) F_P_P_{\text{A,2}} C_{\text{M,2}}
\]

\[
i_{\text{O,2}} = \left( \frac{P_{\text{O,2}}}{P_{\text{O,2}}} + \frac{1}{P_{\text{O,2}}} \right) \left( 4F C_{\text{O,2}} \right) = (P_{\text{O,2}} + P_{\text{O,2}}) 4F C_{\text{O,2}}
\]

\[
i_{\text{A,0}} = \gamma_{\text{M,0}} \frac{C_{\text{M,0}}}{C_{\text{M,ref}}} \left( 1 - \frac{E_{\text{A,0}}} {R \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)} \right) i_{\text{A,0,ref}}
\]

\[
i_{\text{C,0}} = \gamma_{\text{M,0}} \frac{C_{\text{C,0}}}{C_{\text{C,ref}}} \left( 1 - \frac{E_{\text{C,0}}} {R \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)} \right) i_{\text{C,0,ref}}
\]

All of the above equations were used in Mathematica to model the performance of the cell under different operating conditions and fuel sources.
CHAPTER 5: RESULTS AND DISCUSSION

5.1 Stack Testing

After the assembly of the optimized final stack, with a GDL at the anode side and a porous collector plate on the cathode side, while wired in series to collect the current, the stack was tested for leakages by filling it up with deionized water. The water did leak in certain areas, leading to some adjustments in the tightening of screws and the increased sealant used in these areas. After corrections were made, the stack was filled with deionized water and a small amount of pure methanol (about 12mL), in order to activate the MEA’s and to test for any amount of voltage. This test showed a small amount of voltage, yet the stack continued to leak, leading to the use of absorbent pads for soaking methanol. The addition of absorbent pads in the fuel chamber allowed for pure methanol to be loaded without visible fuel leakage, and resulted in slow diffusion. However, clearly leakage still exists in the stack, which reduces performance significantly.

5.1.1 Experiment 1: Pure Liquid Methanol Tests

The first test performed on the completed fuel cell stack was a basic open circuit voltage test using the program FuelCell 7 and the testing station in the Fuel Cell Center in Goddard Hall. The fuel used was 100 mL of pure methanol and was loaded through a hole in the top of the stack using a squirt bottle. The methanol was loaded in a manner as to not touch the cells themselves, and onto an absorbent pad that soaked up the methanol without leaking. From Figure 23, the open circuit voltage (OCV) of the stack wired in series peaked at 4.3 V and remained running for more than 24 hours. The total stack voltage remained constant for about 20 hours at around 3.7 V, or roughly 0.46 V per cell.
The fuel cell stack was reloaded with 100 mL of pure liquid methanol, and a current density test was performed. The current density increased by 0.01 mA/cm$^2$ every minute until the voltage of the cell decreased below 0.01 V. From Figure 24, the peak power in W/cm$^2$ of the stack was about 0.048 W/cm$^2$ at a current density of around 0.5 mA/cm$^2$. The voltage at this point was around 2 V. This figure shows a linear decrease of voltage as the current density increases, which is to be expected. It also shows the parabolic nature of power in relation to current density. The power increases at low current densities, reaches a peak at 0.5, and then drops back to 0 as the current density approaches 1 mA/cm$^2$. 

Figure 23: OCV Graph
5.1.2 Experiment 2: Test Powering a Light Bulb

The next test performed on the fuel cell stack was a qualitative test using 100 ml of pure methanol. The methanol was loaded again into the stack, and the stack was attached to a small camping lantern using alligator clips. The light bulb lit up immediately and shone brightly for almost 2 days, using a small amount of fuel. The bulb required 3 V (two AA batteries) to keep it powered, and the cell provided this amount of voltage for more than 24 hours. The cell stack can very likely power any device only requiring two AA batteries for as long as fuel is reloaded into the fuel chamber.
5.1.3 Experiment 3: Methanol Gel Testing

After the pure methanol testing, a methanol gel was used as fuel. This methanol gel, shown in Figure 26, is similar to Sterno chafing fuel, and was provided by the Fuel Cell Center.
A chassis for housing the methanol fuel was built with 4 stages that could house the methanol gel and distribute it as evenly as possible to all 8 fuel cells. The stack was opened completely in order to load the chassis full of methanol gel, and was then screwed shut. The gel immediately provided a voltage above 4 V, climbing to approximately 4.7 V, before dropping down to 3.8 once it was connected to the Fuel Cell testing station. From Figure 27, the methanol gel was seen to provide a steady voltage of around 3.7 volts for an hour.

![Open Circuit Voltage (Methanol Gel)](image)

**Figure 27: OCV for Gel**

Further tests with the methanol gel proved to be futile as time constraints limited the amount of time that the Fuel Cell testing station was available. The current density test exhausted all of the voltage almost immediately due to the slow diffusion of the methanol gel in comparison to the pure methanol.

It is clear that the performance of the PDMFC was limited by leakages in the assembly.
5.2 Math Modeling Results

After the equations were derived they were entered into the program Mathematica. This program is able to plot different performance curves for the passive fuel cell. The first graph that was plotted was for the methanol gel. In this plot it was assumed that the concentration that reached the anode was 1 molar and the transport constant for the methanol was $5 \times 10^{-4}$ cm/s. The plot can be seen below in Figure 27.

From this graph it can be seen that the OCV of the cell is around .75 volts, which is what is expected for a passive direct methanol fuel cell. As the current applied to the cell is increased a steady decrease in voltage can be seen. This steady decrease reaches a point where the rate of
consumption of electrons is greater than the production of electrons leading to a rapid drop in performance.

The next plot is a performance curve for using pure liquid methanol in a passive cell. For this graph it was assumed that the concentration of methanol at the anode was 6 molar and the transport coefficient is $5 \times 10^{-4}$ cm/s.

![Figure 29: Performance Curve for Pure Methanol](image)

In this graph it can be seen that once again the OCV of the cell is around .75 volts and that a drop in performance is seen once a load is applied. However the drop in voltage when compared to the methanol gel is a lot less dramatic. This is due to the higher concentration of methanol that allows the cell to still produce enough electrons at higher currents.
CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Although the performance of the stack did not achieve peak potential because of leakages, it was still shown that PDMFCs can use pure liquid methanol as a fuel source. Using pure liquid methanol is another advantage that passive stacks have over their active counterparts. In an active stack the fuel chamber is large due to the cells only being able to run using concentrations up to 3 molar, or methanol and water must be mixed continuously. Using pure liquid methanol in a passive cell cuts down on the amount of methanol needed, which reduces the size needed for the fuel chamber. If PDMFCs are to be portable the size of each component has to be as small as possible to cut down on size and weight.

When testing the cell stack using the methanol gel it was found that the performance of the stack was greatly reduced with increasing current densities. This result was seen because there was not enough fuel flow to the cells at high current densities. To counteract the decrease in performance at high current densities a larger amount of methanol gel would need to be added to insure there was enough diffused methanol for the cells. However, this strikes up a problem for PDMFC. As the cell stacks get smaller in size there is a decrease in the size of the fuel chamber. The reduction in the size of the fuel chamber will limit the amount of methanol gel available and the cell stack might not be able to operate at higher current densities. This would limit the use of the methanol gel as a primary fuel source for the stack.

After construction and testing of the cell stack it was clear that there were many improvements that could be made to the design. There are many design flaws that led to poor performance in the cell stack, especially persistent leakage issues, but future work could be done
to fix these flaws. Below we discuss many recommendations for the cell stack and also future prototypes designs that could improve the performance of the cell stack.

6.1 Recommendations for Improving Cell Stack

The biggest decrease in performance when testing the fabricated cell stack was not due to methanol crossover but due to the fact that the cell could not be sealed airtight. Having air leak into the methanol fuel chamber caused fuel loss and overpotentials that caused the overall voltage of each cell to decrease. Allowing methanol to leak from the fuel chamber to the surrounding air affected the fuel utilization of the cell and affected how long the cell was able to perform for a given amount of fuel. It was found that the larger air leaks were due to the individual cells not being tightly sealed to the polycarbonate base. The reason this was seen was because the small plastic screws used to hold each cell down did not provide enough compressive force to form an airtight seal. The screw arrangement for each cell was 4 screws located in the middle of each side of the cell, 1 cm from the outer edge. These screws were able to provide enough force to seal most of the cell to the base, but at the corner of each cell the force was not great enough to create an airtight seal. It is recommended that 4 additional screws be added to the corner of each individual cell to insure they are completely airtight. Once these cells are sealed, the cell should start producing greater voltage and the ability to work at higher current densities.

Refueling the cell stack was an easy process when using absorbent pads and pure liquid methanol. This was the result of a hole that was added to the top of the stack, which allowed for liquid methanol to be poured on the absorbent pad. However this was not the case for the
refueling of methanol gel. Methanol gel was contained in a wire mesh box in the fuel chamber, with multiple levels for the placement of the gel. This method worked extremely well to ensure that each cell was provided methanol, but was difficult to refuel. The problem was that in order to add more gel to the chamber, the stack had to be unscrewed and opened each time. This process was slow and started to strip the threads used to hold the plastic base together, which caused more air leaks in the stack. To eliminate this problem it is recommended that a sealable cover be added to the top of the cell just as the sealable hole was added. This sealable cover could be cut into the top of the base around the screws to still allow the 2 halves of the base to be connected. An O-ring could be used to seal the cover to eliminate any leaks. The addition of a cover on top would protect the stack from damage and also cut down the time it takes for the stack to be refueled.

The testing of the cell stack only utilized two fuel sources: pure liquid methanol and methanol gel. Future work should be conducted using a wide range of fuel to see how different phases and concentrations affect the performance of the cell stack. Testing should also be conducted using fuel sources that are not methanol based, such as furfural, a biofuel. Different fuels may provide more voltage and power density then methanol by decreasing the amount of fuel crossover.

6.2 Future Prototypes

As fuel cell technology continues to advance, a decrease in the size of PDMFC’s should be seen. The cell stack that was constructed for this work showed that passive cell stacks using pure liquid methanol could achieve similar performance curves to stacks that use dilute methanol or methanol gel. However, the stack that was constructed was still extremely bulky and had
excess weight to the design. Below are several designs ideas for prototypes that could facilitate future project in the field of PDMFC’s.

The polycarbonate base that was used for this cell stack was very thick. This design made the stack structurally stable and helped create an airtight seal of the two separate halves, but it also made the design unduly bulky. In future prototypes, this base should be cut down to the bare minimum needed for optimal performance. One idea for a new design would use thin sheets of plastic as the fuel chamber and base. Thin sheets of plastic are a possible replacement because they would still separate the two fuel sources and still allow the connection of individual cells. This however would change the structure of the stack dramatically from the design of the PDMFC built in this work. The thin sheet of plastic could be placed on a thicker plastic support to allow for the use of screws to create a strong seal. The thicker plastic support would not be like the base used in the construction of this stack. The support would be more like a skeleton that would only be necessary where the screws are located. Using thinner plastic would cut down on the overall size and weight of the cell.

Just as the base of the stack was too thick, the thickness of the different components used in the individual cells increased the overall size and weight of the stack as well. The cell stack constructed used 3 different steel plates as current collectors and supports. Each of the steel plates was thicker than necessary, which affected the size of the individual cells and the seal formed when attached to the base. In future prototypes, the current collectors should utilize plates that are thinner while still having the structural integrity to ensure no warping when attached to the fuel chamber. The material used for the current collectors should have the lowest possible electrical resistance to increase the performance of the cell. Future current collectors could even be made out of a material that is not steel. Stainless steel is a poor conductor of
electricity when compared to other metals and was used in this construction due to its strength and cost. To maximize performance a metal should be used that has the strength of steel, but with a lower electrical resistance.

As discussed many times before, the main decrease in performance for the cell stack was the air leaks located in the individual cells. This problem results from the use of weaker plastic screws that were used because of their non-conductive nature. In future prototypes these gaps could be eliminated by attaching the individual cells directly to the fuel chamber without the use of screws. The cells could be attached by either using a type of glue or even have a base design that allows for the cells to be integrated directly into specific slots. Using glue or sealant would ensure an airtight seal, but would also make it difficult to access individual cells if something were to happen in the catalyst layer or MEA. Having specific slots for the cells to slide into could utilize more gasket material, on the outsides of the current collectors, to ensure an airtight seal. If the slots were made a fraction bigger than the individual cells the pressure created when adding gaskets to the outside of the current collectors could create an airtight seal. This method would allow easier access to the individual cells if needed.

Another design for a stack could be a pentagonal prism that has multiple cells located on 4 of the sides around the prism and one side would be empty to serve as a base. The reason this structure is proposed is that it would reduce the overall size of the stack, while ensuring each cell is provided enough fuel. The cells should utilize some of the methods described above such as thinner current collectors and the integration of the individual cells directly to the fuel chamber. The stack would be easily fuel with the addition of a sealable cover at one end of the cell stack. An absorbent material could be inserted into the stack to allow for fueling with pure liquid methanol. Also, methanol gel contained inside of a wire mesh container could also be inserted to
fuel the stack. This method would eliminate cell starving and would utilize a smaller design than the stacks constructed before. An AutoCAD drawing for this prototype can be seen in Figure 29.

Figure 30: Prototype for Passive Stack
APPENDIX 1: REFERENCES


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**APPENDIX 2: MATHEMATICA FILES**

**Methanol Gel**

\[ F = 96487; \alpha A=1/2; \alpha C=1/2; \nu A=+1 \] (* for anode this agrees with Gojkovic et al., 2003*); \[ V C=-2; R=8.314; i_{0,ref}=2.0 \times 10^{-3} (*fitted*); i_{CO,ref}=1.0 \times 10^{-10}; L_A=178 \times 10^{-4}; L_D=260 \times 10^{-4}; L_E=260 \times 10^{-4}; e_D = 0.65; e_E = 0.65; R_t=0; T_{ref}=298; E_A=65000 (*Desai and Neurock (2003) provide a barrier of 60 kJ for CO.S+OH.S=CO2 + H^+ + e^-*); E_C=67000; p_{O,ref}=1; c_{Me,ref}=1 \times 10^{-3}; c_W=5.5 \times 10^{-3} (*mol/cm^3*); \xi=2.9 (*X.Ren and S.Gottesfeld, J.Electrochem.Soc.,148,A87-A93,2001*); D_{O,W}=2.5 \times 10^{-5} (*assumed*); \kappa O=0.144; \kappa Me,D=1.0; \kappa Me,B=0.4 (*Ren, Zawo, 2000, Fig 11*); \phi_{f}=0.75; \rho Pt=21.45; \rho Ru=12.3; \mu=14000; \delta=1.65 (*This has been changed because of missing Bruggeman coefficient in Mathematica files from MDFC paper to fit conductivity data for DMFC of Ren, Zawo, 2000, Fig 8*); \[ v_{ma}=1.255 (*max voltage*); R_t=0; c_{Me,b}=1.0 \times 10^{-3}; c_{Me,0}=\kappa Me,D c_{Me,b}; x_{Me,b}=c_{Me,b}/c_W; v_0=1.214 - 1.4 \times 10^{-4} (T-298)+(R T)/(6 F) Log[(c_{Me,b}/c_W) p_{O,ref}]; D_{O,E} = 0.357(T/352)^{1.823} (*Reid*); D_{Me,W}=2.1 \times 10^{-5} Exp[-(20460/R)(1/T-1/313)] (*This, along with (SubscriptBox[\[ \gamma \], MA]/SubscriptBox[m, MA]=39 m^2/g for black catalyst*)); 
\[ p_{O,in}=x_{O,in}(p_{C}-p_{W}); p_c=1.0; x_{O,in}=0.21; \lambda=20; (*Taken from Ren, Zawo, 2000. For liquid methanol feed. For vapor feed, this would be lower. Further, due to compression, actual \lambda may be lower than this value indicated by sorption isotherm?*) 
\] 
\[ c_{O,ref}=p_{O,ref} / (82 T); c_{O,in}=p_{O,in} / (82 T); \] 
\[ c_{O,b}=c_{O,in}; c_{Me,0}=\kappa Me,D c_{Me,b}; \] 
\[ x_{Me,b}=c_{Me,b}/c_W; \] 
\[ v_0=1.214 - 1.4 \times 10^{-4} (T-298)+(R T)/(6 F) Log[(c_{Me,b}/c_W) p_{O,ref}]; D_{O,E} = 0.357(T/352)^{1.823} (*Reid*); D_{Me,W}=2.1 \times 10^{-5} Exp[-(20460/R)(1/T-1/313)] (*This, along with (SubscriptBox[\[ \gamma \], MA]/SubscriptBox[m, MA]=39 m^2/g for black catalyst*)); 
\[ p_{O,in}=x_{O,in}(p_{C}-p_{W}); p_c=1.0; x_{O,in}=0.21; \lambda=20; (*Taken from Ren, Zawo, 2000. For liquid methanol feed. For vapor feed, this would be lower. Further, due to compression, actual \lambda may be lower than this value indicated by sorption isotherm?*) 
\] 
\[ c_{O,ref}=p_{O,ref} / (82 T); c_{O,in}=p_{O,in} / (82 T); \] 
\[ c_{O,b}=c_{O,in}; c_{Me,0}=\kappa Me,D c_{Me,b}; \] 
\[ x_{Me,b}=c_{Me,b}/c_W; \] 
\[ v_0=1.214 - 1.4 \times 10^{-4} (T-298)+(R T)/(6 F) Log[(c_{Me,b}/c_W) p_{O,ref}]; D_{O,E} = 0.357(T/352)^{1.823} (*Reid*); D_{Me,W}=2.1 \times 10^{-5} Exp[-(20460/R)(1/T-1/313)] (*This, along with (SubscriptBox[\[ \gamma \], MA]/SubscriptBox[m, MA]=39 m^2/g for black catalyst*)); 
\[ p_{O,in}=x_{O,in}(p_{C}-p_{W}); p_c=1.0; x_{O,in}=0.21; \lambda=20; (*Taken from Ren, Zawo, 2000. For liquid methanol feed. For vapor feed, this would be lower. Further, due to compression, actual \lambda may be lower than this value indicated by sorption isotherm?*) 
\]
\[ k_+ = 1.41 \times 10^5 \exp[-(0/(R \ T))]; \text{ (*Vilkar and Datta, 2007*)} \]
\[ k_- = 1.0 \times 10^{13} \exp[-(130000/(R \ T))]; \text{ (*Vilkar and Datta, 2007*)} \]
\[ K = k_+/k_-; \]
\[ \rho_{\text{MA}} = (1-\omega_{\text{Ru}}) \rho_{\text{Pt}} + \rho_{\text{Ru}}; \]
\[ \gamma_{\text{MA}} = \varphi I_{\text{MA}}(6/(\rho_{\text{MA}} d_{\text{MA}})); \]
\[ \gamma_{\text{MC}} = \varphi I_{\text{MC}}(6/(\rho_{\text{Pt}} d_{\text{MC}})); \]
\[ \theta_{\text{CO}} = (K_{c_{\text{Me},0}})/(1 + K c_{\text{Me},0}); \]
\[ \theta_{\text{CO,ref}} = (K_{c_{\text{Me},\text{ref}}})/(1 + K c_{\text{Me},\text{ref}}); \]
\[ i_0 = \gamma_{\text{MAX}}(c_{\text{Me},0})/(1+K c_{\text{Me},0}); \]
\[ i_{\text{CO}} = \gamma_{\text{MCX}}(c_{\text{O},b})/\exp[-(E_{\text{C}}/R)(1/T-1/T_{\text{ref}})]; \]
\[ D_{\text{Me,D,e}} = 0.975 \exp[-(30975/(R \ T))]; \text{ (*Fitted to limiting current density in Fig 3 of Chiu, 2011. Also presumably includes the partition coefficient, Subscript[\kappa, \text{Me,D}], although assumed here as unity, and its temperature variation, accounting for the higher activation energy than Subscript[D, \text{Me,W}]*)} \]
\[ x = 1/k_{\text{Me}}; P_{\text{Me,D,e}} = 1/(L_{\text{D}}/(\kappa_{\text{Me,D}} D_{\text{Me,D,e}})+x); \]
\[ h_{\text{C}} = 0.3; \text{ (*Oxygen diffusion film thickness - assumed simply to estimate the gas-phase MT coeff - alternatively different values of MT coeff may be assumed*)} \]
\[ k_{\text{O}} = 2.696 D_{\text{O,E}}/h_{\text{C}}; \]
\[ q_{\text{W}} = 0.5 \text{ (*or 0.4*)(*for liquid feed this is high and should be virtually independent of current*)(*For vapor feed, may assume Subscript[q, \text{W}]=2.0 y assumed proportional to water flux or current*)}; \]
\[ P_{\text{O,E,e}} = 1/(L_{\text{E}}/(\kappa_{\text{O}}(1-(q_{\text{W}})/1.5 D_{\text{O,E}})+1/k_{\text{O}})); \]
\[ i_{\text{AL}} = 6F P_{\text{Me,D,e}} c_{\text{Me,b}}; \]
\[ i_{\text{CL}} = 4F P_{\text{O,E,e}} c_{\text{O,b}}; \]
\[ i_{\text{X,Me,L}} = \kappa_{\text{Me,B}}(6F)/L_{\text{B}}(c_{\text{Me,b}}); \]
\[ P_{\text{O,D,e}} = 1/(L_{\text{D}}/(\kappa_{\text{O}} D_{\text{O,W}} \kappa_{\text{O}})); \]
\[ i_{\text{X,Me}} = (((i_{\text{X,Me,L}}+3(\kappa_{\text{Me,B}}/\kappa_{\text{Me,D}})) x_{\text{Me,b}} y)/(1-y/i_{\text{AL}}))/(1+1/i_{\text{AL}}(i_{\text{X,Me,L}}+3(\kappa_{\text{Me,B}}/\kappa_{\text{Me,D}})) x_{\text{Me,b}} y)); \]
\[ \eta_{\text{A}} = (R \ T)/(\alpha_{\text{A}} v_{\text{A}} F) \text{ ArcSinh}((y+i_{\text{X,O}})/(2 i_{\text{A}}))/(1-(y+i_{\text{X,O}})/i_{\text{AL}})(1+1/i_{\text{AL}}(i_{\text{X,Me,L}}+3(\kappa_{\text{Me,B}}/\kappa_{\text{Me,D}})) x_{\text{Me,b}} y)); \]
\[ \eta_{\text{C}} = (R \ T)/(\alpha_{\text{C}} v_{\text{C}} F) \text{ ArcSinh}((y+i_{\text{X,Me}})/(2 i_{\text{C}}))/(1-(y+i_{\text{X,Me}})/i_{\text{CL}})); \]
\[ \eta_{\text{B}} = y (L_{\text{B}}/\sigma_{\text{B}}); \eta_{\text{I}} = y R_{\text{I}}; \]
\[ \Psi = v_{\text{0}} + \eta_{\text{C}}; \]
\[ V = v_{\text{0}} - \eta_{\text{A}} + \eta_{\text{C}} - \eta_{\text{B}} - \eta_{\text{I}}; \]
\[ P = V y; \]
\[ q = (y+i_{\text{X,Me}}+i_{\text{X,O}}) v_{\text{ma}} - P; \]
\[ \Xi = P (1/(v_{\text{ma}})(1/(y+i_{\text{X,Me}}+i_{\text{X,O}}))100; \]
Pure Liquid Methanol

\[ F = 96487; \alpha_A=1/2; \alpha_C=1/2; \nu_A=+1 \text{ (* for anode this agrees with Gojkovic et al., 2003*)}; \nu_C=-2; R=8.314; 1_{A,0,ref}=2.0 \times 10^{-3} \text{ (*fitted*)}; 1_{C,0,ref}=1.0 \times 10^{-10}; L_{B}=178 \times 10^{-4}; L_{D}=260 \times 10^{-4}; L_{E}=260 \times 10^{-4}; \varepsilon_D=0.65; \varepsilon_E=0.65; R_c=0; T_{ref}=298; E_A=65000\text{(*Desai and Neurock (2003) provide a barrier of 60 kJ for CO}_2+\text{OH}_2=\text{CO}_2 + \text{H}^+ + \text{e}^-\text{*}); E_C=67000; p_{O,ref}=1; c_{Me,ref}=1 \times 10^{-3}; c_{W}=55.5 \times 10^{-3} \text{(*mol/cm}^3\text{*)}; \theta=2.9 \text{(*X.Ren and S.Gottesfeld,J.Electrochem.Soc.,148,A87-A93,2001*)}; D_{O,W}=2.5 \times 10^{-5} \text{(*assumed*)}; \kappa_O=0.144; \kappa_{Me,D}=1.0; \kappa_{Me,B}=0.4 \text{(*Ren, Zawo, 2000, Fig 11*)}; \phi_I=0.75; \rho_{Pt}=21.45; \rho_{Ru}=12.3; E_{i,ref}=14000; \delta=1.65 \text{(*fitted to conductivity data for DMFC of Ren, Zawo, 2000, Fig 8*)}; v_{ma}=1.255 \text{(*max voltage*)}; R_I=0; c_{Me,in}=6.0 \times 10^{-3} \text{(*mol/cm}^3\text{*)}; a=5.3 \text{(*du Pont MEAs area*)}; h=0.1; l=45; n=1; \text{(*Flow channel height, length, and number of parallel channels*)}; m_{MA}=4.0 \times 10^{-3}; m_{MC}=2.0 \times 10^{-3}; \omega_{Ru}=0.5; d_{MA}=2.7 \times 10^{-7}; d_{MC}=2.7 \times 10^{-7} \text{(* These catalysts are C supported frm du Pont. Hogarth and Ralph give Subscript\[\gamma, MA]/Subscript[m, MA]=39m}^2/g \text{for black catalyst*)}; Q_A=5/60; Q_C=150/60; \text{(*Volumetric anode and cathode flow rates, cm}^3/s\text{*)}; p_W=\exp[11.676 - 3816.44/(T - 46.13)]; \text{(*vapor pressure of water in cell*)}; p_{O,in}=x_{O,in}(p_C - p_W); p_C=1.0; x_{O,in}=0.21; c_{Me,b}=c_{Me,in} -(a \cdot y)/(12 \times F \times Q_A); \text{(*Current should actually also include crossover current*)}; \lambda=20 \text{(*Taken from Ren, Zawo, 2000. For liquid methanol feed. For vapor feed, this would be lower. Further, due to compression, actual \lambda may be lower than this value indicated by sorption isotherm??*)}; K_A=6.2 \exp[(-(52300)/(R)(1/T-1/298))]; c_{H_0} = 1/(18 \lambda); K = k_+/(k_-); K_A=(1-\omega_R) \rho_{Pt} + \omega_R \rho_{Ru};
\[\gamma_{MA} = \varphi_{I} m_{MA} (6 / (\rho_{MA} d_{MA})) ;
\]
\[\gamma_{MC} = \varphi_{I} m_{MC} (6 / (\rho_{Pt} d_{MC})) ;
\]
\[\theta_{CO} = (K c_{Me,0}) / (1 + K c_{Me,0}) ;
\]
\[\theta_{CO,ref} = (K c_{Me,ref}) / (1 + K c_{Me,ref}) ;
\]
\[i_{A0} = \gamma_{MA} x (c_{Me,0} / c_{Me,ref}) (1 - \theta_{CO}) / (1 - \theta_{CO,ref}) \exp[-(E_{A} / R)(1/T - 1/T_{ref})] i_{A0,ref} ;
\]
\[i_{C0} = \gamma_{MC} x (c_{O,b} / c_{O,ref}) \exp[-(E_{C} / R)(1/T - 1/T_{ref})] i_{C0,ref} ;
\]
\[\tau_{Me} = Q_{A} / (n h^{2} l) ;
\]
\[k_{Me} = 5 \times 10^{-4} ;
\]
\[D_{Me,D,e} = 0.975 \exp[-(30975 / (R T))] ;(*Fitted to limiting current density in Fig 3 of Chiu, 2011. Also presumably includes the partition coefficient, Subscript[\kappa, Me,D], although assumed here as unity, and its temperature variation, accounting for the higher activation energy than Subscript[D, Me,W]*)
\]
\[P_{Me,D,e} = 1 / (L_{D} / (\kappa_{Me,D} D_{Me,D,e}) + 1 / k_{Me}) ;
\]
\[\tau_{O} = Q_{C} / (n h^{2} l) ;
\]
\[k_{O} = 2.696 D_{O,E} / h ;
\]
\[q_{W} = 0.5 (*or 0.4*)(*for liquid feed this is high and should be virtually independent of current*)(*For vapor feed, may assume Subscript[q, W] = 2.0 y assumed proportional to water flux or current*);
\]
\[P_{O,E,e} = 1 / (L_{E} / (\kappa_{O} (1 - q_{W}) 1.5 D_{O,E}) + 1 / k_{O}) ;
\]
\[i_{X,Me,L} = \kappa_{Me,B} (6F) / L_{B} c_{Me,b} ;
\]
\[P_{O,D,e} = 4F c_{O,b} P_{O,D,e} + \square_{B} D_{O,W} \kappa_{O} ;
\]
\[i_{X,O} = 4F c_{O,b} P_{O,D,e} + \square_{B} D_{O,W} \kappa_{O} ;
\]
\[i_{X,Me} = (i_{X,Me,L} + 3 (\kappa_{Me,B} / \kappa_{Me,D}) x_{Me,b} y) (1 - y / i_{AL}) / (1 + 1 / i_{AL} (i_{X,Me,L} + 3 (\kappa_{Me,B} / \kappa_{Me,D}) x_{Me,b} y)) ;
\]
\[\eta_{A} = (R T) / (\alpha_{A} v_{A} F) \arcsinh((y + i_{X,O}) / (2 i_{A0}) / (1 - (y + i_{X,O}) / i_{AL}) (1 + 1 / i_{AL} (i_{X,Me,L} + 3 (\kappa_{Me,B} / \kappa_{Me,D}) x_{Me,b} y))) ;
\]
\[\eta_{C} = (R T) / (\alpha_{C} v_{C} F) \arcsinh((y + i_{X,Me}) / (2 i_{C0}) / (1 - (y + i_{X,Me}) / i_{CL})) ;
\]
\[\eta_{B} = y (L_{B} / \sigma_{B}) ; n_{I} = y R_{f} ;
\]
\[\Psi = v_{0} + \eta_{C} ;
\]
\[V = v_{0} - \eta_{A} + \eta_{C} - \eta_{B} - \eta_{I} ;
\]
\[P = V y ;
\]
\[q = (y + i_{X,Me} + i_{X,O}) v_{ma} - P ;
\]
\[\Xi = P (1 / v_{ma}) (1 / (y + i_{X,Me} + i_{X,O})) 100 ;
\]
APPENDIX 3: MSDS SAFETY SHEETS

Liquid Methanol

MATERIAL SAFETY DATA SHEET

This Material Safety Data Sheet (MSDS) complies with the United Nations Globally Harmonized System (GHS) of Classification and Labeling. Second revised Edition and meets or exceeds the Canadian and United States Requirements for Hazard Communication.

1. Product and Supplier Identification

Product Name: Methanol
GHS Product Identifier: Methanol
Recommended Use: Solvent, fuel, feedstock

Restrictions on Use: Do not use in a confined area without proper ventilation. Contact lenses may cause further damage in case of splash into eye. Avoid use near heat, flames, sparks, and other sources of ignition.

Product: Methanol (CH₃OH) Methanex Tel. #: (604) 681-2600
Synonyms: Methanol, methyl hydrate, wood spirit, methyl hydroxide
Emergency Tel. #: 1-800-202-8200 (CHEMTREC) (Canada and USA)

Company Identification: Methanex Corporation
1800 Waterfront Centre
206 Burrard Street
Vancouver, B.C.
V6C 3M1

Importer: Methanex Methanol Company
15361 Dallas Parkway, Suite 900
Addison, Texas 75001
Telephone: (972) 702-0908

2. Hazards Identification

Classification: Flammable Liquid, Category 1, Acute Toxicity Category 1*, Reproductive Toxicity 1B, Specific Target Organ Toxicity (Repeated Exposure)

Label:

Hazard Communication: DANGER! Extremely flammable liquid and vapour. Fatal if swallowed. May damage fertility or the unborn child (fetotoxic and teratogenic effects). May cause damage to eyes and central nervous system if ingested or inhaled.

*Note: Assigned to classification based on human experience rather than the strict application of classification criteria set out in the Recommendations on the Transport of Dangerous Goods, Model Regulations Special Provision 270.

Hazards: Colourless liquid, with a mild, characteristic alcohol odour when pure. Crude methanol may have a repulsive, pungent odour. Hygroscopic (moisture absorbing).

FLAMMABLE LIQUID AND VAPOUR: Burns with a clean, clear flame, which is almost invisible in daylight, or a light blue flame. Can decompose at high temperatures forming carbon monoxide and formaldehyde.
Methanol

Confined space toxicity hazard. Mild central nervous system depressant following inhalation, skin absorption or ingestion. May cause headache, nausea, dizziness, drowsiness, and un-coordination. Severe vision effects, including increased sensitivity to light, blurred vision, and blindness may develop following an 8-24 hour symptom-free period. Coma and death may result.

IRRITANT: Causes eye irritation. Aspiration hazard. Swallowing or vomiting of the liquid may result in aspiration (breathing) into the lungs.

POSSIBLE REPRODUCTIVE HAZARD: May cause fetotoxic (toxic to the fetus during the latter stages of pregnancy, often through the placenta) and teratogenic effects (causing malformations of the fetus), based on animal information.

NFPA Ratings: (Health, Fire, Reactivity): 1, 3, 0

3. Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>% (w/w)</th>
<th>Exposure Limits (ACGIH)*</th>
<th>L.D_{50}</th>
<th>L.C_{50}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (CAS 07-50-1)</td>
<td>90-100</td>
<td>TLV-TWA: 200 ppm, skin; TLV-STEEL: 250 ppm, skin; FEL-TWA: 200 ppm, skin; FEL-STEEL: 250 ppm, skin; IDLH: 6900 ppm. acute inhalation toxicity to animals; TLV Basal critical effects: neuropathy, vision, central nervous system (CNS)</td>
<td>5628 mg/kg (oral/rat); 15900 mg/kg (dermal/rabbit)</td>
<td>54000 ppm (inhalation/rat)</td>
</tr>
</tbody>
</table>

* Exposure limits may vary from time to time and from one jurisdiction to another. Check with local regulatory agency for the exposure limits in your area. ACGIH, American Conference of Governmental Industrial Hygienists.

4. First Aid Measures

Note: Emergency assistance may also be available from the local poison control centre.

Eye Contact: Remove contact lenses if worn. In case of contact, immediately flush eyes with plenty of clean running water for at least 15 minutes, lifting the upper and lower eyelids occasionally. Obtain medical attention.

Skin Contact: In case of contact, remove contaminated clothing. In a shower, wash affected areas with soap and water for at least 15 minutes. Seek medical attention if irritation occurs or persists. Wash clothing before reuse. Prolonged contact with methanol may defat skin tissue, resulting in drying and cracking.

Inhalation: Remove to fresh air, restore or assist breathing if necessary. Obtain medical attention.

Ingestion: Swallowing methanol is potentially life threatening. Onset of symptoms may be delayed for 18 to 24 hours after ingestion. If conscious and medical aid is not immediately available, do not induce vomiting. In actual or suspected cases of ingestion, transport to medical facility immediately.

NOTE TO PHYSICIAN: Acute exposure to methanol, either through ingestion or breathing high airborne concentrations can result in symptoms appearing between 40 minutes and 72 hours after exposure. Symptoms and signs are usually limited to the Central Nervous System (CNS), eyes and gastrointestinal tract. Because of the CNS’s effects of headache, vertigo, lethargy and confusion, there may be an impression of ethanol intoxication. Blurred vision, decreased acuity and photophobia are common complaints. Treatment with ipecac or lavage is indicated in any patient presenting within two hours of ingestion. A profound metabolic acidosis occurs in severe poisoning and serum bicarbonate levels are a
more accurate measure of severity than serum methanol levels. Treatment protocols are available from most major hospitals and early collaboration with appropriate hospitals is recommended.

Ethanol significantly decreases the toxicity of methanol because it competes for the same metabolic enzymes, and has been used to treat methanol poisoning.

5. Fire Fighting Measures

**Suitable Extinguishing Media:** Extinguishing Media: Small fires: Dry chemical, CO₂, water spray. Large fires: Water spray (see note in Unsuitable Extinguishing Media). AFF(R) (Aqueous Film Forming Foam (alcohol resistant)) type with either a 3% or 6% foam proportioning system.

**Unsuitable Extinguishing Media:** General purpose synthetic foams or protein foams may work, but much less effectively. Water may be effective for cooling, but may not be effective for extinguishing a fire because it may not cool methanol below its flash point.

**Specific Hazards:** Methanol vapours may burn with an invisible flame. During a fire, carbon monoxide, carbon dioxide and irritation and toxic gases such as formaldehyde may be generated. Vapours can accumulate in confined spaces resulting in a toxicity and flammability hazard. Closed containers may rupture violently and suddenly release large quantities of methanol when exposed to fire or excessive heat for a sufficient period of time. Vapours are slightly heavier than air and may travel long distances toward sources of ignition.

**Hazardous Combustion Products:** Toxic gases and vapours; oxides of carbon and formaldehyde.

**Fire Fighting Instructions:** Methanol burns with a clean clear flame that is almost invisible in daylight. Stay upwind! Isolate and restrict area access. Concentrations of greater than 25% methanol in water can be ignited. Use fire water spray or fog to control fire spread and cool adjacent structures or containers. Certain fire control water for later disposal. Fire fighters must wear full face, positive pressure, self-contained breathing apparatus or airline and appropriate protective fire fighting clothing as per NFPA. Note that methanol fires may require proximity suits. Take care not to walk through any spilled chemical.

**Special Information:** Vapours can flow along surfaces to distant ignition sources and flash back.

6. Accidental Release Measures

**Overview:** Flammable liquid! Can burn without a visible flame. Release can cause an immediate risk of fire and explosion. Eliminate all ignition sources. Stop leak and use absorbent materials. If necessary, contain spill by dikeing. Fluorocarbon alcohol resistant foams may be applied to spill to diminish vapour and fire hazard. Maximize methanol recovery for recycling or re-use. Restrict access to area until completion of cleanup. Ensure cleanup is conducted by trained personnel only. Wear adequate personal protection and remove all sources of ignition. Notify all governmental agencies as required by law.

**Personal Protection:** Full face, positive pressure self-contained breathing apparatus or airline, and fire resistant protective clothing with chemical resistant splash suit must be worn. If product ignites, approach and fire fighting must be done with appropriate fire fighting clothing.

**Environmental Precautions:** Biodegrades easily in water. Methanol in fresh or salt water may have serious affects on aquatic life. A study on methanol's toxic affects on sewage sludge bacteria reported little effect on digestion at 0.1% while 0.5% methanol retarded digestion. Methanol will be broken down to carbon dioxide and water.

**Remedial Measures:** Flammable liquid. Release can cause an immediate fire/explosion hazard. Eliminate all sources of ignition, stop leak and use absorbent materials. Collect liquid with explosion proof pumps. Do not walk through spill product as it may be on fire and not visible.

**Small Spills:** Soak up spill with non-combustible absorbent material. Recover methanol and dilute with water to reduce fire hazard. Prevent spilled methanol from entering sewers, confined spaces, drains, or waterways. Restrict access to unprotected personnel. Put material in suitable, covered, labeled containers. Flush area with water.
Large Spills: If necessary, contain spill by diking. Fluorocarbon alcohol resistant foams may be applied to spill to diminish vapour and fire hazard. Maximize methanol recovery for recycling or reuse. Collect liquid with explosion proof pumps.

7. Handling and Storage

Precautions for Handling: No smoking or open flame in storage, use or handling areas. Use explosion proof electrical equipment. Ensure proper electrical grounding procedures are in place.

Storage: Store in totally enclosed equipment, designed to avoid ignition and human contact. Tanks must be grounded, vented, and should have vapour emission controls. Tanks must be diked as per NFPA or API Standards. A flammable mixture of methanol vapour and air is possible inside a storage tank or transportation tank, and handlers should take appropriate precautions to reduce the risk of ignition. Handlers must eliminate ignition sources or purge the tank with an inert gas such as nitrogen. All equipment must be grounded - bonded when transferring product in order to avoid static discharge from the equipment, and subsequent possible fire. Avoid storage with incompatible materials. Anhydrous methanol is non-corrosive to most metals at ambient temperatures except for lead, nickel, monel, cast iron and high silicon iron. Coatings of copper (or copper alloys), zinc (including galvanized steel), or aluminum are unsuitable for storage. These materials may be attacked slowly by the methanol. Storage tanks of welded construction are normally satisfactory. They should be designed and built in conformance with good engineering practice for the material being stored. While plastics can be used for short term storage, they are generally not recommended for long-term storage due to deterioration effects and the subsequent risk of contamination.

Corrosion rates for several construction materials:

- <0.508 mm/year: Cast iron, monel, lead, nickel
- <0.051 mm/year: High silicon iron
- Some attack: Polyethylene
- Satisfactory: Neoprene, phenolic resins, polyesters, natural rubber, butyl rubber
- Resistant: Polyvinyl chloride, unplasticized

8. Exposure Controls, Personal Protection

Occupational Controls: ACGIH TLV-TWA: 200 ppm, skin (262 mg/m³);
TLV-STEL: 250 ppm, skin (328 mg/m³);
PEL-TWA: 200 ppm, skin
PEL-STEL: 250 ppm, skin
TLV Basis: critical effects: neuropathy, vision, central nervous system(CNS)
IDLH: 6000 ppm, acute inhalation toxicity to animals

Engineering Controls: In confined areas, local and general ventilation should be provided to maintain airborne concentrations below permissible exposure limits. Ventilation systems must be designed according to approved engineering standards.

Respiratory Protection: NIOSH/OSHA recommendations for methanol concentrations in air:

- Up to 2000 ppm: supplied air respirator
- Up to 6000 ppm: supplied air respirator operated in a continuous-flow mode.
- Up to 6000 ppm: supplied air respirator with a tight-fitting facepiece operated in a continuous-flow mode; or Full-facepiece self-contained breathing apparatus or Full-facepiece supplied air respirator.

Cartridge type respirators are NOT recommended.

Emergency or Planned entry into unknown concentrations or IDLH (immediately dangerous to life or health) conditions:
Respirator selection must be done by a qualified person and be based upon a risk assessment of the work activities and exposure levels. Respirators must be fit tested and users must be clean shaven where the respirator seals to the face. Exposure must be kept at or below the applicable exposure limits and the maximum use concentration of the respirator must not be exceeded.

Positive pressure, full-facepiece self-contained breathing apparatus, or Positive pressure, full-facepiece supplied air respirator with an auxiliary positive pressure self-contained breathing apparatus.

Skin Protection: Butyl and nitrile rubbers are recommended for gloves. Check with manufacturer. Wear chemical resistant pants and jackets, preferably of butyl or nitrile rubber. Check with manufacturer.

Eye and Face Protection: Face shield and chemical splash goggles when transferring is taking place. Contact lenses should not be worn when working with methanol.

Footwear: Chemical resistant and as specified by the workplace.

Other: Eyewash and showers should be located near work areas. NOTE: PPE must not be considered a long-term solution to exposure control. PPE usage must be accompanied by employer programs to properly select, maintain, clean, fit and use. Consult a competent industrial hygiene resource to determine hazard potential and/or the PPE manufacturers to ensure adequate protection.

Careful consideration must be made of the added danger of the concentration being in the LEL/UEL range and so there may be a fire/explosion hazard.

### 9. Physical and Chemical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Liquid, clear, colourless</td>
</tr>
<tr>
<td>Odour</td>
<td>Mild characteristic alcohol odour</td>
</tr>
<tr>
<td>Odour Threshold: detection</td>
<td>4.2 - 5900 ppm</td>
</tr>
<tr>
<td>Odour Recognition:</td>
<td>100 ppm (geometric mean)</td>
</tr>
<tr>
<td>Odour Recognition:</td>
<td>53 - 9840 ppm</td>
</tr>
<tr>
<td>Odour Recognition:</td>
<td>990 ppm (geometric mean)</td>
</tr>
<tr>
<td>pH</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>-97.8°C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>94.7°C</td>
</tr>
<tr>
<td>Boiling Range:</td>
<td>Not determined</td>
</tr>
<tr>
<td>Flash Point</td>
<td>11.0°C</td>
</tr>
<tr>
<td>Solubility</td>
<td>Completely soluble</td>
</tr>
<tr>
<td>Partial Coefficient:</td>
<td>Log P (oct) = -0.82</td>
</tr>
<tr>
<td>Vapour Pressure:</td>
<td>12.6 kPa @ 20°C</td>
</tr>
<tr>
<td>Upper Explosive Limit (UEL)</td>
<td>38.5 %</td>
</tr>
<tr>
<td>Lower Explosive Limit (LEL)</td>
<td>6%</td>
</tr>
<tr>
<td>Auto Ignition Temperature</td>
<td>454°C</td>
</tr>
<tr>
<td>Solvent Solubility:</td>
<td>Soluble in all proportions in ethanol, benzene, other alcohols, chloroform, diethyl ether, other ethers, esters, ketones and most organic solvents.</td>
</tr>
<tr>
<td>Critical Temperature:</td>
<td>239.4°C</td>
</tr>
<tr>
<td>Specific Gravity:</td>
<td>0.191 @ 20°C</td>
</tr>
<tr>
<td>Evaporation Rate:</td>
<td>4.1 (n-Butyl Acetate = 1)</td>
</tr>
<tr>
<td>Vapour Density:</td>
<td>1.105 @ 15°C (air = 1)</td>
</tr>
<tr>
<td>Decomposition Temperature:</td>
<td>Not determined</td>
</tr>
<tr>
<td>Sensitivity to Impact:</td>
<td>No</td>
</tr>
<tr>
<td>Sensitivity to Static Charge:</td>
<td>Low</td>
</tr>
</tbody>
</table>

### 10. Stability and Reactivity

Chemical Stability: Stable as supplied.

Hazardous Reactions: Yes. Avoid contact with strong oxidizers, strong mineral or organic acids, and strong bases. Contact with these materials may cause a violent or explosive reaction. May be corrosive to lead, aluminum, magnesium, and platinum.

Conditions to Avoid: Avoid contact with sparks, heat, open flame, or ignition sources.

Incompatibility: Yes. Avoid contact with strong oxidizers, strong mineral or organic acids, and strong bases. Contact with these materials may cause a violent or explosive reaction. May be corrosive to lead, aluminum, magnesium, and platinum. May react with metallic aluminum or magnesium and generate hydrogen gas. May attack some forms of plastic, rubber, and coatings.

Hazardous Decomposition Products: Formaldehyde, carbon dioxide, and carbon monoxide.

Hazardous Polymerization: Will not occur.
11. Toxicological Information

Signal Word/Label: DANGER! Extremely flammable liquid and vapour. Fatal if swallowed. May damage fertility or the unborn child (fetotoxic and teratogenic effects). May cause damage to eyes and central nervous system if ingested or inhaled.

Primary Routes of Entry:

- Skin Contact: Yes
- Skin Absorption: Yes
- Eye Contact: Yes
- Ingestion: Yes
- Inhalation: Yes

Emergency Overview: Colourless liquid, with a mild, characteristic alcohol odour when pure. Crude methanol may have a repulsive, pungent odour. Hygroscopic. Can decompose at high temperatures forming carbon monoxide and formaldehyde. Confined space toxicity hazard. Mild central nervous system depressant following inhalation, skin absorption or ingestion. May cause headache, nausea, dizziness, drowsiness, and incoordination. Severe vision effects, including increased sensitivity to light, blurred vision, and blindness may develop following an 8-24 hour symptom-free period. Coma and death may result. Causes eye irritation. Aspiration hazard. Swallowing or vomiting of the liquid may result in aspiration (breathing) into the lungs. May cause fetotoxic (toxic to the fetus during the latter stages of pregnancy, often through the placenta) and teratogenic effects (causing malformations of the fetus), based on animal information.

Acute Exposure:

Inhalation: Inhalation of high airborne concentrations can also irritate mucous membranes, cause headaches, sleepiness, nausea, confusion, loss of consciousness, digestive and visual disturbances and even death. NOTE: Olfactory threshold of methanol is several times higher than the TLV-TWA. Depending upon severity of poisoning and the promptness of treatment, survivors may recover completely or may have permanent blindness, vision disturbances and/or nervous system effects. Concentrations in air exceeding 1000 ppm may cause irritation of the mucous membranes.

Skin Contact: Methanol is moderately irritating to the skin. Methanol can be absorbed through the skin and harmful effects have been reported by this route of entry. Effects are similar to those described in “Inhalation”.

Eye Contact: Methanol is a mild to moderate eye irritant. High vapour concentration or liquid contact with eyes causes irritation, tearing and burning.

Ingestion: Swallowing even small amounts of methanol could potentially cause blindness or death. Effects of sub lethal doses may be nausea, headache, abdominal pain, vomiting and visual disturbances ranging from blurred vision to light sensitivity.

Chronic Exposure:

Irritancy: Prolonged contact with skin may defat tissue causing dermatitis or aggravate existing skin problems.

Sensitization: None reported.
Carcinogenicity: Not listed by IARC, NTP, ACGIH, or OSHA as a carcinogen.

Teratogenicity: Methanol has produced fetotoxicity in rats and teratogenicity in mice exposed to high concentrations of methanol vapours.

Reproductive Toxicity: Information available does not suggest that methanol is a reproductive toxin.

Mutagenicity: There is insufficient information available to conclude that methanol is mutagenic.

Synergistic Products: In animals, high concentrations of methanol can increase the toxicity of other chemicals, particularly liver toxins like carbon tetrachloride. Ethanol significantly reduces the toxicity of methanol because it competes for the same metabolic enzymes, and has been used to treat methanol poisoning.

Potential for Accumulation: Methanol is readily absorbed into the body following inhalation and ingestion. Skin absorption may occur if the skin is broken or exposure is prolonged. Once absorbed, methanol is rapidly distributed to body tissues. A small amount is excreted unchanged in exhaled air and the urine. The rest is first metabolized to formaldehyde, which is then metabolized to formic acid and/or formate. The formic acid and formate are eventually converted to carbon dioxide and water. In humans, methanol clears from the body, after inhalation or oral exposure, with a half-life of 1 day or more for high doses (greater than 1000 mg/kg) or about 1.5-3 hours for low doses (less than 100 mg/kg or 76.5-230 ppm (100-300 mg/m³)).

Medical Conditions Aggravated by Exposure: Persons with pre-existing skin disorders, eye problems, respiratory conditions, or impaired liver or kidney functions may be more susceptible to the effects of this substance.

12. Ecological Information

Environmental toxicity: DO NOT discharge into sewer or waterways.

Methanol:

- LC₅₀ Pimephales promelas (fathead minnows) 26.4 g/L/96 hr, (28-29 days old), confidence limits = 20.5-32.4. Test conditions: Water temp = 25°C, dissolved oxygen = 7.3 mg/L, water hardness = 43.6 mg/l CaCO₃, alkalinity = 46.6 mg/l CaCO₃, tank volume = 8.3 L, additions = 5.71 V/O, pH = 7.66
- LC₅₀ Pimephales promelas (Fathead minnow, 28-32 day old, 0.126 g) 29.7 mg/L/24 hr; flow-through, 23.3±2°C, hardness 46.4 mg/L CaCO₃, pH 7.0±0.0
- LC₅₀ Pimephales promelas (Fathead minnow, 30 day old 0.12 g) 28.1 mg/L/96 hr; flow-through, 24-25°C, hardness 45.5 mg/L CaCO₃, pH 7.5
- LC₅₀ Daphnia pulex (Water flea, <24 hr old) 10.5 mg/L/18 hr; static, 22°C, hardness 23±2 mg/L CaCO₃
- EC₅₀ Daphnia obtusa (Water flea, <24 hr old; immobilization) 23.5 mg/L/24 hr; static, 20±1°C, hardness 250 mg/L CaCO₃, pH 7.5±0.2
- EC₅₀ Daphnia obtusa (Water flea, <24 hr old; immobilization) 22.2 mg/L/48 hr; static, 20±1°C, hardness 250 mg/L CaCO₃, pH 7.5±0.2

log Kow = -0.62 - 0.66
Half-life (hr) air: 427
Half-life (hr) H₂O surface water: 9.3 - 64
Henry’s Law constant (atm m³/mol): 4.5x10⁻ⁱ⁰
BOD 5 if unstated: 0.76 - 1.12
COD: 1.05 - 1.50, 99%
ThOD: 1.35
BOD: 0.2 - 10
TLm(48 hr): 8000mg/L (trout)
Toxicity Anthropa: NOEL 10 g/L/48 hr (Daphnia)
HSNO Classification: 8.3C – Harmful to terrestrial vertebrates
Methanol in fresh or salt water may have serious effects on aquatic life. A study on methanol's toxic effects on sewage sludge bacteria reported little effect on digestion at 0.1% while 0.5% methanol retarded digestion. Methanol will be broken down into carbon dioxide and water.

Environmental Fate:

Biodegradability: Biodegrades easily in water and soil.

Bioaccumulation:

- **TERRESTRIAL FATE:** Based on a classification scheme, an estimated Koc value of 1 determined from a structure estimation method indicates that methanol is expected to have very high mobility in soil. Volatilization of methanol from moist soil surfaces is expected to be an important fate process given a Henry's Law constant of 4.55x10^-6 (atm m^3/mol). The potential for volatilization of methanol from dry soil surfaces may exist based upon a vapor pressure of 127 mm Hg. Biodegradation is expected to be an important fate process for methanol.

- **AQUATIC FATE:** Based on a classification scheme, an estimated Koc value of 1, determined from a structure estimation method, indicates that methanol is not expected to adsorb to suspended solids and sediment. Volatilization from water surfaces is expected based upon a Henry's Law constant of 4.55x10^-4 (atm m^3/mol). Using this Henry's Law constant and an estimation method, volatilization half-lives for a model river and model lake are three and 35 days, respectively. According to a classification scheme, a BCF of less than 10 measured in fish, suggests bioconcentration in aquatic organisms is low. Hydrolysis and photolysis in sunlit surface waters is not expected to be an important environmental fate process for methanol since this compound lacks functional groups that hydrolyze or absorb light under environmentally relevant conditions. Methanol has been shown to undergo rapid biodegradation in a variety of screening studies using sewage seed and activated sludge inoculum, which suggests that biodegradation will occur in aquatic environments.

- **ATMOSPHERIC FATE:** According to a model of gas/particle partitioning of semi volatile organic compounds in the atmosphere, methanol, which has a vapor pressure of 127 mm Hg at 25°C, is expected to exist solely as a vapor in the ambient atmosphere. Vapor-phase methanol is degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 17 days, calculated from its rate constant of 9.4x10^-15 cm^3/molecule-sec at 25°C.

### 13. Disposal Considerations

Review federal, provincial or state, and local government requirements prior to disposal. Store material for disposal as indicated in Section #7: Handling and Storage. Disposal by controlled incineration or by secure landfill may be acceptable. Recycle wherever possible. Large volumes may be suitable for re-distillation or, if contaminated, incinerated. Can be disposed of in a sewage treatment facility. Methanol levels of up to 0.1% act as a food source for bacteria; above this level may be toxic to bacteria. When pumping through sewage collection systems, the level of methanol should be kept below the flammable range (a 25% methanol/water mixture is non-flammable at temperatures below 36°C). 1 ppm of methanol is equivalent to 1.5 ppm BOD loading in the sewage plant.

**Container disposal:**

Empty containers may contain hazardous residue. Return to supplier for reuse if possible. Never weld, cut or grind empty containers. If disposing of containers, ensure they are well rinsed with water, then disposed of at an authorised landfill. After cleaning, all existing labels should be removed.
14. Transport Information

Canada Transportation of Dangerous Goods (TDG): UN 1230, Methanol, Class 3(6.1), P.G. II
Limited Quantity: ≤ 1 litres
ERG Guide Number: 131

United States Department of Transport (49CFR): UN 1230, Methanol, Class 3, P.G. II
(Domestic Only)
(RQ 5000 lbs/2270 kg)
Limited Quantity: ≤ 1 litres
ERG Guide Number: 131

International Air Transport Association (IATA): UN 1230, Methanol, Class 3(6.1), P.G. II
Packaging Instruction (passenger aircraft): 305, 1 litre maximum per package

International Maritime Organization (IMO): UN 1230, Methanol, Class 3(6.1), P.G.II,
Flash Point = 11°C
EmS No. F-E, S-D
Stowage Category “B”, Clear of living quarters

Marine Pollutant: No

15. Regulatory Information

CANADIAN FEDERAL REGULATIONS:

CEPA, DOMESTIC SUBSTANCES LIST: Listed (Canadian Environmental Protection Act
(CEPA) Schedule I)

WHMIS CLASSIFICATION: B2, D1B, D2A, D2B

UNITED STATES REGULATIONS:

40CFR 116-117 (EPA): Hazardous
40CFR 355, Appendices A and D: Subject to Emergency Planning and Notification
40CFR 372 (SARA Title III): Listed
40CFR 302 (CERCLA): Listed

TOXIC SUBSTANCES CONTROL ACT (TSCA): Listed in the inventory.
# Methanol Gel

## MATERIAL SAFETY DATA SHEET

**GEL HEAT™ BLUE  GEL METHANOL CHAFING DISH FUEL**

24 hour emergency assistance: CHEMTREC 1-800-424-9300 day or night. Outside the continental United States, call CHEMTREC at 1-703-527-3567 (collect calls accepted).

Hollowick urges the customer receiving the Material Safety Data Sheet (MSDS) to study it carefully to become aware of hazards, if any, of the product involved. In the interest of safety, you should (1) notify your employees, agents and contractors of the information on this sheet, and (2) furnish a copy to each of your customers to inform their employees as well.

### SECTION I – PRODUCT INFORMATION

<table>
<thead>
<tr>
<th>TRADE NAME:</th>
<th>GEL HEAT™ BLUE GEL METHANOL CHAFING DISH FUEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>PACKAGE:</td>
<td>Cams (72 per case)</td>
</tr>
<tr>
<td>SYNONYMS:</td>
<td>Gel (or jelled) Methanol (Consumer Commodity)</td>
</tr>
<tr>
<td>PRODUCT IB:</td>
<td>Mixture, CAS number not applicable</td>
</tr>
<tr>
<td>CHEMICAL FAMILY:</td>
<td>Not applicable</td>
</tr>
<tr>
<td>GENERAL INFORMATION:</td>
<td>A gel alcohol fuel for warming food in chafing dishes only. The fuel is methanol in a colloidal gel.</td>
</tr>
<tr>
<td>DATE PREPARED:</td>
<td>December 1, 2020</td>
</tr>
</tbody>
</table>

### SECTION II – HAZARDOUS INGREDIENTS/IDENTITY INFORMATION

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>CAS RN.</th>
<th>WT/WT%</th>
<th>TLV (UNITS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>67-65-1</td>
<td>74.8</td>
<td>200 ppm</td>
</tr>
<tr>
<td>Acetone</td>
<td>67-64-1</td>
<td>0.4</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>Denatured Benzoate</td>
<td>379-33-0</td>
<td>Trace</td>
<td></td>
</tr>
</tbody>
</table>

### SECTION III – PHYSICAL/CHEMICAL CHARACTERISTICS

- **APPEARANCE AND ODOR:** Blue gel with alcohol odor
- **SPECIFIC GRAVITY (H2O=1) at 80 °F:** Not applicable
- **% VAPOR BY VOLUME:** 95%
- **SOLUBILITY IN WATER:** Slightly soluble
- **pH:** Not applicable

### SECTION IV – FIRE AND EXPLOSION HAZARDS

- **FLASH POINT:** Tag Closed Cup 54 °F (12.2 °C)
- **IGNITION TEMPERATURE:** 410 °F
- **EXTINGUISHING MEDIA:** Carbon dioxide, dry chemical, water mist or fog
- **SPECIAL FIREFIGHTING PROCEDURES:**
  - Do not use high-pressure stream of water to extinguish burning material
  - Unusual fire or explosion hazard: Closed can exposed to flame and heat may erupt scattering burning fragments.

### SECTION V – REACTIVITY DATA

- **STABILITY:** Stable
- **CONDITIONS AND MATERIALS TO AVOID:** Heat, open flame, strong oxidizers
- **HAZARDOUS DECOMPOSITION PRODUCTS:** None known
- **HAZARDOUS POLYMERIZATION:** Will not occur
SECTION VI – HEALTH/HAZARD DATA

EYES: Can cause moderate irritation, redness, tearing
SKIN: Prolonged or repeated contact can cause moderate irritation, dermatitis.
BREATHING: Excessive inhalation of vapors can cause nasal and respiratory irritation
SWALLOWING: Can cause gastrointestinal irritation, nausea, vomiting and diarrhea

SECTION VII – EMERGENCY FIRST AID PROCEDURE

IF ON SKIN: Thoroughly wash exposed area with soap and water. Remove contaminated clothing. Launder contaminated clothing before re-use.
IF IN EYES: Flush with large amounts of water, lifting upper and lower lids occasionally. GET MEDICAL ATTENTION.
IF SWALLOWED: If victim is conscious, give two glasses of water, induce vomiting immediately by sticking finger down throat. Call a physician. Never give anything by mouth to an unconscious person.
IF INHALED: Move individual to fresh air.

SECTION VIII – OCCUPATIONAL EXPOSURE LIMITS

THRESHOLD LIMIT VALUE: Not established

SECTION IX – EMPLOYEE PROTECTION

RESPIRATORY PROTECTION: Not required under normal conditions of use
VENTILATION: Not required under normal conditions of use

SECTION X – ENVIRONMENTAL PROTECTION

ENVIRONMENTAL PRECAUTIONS: Keep away from fire and other ignition sources. Avoid spills and leaking of this material. Absorb spilled material using paper, floor absorbents or other absorbent material. Ventilate the area.

SECTION XI – REGULATORY CONTROLS

DEPARTMENT OF TRANSPORTATION (DOT):
DOT CLASSIFICATION: ORM-D
DOT PROPER SHIPPING NAME: Consumer Commodity:ORM-D
DOT EMERGENCY GUIDE NUMBER: Not applicable

SECTION XII – SARA TITLE III

Components present in this product at a level which could require reporting under the statute (Section 313) are:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CAS #</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>67-56-1</td>
<td>74.8%</td>
</tr>
<tr>
<td>Acetone</td>
<td>67-64-1</td>
<td>1.4%</td>
</tr>
</tbody>
</table>

The information contained herein is furnished without warranty of any kind. Employers should use this information only as a supplement to other information gathered by them and must conduct testing and/or make independent determinations of suitability and completeness of information from all sources to assure proper use of these materials and the safety and health of employees.

HOLLOWICK INC. GEL HEAT™ BLUE GEL METHANOL CHAFING DISH FUEL