ABSTRACT

High system cost and large size are two barriers preventing mainstream commercial viability of proton exchange membrane fuel cells. These barriers can be addressed by (a) improving water management in the cell for a higher power density at lower cost and (b) reducing the cost and size of balance of plant components. The cathode reactant humidification system directly affects the water management of the cell and is one of the most expensive balance of plant components in the system.

A thermodynamic model of a cathode gas to gas membrane humidifier was implemented. The model considers two-phase heat and mass transfer along two parallel, one-dimensional channels in counter flow operation.

A single channel humidifier was constructed with the capability of measuring temperature and dew point temperature profiles along the channel. Dew point profiles and the effect of flow rate on the outlet dew point were measured at 30, 50, and 70°C isothermal cases with fully saturated wet-side inlet conditions. Water flux across the membrane was constant along the channel and the outlet dew point decreased with dry-side flow rate for all cases. The effect of wet-side flow rate was minor.

The experimental data were compared to the thermodynamic model using membrane diffusivity from four published correlations and three different techniques. The different diffusivity correlations affected model predictions of moisture flux by up to 86%, demonstrating that fitted membrane parameters must be used if modeling accuracy is expected. Calculating diffusivity at the average membrane water content of the two sides of the membrane was shown to be a better approximation than using an average
relative humidity. Also, the model over-predicted the outlet dew point more at lower temperatures than at higher temperatures compared to the experimental data.

Finally, a 5kW humidifier design was simulated at a pressure of 1 atm with 65°C fully-saturated and 25°C completely-dry conditions at the wet-side and dry-side inlets, respectively. Analysis revealed that modeling moisture transfer using humidity ratio as a driving force can lead to unphysical results under non-isothermal conditions with high moisture flux. Pressure drop estimations using an all-vapour, Darcy friction factor analysis were very low compared to measured data and a fitted flow restriction equation was suggested.

**Keywords:** humidifier, membrane, fuel cell, water management, mass transfer, single phase
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<td>$A_{cs}$</td>
<td>Channel cross sectional area</td>
<td>$[m^2]$</td>
</tr>
<tr>
<td>$A$</td>
<td>Membrane surface area</td>
<td>$[m^2]$</td>
</tr>
<tr>
<td>$a$</td>
<td>Concentration of sulfonate sites, $a=1789$</td>
<td>$[mol(SO_3^-) m^3]$</td>
</tr>
<tr>
<td>$\tilde{a}$</td>
<td>Chemical activity</td>
<td>$[0,1]$</td>
</tr>
<tr>
<td>$Bi$</td>
<td>Biot number</td>
<td></td>
</tr>
<tr>
<td>$C$</td>
<td>Constant parameters for sorption curve equation, Hyland and Wexler equation, and orifice pressure drop correlation</td>
<td></td>
</tr>
<tr>
<td>$C'$</td>
<td>Vapour concentration (Ch.2 only)</td>
<td>$[mol m^3]$</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Specific heat capacity at constant pressure</td>
<td>$[J mol^{-1} K^{-1}]$</td>
</tr>
<tr>
<td>$d'$</td>
<td>Channel depth</td>
<td>$[m]$</td>
</tr>
<tr>
<td>$D, D_t$</td>
<td>Diffusion coefficient</td>
<td>$[m^2 s^{-1}]$</td>
</tr>
<tr>
<td>$D_n$</td>
<td>Product of diffusion coefficient and membrane density</td>
<td>$[kg m^{-2} s^{-1}]$</td>
</tr>
<tr>
<td>$f$</td>
<td>Darcy friction factor</td>
<td></td>
</tr>
<tr>
<td>$g$</td>
<td>Mass transfer function per unit length</td>
<td>$[kg s^{-1} m^{-1}]$</td>
</tr>
<tr>
<td>$h_{sup}$</td>
<td>Heat of vaporization</td>
<td>$[J kg^{-1}]$</td>
</tr>
<tr>
<td>$h$</td>
<td>Specific enthalpy</td>
<td>$[J kg^{-1}]$</td>
</tr>
<tr>
<td>$h_a$</td>
<td>Convection heat transfer coefficient, or conductance</td>
<td>$[kg m^{-2} s^{-1}]$</td>
</tr>
<tr>
<td>$h_m$</td>
<td>Convection mass transfer coefficient, or conductance</td>
<td>$[kg m^{-2} s^{-1}]$</td>
</tr>
<tr>
<td>$J$</td>
<td>Water flux</td>
<td>$[mol s^{-1} m^{-2}]$ or $[kg s^{-1} m^{-2}]$</td>
</tr>
<tr>
<td>$J_{w}$</td>
<td>Steady state water flux across membrane</td>
<td>$[mol s^{-1} m^{-2}]$</td>
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<td>$\overline{J}_{mem, H_2O}$</td>
<td>Average water flux across membrane</td>
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<tr>
<td>$K_c$</td>
<td>Entrance pressure loss coefficient</td>
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<tr>
<td>$K_e$</td>
<td>Exit pressure loss coefficient</td>
<td></td>
</tr>
<tr>
<td>$k$</td>
<td>Rate constant for condensation rate equation</td>
<td>$[s^{-1}]$</td>
</tr>
<tr>
<td>$L$</td>
<td>Length of channel</td>
<td>$[m]$</td>
</tr>
<tr>
<td>$Le$</td>
<td>Lewis number</td>
<td></td>
</tr>
<tr>
<td>$M$</td>
<td>Number of permeable channel walls</td>
<td></td>
</tr>
<tr>
<td>$MW$</td>
<td>Molecular weight</td>
<td>$[kg mol^{-1}]$</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>Mass flow rate</td>
<td>$[kg s^{-1}]$</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of channels</td>
<td></td>
</tr>
<tr>
<td>$Nu$</td>
<td>Nusselt number</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>Number of moles</td>
<td>$[mol]$</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$P_i$</td>
<td>Partial pressure of species $i$</td>
<td>$[Pa]$</td>
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<tr>
<td>$Q$</td>
<td>Volumetric flow rate</td>
<td>$[SLPM]$ (at 25°C and 1 atm)</td>
</tr>
<tr>
<td>$q'$</td>
<td>Heat transfer rate to surroundings per unit length</td>
<td>$[W m^{-1}]$</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
<td></td>
</tr>
<tr>
<td>$R_e^2$</td>
<td>Coefficient of determination</td>
<td></td>
</tr>
<tr>
<td>$Sh$</td>
<td>Sherwood number</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>$[K]$ or $[\degree C]$</td>
</tr>
<tr>
<td>$T_d$</td>
<td>Dew point above liquid water</td>
<td>$[K]$ or $[\degree C]$</td>
</tr>
<tr>
<td>$t_{mem}$</td>
<td>Membrane thickness</td>
<td>$[m]$</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>$[s]$</td>
</tr>
<tr>
<td>$U$</td>
<td>Overall heat transfer coefficient</td>
<td>$[W m^{-2} K^{-1}]$</td>
</tr>
<tr>
<td>$U_{sur}$</td>
<td>Overall heat transfer coefficient to surroundings</td>
<td>$[W m^{-2} K^{-1}]$</td>
</tr>
</tbody>
</table>
**Overall heat transfer coefficient across membrane** \( U_{\text{mem}} \) \[ \text{W m}^{-2} \text{K}^{-1} \]

**Water uptake** \( u \) \[ \text{kg H}_2\text{O (kg dry membrane)}^{-1} \]

**Maximum water uptake capacity** \( u_{\text{max}} \) \[ \text{kg H}_2\text{O (kg membrane)}^{-1} \]

**Mass averaged velocity** \( V \) \[ \text{m s}^{-1} \]

**Molar volume** \( V \) \[ \text{m}^3 \text{mol}^{-1} \]

**Effective perimeter for heat transfer to surroundings** \( w \) \[ \text{m} \]

**Distance along channel measured from dry-side inlet** \( x \) \[ \text{m} \]

**Molar fraction of species \( i \)** \( x_i \) \[ \text{mol} i \text{ (mol total)}^{-1} \]

**Greek**

- \( \gamma_u \) Absorption coefficient \[ \text{m s}^{-1} \]
- \( \gamma_d \) Desorption coefficient \[ \text{m s}^{-1} \]
- \( \varepsilon \) Effectiveness \[ 0,1 \]
- \( \delta \) Proportionality constant in diffusion equation
- \( \phi \) Relative humidity
- \( \zeta \) Specific humidity \[ \text{kg H}_2\text{O (kg total)}^{-1} \]
- \( \omega \) Humidity ratio \[ \text{kg H}_2\text{O (kg dry air)}^{-1} \]
- \( \rho \) Density \[ \text{kg m}^{-3} \]
- \( \sigma \) Surface tension \[ \text{Nm}^{-1} \]
- \( \sigma \) Ratio of open area to total frontal area
- \( k \) Thermal conductivity \[ \text{W m}^{-1} \text{K}^{-1} \]
- \( \xi \) Dummy variable
- \( \lambda \) Membrane water content \[ \text{mol H}_2\text{O/mol SO}_3 \]
- \( \lambda^* \) Equilibrium membrane water content \[ \text{mol H}_2\text{O/mol SO}_3 \]
- \( \lambda_{liq} \) Liquid-equilibrated membrane water content, 22 \[ \text{mol H}_2\text{O/mol SO}_3 \]
- \( \theta \) Dimensionless weighting parameter
- \( \eta \) Fraction of latent heat release transferred to the dry-side stream \[ 0,1 \]
- \( \Gamma \) Overall mass transfer coefficient \[ \text{kg m}^{-2} \text{s}^{-1} \]
- \( \psi \) Membrane diffusion mass transfer resistance \[ \text{kg}^{-1} \text{s m}^{-2} \]
- \( \mu \) Chemical potential \[ \text{J mol}^{-1} \]

**Subscript**

- \( l, 2 \) Chamber side index (1=wet chamber, 2=dry chamber)
- \( \text{air} \) Air
- \( \text{DI} \) Dry-side channel inlet (also used as an abbreviation)
- \( \text{DO} \) Dry-side channel outlet (also used as an abbreviation)
- \( \text{dry} \) Dry-side channel
- \( \text{H}_2 \) Hydrogen
- \( \text{H}_2\text{O} \) Water
- \( \text{in} \) referring to inlet quantity
- \( \text{l} \) Liquid phase
- \( \text{mem} \) Membrane
- \( \text{O}_2 \) Oxygen
- \( \text{out} \) referring to outlet quantity
- \( \text{surr} \) Surroundings
- \( v \) Vapour phase
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDC</td>
<td>Constant Diffusion Coefficient model</td>
</tr>
<tr>
<td>DPAT</td>
<td>Dew Point Approach Temperature $[^{°C}]$ or $[K]$</td>
</tr>
<tr>
<td>EE</td>
<td>Enthalpy (or total) Effectiveness</td>
</tr>
<tr>
<td>EOD</td>
<td>Electro-Osmotic Drag</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas Diffusion Layer</td>
</tr>
<tr>
<td>LE</td>
<td>Latent Effectiveness</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane Electrode Assembly</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton Exchange Membrane</td>
</tr>
<tr>
<td>PEMFC</td>
<td>PEM Fuel Cell</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>SE</td>
<td>Sensible Effectiveness</td>
</tr>
<tr>
<td>VDC</td>
<td>Variable Diffusion Coefficient model</td>
</tr>
<tr>
<td>WRR</td>
<td>Water Recovery Ratio</td>
</tr>
</tbody>
</table>

### Superscript

- $e$: equilibrium water content value
- $D$: referring to the dry (or sweep) side
- $sat$: Value at saturation
- $W$: referring to the wet (or feed) side
- $\ast$: Outlet quantity
- $\cdot$: Per unit length

### Abbreviations

- wet: Wet-side channel
- WI: Wet-side channel inlet (also used as an abbreviation)
- WO: Wet-side channel outlet (also used as an abbreviation)
- $x$: All probe locations along channel
If there is any merit or glory that arises from this thesis, I desire for that glory to be given to God. It is He who has blessed me with not only food, shelter, and a peaceful country, but also a wonderful family, beautiful wife, and a university education.

From the depth of my heart I also thank my wife Katie for her loving comfort, encouragement, and patience throughout the course of this research. As work hours increased, she encouraged me all the more and without that support this thesis would not be the quality that it is. On another personal note, I pay tribute to my parents, who have always loved me and supported my every endeavour.

The academic content of this thesis is the result of assistance from many people. My supervisor Dr. Walter Mérida was instrumental in the success of this thesis project. His enthusiasm for the subject matter and willingness to lend assistance were very beneficial in the completion of this work. Thanks also goes to everybody in my research group, with specific mention to Tatiana Romero, Omar Herrera, Saul Pazos-Knoop, David Kadylak, and Amir Niroumand. Thank you not only for the academic discussions, but also the numerous Spanish lessons and fun friendship. I'm also appreciative of Chad Comeault and James Dean at dPoint Technologies for getting me started on this interesting project and for the many helpful discussions along the way. Finally, I would like to thank Dr. Martin Davy, James Dean, and Dr. Walter Mérida for the time they have invested being on my examination committee.

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The work contained in Appendix C was a collaborative effort with fellow graduate student Tatiana Romero\textsuperscript{ab}, professor Walter Mérida\textsuperscript{ab} from the Department of Mechanical Engineering, and professor Brian Wetton\textsuperscript{c} from the Department of Mathematics at the University of British Columbia. The project originated with T. Romero who identified the need for progress in the area of mass transfer resistance in Nafion membranes and designed an experimental setup to assist in meeting that need. She also contributed the experimental data. W. Mérida assisted in the design of the experimental setup and in funding the resources required to carry out the work. B. Wetton lended assistance by guiding the development of the mathematical model. P. Cave, the current author, implemented and verified the model, performed the data analysis, and took on the central role in preparing the manuscript to date.

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1. Introduction

Proton Exchange Membrane (PEM) fuel cells, also known as Polymer Electrolyte fuel cells, describe the class of fuel cells that employ proton-conducting polymers as the ionic conductor. PEM fuel cells are attractive primarily because they have such a diverse range of power applications. Products have already been marketed with rated power as low as 1 W (e.g. Angstrom Power’s A2 Fuel Cell Flashlight) and as high as 300 kW (e.g. Ballard Power’s Mark 902 fuel cell module in a transit bus application). Part of their appeal is also due to their low operating temperatures, ease of start-up, ability to work in any orientation, and lack of corrosive fluids. A final advantage is that the thinness of the membrane electrode assembly (MEA) and planar architecture result in a compact fuel cell suitable for use in portable applications [1].
PEM fuel cells are not without their disadvantages. High cost, due in part to the expensive platinum catalyst and proton exchange membrane, is preventing their commercial viability. Fuel storage has also proven to be a challenge. Hydrogen, a primary fuel candidate, is not yet widely available and its storage systems have low gravimetric and volumetric storage densities. Additional challenges to be overcome include water management, limited durability, poor tolerance to fuel contamination, and difficulty starting-up under diverse operational conditions (e.g., sub-zero temperatures) [2]. Detailed descriptions of the components and processes found in a PEM fuel cell can be found in textbooks such as [1-4].

The research focus of this thesis is the water transport in membranes within the context of PEM fuel cell applications. Specifically, the characterization of membrane humidifiers for cathode reactant humidification was considered. Reactant humidification subsystems are among the most expensive components in the balance of plant, and in addition can be a key performance enhancer. Technological improvements to reactant humidification will have a beneficial impact on the overall system power density and cost.

The remainder of this introductory chapter covers the pertinent background information and summarizes related research. First, the need for reactant humidification is explained, followed by a description of the various humidification strategies. Next, a review of moisture transport in membranes is presented followed by a discussion on humidification metrics. Finally, the specific objectives and role of the current project in the larger framework of research is presented.
1.1. Water management

Several of the technological challenges surrounding PEM fuel cells are directly or indirectly related to water management. The solid polymer electrolyte must remain adequately hydrated to efficiently conduct protons. A variation of relative humidity from 85 to 35% causes a full order of magnitude reduction of the protons conductivity of Nafion from 0.09 to 0.009 Scm\(^{-1}\) \[5\]. At the other extreme, too much water will flood the catalyst layers and reaction sites, increasing mass transport losses. The resulting limited operational envelope as judged by cathode exhaust relative humidity is conceptually depicted in Figure 1.1. A delicate balance must be struck when managing the water fluxes in a fuel cell, and many aspects must be considered and understood to properly maintain this balance.

Figure 1.1. Limited operational envelope of a PEM fuel cell. (Modified from [1])
1.1.1. Water flux sources

In an operating PEM fuel cell, there are two types of water sources and two important water transport mechanisms across the membrane. The sources are the water produced by the oxygen reduction reaction at the cathode and the water carried into the cell by the reactant streams. In addition to affecting the flux of water entering the cell, the humidity of the reactants influences the drying effect of the gas streams.

The two types of water transport in the cell are back diffusion and electro-osmotic drag (EOD). Due to the water production at the cathode, a concentration gradient is established that moves water to the anode. The term back diffusion is used loosely here, because other transport mechanisms have been used to quantify the same flux. In the case of a fully humidified or flooded membrane where there is no concentration gradient, a pressure differential between anode and cathode can result in convection driven transport. This topic is expounded in Section 1.3 “Moisture transport in membranes”. The second type of water transport, EOD, occurs because water is a polar molecule and there is an electrostatic force of attraction to charged ions. The migration of protons from anode to cathode in the membrane consequently ‘drags’ a number of water molecules with it.

![Figure 1.2. Back diffusion and EOD water transport mechanisms in a PEMFC](image-url)
1.1.2. Need for reactant humidification

The water produced internally by the oxidant reduction reaction is generally not enough to ensure the membrane is sufficiently hydrated everywhere in the cell. The drying effect of the reactant streams removes this product water from the GDL and leaves the membrane dry, especially at the beginning of the flow field channels. To compound the problem, it is desirable to operate the cell at higher temperatures in order to minimize activation losses, but this drying effect becomes more pronounced at higher temperatures due to the exponentially increasing nature of the saturation vapour pressure curve.

Reactant humidification is necessary to ensure the entire membrane area is well-humidified. A more humidified membrane has higher protonic conductivity and longer lifetime.

1.2. Existing humidification schemes

Water management in PEM fuel cells is currently performed by either attempting to retain product water or humidifying one or both reactants to ensure the membrane is well-humidified. Removal of excess water to prevent flooding is controlled by adjusting the humidity content, pressure, and temperature in the flow channels [6].

For anode humidification, excess hydrogen exits the cell with a high humidity due to the back diffusion of water from the cathode. A hydrogen recirculation pump, which is in place for fuel economy reasons, returns this moist hydrogen to the inlet stream where it partially humidifies the dry inlet hydrogen.

Although it is possible to humidify only the anode reactant, including cathode humidification yields higher performance [7]. Cathode humidification is the focus of this review. Figure 1.3 shows conceptually how a cathode humidifier fits into the PEM fuel
cell system. A blower (or compressor in high pressure applications) supplies a dry air stream (location 1) which passes through the humidification device before reaching the cathode inlet (2). The stream usually leaves the fuel cell cathode fully saturated (3) and is vented as exhaust. In a recuperative type humidifier such as enthalpy wheels or membrane humidifiers (explained below), the moisture from the exhaust stream is recycled and passed back to the inlet stream (5).

![Figure 1.3. Conceptual balance of plant diagram](image)

A variety of humidification schemes have been attempted, broadly categorized as self humidifying, internal, or external.

### 1.2.1. Self humidification

With proper material selection in the gas diffusion layer (GDL), a system can be designed that retains product water close to the membrane and therefore does not need reactant humidification [7-14]. Watanabe and co-workers have reported on self-humidified PEMFCs using a very thin membrane impregnated with particles of SiO$_2$, TiO$_2$, and Pt [8]. The oxides are highly hygroscopic and increase water retention. The noble catalyst enhances water production from H$_2$(g) and O$_2$(g) that diffuse through the thin
membrane and react internally. These authors maintain that the parasitic fuel losses are justified by the improved performance of the ionic conductor.

Self-humidification greatly reduces BOP complexity but cell performance is less than what could be achieved with extra humidification. In higher power applications (>5kW) or medium-to-high temperatures (>60°C), the benefit of reduced system complexity becomes marginalized by the larger and heavier system size (a result of low gravimetric and volumetric power density). Also, the effects on membrane longevity and the MEA response to sudden changes in current density are not clear.

1.2.2. Internal humidification

Internal humidification usually incorporates a dedicated humidification module located upstream from the electrochemically active section in a PEM fuel cell stack. As a result, a fraction of the stack volume is devoted to reactant conditioning [15-17]. In conventional designs, highly purified water is used to condition the reactants, and serve as a heat exchange fluid to maintain the desired cell operating temperature. The water must be de-ionised to avoid contamination of the membranes, and to minimize the possibility of electrical short-circuits (additional filtering and purification hardware is required). In typical systems, a single coolant loop is concurrently pumped through the humidification module and through cooling elements placed at evenly spaced locations within the stack. The internal humidification mechanisms vary, but a few illustrative approaches will be described.

- **Internal membrane humidifiers:** Relies on a water-permeable membrane separating two compartments upstream of the electrochemically active section. Liquid water flowing through channels in one compartment diffuses across the
permeable membrane and is evaporated upon exposure to the flowing reactant gases. The rate of evaporation is controlled by varying the temperature, pressure, and flow rate of liquid water and dry reactants. Related research can be found in [18] and [19].

- **Internal direct liquid water injection**: Liquid water is injected via porous, interdigitated flow field plates [20, 21]. With these flow field plates, the reactant inlets and outlets are not connected directly, and excess gas must diffuse through the GDL and underneath the lands of the plates. Fluid head is lost by forcing the gases through the porous layers, resulting in large pressure drops and lower efficiencies. However, this method could prove beneficial for applications using enriched oxidant streams and microscopic fuel cell systems that do not rely on traditional fuel storage or delivery methods.

- **Wicks and Sponges**: Water absorbing sponges [22] and porous fiber wicks [23] have also been proposed as internal water management schemes. The sponges sit between the flow field plate and GDL. A wicking action absorbs liquid water from near the reactant outlet and moves the water through the sponge towards the reactant inlet, where it is used to humidify the incoming dry gas. Similarly, the porous fiber wicks are embedded into the membrane and wick water from an external reservoir to dry areas of the membrane.

### 1.2.3. External humidification

Several strategies exist that remove the integrated humidification device from within the stack to a centralized location outside of the stack. This simplifies the stack construction and provides a modular design.
• **Saturation bubblers:** A porous nozzle at the bottom of a sealed water reservoir disperses the gases into small bubbles—enabling them to become saturated with water vapour. The temperature and pressure in the reservoir control the humidification level. This humidification approach is impractical in portable or mobile applications, but could provide a simple solution for residential and stationary applications.

• **Direct-injection or spraying:** An atomizer is used to add a known amount of water externally. This technique provides very good control of the humidification levels, and can enhance the thermal management of larger stacks (e.g., by providing additional evaporative cooling for the compressed reactants) [24, 25]. The system complexity and large number of components increases the balance of plant size and cost.

• **Membrane humidifiers:** Employ a water-permeable membrane to transfer moisture from cathode exhaust stream to cathode inlet stream. These recuperative devices are simple and cost effective, but are limited in effectiveness and have a noticeable pressure drop. Typical architectures are shell-and-tube or plate-and-frame, both derived from heat exchanger technology. These are the focus of this work and will be explained in more detail in the coming chapters. Known commercial vendors are Perma Pure LLC, EnerFuel Inc (both shell-and-tube), and dPoint Technologies (plate-and-frame).

• **Enthalpy wheel:** Involves rotating a desiccant-coated porous cylinder which adsorbs moisture while exposed to the wet stream and desorbs it while exposed to the dry stream. These are high efficiency enthalpy exchangers, but involve
numerous parts, have substantial parasitic load to operate the rotary motor, and are relatively expensive. The only known commercial product is Emprise Corporation’s Humidicore™.

1.2.4. Similar technologies: Energy recovery ventilators

In hot climates, energy recovery ventilators (ERV’s) are used to condition the air entering a building. These devices are similar to membrane humidifiers and enthalpy wheels; the only difference is that they are being used in reverse. Hot, humid air from outside is passed through the ERV to transfer its heat and humidity to the cooler, drier air leaving the building as exhaust. Every unit of energy recovered with these devices is at least one less unit that must be consumed by the air conditioning unit. In hot and humid cities like Hong Kong, China, an ERV can reduce air conditioning loads by over 50%, compared to 10% when only using a heat recovery ventilator (which only exchanges sensible heat) [26]. Similar moisture-transferring devices can also be found in air drying applications.

Zhang and Niu from China have published numerous studies related to membrane-based ERVs for air conditioning in buildings [27-34]. In 2002, they developed and applied the heat exchanger $\varepsilon$-NTU (Effectiveness-Number of Transfer Units) method of analysis to heat and humidity exchangers [34]. Simonson and Besant had done the same for enthalpy wheels in 1999 [35, 36], also in the context of ERV’s. The $\varepsilon$-NTU method, however, is limited to single phase conditions. In a membrane humidifier for PEMFC application, the saturated wet-side stream will cool and condense to cause two phase flow over one side of the membrane.
1.3. **Moisture transport in membranes**

There is no common method to model water transport for all membranes. The manner in which thermodynamic potential driving force is represented depends on the type of membrane and operating conditions. Examples of parameters used to represent the driving gradient include mass fraction, absolute humidity, density, concentration, partial pressure, total pressure, etc. While often these properties can be calculated from each other, the modeling choice affects the magnitude of coefficients used in governing equations. The ensuing discussion of modeling techniques is limited to steady state conditions and because the channel lengths in humidifiers (>100mm) are much larger than membrane thickness (0.050 – 0.2 mm), the transport equations are approximated to be one-dimensional across the membrane. First, a brief discussion on suitable membranes is presented.

1.3.1. **Membrane types**

Several volumes have been written (e.g.,[37, 38]) on the structure and applications of various membrane types and detailed discussion is beyond the scope of this work. Target membranes for fuel cell humidifiers shall exhibit very high water to air selectivity. A few examples of such membranes are polyethersulphone, cellulose triacetate, silica-impregnated polyethylene, and polyvinylchloride membranes. These membranes are 460 to 30,000 times more permeable to water than to air [39].

The sulfonated polytetrafluoroethylene (PTFE) membrane Nafion, made by DuPont, was one of the membranes used in this work. Although Nafion was developed and is primarily used as an electrolyte, its ability to selectively transport water while resisting oxygen and nitrogen crossover also makes it a prime candidate for the moisture transport.
exchange media in membrane humidifiers. It is the membrane of choice of Perma Pure Inc. in their shell and tube humidifiers. Nafion has a wide spectrum of pores ranging from 1 to 100 nm, with an average of 2 nm [40]. For further reading on Nafion, the reader is referred to the 2004 comprehensive review "State of Understanding of Nafion" by Mauritz and Moore [41].

1.3.2. Solution-Diffusion

Water transport through dense membranes is commonly assumed to follow an absorption, diffusion, and desorption process. The appropriate equation for steady state water flux, $J$, is Fick's first law.

$$J_{H_2O}^{\text{diff}} = -D_{\xi} \frac{d\xi}{dy} \quad (1.1)$$

where $\xi$ is a dummy variable representing the chosen driving gradient parameter (e.g. chemical potential, density, concentration, mass fraction etc), and $D_{\xi}$ is the effective diffusion coefficient, or diffusivity, with respect to that driving force. In Nafion-related literature, it is most common to use a concentration [mol m$^{-3}$] gradient normalized per sulfonate site. The equivalent parameter is referred to as the water content, $\lambda$ [mol H$_2$O (mol SO$_3^-$)$^{-1}$].

In this case, Eqn.(1.1) becomes: [42, 43]

$$J_{H_2O}^{\text{diff}} = -a D_{\lambda} \frac{d\lambda}{dy} \quad (1.2)$$

where $a$ is the concentration of sulfonate sites in a dry membrane, $a = \rho_{\text{mem,dry}} / M_{\text{mem,dry}}$. Springer [44] is credited as one of the first to use this diffusion model for water transport in PEMFC literature.
1.3.2.1 Sorption Curves

Any hygroscopic material will achieve a moisture content dependent on the temperature and humidity of its surroundings. Generally, this amount of moisture is characterized as a function of relative humidity, and plotted as a sorption curve. The sorption curve starts at zero for zero humidity for every material, and at low temperatures (e.g., 15 to 50°C), the sorption curve is generally independent of temperature [45].

The water uptake capacity, $u$, of the membrane is defined as the amount of water absorbed per unit dry weight of the membrane [46]. For use with ion exchange membranes such as Nafion, the water content, $\lambda$, is defined as the number of water molecules per cationic site. The equivalent weight (EW) is defined as:

$$EW = \frac{\text{weight of dry polymer sample [g]}}{\text{number of acid groups [mol]}}$$  \hspace{1cm} (1.3)

The ion exchange capacity is the inverse of EW.

Theoretical equations to interpret the shapes of sorption curves include the Brunauer-Emmett-Teller (BET) and Guggenheim-Anderson-de Boer (GAB) equations [47]. The Flory-Huggins model is a more thermodynamically rigorous technique to derive a sorption curve for ion exchange membranes used by Futerko and Hsing [48].

Often it is more practical to use an empirical fitted relationship to describe the sorption curve. If the sorption shape is sigmoidal, a 3rd degree polynomial will suffice [49, 50]. These sorption curves can be obtained by weighing a sample in controlled chamber with known relative humidity. Once the sample mass achieves a steady state, the net mass of absorbed water can be calculated and, if desired, normalized to the dry membrane weight. Generally, a hysteresis in the sorption curve will occur as a result of whether the sample has absorbed or desorbed moisture to reach the equilibrium...
condition, with the former yielding lower moisture content values and the latter higher moisture content values.

The water content for Nafion is generally calculated as a function of relative humidity from equilibrium sorption curves obtained from Zawodzinski [50] at 303 K or Hinatsu [49] at 353 K. It has been observed that liquid-equilibrated Nafion has a higher water uptake capacity than when equilibrated with saturated vapour which has the same activity value (so called Schroeder's Paradox)[51]. The water content of liquid equilibrated membrane does not vary significantly with temperature with a typical water content value of 22 [50].

Alternatively, the following two parameter relationship can be used to approximate the sorption curve for several types of hygroscopic materials [33]:

\[ u = \frac{u_{\text{max}}}{1 - C + C / \phi} \]  

(1.4)

where \( u_{\text{max}} \) is the maximum water uptake capacity and \( C \) determines the shape of the sorption curve. For molecular sieves, \( C<1 \); for silica gel, \( C=1 \); and for polymers, \( C>1 \).

1.3.3. Permeability

The permeability method, or hydraulic method, is an application of the Darcy's law fluid flow correlation. Though Darcy's law is an experimental relationship, it can be derived from the governing conservation of momentum (Navier-Stokes) equation and is applicable in a wide range of problems where viscous laminar transport through porous media is involved. Hence, it is commonly applied to porous membranes, or in special cases non-porous membranes (i.e., when they are liquid-equilibrated and liquid water has formed interconnected channels through the membrane).
\[ J_{perm}^{H_2O} = -\frac{k_p \, dP}{\mu \, dy} \]  \hspace{1cm} (1.5)

\[ J_{perm}^{H_2O} = \frac{J_{perm}^{\ast}}{V_{H_2O}} \]  \hspace{1cm} (1.6)

where \( \mu \) is the fluid viscosity, \( k_p \) is the permeability, \( P \) is total pressure, and \( J_{perm}^{\ast} \), the discharge velocity, is in volumetric units \([m^3 s^{-1} m^{-2} \rightarrow ms^{-1}]\) as opposed to \([mol s^{-1} m^2]\).

The partial molar volume of water, \( V_{H_2O} \), can be used to convert the discharge velocity into a molar flux via Eqn.(1.6). In multiphase flow, the discharge flux of each phase \( i \) can be determined using phase permeability, \( k_{pi} \), phase viscosity, \( \mu_i \), and partial pressure, \( P_i \).

The hydraulic models within a PEMFC context started with the work of Bernardi and Verbrugge [52] and Verbrugge and Hill [53].

A permeation coefficient, \( \psi \), is the product of the diffusivity and solubility. This allows Henry’s law of solubility and Fick’s law of diffusion to be combined into one equation:

\[ J_{i}^{HF} = -\psi_i \frac{dP_i}{dy} \]  \hspace{1cm} (1.7)

This equation is usually used for permeation of gases into the membrane and is more useful for reactant gas crossover calculation than moisture transfer. As a dilute-solution transport equation, it is only valid when gases are in very low concentrations and interact only with the solvent (i.e., they do not alter the chemical potential of any species in the membrane) [54].

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1.3.4. Concentrated solution

Species transport may also be described according to concentrated solution theory [54, 55]. In this case, the driving force is the chemical potential gradient:

$$\nabla \mu_{H_2O} = RT \ln \nabla \tilde{a}_{H_2O} + \nabla \tilde{V}_{H_2O} \nabla P$$

(1.8)

where $\mu$ is the chemical potential, $\tilde{a}$ is the chemical activity, $T$ is temperature, and $R$ is the gas constant. This method bridges the gap between diffusion and hydraulic models in that it is applicable in both the vapour and liquid phases. In the liquid phase, there is no activity gradient and it reduces to a pressure driven process just as in the hydraulic model.

1.3.5. Thermo-diffusion

The presence of temperature gradients can complicate moisture transport analysis. Heat flux in a material has been observed to affect moisture transport, a phenomenon named thermo-diffusion, or the Soret effect. In some arrangements the molecular or particle flux is in the same direction as the heat flux [56], whereas in other situations the material flux is opposite the heat flux. Studies have shown that thermo-osmotic flux in cation exchange membranes such as Nafion occurs opposite the temperature gradient, that is, from cold to hot regions [57, 58]. However, the magnitude of this flux is small compared to other flux terms (e.g., diffusion caused by concentration gradients).

The mechanism behind thermo-diffusion is not well understood, but it is suspected to be caused by gradients in solvent entropy [57, 59]. Two possible explanations of the mechanism that would explain transport in the same direction as the temperature gradient are shown in Figure 1.4 and described as follows:
1. Due to the effect of temperature on surface tension, a gradient in temperature results in a gradient in surface tension, $\sigma$, of the same direction which enables droplets to flow.

2. Higher temperatures will expand trapped air bubbles and result in an increase of air pressure, which translates into pushing the slugs of water in the direction of lower temperature.

![Figure 1.4. Temperature gradients causing a) surface tension and b) capillary pressure driven moisture transport in capillaries adapted from [56]](image)

1.3.6. Surface mass transfer

A commonly adopted engineering postulate is that the mass flux across the interface is proportional to the difference between the driving parameter (e.g., density, concentration, etc) evaluated at the surface and the bulk fluid adjacent to the surface.

$$ J = h_m (\xi - \xi_w) $$

(1.9)

where the constant of proportionality, $h_m$, is called either the surface mass transfer conductance, adsorption/desorption coefficient, or convective mass transfer coefficient. In the context of sorption, the interface and bulk fluid driving force parameters, $\xi$,
correspond to the non-equilibrium and equilibrium sorbed value of water content, respectively, and the mass transfer conductance is denoted by $\gamma$.

### 1.4. Humidification metrics

A desirable recuperative type cathode humidifier has:

- a high moisture transfer effectiveness,
- low device pressure drop,
- small size,
- low cost,
- high lifetime (durability),
- low weight,
- minimal air crossover (whether wet or dry), and
- high maximum operating temperature and pressure.

The moisture transfer effectiveness and, to a lesser extent, pressure drop and size, are considered in this work. Several metrics to measure a humidifier's moisture-transferring ability have been used in the past. In this section, several commonly used humidity indicators are defined and then advantages and disadvantages of their use as humidifier performance metrics are discussed.

#### 1.4.1. Definition of terms

In a multi-component mixture, the terms gas and vapour refer to the non-condensable and condensable component, respectively. In this work, vapour always refers to water. The wet-side, donor side, and feed side are synonyms for the cathode
exhaust side of the membrane, which is more humid. The dry-side, receiver side, permeate, and sweep all refer to the stream that is being humidified.

The **saturation vapour pressure**, $P_{H_2O}^{sat}$, is the partial pressure of water present when in equilibrium with a flat liquid water surface. There are numerous empirical relationships to quantify this as a function of temperature, including the Goff-Gratch, Hyland and Wexler, and Magnus Teten equations to list a few. The Hyland and Wexler equation was used throughout this work and is written below:

$$\ln P_{H_2O}^{sat} = \frac{C_1}{T} + C_2 + C_3T + C_4T^2 + C_5T^3 + C_6 \ln(T)$$

(1.10)

where $T$ is in Kelvin and $P_{H_2O}^{sat}$ is in Pa. The constant coefficients are listed in Table 1.1.

The deviation between most empirical equations is $<1.0\%$ for $-40 < T < 100^\circ$C.

Table 1.1. Coefficients for the Hyland and Wexler equation. Units for each coefficient change to give a pure number on the right side of Eqn.(1.10).

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>$-0.5802206 \times 10^4$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$0.13914993 \times 10^1$</td>
</tr>
<tr>
<td>$C_3$</td>
<td>$-0.48640239 \times 10^{-1}$</td>
</tr>
<tr>
<td>$C_4$</td>
<td>$0.41764768 \times 10^{-4}$</td>
</tr>
<tr>
<td>$C_5$</td>
<td>$-0.14452093 \times 10^{-7}$</td>
</tr>
<tr>
<td>$C_6$</td>
<td>$0.65459673 \times 10^1$</td>
</tr>
</tbody>
</table>

In this work, dew points below $0^\circ$C refer to the temperature at which the parcel of moist air would be saturated above super cooled liquid water. This is distinct from the frost point, which correlates moisture content to the saturation pressure above a frozen surface (i.e., ice). In all cases, however, negative dew point values indicate very low water concentrations.

### 1.4.1.1 Measures of humidity

The **relative humidity**, $\phi$, is the ratio of mole fraction of water vapour to the mole fraction that would be present at saturation under the same temperature. Assuming an ideal gas, it is also the ratio of vapour pressure to saturation vapour pressure.
CHAPTER 1

\[
\phi = \frac{n_{H_2O}}{n_{H_2O}^{sat}} = \frac{P_{H_2O}}{P_{H_2O}^{sat}}
\]  

(1.11)

Specific humidity, \( \zeta \), is the ratio of mass of water to the total mass of the sample (air plus water):

\[
\zeta = \frac{m_{H_2O}}{m_{total}}
\]  

(1.12)

The humidity ratio, \( \omega \), (also commonly referred to as the mixing ratio or moisture content) is the mass ratio of water to dry air:

\[
\omega = \frac{m_{H_2O}}{m_{dry\ air}}
\]  

(1.13)

In chemical engineering, the humidity ratio is referred to as absolute humidity [45]. However, in Heating, Ventilation, and Air Conditioning (HVAC) engineering, the absolute humidity is the ratio of mass of water vapour to total volume of the sample [60].

The degree of saturation (or percentage absolute humidity in chemical engineering) is the ratio of humidity ratio to humidity ratio at saturation at the same temperature and pressure.

The thermodynamic wet-bulb temperature is the temperature at which water evaporating into air can adiabatically and simultaneously bring the air to saturation at the same pressure. By definition, it satisfies a conservation of enthalpy equation for the moist air:

\[
\text{(initial enthalpy) + (added energy to bring vapour to saturation) = (enthalpy of saturated air)}
\]

\[
h + (\omega_s^{sat} - \omega)h_w^{sat} = h_s^{sat}
\]  

(1.14)

where \( \omega_s^{sat} \), \( h_w^{sat} \), and \( h_s^{sat} \) are the saturation humidity ratio, specific enthalpy of water, and the specific enthalpy of the mixture at saturation, all evaluated at the wet bulb.
temperature, $T_{wb}$ [60]. Note that this is the thermodynamic definition of wet-bulb temperature, and slight corrections to the measured wet-bulb temperature are necessary, depending on the physical device used and temperature.

1.4.2. **Quantifying humidifier performance**

Before critically analyzing various humidifier performance metrics that have been identified, it should be clarified that there is no single metric that is universally more appropriate. The choice of performance metric often depends on whether one is comparing different humidifiers at identical conditions or comparing the same humidifier at different conditions. Furthermore, it also depends on whether the variable of interest is the absolute amount of water in the flow [kg s$^{-1}$ or mol s$^{-1}$] or a relative ratio of water to gas.

1.4.2.1 **Outlet humidity measures**

The dew point, relative humidity, specific humidity, humidity ratio, degree of saturation, or wet bulb temperature of the dry-side outlet stream provide relative measures of the humidifier performance. The term relative is used because they offer no indication of the absolute amount of water carried in the stream (i.e., they do not consider flow rates). For example, an outlet relative humidity must be reported with temperature, pressure, and air flow rate to quantify the mass flow rate of water. Furthermore, there is no indication of the maximum value of dew point or relative humidity that could be attained under the operating conditions. For example, an outlet dew point of 30°C is poor if the wet side inlet, $T_{d,wi}$, is 70°C; but is much better if $T_{d,wi}=35$°C. Outlet humidity measures are suitable performance metrics only if the absolute amount of water is not of primary interest.
1.4.2.2 Dew point approach temperature

The **dew point approach temperature**, DPAT, is the difference in dew point between the wet-side inlet (WI—location 3 in Figure 1.3) and dry-side outlet (DO—location 2 in Figure 1.3). This measure provides an indication of how close the outlet dew point was to the maximum that could have been achieved, similar to an approach temperature or pinch temperature in heat exchanger analysis. A lower DPAT indicates better performance in humidifiers.

When comparing the same or different humidifiers at conditions with constant wet side inlet dew point, the DPAT provides a practical evaluation of the performance. To exemplify an area of caution when using DPAT, consider the case where a non-perfect humidifier is run with \( T_{d,wi}=40^\circ C \) and yields a DPAT of 5°C. If it is then run under the same flows with \( T_{d,wi}=80^\circ C \) and yields a DPAT of 30°C, the DPAT performance as measured by the DPAT is worse, even though it has in fact transferred more water. Also, DPAT is a skewed scale due to the non-linear nature of the saturation vapour pressure curve; a 3°C DPAT is not twice as good as a 6°C DPAT.

1.4.2.3 Gravimetric measures

The total water transfer is calculated as the difference in amount of water between inlet and outlet in either stream. The average water flux is the total water transfer normalized by total membrane area:

\[
\bar{J}_{\text{mem, H}_2\text{O}} = \frac{\dot{m}_{H_2O, DO} - \dot{m}_{H_2O, DI}}{A}
\]  

(1.15)

where \( \dot{m}_{H_2O, DO} \) and \( \dot{m}_{H_2O, DI} \) are the mass flow rates of water at the dry-side outlet and dry-side inlet, respectively. Either the total water transfer or average water flux are
suitable metrics when comparing the same humidifier at different operating conditions. If comparing different humidifiers, the average water flux indicates which humidifier is performing more efficiently (on a basis of available membrane area) but only the total water transfer is suitable if the objective is to determine which is better in absolute terms. Note, however, that these metrics have no indication of the maximum amount that could have been transferred.

1.4.2.4 Effectiveness measures

Several 1st Law effectiveness metrics have been identified that normalize humidifier performance on a scale from 0 to 1. The sensible, moisture (or latent), and total (or enthalpy) effectiveness relate the effectiveness of sensible heat, moisture, and total enthalpy transfer, respectively [61].

\[
\varepsilon = \frac{\dot{m}_{air,DI}(\xi_{DO} - \xi_{DI})}{(\dot{m}_{air})_{min}(\xi_{WI} - \xi_{DL})}
\] (1.16)

where the dummy variable, \(\xi\), is either the temperature (\(T\)), humidity ratio (\(\omega\)), or enthalpy (\(h\)) depending on whether the sensible effectiveness (SE), latent effectiveness (LE), or enthalpy effectiveness (EE) is being calculated. Note that a constant specific heat capacity for the mixture is assumed in this expression for sensible effectiveness.

The water recovery ratio (WRR) is defined as the ratio of the total water transferred to the dry stream to the quantity of water supplied to the humidifier via the wet stream [62].

\[
WRR = \frac{\dot{m}_{H2O,DO} - \dot{m}_{H2O,DI}}{\dot{m}_{H2O,WI}}
\] (1.17)
CHAPTER 1

After inspection, it was determined that WRR is a special case of LE that is valid when the air flow rates on wet and dry sides are balanced (i.e., equal) and the water entering the dry-side inlet (DI—location 1 in Figure 1.3) is negligible. The SE is a measure of heat transfer; not mass transfer, and therefore is of limited use in humidifier design. The LE and EE are useful measures and correct the WRR in the case of partially humidified dry side inlet conditions or unbalanced flows. EE can be misleading from a moisture transfer point of view if the sensible heat exchange makes up the bulk of the total enthalpy exchange. The LE is the better of the four to isolate moisture-transferring effectiveness. Effectiveness terms give an immediate indication of how well the humidifier is performing under the conditions, but they convey neither the absolute amount of water nor a measure of humidity of the outlet stream.

Finally, a deficiency of all of these effectiveness parameters is that they only consider mass and energy conservation. Second law considerations such as irreversibilities due to heat transfer, phase changes, absorption/desorption, and friction losses are not accounted for so a thermodynamic maximum performance is difficult to predict.

1.5. Overview of thesis

An overview of the thesis structure is presented in Figure 1.5. The second chapter develops a thermodynamic model of a plate and frame membrane humidifier. The third chapter presents an experimental study on the effect of flow rate and channel location on moisture transfer in a single channel counter flow membrane humidifier. A single channel provides the ability to impose known hydrodynamic and thermal conditions. Next, this data was compared against the predictive thermodynamic model using existing
diffusion correlations from literature (Chapter 4). Finally, the same model was extended to consider an existing commercial humidifier in the fifth chapter. The concluding chapter summarizes key contributions to the field and identifies areas where future work is needed.

**Research Problem:** There are no identified thermodynamically-grounded tools to aid the development of membrane fuel cell humidifiers

**Hypothesis:** Moisture flux can be predicted with a nor-isothermal model of two parallel 1D channels encompassing techniques from other related technologies

| Ch 1 | Introduction |
| Ch 2 | Model description |
| Ch 3 | Experimental study |
| Ch 4 | Single channel Nafion humidifier under isothermal conditions |
| Ch 5 | A 5kW humidifier with unknown membrane under nor-isothermal conditions |
| Ch 6 | Conclusions |

**Specific Objectives Addressed**

1. Develop a thermodynamically-grounded tool to aid in the development of membrane fuel cell humidifiers
2. Experimentally collect information on the effect of flow rate and channel location on water transfer
3. Validate model predictions for effect of flow rate and channel location
4. Evaluate and compare diffusion coefficient correlations from literature
5. Apply model to application-relevant geometry and conditions
6. Evaluate suitability of modeling techniques from enthalpy exchangers in different applications (namely ERV's)

**Figure 1.5. Thesis overview**

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Table 1.2 lists factors that affect moisture transport across the membrane. This thesis considers only diffusion transport methods and hence does not consider convection-driven transport (i.e., permeation). Some of the factors, such as flow rates and temperature, are considered more than others.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>• channel height a</td>
<td>Affects heat and mass transfer coefficients, and fluid velocity via cross sectional area.</td>
</tr>
<tr>
<td>• channel width a</td>
<td>Affects heat and mass transfer coefficients, and fluid velocity via cross sectional area.</td>
</tr>
<tr>
<td>• channel length a</td>
<td>Affects useable membrane area.</td>
</tr>
<tr>
<td>• number of channels a</td>
<td>Affects flow rate per channel.</td>
</tr>
<tr>
<td>• membrane structure</td>
<td>Affects whether transport is convective (pressure-driven) or diffusive (concentration-driven).</td>
</tr>
<tr>
<td>• membrane diffusivity a</td>
<td>Affects diffusive mass transfer resistance.</td>
</tr>
<tr>
<td>• membrane permeability</td>
<td>Affects convective mass transfer resistance.</td>
</tr>
<tr>
<td>• membrane thickness a</td>
<td>Affects mass transfer resistance.</td>
</tr>
<tr>
<td>• temperature or temperature difference a</td>
<td>Affects relative humidity, thermo-diffusion, and condensation rate. Also affects membrane and fluid properties.</td>
</tr>
<tr>
<td>• pressure b or pressure difference</td>
<td>Affects convective driving gradient. Also affects membrane and fluid properties.</td>
</tr>
<tr>
<td>• relative humidity or relative humidity difference a</td>
<td>Affects water uptake and hence diffusion driving gradient.</td>
</tr>
<tr>
<td>• wet side flow rate or velocity a</td>
<td>Affects residence time.</td>
</tr>
<tr>
<td>• dry side flow rate or velocity a</td>
<td>Affects residence time.</td>
</tr>
<tr>
<td>• mixture composition (nitrogen, oxygen, water) ac</td>
<td>Affects fluid properties.</td>
</tr>
<tr>
<td>• two phase vs. single phase flow ad</td>
<td>Consequence of other conditions, but may cause a non-continuous change in transport ability.</td>
</tr>
<tr>
<td>• turbulent vs. laminar</td>
<td>Consequence of other conditions, but may cause a non-continuous change in transport ability.</td>
</tr>
</tbody>
</table>

a – Considered in this thesis.  
b – Capability for non-atmospheric pressures was built in to the model but never used. Not all fluid properties were made dependent on pressure.  
c – Oxygen-depleted air on wet side was not considered.  
d – Included for thermal calculations, but not for membrane moisture transfer.

Figure 1.6 shows where the area of PEMFC membrane humidifiers falls within the broader framework of literature. While related areas such as polymer membrane-based diffusion, PEMFC water management, and compact heat exchangers have been
studied intensively for decades, the specific application of membrane humidifiers for PEMFC applications has only recently begun to see more research.

Chen and Peng (2005)[63] are the only known group to model a PEMFC gas-to-gas membrane humidifier. They constructed a dynamic Simulink model to study the transient response of the humidifiers from a control systems context. As mentioned earlier, other pertinent models were found in ERV technology literature but these have not been applied to conditions relevant to PEMFC membrane humidifiers [33, 34]. In PEMFC literature (for studies within the actual cell), a few models have considered the significance of surface mass transfer effects for hydrophilic membranes [43, 63-65]. The work of Ge et al [43] focused specifically on characterizing surface absorption and
desorption coefficients for Nafion. Similar effects are expected to be significant in membrane humidifiers.

Most experimental efforts to examine PEMFC membrane humidifiers involve condensing the outlet stream to obtain a time and space-averaged flux value for moisture transport across the membrane [66]. These flux values have been tabulated against geometric parameters such as the ratio of residence time (e.g., the residence time that water molecules spend in the flow channel) to diffusion time (e.g., the time required to diffuse through air over the depth of the channel) [66, 67]. This ratio has been used successfully to specify the channel sizing for planar humidifiers. Other experimental work was provided by Park et al. in 2005 [19], who reported data for liquid water-to-gas internal humidification using multiple membranes.

To summarize, the current work identifies relevant elements of PEMFC and ERV research and applies them to PEMFC membrane humidifiers with the goal of developing a thermodynamically-grounded technique to predict moisture transfer performance. The attributes, relevance, and limitations of the most related literature are listed in Table 1.3.
Table 1.3. Summary of most relevant literature, including Niu and Zhang [33], Zhang and Niu [34], Ge et al [43], Park et al [19], and Huizing [66]

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>PEMFC reactant humidification</th>
<th>Membrane (d) humidifiers</th>
<th>Surface mass transfer Model</th>
<th>Experimental</th>
<th>Relevance</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niu and Zhang</td>
<td>2001</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>Discussed moisture transfer resistance for membranes</td>
<td>Crossflow exchanger, ERV conditions only (single phase)</td>
</tr>
<tr>
<td>Zhang and Niu</td>
<td>2002</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>Developed NTU method for moisture transfer</td>
<td>Limited validation, ERV conditions only (single phase)</td>
</tr>
<tr>
<td>Ge et al</td>
<td>2005</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>Quantified surface sorption coefficients</td>
<td>Isothermal conditions, short channel length</td>
</tr>
<tr>
<td>Park et al</td>
<td>2005</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>Performance testing with variable flow rate and temperature</td>
<td>For internal membrane humidification, liquid to gas only</td>
</tr>
<tr>
<td>Chen and Peng</td>
<td>2005</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>Transient thermodynamic model of external membrane humidifier</td>
<td>No experimental validation, assumes log mean temperature difference correlations</td>
</tr>
<tr>
<td>Huizing</td>
<td>2007</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>Recent study of design and membrane selection of PEMFC gas-to-gas membrane humidifiers</td>
<td>Experimental work only, moisture transfer prediction based on empirical coefficient</td>
</tr>
<tr>
<td>Cave</td>
<td>2007</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>Only Chen has proposed a similar thermodynamic model for PEMFC gas-to-gas membrane humidifiers. The current work is the first to consider ERV modeling techniques and membrane surface mass transfer resistances. Only Huizing has experimentally studied PEMFC gas-to-gas membrane humidifiers. The current work is the first to consider unbalanced flow rates and channel location effects.</td>
<td>(Relevant chapter number in parentheses)</td>
</tr>
</tbody>
</table>

29
2. Model description

2.1. Chapter overview

A thermodynamic model was developed and implemented with the objective of predicting moisture transfer performance in a plate and frame membrane fuel cell humidifier. The model is presented here. The ability to accurately predict moisture transfer strongly depends on the type of membrane employed as the moisture exchange media. Nafion was used in a single channel experimental study for validation and thus is given specific treatment throughout the development. A generic method to model alternative membranes is also considered, subject to the limitation that the solution-diffusion model is appropriate for the unknown membrane.
2.2. **Humidifier discretization**

A plate and frame membrane humidifier consists of a stack of membrane layers and flow-guiding plates. In a counter flow arrangement, the humid air and dry air flows in opposite directions on adjacent sides of the membrane in a channel geometry determined by the flow field plate design.

This geometry was discretized by considering two parallel 1-D channels on opposite sides of the membrane layer. Assuming equal flow sharing among all channels, the number of plates and number of channels per plate determined the amount of flow passing through each channel.

2.3. **Model description**

This model is a pseudo 2-D (two parallel 1-D channels), steady state, finite volume approach to the heat and mass transfer equations involved. The advantage to this numerical approach compared to other heat transfer analysis techniques (e.g., $\varepsilon$-NTU method) is that it provides a spatial map of the state properties and indicates where most of the heat and mass transfer are taking place. In addition, the $\varepsilon$-NTU method applied to heat and mass transfer through membranes is relatively new, has not yet been shown robust under PEMFC-relevant conditions, and has not been demonstrated for two phase flow. See Appendix A "Limitations of $\varepsilon$ -NTU method for heat and mass transfer" for more details.

Figure 2.1 shows a control volume with surface-averaged heat and mass fluxes.
2.3.1. Assumptions

1. Ideal gas law valid throughout.

2. Fully developed, laminar flow on both sides.

3. Negligible changes in kinetic and gravitational potential energies of gases.

4. Solution-diffusion moisture transport mechanism is valid and Soret thermo-diffusion effects are negligible.

5. Equal flow sharing and similar boundary conditions among all channels.

6. Vapour and fluid phases move at same velocity and homogeneously (i.e., zero-slip flow model.)

7. No reactant gas crossover.

8. Overall moisture transport is diffusion-limited (since diffusivity of water in air is much higher than diffusivity of water in membrane), unless it is specified that surface mass transfer resistances are being considered.
2.3.2. Conservation of mass

Each stream (wet-side and dry-side) is a mixture of air and water. Assuming no air crossover, the flow rate of the dry gas remains constant for both sides \( \left( \frac{d \dot{m}_{\text{air}}}{dx} = 0 \right) \).

The 1D conservation of mass equation for the dry-side (superscript \( D \)) yields:

\[
\frac{d \dot{m}_{H_2O}^D}{dx} = g \left( \dot{m}_{H_2O}^D, T^D, \dot{m}_{H_2O}^W, T^W, \dot{m}_{\text{air}}^D \right)
\]

where the superscript \( W \) refers to the adjacent cell in the wet-side stream. The function \( g \) represents the mass transfer of water across the membrane from wet-side to dry-side. This function depends on the membrane, and is expounded in Section 2.4.

Condensation is expected on the wet-side so the vapour component ODE is adjusted to account for the phase distribution:

\[
\frac{d \dot{m}_{H_2O,v}^W}{dx} = g \left( \dot{m}_{H_2O}^W, T^W, \dot{m}_{H_2O}^D, T^D, \dot{m}_{\text{air}}^W \right) \frac{d \dot{m}_{H_2O,l}^W}{dx}
\]

where the change in liquid component is given by a rate of condensation equation [24]:

\[
\frac{d \dot{m}_{H_2O,l}^W}{dx} = - \frac{k \omega d (MW_{H_2O})}{RT} (P_{H_2O} - P_{H_2O}^{sat})
\]

where \( k \) is a rate constant, \( \omega \) is channel width, \( d \) is channel depth, and \( MW_{H_2O} \) is the molecular weight of water. The rate constant \( k \) was set to 1.0 based on [24]. For typical humidifier channel geometries, it should be sufficiently high that condensation occurs very quickly at relative humidity's greater than 1.
2.3.3. Conservation of energy

It can be shown (Appendix B) that the conservation of energy applied to the control volumes on the dry and wet sides, respectively, provide the following ODE equations for channel temperatures:

$$\frac{dT^D}{dx} = \frac{U_{memb} (T^w - T^D) + U_s (T_{surr} - T^D) + \eta |h_{vap}|}{c_{p,air} m^D_{air} + c_{p,H2O} m^D_{H2O}} \frac{dm^w_{H2O}}{dx}$$  (2.4)

$$\frac{dT^w}{dx} = \frac{U_{memb} (T^D - T^w) + U_s (T_{surr} - T^w) + (1 - \eta) |h_{vap}|}{c_{p,air} m^w_{air} + c_{p,H2O} m^w_{H2O}} \frac{dm^w_{H2O}}{dx}$$  (2.5)

where $|h_{vap}|$ is the heat of vaporization, $\eta$ is fraction of heat transferred to the dry side membrane during condensation, $U_s$ and $U_{memb}$ are the series conductance of heat transfer to the surroundings and across the membrane, respectively, per unit length. Using $\eta$ was selected instead of solving a minimum 4 point, 1D thermal flux balance in the $y$-direction at every station along the $x$-axis. This is justifiable because the membrane thermal conduction resistance is negligible compared to convective heat transfer resistance, so the membrane is essentially at the same temperature on both wet and dry sides [34]. The heat released during condensation then is transferred directly to one of the two streams. Since in the cases studied here, the temperature gradient is always from wet side to dry side, $\eta$ was set to 1. The liquid water present in the wet side channel also has an effect as an extra thermal mass, included in the denominator.

The overall heat transfer coefficient across the membrane per unit length, $U_{memb}$, was defined as:
where \( w \) is the channel width, \( M \) is the number of walls transferring heat (either 1 for a single channel humidifier or 2 for a stacked plate and frame humidifier), and \( \kappa_{\text{mem}} \) are the membrane thickness and conductivity, respectively. The convective heat transfer coefficients, \( h \), were found from the Nusselt number, \( Nu \):

\[
h = \frac{Nu \kappa}{D_h}
\]

where the conductivity of the moist air, \( \kappa \), was calculated using data obtained from [60] and the hydraulic diameter is \( D_h = 2wd/(w+d) \). The Nusselt number is usually given as a function of Reynolds number and Prandtl number. For laminar flow, however, it reduces to a function of channel geometry and boundary conditions. Traditional assumptions to obtain Nusselt numbers assume either constant temperature or constant heat flux boundary conditions. Although neither of these truly describe the naturally formed boundary conditions in a heat and mass exchanger, constant heat flux will be assumed because it has been shown to provide a better approximation to true boundary conditions [68]. For the single channel humidifier analysis (a square channel), the Nu number is 3.61 [69]. For a stacked plate and frame humidifier with the heat transfer occurring across two opposing walls, the Nu number was interpolated from data in [70] as a function of aspect ratio (AR=d/w).
The heat loss to surroundings was modeled with an overall heat transfer coefficient per unit length.

$$q_{\text{surr}} = \dot{U}_s (T_{\text{surr}} - T)$$  \hspace{1cm} (2.8)

where $q_{\text{surr}}$ was the heat lost per unit length, $T_{\text{surr}}$ was the temperature of the surroundings, and the overall heat transfer coefficient $\dot{U}_s$ was determined by fitting experimental data with no latent heat transfer occurring.

### 2.4. Mass transfer function

#### 2.4.1. Nafion

The mass transfer per unit length function, $g$, for Nafion, was modeled as follows:

$$g = awM (MW_{H_2O}) \Gamma (\lambda^w - \lambda^D)$$  \hspace{1cm} (2.9)

$$\Gamma = \left( \frac{1}{\gamma^D} + \frac{t_{\text{mem}}}{D} + \frac{1}{\gamma^W} \right)^{-1}$$  \hspace{1cm} (2.10)

where $a$ is the concentration of sulfonate sites, $\Gamma$ is the overall mass transfer coefficient and $MW_{H_2O}$ is the molecular weight of water. This form is flexible in that it can accommodate or neglect the effect of surface mass transfer conductances, $\gamma$.

The amount of water sorbed by a membrane can be mapped to relative humidity, $\phi$, of the adjacent bulk vapour by sorption curves. For Nafion, it is common to

---

Table 2.1. Nusselt numbers for laminar flow with two walls transferring heat [70]

<table>
<thead>
<tr>
<th>$AR = d/w$</th>
<th>$Nu$</th>
<th>$AR = d/w$</th>
<th>$Nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.541</td>
<td>0.7</td>
<td>4.192</td>
</tr>
<tr>
<td>0.1</td>
<td>6.399</td>
<td>1.0</td>
<td>3.703</td>
</tr>
<tr>
<td>0.2</td>
<td>5.703</td>
<td>1.43</td>
<td>3.173</td>
</tr>
<tr>
<td>0.3</td>
<td>5.224</td>
<td>2.0</td>
<td>2.657</td>
</tr>
<tr>
<td>0.4</td>
<td>4.884</td>
<td>2.5</td>
<td>2.333</td>
</tr>
<tr>
<td>0.5</td>
<td>4.619</td>
<td>3.33</td>
<td>1.946</td>
</tr>
</tbody>
</table>
interpolate two sorption curves at different temperatures, available from [49] and [44]. This procedure is the same as that of [43].

\[ \lambda_{\text{mem}} = \lambda_{303} + \frac{\lambda_{353} + \lambda_{303}}{50} (T - 303) \]

\[ \lambda_{303} = 0.043 + 17.81\phi - 39.85\phi^2 + 36.0\phi^3 \]

\[ \lambda_{353} = 0.300 + 10.8\phi - 16.0\phi^2 + 14.1\phi^3 \]  

\[ \text{(2.11)} \]

### 2.4.1.1 Diffusion coefficient correlations

The procedure for calculating the diffusion coefficient for Nafion is a topic of ongoing debate in the literature and will be discussed in this work. There are variations in Nafion diffusion coefficients as large as 3 orders of magnitude in the literature due to the variety of different techniques used to measure them [71].

In Chapter 4, results from four different diffusivity correlations are compared. Zawodzinski et al [72] measured the self-diffusion coefficient of water in Nafion using nuclear magnetic resonance spectroscopy. Motupally et al [42] converted this data into an equation for the equivalent Fickian diffusion coefficient (i.e., in the presence of a gradient):

\[ D_{\lambda} = D_{\lambda,\phi} \exp \left( -\frac{2436}{T_{\text{mem}}} \right) \]

\[ D_{\lambda,\phi} = \begin{cases} 
3.10 \times 10^{-7} \lambda \left( -1 + e^{0.28\lambda} \right) & 0 < \lambda_{\text{mem}} \leq 3 \\
4.17 \times 10^{-8} \left( 1 + 161e^{-3} \right) & 3 < \lambda_{\text{mem}} < 17 
\end{cases} \]  

\[ \text{(2.12)} \]

Chen and Peng [63] also used a piecewise correlation:
\[ D_\lambda = D_{\lambda,0} \exp \left( \frac{2416}{303} \frac{2416}{T_{\text{mem}}} \right) \]

\[
D_{\lambda,0} = \begin{cases} 
10^{-10} & \lambda_{\text{mem}} < 2 \\
10^{-10} (1 + 2(\lambda_{\text{mem}} - 2)) & 2 \leq \lambda_{\text{mem}} \leq 3 \\
10^{-10} (3 - 1.76(\lambda_{\text{mem}} - 3)) & 3 < \lambda_{\text{mem}} < 4.5 \\
1.25 \times 10^{-10} & \lambda_{\text{mem}} \geq 4.5 
\end{cases} \tag{2.13}
\]

The piecewise correlations in Eqns.(2.12) and (2.13) arise from the mapping of self diffusion coefficient to Fickian diffusion coefficient [42].

Two other relationships were also chosen for evaluation here. Data from Fuller [73] has been expressed by [42] as:

\[ D_\lambda = 2.1 \times 10^{-7} \lambda \exp \left( -\frac{2436}{T_{\text{mem}}} \right) \tag{2.14} \]

and the results from Nguyen and White [24] converted into a function of water content gives:

\[ D_\lambda = \left( 1.76 \times 10^{-9} + 1.94 \times 10^{-8} \lambda \right) \exp \left( -\frac{2436}{T_{\text{mem}}} \right) \tag{2.15} \]

Eqns.(2.14) and (2.15) were gathered using steady state flux data, as opposed to Eqns.(2.12) and (2.13) which measured the self diffusion coefficient and then converted them to Fickian diffusion coefficients.

2.4.1.2 Diffusion coefficient calculation method

In addition to different diffusion coefficient correlations available in literature, there are different ways to employ them in along-the-channel calculations. To compare these methods, each of the four diffusion coefficient correlations was calculated according to one of the following three methods.
The first method is that used by Chen and Peng. They evaluate the diffusion coefficient at location $x$ along the channel using the $\lambda_{\text{mem}}$ corresponding to the average relative humidity between the wet side and dry side at $x$.

$$\lambda_{\text{mem}} = \lambda_{\text{mem}} \text{ at } \left( \frac{\phi^w + \phi^D}{2} \right)$$

(2.16)

$$D = D_{\lambda}(\lambda_{\text{mem}}, T_{\text{mem}})$$

Second, it was hypothesized that evaluating the diffusion coefficient at the average water content instead of average relative humidity would provide a more accurate approximation.

$$\lambda_{\text{mem}} = \left( \frac{\lambda^w + \lambda^D}{2} \right)$$

(2.17)

$$D = D_{\lambda}(\lambda_{\text{mem}}, T_{\text{mem}})$$

The third method considered does not use an average membrane water content, but instead integrates across the membrane to find the true flux. This approach was used by [42] and [43], but numerically integrating under non-smooth functions like Eqns.(2.12) and (2.13) can be computationally expensive.

$$g = \frac{awM(MW_{H2O})}{t_{\text{mem}}} \int_{\phi^w}^{\phi^D} D_{\lambda} d\lambda$$

(2.18)

2.4.1.3 Surface mass transfer resistances

The last section of Chapter 4 examines the effects including surface mass transfer resistances. The mass transfer conductance for absorption and desorption, $\gamma_a$ and $\gamma_d$, for Nafion were calculated according to recently proposed equations from Ge et al [43]:

$$\gamma_a = 1.14 \times 10^{-5} f_v \exp\left(2416\left(\frac{1}{303} - \frac{1}{T}\right)\right)$$

(2.19)

$$\gamma_d = 4.59 \times 10^{-5} f_v \exp\left(2416\left(\frac{1}{303} - \frac{1}{T}\right)\right)$$

(2.20)

where the volume fraction of water, $f_v$, is given by:
where $V_{H2O}$ is the partial molar volume of liquid water ($1.82 \times 10^{-5} \text{ m}^3 \text{mol}^{-1}$) and $V_{mem}$ is the partial molar volume of dry membrane, $V_{mem} = EW/\rho_{mem,dry} = 5.50 \times 10^{-4} \text{ m}^3 \text{mol}^{-1}$.

Presumably, Ge et al. have assumed there is 1 SO$_3^-$ site per mer of membrane, though the validity of this assumption is a matter of debate. Values of $\gamma_a$ and $\gamma_d$, where then used to find the overall mass transfer coefficient with Eqn.(2.10). When surface effects were used in tandem with Eqn.(2.18), Eqn.(2.18) was divided by $\left(\lambda^w - \lambda^d\right)$ to obtain an effective diffusion coefficient that only accounts for bulk membrane resistance. This effective diffusion was then used in Eqn.(2.10).

### 2.4.2. Unknown membranes

The sorption curve for non-ionic membranes and desiccants can be modeled generically by the parametric function in Eqn.(2.22) [68].

$$u = \frac{u_{max}}{1 - C + C / \phi} \quad (2.22)$$

where $u_{max}$ is the maximum water uptake of the membrane in [kg H$_2$O (kg membrane)$^{-1}$], $C$ is a parameter describing the shape of the sorption shape, and $\phi$ is the relative humidity of adjacent gas.

If convective mass transfer resistance is neglected, the mass transfer function $g$ is:

$$g = \frac{wMD_u}{t_{mem}} \left( u^w - u^d \right) \quad (2.23)$$
where $D_u$ is very distinct from $D_x$. $D_u$ is a lumped term of the true diffusion coefficient [m$^2$s$^{-1}$] and membrane density [kg m$^{-3}$]. The units of $D_u$ are [kg m$^{-1}$ s$^{-1}$] compared to $D_x$ which has units [m$^2$s$^{-1}$]. The diffusivity is assumed constant for unknown membranes.

If convective mass transfer resistance is not neglected, an alternate formulation derived by Niu and Zhang in [68] for ERV technology, is:

$$g = wM \Gamma \left( \omega^w - \omega^D \right)$$

(2.24)

where the overall membrane mass transfer coefficient $\Gamma$ is given by:

$$\Gamma = \left( \frac{1}{h_M^w} + \Psi + \frac{1}{h_M^D} \right)^{-1}$$

(2.25)

and the diffusion mass transfer resistance $\Psi$ is given by: [68]

$$\Psi = \frac{t_{mem} \cdot 10^6 \left( 1 - C + C/u^D \right)^2 \left( u^D \right)^2}{D_u \exp \left( 5294/T^D \right) \mu_{max} C}$$

(2.26)

The convective mass transfer conductance's, $h_M$, are arrived at by means of the Chilton Colburn heat and mass transfer analogy relating Sherwood number (Sh) to Nusselt number and Lewis number (Le).

$$Sh = Nu \cdot Le^{\frac{1}{3}} = \frac{h_M D_h}{D_{air-H_2O}}$$

(2.27)

where $D_{air-H_2O}$ is the diffusivity of water in air, and the Lewis number is the ratio of Schmidt number to Prandtl number, or:

$$Le = \frac{\kappa}{\rho \cdot c_p \cdot D_{air-H_2O}}$$

(2.28)
After calculating the Lewis number for the stream and Nusselt number from Table 2.1, \( h_M \) is found from Eqn.(2.27). The suitability of using this mass transfer technique for fuel cell humidifiers was considered in Section 5.4.4 and Appendix A.

2.5. **Implementation**

The four state variables selected were \( \dot{m}_{H_2O}^w \), \( \dot{m}_{H_2O}^D \), \( T^w \), and \( T^D \). The governing equations were coded with MATLAB as a boundary value problem using the `bvp4c.m` function. BVP4c approximates the solution on each mesh interval by a cubic polynomial, satisfying the equations to a prescribed tolerance [74]. The relative error tolerance was set to \( 1 \times 10^{-3} \), meaning the maximum change in any state variable with continued iteration was 0.1%. Mesh size was adapted automatically by the solver.
3. Experimental study\textsuperscript{b}

3.1. Chapter overview

There is a gap in existing membrane humidifier literature between simulations based on numerical models and macroscopic experimental studies. The former provide complete spatial mapping of humidity and temperature while the latter rely on time and space-averaged fluxes. Humidity measurements at different locations along the channels would both address this gap in existing literature and assist in validating the model presented in Chapter 2.

\textsuperscript{b} A version of this chapter has been submitted for publication to the Journal of Power Sources. P.Cave, W.Mérida. “Water flux in membrane fuel cell humidifiers: Flow rate and channel location effects”
A straight, single channel membrane humidifier was constructed to measure temperature and moisture profiles along both the donor and receiver channels. A persulfonic Nafion membrane was used as the water exchange medium. Single-phase vapour to vapour results are reported for counter flow operation. Specifically, flow rate and channel location effects on outlet dew point at different temperatures are considered.

3.2. Setup

The experimental setup consisted of a single channel membrane humidifier as illustrated in Figure 3.1. A 1 cm x 1cm x 20 cm flow channel was machined into two plates, which were then mated together with Nafion 117 membrane as the hygroscopic separator. The Nafion was pretreated by boiling in a 3wt% H$_2$O$_2$ solution for 2 hours, rinsing with de-ionized water, boiling in 1.0 M H$_2$SO$_4$ for 2 hours, and finally rinsing and storing in de-ionized water. The membrane was removed from de-ionized water and exposed to ambient room temperature and humidity conditions for at least 24 hours prior to testing. Five evenly-spaced 1/16” probe holes were drilled into the flow channels for thermocouple or dew point sensor placement. Calibrated type-T unsheathed thermocouples were used due to their reasonable accuracy, suitability in moist air environments, and small size (to minimize interference with the flow distribution in the channel).
A Vaisala HMT337 dew point transmitter was used to measure moisture content. Because this is a polymer-based capacitive sensor, an effort was made to ensure the probe temperature was equal to the process temperature. The dew point probe was placed in a cavity, and at the time of measurement a sample of gas from the channel was allowed to flow through this cavity to provide a more accurate dew point measurement. The Vaisala meter measures relative humidity at ± 2% and temperature at ± 0.2°C and converts these measurements to dew point. The Hyland and Wexler equation was used to relate saturated water vapour pressure to temperature (Eqn.(1.10)).
Figure 3.2. Experimental setup schematic

Figure 3.2 shows the experimental setup. The dry side stream (or receiver side) was delivered through a mass flow controller and heated to the desired inlet temperature, $T_{Di}$. The wet side stream (or donor side) passed through a mass flow controller, a saturation point bubbler humidifier, and then heated to the desired temperature, $T_{Wi}$. The moisture content of this stream was controlled by the temperature and pressure in the bubbler. In actual operation, the wet side stream, coming from the cathode exhaust, would be oxygen-depleted moist air. In this work, regular air was used on both sides.

3.3. Methodology

Three related questions were addressed in this experimental study. First, in this configuration, the heat lost to the surroundings was comparable to the enthalpic flow through the humidifier and thus not negligible. The first step then was to characterize and quantify the heat loss of the humidifier. A stream may gain or lose heat energy through the channel walls to the surroundings, through the membrane to the opposite stream, and
through latent heat transfer in the presence of phase changes. Single phase conditions were imposed throughout this study for simplicity, although in practical operating conditions there may be condensation on the wet side.

Next, the effects of flow rates were studied. The effect of flow rates on humidifier performance is of utmost interest in humidifier design because it characterizes the humidifier just as a polarization curve characterizes a fuel cell. The fuel cell system’s air flow rate will be determined by the stoichiometric ratio and current demands, so it is desirable to characterize the humidifier’s moisture-transferring ability as a function of flow rate. Furthermore, membrane humidifiers are currently passive devices, humidifying the reactant as much as possible before entering the cell. However, in some operating regimes or future applications, it may be desirable to control the humidity over a range. One example of a control mechanism is a dry air bypass gate as suggested in [63]. In this case, there would be a differential flow on either side of the membrane. It would then be advantageous to fully understand the tradeoffs of changing wet side and dry side flow rates individually.

A randomized full-factorial experiment was carried out consisting of 3 levels of both wet side and dry side flow rates. Three replications of each combination of these two variables were carried out under four different sets of conditions, making a total of 27 measurements for each set of conditions. The experimental conditions for each case are summarized in Table 3.1.

The third portion of this study aimed to provide information regarding the streamwise variation in moisture flux. Knowing where most of the moisture transfer occurs in counter flow mode could provide valuable information leading to optimization of the
channel length. Two replications with randomization were taken at each of the 10 probe locations. This was performed for the same four sets of conditions.

The seven independent variables in this arrangement are: dry side inlet temperature, dew point, and flow rate ($T_{Di}, T_{d,Di}$, and $Q_{air,Di}$), wet side inlet temperature, dew point, and flow rate ($T_{Wi}, T_{d,Wh}$, and $Q_{air,Wh}$) and the temperature of the surroundings ($T_{surr}$). The dependent variables can include temperatures or dew points at the 10 probe locations, $T_x$ or $T_{d,x}$. Due to the high number of variables, four individual cases representing different operating regimes were considered. The case definitions and experimental testing approach is shown in Table 3.1: Testing matrix.
### Chapter 3

#### Table 3.1. Testing matrix

<table>
<thead>
<tr>
<th>Case</th>
<th>Research Focus</th>
<th>Fixed Temperatures in [°C]</th>
<th>Independent</th>
<th>Dependent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Flows in [SLPM]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Heat loss to surroundings</td>
<td>$T_{Di} = 85$</td>
<td>Stream wise location</td>
<td>$T_x$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{d,Di} = -40$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Q_{air,Di} = 1.0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{wi} = 85$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{d,wi} = -40$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Q_{air,wi} = 1.0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{surr} = 21$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 1</td>
<td>Effect of flow rates on moisture transfer</td>
<td>$T_{Di} = 25$</td>
<td>$0.4 &lt; Q_{air,Di} &lt; 1.0$</td>
<td>$T_{d,DO}$</td>
</tr>
<tr>
<td>Non-isothermal case.</td>
<td></td>
<td>$T_{d,Di} = -40$</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>$T_{wi} = 80$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{d,wi} = 25^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Streamwise variation in moisture flux</td>
<td>As above, with: $Q_{air,Di} = 1.0$</td>
<td>Stream wise location</td>
<td>$T_x$, $T_{d,x}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Q_{air,wi} = 1.0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cases 2, 3, and 4*</td>
<td>Effect of flow rates on moisture transfer under isothermal conditions</td>
<td>$T_{Di} = T_{surr}$</td>
<td>$0.4 &lt; Q_{air,Di} &lt; 1.0$</td>
<td>$T_{d,DO}$</td>
</tr>
<tr>
<td>Isothermal cases at low, medium, and high temperatures, respectively.</td>
<td></td>
<td>$T_{d,Di} = -40$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{wi} = T_{surr}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{d,wi} = T_{surr}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Where $T_{surr} = 30$ (Case 2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{surr} = 50$ (Case 3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{surr} = 70$ (Case 4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Streamwise variation in moisture flux</td>
<td>As above, with: $Q_{air,Di} = 1.0$</td>
<td>Stream wise location</td>
<td>$T_{d,x}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Q_{air,wi} = 1.0$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a This is the maximum dew point allowable to ensure no condensation occurs in the wet side as the temperature drops; limited by humidifier heat loss to the surroundings.

*b These cases use an oven to impose isothermal conditions.

### 3.4. Experimental considerations

#### 3.4.1. Measurement technique

Figure 3.3 illustrates the dew point measurement technique. In steady state, if the convective velocity of the air/water mixture along the channel is greater than the diffusive velocity of water in air across the channel, then a significant concentration gradient in the y-direction will develop. As a result, the sample probe location on the wall...
opposite the membrane may measure an artificially low concentration value on the dry side and an artificially high concentration value on the wet side. This effect will become more noticeable further along the channel where concentration gradients grow larger and the mixture is no longer well-mixed. To mitigate this effect, the channel exit stream was partially restricted during measurements to force a larger sample of air/water mixture through the sensing cavity.

![Diagram of measurement technique](image)

**Figure 3.3.** The measurement technique showing conceptually the concentration gradients across the channel and their effect on measurement precision

### 3.4.2. Flow correction

As a result of the experimental set up shown in Figure 3.2, one must consider the addition of water when stating the actual wet side flow rate delivered to the membrane humidifier. The amount of added water is quantified, assuming an ideal gas mixture and 100% effective bubbler, via:

$$\dot{m}_{H_2O} = \frac{P_{H_2O}^{sat}}{P - P_{H_2O}^{sat}} \frac{MW_{H_2O}}{MW_{air}} \dot{m}_{air}$$  \((3.1)\)
where $P_{H2O}^{sat}$ is the saturation pressure at the bubbler temperature, and $P$ is the total pressure in the bubbler. The mass flow rate of water and air are summed to determine the actual flow composition and rate delivered to the membrane humidifier. For reference, Figure 3.4 has been included to show the appropriate correction factors (either volumetric or gravimetric) to obtain the total flow rate of the mixture. Higher backpressure build up at the saturation bubbler results in less water being evaporated by the flow. Should one not account for these corrections, the maximum error will be found in cases with high dew point and high flow rates (which cause higher back pressures). The sensitivity to dew point is much higher than to bubbler pressure.

![Figure 3.4. Volumetric and mass flow rate correction factors due to addition of water for various bubbler backpressures](image)

3.5. Results and discussion

3.5.1. Heat loss to surroundings

The amount of heat lost to the surroundings was quantified by how it affects the temperature profiles in co-flow operation with both inlet streams flowing dry air at the
same temperature. Neglecting changes in potential or kinetic energy, the heat loss per unit length for this configuration, \( q' \) [W m\(^{-1}\)], was calculated according to the equation:

\[
q' = -\frac{d(mc_p T)}{dx} = -mc_p \frac{dT}{dx}
\]  

(3.2)

The derivative of the quadratic fit \((R^2 = 1.00)\) shown in Figure 3.5, the appropriate flow rate, and the specific heat capacity of dry air \((c_p=1007 \text{ J/kg/K})\) were used to calculate the heat loss rate. If the heat loss to the surroundings is modeled with an overall heat transfer coefficient, the following equation applies [69]:

\[
q' = Uw(T_{surr} - T)
\]  

(3.3)

The product of overall heat transfer coefficient, \( U \), and effective perimeter, \( w \), can be extracted from the slope of a linear fit in a plot of \( q' \) vs. \((T_{surr} - T)\)(Figure 3.6).

![Figure 3.5. The temperature profile and the heat loss rate to surroundings with dry air in coflow mode (1.0 SLPM)](image)

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A value of $U_w = 0.149 \pm 0.023 \, \text{W} \, \text{K}^{-1} \, \text{m}^{-1}$ at a 95% confidence interval was obtained for this particular experimental setup. The $U_w$ term can be assumed constant for fully developed laminar flows because the Nusselt numbers, thermal conductivity of air, and consequently convective heat transfer coefficients all remain approximately constant.

### 3.5.2. Effect of unbalanced flow rates on humidification performance

Reporting solely the outlet dew point or relative humidity, as done in [19], as the performance variable can be misleading because it is possible and common to find that a lower outlet dew point at a higher flow rate can represent more mass of water transferred than a higher dew point reading at a lower flow rate. Therefore, the average water flux across the membrane and latent effectiveness (LE) performance indicators are also considered in the current section. The water recovery ratio (WRR) is not suitable as an effectiveness measure as LE for this study because the dry side and wet side flow is not always balanced (equal). The theoretical maximum amount of transferable water is limited by what can be carried in the stream with the lowest flow rate. Contours of these three metrics for the ranges of flow studied are shown in Figures 3.7-3.10.
Figure 3.7. CASE 1 (Non-Isothermal) – Measured effect of flow rates on a) Outlet dew point, b) Average water flux, and c) Latent effectiveness

Figure 3.8. CASE 2 (Isothermal, 30°C) - Measured effect of flow rates on a) Outlet dew point, b) Average water flux, and c) Latent effectiveness
Two observations can be made with regard to Figures 3.7a, 3.8a, 3.9a, and 3.10a. First, in all cases the outlet dew point increases at lower dry side flow rates. This result might be expected since lower flow rates give both the dry gases a longer residence time in the channel, allowing for more moisture to be evaporated from the membrane surface. Second, the effect of the dry side flow rate on outlet dew point is generally much more pronounced than the wet side flow rate (evidenced by the near-vertical contour lines).
This suggests that an abundance of moisture exists at the membrane interface on the dry side and it is only the dry side’s time in the channel that limits how much water is evaporated. Translating this to a practical design consideration, a bypass gate or bleed valve that reduces the wet side flow rate through the humidifier will reduce the pressure drop through the wet side with minimal loss in moisture transfer performance.

Figures 3.7b, 3.8b, 3.9b, and 3.10b uncover no clear trends from case to case. However, it should be noted that a higher outlet dew point does not necessarily mean that more moisture has been transferred (in many cases the opposite is true). This is an important consideration when comparing performance data because using dew point alone may lead to erroneous interpretations. For example, Park et al [19] concluded that flux across the membrane increases with an increase in flow rates, whereas Ge et al [43], in a similar application, concluded that the outlet dew point decreases with increasing flow rates. The two conclusions appear in conflict, but are solely the result of the metric used to indicate performance. A second observation with respect to these graphs is that there exists an optimal combination of flow rates that yields the highest water flux. However, this optimum varies with operating conditions in an unclear way and in some cases is not reliably discernible with the data presented here (Figure 3.10b). Nonetheless, the importance of such information can be illustrated with an example. If operating at 50°C (Figure 3.9b) with both $Q_{air, D}$ and $Q_{air, WI}$ at 1.0 SLPM, bypassing a portion of the dry side flow to allow only 0.7 SLPM through the dry side of the humidifier would enable more water to be transferred. The two streams could then be remixed with a higher specific humidity than if all of the dry air had been passed through the humidifier.
A common characteristic on all of the latent effectiveness graphs is a degree of symmetry about a line of equal flow rates (45°C angle on the graphs). This is a consistent trend with sensible effectiveness is heat exchanger technology [61] and is a result of the minimum flow rate limiting the maximum potential water transfer. The implication is that an unbalanced humidity exchanger is more effective than a balanced heat exchanger. Note, however, that a high effectiveness rating (a relative measure) does not necessarily mean the design will meet its performance specification in absolute terms [kg s⁻¹ m⁻²]. As the temperature increases from Case 2 to Case 4, the LE values become progressively smaller. At equal flows of 0.7 SLPM, the WRR goes from 0.16 at 30°C to 0.082 at 70°C. The reason for this is because the higher temperature dew points carry a lot more water into the system, but the humidifier is not well-enough designed to transfer a significant portion of it to the dry side.

The estimated accuracy (based on sensor accuracy) and precision (standard deviation between replications) of these results are summarized in Table 3.2. At higher temperatures, even small error in measurement can result in large errors in the calculated values of average water flux and latent effectiveness.
Table 3.2. Calculated accuracy and precision estimates for dew point readings in factorial experiments

<table>
<thead>
<tr>
<th>Wet Side Flow Rate [SLPM]</th>
<th>Dry Side Flow Rate [SLPM]</th>
<th>ACCURACY a [± °C]</th>
<th>PRECISION b [± °C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Case 1</td>
<td>0.4</td>
<td>1.38</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>1.41</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.47</td>
<td>1.79</td>
</tr>
<tr>
<td>Case 2</td>
<td>0.4</td>
<td>0.80</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>0.71</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.70</td>
<td>0.91</td>
</tr>
<tr>
<td>Case 3</td>
<td>0.4</td>
<td>0.90</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>0.86</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.85</td>
<td>1.00</td>
</tr>
<tr>
<td>Case 4</td>
<td>0.4</td>
<td>1.22</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>1.10</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.20</td>
<td>1.49</td>
</tr>
</tbody>
</table>

a Based on manufacturer’s published accuracy limits for given conditions.
b Based on standard error of three replications.

3.5.3. Stream wise variation in moisture flux

The measured dew point profiles and calculated mass flow of water (via Eqn.(3.1) with \( P_{\text{H}_2\text{O}}^{na} \) replaced with the water vapour partial pressure \( P_{\text{H}_2\text{O}} \) ) are shown in Figures 3.11 to 3.14. For these figures, the arrows indicate direction of flow and the error bars shown are the manufacturer’s stated accuracy limits or the standard deviation of the replications, whichever is higher.

![a)Measured Dew Point Profile](image1)

![b)Calculated Mass Flow of Water](image2)

Figure 3.11. Measured moisture profiles - CASE 1 (Non-isothermal)
Figure 3.12. Measured moisture profiles - CASE 2 (Isothermal, 30°C)

Figure 3.13. Measured moisture profiles - CASE 3 (Isothermal, 50°C)
CHAPTER 3

Figure 3.14. Measured moisture profiles - CASE 4 (Isothermal, 70°C)

In all cases, the mass flow rate of water in the channels (Figures 3.11b, 3.12b, 3.13b, and 3.14b) appears to change linearly along the channel. Table 3.3 summarizes the fitted linear models. Although no phenomenological significance can be ascribed to the linear profile, it provides a useful empirical correlation for engineering design. A linear profile implies that the flux across the membrane is approximately constant along the length of the channel.

Table 3.3. Calculated average water fluxes from Figures 3.11b, 3.12b, 3.13b, and 3.14b

<table>
<thead>
<tr>
<th>Case</th>
<th>Wet Side</th>
<th>Dry Side</th>
<th>Wet Side</th>
<th>Dry Side</th>
<th>Statistically different slopes *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated Flux Value [x10^-5 kg s^-1 m^-2]</td>
<td>Estimated Error in Flux Value [x10^-5 kg s^-1 m^-2]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 1</td>
<td>0.51</td>
<td>0.040</td>
<td>Yes</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 2</td>
<td>3.60</td>
<td>0.202</td>
<td>No</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.04</td>
<td>0.436</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 3</td>
<td>8.25</td>
<td>0.669</td>
<td>No</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.76</td>
<td>0.502</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 4</td>
<td>21.3</td>
<td>7.58</td>
<td>No</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.6</td>
<td>1.67</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* At a 0.05 significance level, determined by t-test.

With the net change in water flow rate presented in the margins of Figures 3.11b-3.14b, it is possible to compare the amount of water lost from the wet side to the amount
of water gained by the dry side. Although the difference was only statistically significant in Case 1, the amount of water 'lost' by the wet side is slightly higher than the water being 'gained' by the dry side stream. The possibility of a leak is unlikely; a more probable cause may be a result of measurement technique. As mentioned in section 3.4, the effect of concentration gradient across the channel may cause dry side measurements to be lower and wet side measurements to be higher than their true values.

3.6. **Chapter summary**

In this chapter, the effects of flow rates and channel location on performance of a single channel planar membrane humidifier operating under single phase conditions are reported. First, the heat loss to the surroundings was quantified and found to affect the overall performance significantly. Second, results from varying flow rates indicate that lower flow rates lead to higher outlet dew point values of the receiver stream which can be related to longer residence times. It was also found that moisture transfer is more strongly influenced by the flow rate through the receiver side than the donor side. Finally, five-point dew point profiles for both donor and receiver sides are reported for various temperature conditions. No stream wise variation in moisture flux was observed under isothermal conditions, and the average flux value increased from $3.3 \times 10^{-5}$ kg s$^{-1}$ m$^{-2}$ at $30^\circ$C to $2.0 \times 10^{-4}$ kg s$^{-1}$ m$^{-2}$ at $70^\circ$C under fully humidified donor-side inlet conditions.
4. Single channel Nafion humidifier under isothermal conditions

4.1. Chapter overview

The experimental study in Chapter 3 supplied a large amount of data to membrane humidifier research efforts. However, it is the ability to predict humidifier performance that will be most valuable to the development and design of optimal humidifiers. To work towards this end, the model developed in Chapter 2 was applied to the single channel humidifier used in Chapter 3. This study aims to validate the model under isothermal, single-phase conditions and assess the accuracy of existing Nafion modeling techniques. To clarify, the objective of this study is not simply to use fitted model parameters to reproduce the data, but rather to evaluate differences among existing correlations and
make recommendations on what techniques are most suitable for the particular geometry and conditions.

4.2. Experimental details

Model results were evaluated against experimental results from Chapter 3. These results were obtained from a 1 cm x 1 cm x 20 cm single channel humidifier in counter flow operation using Nafion 117 as the water-permeable membrane. The discussions in Sections 4.3.1-4.3.4, and 4.3.6 consider only the balanced flow conditions ($Q^W=Q^D=0.4, 0.7,$ and 1.0 SLPM) and three isothermal conditions ($T=30, 50,$ and $70^\circ C$). Section 4.3.5 compares simulations against data from all the flow rates for the $50^\circ C$ isothermal case. For complete experimental details, the reader is referred to Chapter 3. The parameters used in the simulations are summarized in Table 4.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel width ($w$)</td>
<td>0.01 m</td>
<td>Chapter 3</td>
</tr>
<tr>
<td>Channel depth ($d$)</td>
<td>0.01 m</td>
<td>Chapter 3</td>
</tr>
<tr>
<td>Channel length ($L$)</td>
<td>0.2 m</td>
<td>Chapter 3</td>
</tr>
<tr>
<td>Area of membrane ($A=wL$)</td>
<td>0.002 m$^2$</td>
<td>Chapter 3</td>
</tr>
<tr>
<td>Membrane dry thickness ($t_{mem}$)</td>
<td>$1.83 \times 10^{-4}$ m</td>
<td>[43, 54]</td>
</tr>
<tr>
<td>Membrane molecular weight ($M_{mem}$)</td>
<td>1.1 kg mol$^{-1}$</td>
<td>[43, 54]</td>
</tr>
<tr>
<td>Membrane density ($\rho_{mem}$)</td>
<td>2000 kg m$^{-3}$</td>
<td>[43, 54]</td>
</tr>
<tr>
<td>Ionic site concentration ($\alpha=\rho_{mem}/M_{mem}$)</td>
<td>1818 mol m$^{-3}$</td>
<td>[43, 54]</td>
</tr>
<tr>
<td>Total pressure ($P$)</td>
<td>101325 Pa</td>
<td></td>
</tr>
<tr>
<td>Water content ($\lambda$)</td>
<td>Eqn.(2.11)</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient ($D_x$)</td>
<td>Eqn.(2.12), (2.13), (2.14), or (2.15)</td>
<td></td>
</tr>
<tr>
<td>Volume fraction of membrane ($\overline{V}_{mem}$)</td>
<td>$5.50 \times 10^{-4}$ m$^3$ mol$^{-1}$</td>
<td>[43]</td>
</tr>
<tr>
<td>Volume fraction of water ($\overline{V}_{H_2O}$)</td>
<td>$1.8 \times 10^{-5}$ m$^3$ mol$^{-1}$</td>
<td>[43]</td>
</tr>
</tbody>
</table>
4.3. Results and discussion

4.3.1. Comparison of methods of evaluating diffusion coefficient

Three modeling techniques to evaluate the diffusion coefficient were compared. As detailed in Section 2.4.1.2, the diffusion coefficient equations were evaluated at A) the water content derived from the average relative humidity between wet and dry sides, B) the average water content between wet and dry sides, or C) integrating across the thickness of the membrane. Since method C is the most rigorous technique, it is the value against which the other two methods will be evaluated. Figure 4.1 shows the errors of methods A and B evaluated against method C for every temperature and balanced flow combination. The four diffusion coefficient correlations considered here are those of Zawodzinski, Nguyen, Chen, and Fuller (Eqns.(2.12),(2.14),(2.15), and (2.13) respectively). The latent effectiveness was selected as an appropriate metric for output comparison. It should be noted that the scatter of error is of primary interest here rather than the magnitudes of latent effectiveness. The sums of squared errors for each of the 4 different diffusion correlations, along with a total tally, are listed in Table 4.2.
Figure 4.1. Error scatter in simulated latent effectiveness caused by evaluating diffusion coefficient at average relative humidity (solid markers) or water content (open markers), using correlations from Zawodzinski, Nguyen, Fuller (all via [42]), and Chen [63].

Table 4.2. Sum of squared errors for data in Figure 4.1

<table>
<thead>
<tr>
<th>Sum of Squared Errors</th>
<th>Zawodzinski</th>
<th>Nguyen</th>
<th>Chen</th>
<th>Fuller</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Using average $\phi$</td>
<td>0.3457</td>
<td>0.0081</td>
<td>0.0189</td>
<td>0.1279</td>
<td>0.5007</td>
</tr>
<tr>
<td>Using average $\lambda$</td>
<td>0.0383</td>
<td>0.0000</td>
<td>0.0136</td>
<td>0.0000</td>
<td>0.0519</td>
</tr>
</tbody>
</table>

It is clear from Figure 4.1 and Table 4.2 that evaluating the diffusion coefficient at $\lambda_{\text{zen}} = (\lambda^w + \lambda^D)/2$ is more consistently reliable over a broad range of temperatures, flow rates, and diffusion correlations than proceeding from an average relative humidity as was suggested in [63]. The sum of squared errors over the 36 data points was almost 10 times lower using the average water content.
Looking at the individual diffusion coefficient correlations, the Nguyen and Fuller equations showed much less susceptibility to error than the Zawodzinski and Chen correlations. The reason for this can be linked to the latter two suggesting a maximum diffusion coefficient near $\lambda=3$ and therefore having a non-monotonic function. Using an average water content value between a saturated value ($\sim \lambda=10$) and a near-dry value ($\sim \lambda=1$) increases the likelihood of falling near the water content that yields the maximum diffusion coefficient. This would yield an artificially high diffusion coefficient and, consequently, a high latent effectiveness. Indeed, all but 1 of the 18 data points from these two correlations show an over-predicted latent effectiveness resulting from the assumptions.

The Fuller and Nguyen equations exhibit zero error when the average water content approximation is used. This is a direct consequence having a linear dependence of diffusion coefficient on water content. Of all four correlations studied, the Nguyen equation is the least susceptible to error caused by either assumption. The accuracy of the magnitude of these diffusion coefficients will be evaluated next.

4.3.2. Evaluation of diffusion coefficient magnitudes

The accuracy of calculated flux values was found to be highly dependent on the magnitude of diffusivity provided by the chosen correlation. Figures 4.2, 4.3, and 4.4 depict the outlet dew point as a function of flow rate for the 30, 50, and 70°C isothermal conditions, respectively. For all cases, the water content on both sides of the membrane was averaged to evaluate the diffusion coefficient. The outlet dew point is an acceptable response variable because we are only comparing the magnitude and trends obtained by different correlations at the same conditions; not evaluating performance at different
conditions. The error bars shown are the higher of manufacturer's recommended accuracy or standard deviation of three replications, as reported in Chapter 3.

Figure 4.2. Comparison of experimental data with simulated results using different diffusion coefficient relationships from literature, CASE 2 - 30°C Isothermal
Figure 4.3. Comparison of experimental data with simulated results using different diffusion coefficient relationships from literature, CASE 3 - 50°C Isothermal

Figure 4.4. Comparison of experimental data with simulated results using different diffusion coefficient relationships from literature, CASE 4 - 70°C Isothermal
It can be seen from Figures 4.2, 4.3, and 4.4 that the model accurately captures the trend that increasing flow rate decreases the outlet dew point. However, large variations in the magnitude are observed depending on the diffusion coefficient correlation used. The Fuller and Chen correlations predict on average 16 and 22°C higher than the experimental values, respectively. The Zawodzinski and Nguyen correlations fare much better but the maximum error is still significant (up to 6°C). It is without question that the careful selection of a diffusion coefficient correlation is paramount to any degree of success in a predictive model.

4.3.3. Temperature dependency of diffusion coefficients

The effect of temperature on the diffusion coefficient has not been subject to much research in the literature. One of two common forms of dependencies are used, both intended to exhibit an Arrhenius dependence on temperature:

\[
D_\lambda = D_{\lambda,0} \exp \left( \frac{E_a}{R} \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T_{\text{mem}}} \right) \right) \tag{4.1}
\]

\[
D_\lambda = D_{\lambda,0} \exp \left( - \frac{E_a}{RT_{\text{mem}}} \right) \tag{4.2}
\]

The value for \(E_a\), the activation energy of diffusion, has been reported by Yeo and Eisenburg in 1977 to be 4.8 kcal mol\(^{-1}\) (20 096 J mol\(^{-1}\)) [75] and by Verbrugge et al in 1992 to be 4.3 kcal mol\(^{-1}\) (18 003 J mol\(^{-1}\)) [76]. These values are still used today. The reference temperature, \(T_{\text{ref}}\), is the temperature at which \(D_{\lambda,0}\) is known. The second form, Eqn.(4.1), provides for an easier interpretation of \(D_{\lambda,0}\) since the magnitude of the temperature correction is on the order of 1 and hence close in magnitude to \(D_\lambda\). In
Eqn.(4.2), the temperature correction is on the order of $10^{-4}$, so $D_{x,0}$ is consequently much larger than $D_x$ and can be misleading.

From Figures 4.2 to 4.4, the trend of the Zawodzinski and Nguyen relationships is for the total water flux to be overestimated at lower temperatures and underestimated at higher temperatures. This trend is elucidated in Figure 4.5.

![Figure 4.5. Effect of temperature on the over-prediction of outlet dew point for the two best diffusion coefficient correlations. The 0.4, 0.7, and 1.0 SLPM flows are included. Over-prediction is simulated outlet dew point minus experimental outlet dew point.](image)

Accordingly, a lower activation energy would provide a better temperature correction. The effect that lowering the activation energy had on the temperature dependence is shown in Figure 4.6 for the Nguyen equation. Unfortunately, increasing the activation energy also increased the magnitude of diffusion coefficient for all
temperatures and the over-predictions were larger in magnitude despite being constant with temperature. A value of $E_a = 14965 \, J \, mol^{-1}$ was observed to accurately reflect the temperature dependence.

![Graph showing effect of temperature on over-prediction of outlet dew point for various activation energies, using Nguyen equation and 1.0 SLPM. Over-prediction is the simulated outlet dew point minus experimental outlet dew point.](image)

Figure 4.6. Effect of temperature on over-prediction of outlet dew point for various activation energies, using Nguyen equation and 1.0 SLPM. Over-prediction is the simulated outlet dew point minus experimental outlet dew point.

Alternatively, the diffusivity relationships can be converted to the form of Eqn.(4.1) and the reference temperature changed in tandem with activation energy to provide a fit. This approach, however, is equivalent to changing the magnitude of $D_{\lambda,o}$ and that was not the objective of this analysis. This analysis was only intended to evaluate the suitability of currently existing diffusion coefficient correlations.
4.3.4. Streamwise variation in moisture flux: comparison with experimental data

The change in dew point along the length of the channel is shown in Figure 4.7. The Nguyen and Zawodzinski diffusion coefficient correlations were used for this study since they were shown to provide the most accurate outlet dew point \((x/L = 1)\). The 50°C isothermal case was be considered. The 1.0 SLPM case was simulated in order to compare with experimental data presented in Chapter 3.

![Figure 4.7. Simulated and experimental temperature and dew point profiles for a) Nguyen and b) Zawodzinski diffusion coefficient equations, for the 50°C isothermal case with 1.0 SLPM on both sides. Arrows indicate direction of flow.](image)

The simulations follow the general trend of the experimental data, with a rapid rise of dew point in the initial quarter of the channel and gradually tapering off. This trend was expected because for a given flow rate and pressure, less water is required to increase from, for example, a -30 to a -10°C dew point compared to an increase from 0 to 10°C dew point. This non-linear scale is a result of the concave dependency of saturated vapour pressure on temperature (i.e., \( \frac{d^2 P_{H2O}}{dT^2} > 0 \)).

At this condition of temperature and flow rate, the Zawodzinski relationship follows the experimental channel profile more closely. However, this was not the case...
under all temperatures. Therefore no recommendation can be made about which relationship is more suitable.

Despite the non-uniform increase in dew point, the simulated mass flow rate of water vapour in the channels increased relatively uniformly with position. This is shown in Figure 4.8. This linearity implies that the water flux across the membrane is near-constant along the length of the channel, as was concluded in Chapter 3. At some conditions, a small convexity was observed, implying higher flux across the membrane at lower $x$ locations.

Figure 4.8. Simulated mass flow rate of water present in the channels according to location, using Zawodzinski's diffusion coefficient correlation, 50°C isothermal case, and 1.0 SLPM
4.3.5. Effect of unbalanced flow rates: comparison with experimental data

Section 3.5.2 presented the effects of unbalanced flow rates on humidifier performance. Although the effect of flow rates on outlet dew point was clear, little useful information could be extracted about the effect of unbalanced conditions on the average water flux or latent effectiveness. The 50°C isothermal case was simulated to observe the trends produced by the model for comparison purposes. The Nguyen diffusion relationship was used since it provided the most accurate outlet dew point predictions at 50°C (see Figure 4.3).

Figure 4.9. Simulated contour plots of effect of flow rates on a) Outlet dew point, b) Average water flux, and c) Latent effectiveness for the 50°C isothermal case, using Nguyen’s diffusivity correlation

Figure 4.9a showing outlet dew point matches very well in both magnitude and trend with the experimental data presented in Section 3.5.2. The average water flux and latent effectiveness, however, show much smoother trends. The difference is likely caused by the sparse data and linear contour approximations in the experimental data set. The latent effectiveness again shows symmetry about the line of equal flow rates (a 45° line on the contour plot). The small asymmetry observed is because the wet side stream is

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carrying more water and thus has a higher total flow rate than the dry side. This effectively scales the y-axis and causes the slight asymmetry.

4.3.6. Surface mass transfer coefficients

In the previous analyzes, it was assumed that overall mass transfer across the membrane was rate-limited by diffusion. Evidence has recently been put forward by several authors [43, 65, 71] suggesting that there are situations where the adsorption and desorption mechanisms cannot be overlooked as insignificant or negligible. Eqns.(2.19) and (2.20) were used to assess the impact of such a resistance on performance. Figure 4.10 shows the adjusted performance at 50 and 70°C for comparison with Figures 4.3 and 4.4.

![Comparison of experimental data with simulated results using different diffusion coefficient relationships from literature, with surface mass transfer effects according to Ge, at a) 50°C isothermal and b) 70°C isothermal](image)

The effect of including absorption and desorption mass transfer coefficients significantly lowered the outlet dew point. Table 4.3 summarizes the drop in outlet dew point for each diffusion coefficient correlation and flow rate. One can see that the effect of surface resistances were much more pronounced when using the Chen and Fuller
correlations, which are the two equations that had initially over-predicted the experimental data the most. This phenomenon makes sense considering Eqn.(2.10). If the magnitude of diffusion coefficient was high, the diffusion resistance \( t_{menv}/D_a \) would be small. It follows that the surface resistances \( 1/\gamma_a + 1/\gamma_d \) will make up a greater proportion of the series sum of resistances and has a greater effect on the solution.

Table 4.3. Change in outlet dew point \( [\degree C] \) caused by including surface absorption and desorption coefficients for the 50 and 70\degree C isothermal cases

<table>
<thead>
<tr>
<th>Correlation</th>
<th>CASE 3 - 50\degree C Isothermal</th>
<th>CASE 4 - 70\degree C Isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flows in SLPM</td>
<td>Average</td>
</tr>
<tr>
<td>Zawodzinski</td>
<td>0.4</td>
<td>-2.1</td>
</tr>
<tr>
<td>Nguyen</td>
<td>-1.8</td>
<td>-2.3</td>
</tr>
<tr>
<td>Chen</td>
<td>-5.1</td>
<td>-6.4</td>
</tr>
<tr>
<td>Fuller</td>
<td>-5.7</td>
<td>-6.9</td>
</tr>
</tbody>
</table>

Having established that diffusion is not necessarily the rate-limiting process and that surface mass transfer must be properly understood, a mathematical technique to differentiate and quantify diffusion and desorption coefficients using transient permeation measurements was developed. The progress made on this investigation to date is detailed in Appendix C.

4.4. Chapter summary

The predictive thermodynamic model was used to interpret the data reported in Chapter 3 and evaluate the suitability of existing diffusion modeling techniques for humidifier modeling. It was shown that if an engineering approximation is to be made when evaluating the diffusion coefficient, averaging the water content is more reliable and more accurate than averaging the relative humidity on either side of the membrane. Without including surface mass transfer resistances, the diffusion coefficient
relationships from Nguyen and Zawodzinski were the most accurate correlations. The maximum errors compared to experiment data found using the Nguyen relationship was 14% in outlet dew point and 21% in average water flux. Surface mass transfer resistances were found to be non-negligible.
5. A 5kW humidifier with unknown membrane and non-isothermal conditions

5.1. Chapter overview

The work presented thus far built the foundations required to reach the overall objective—to develop a thermodynamic model that can be used to assist in the design of new membrane humidifiers. Such a model would predict the effects of geometry (channel width, depth, number of channels, and channel length) and operating conditions (inlet temperatures, humidity’s, flow rates, and pressures) on moisture transfer.

This final chapter applies the model to application-relevant geometry and conditions. Non-isothermal conditions, two phase flow, and the ability to accommodate membranes other than Nafion are considered here since these features were not employed
in the previous chapter. Also, a post-processing module that estimates pressure drop was used.

A brief humidifier description section summarizes the geometry of a commercially available plate and frame humidifier and the means by which experimental data were gathered. Next, the pressure drop calculations are explained. The results section examines the effects of varying the unknown membrane parameters, the effect of flow rate on this geometry, and the effect of including surface mass transfer resistances. A section on using the model as a design tool completes the discussion.

5.2. **Humidifier description**

A 5 kW plate and frame humidifier was considered in this study, based on the Dx5-51 product from dPoint Technologies. Plate and frame humidifiers are constructed by stacking plates (with channel ribs guiding the flow) and membrane layers. For modeling purposes, the humidifier was discretized by only considering one of the \( N \) parallel wet-side and dry-side channels. The number of plates and number of channels per plate was irrelevant. This discretization assumed that the channels have equal lengths, flow distribution, and boundary conditions. Heat loss to the surroundings was ignored because it is a property of the physical humidifier size and housing and will not scale as proportional to the number of channels. Nonetheless, the enthalpy lost to the surroundings was expected to be small in comparison with the enthalpy flow through the device (i.e., <5%). This similar-channels assumption also neglected that the end plates only have one surface for mass transfer instead of two.
CHAPTER 5

The relevant humidifier information is provided in Table 5.1. The operating conditions, unless otherwise indicated, were defined by a set of design conditions listed in Table 5.2, based on typical low pressure and temperature system operation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>5 kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum rated flow (Q)</td>
<td>350 SLPM</td>
</tr>
<tr>
<td>Channel width (w)</td>
<td>0.003 m</td>
</tr>
<tr>
<td>Channel depth (d)</td>
<td>0.0016 m</td>
</tr>
<tr>
<td>Channel length (L)</td>
<td>0.255 m</td>
</tr>
<tr>
<td>Number of channels (N)</td>
<td>520</td>
</tr>
<tr>
<td>Membrane dry thickness (t_{mem,dry})</td>
<td>1.75 x 10^{-4} m</td>
</tr>
<tr>
<td>Membrane maximum water uptake (u_{max})</td>
<td>0.3 kg kg^{-1}</td>
</tr>
<tr>
<td>Membrane sorption curve parameter (C)</td>
<td>5</td>
</tr>
<tr>
<td>Membrane diffusion coefficient (D)</td>
<td>9 x 10^{-7} kg m^{-2} s^{-1}</td>
</tr>
<tr>
<td>Heat transfer coefficient to surroundings</td>
<td>0</td>
</tr>
<tr>
<td>Constant in rate of condensation equation</td>
<td>1.0</td>
</tr>
<tr>
<td>a – Unless otherwise indicated</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2. Standard low temperature and pressure test conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_{wi}</td>
<td>65 °C</td>
</tr>
<tr>
<td>T_{d,wi}</td>
<td>65 °C</td>
</tr>
<tr>
<td>T_{DI}</td>
<td>25 °C</td>
</tr>
<tr>
<td>T_{D,DI}</td>
<td>-30 °C</td>
</tr>
<tr>
<td>T_{sur}</td>
<td>21 °C</td>
</tr>
<tr>
<td>P_{w}</td>
<td>1 atm</td>
</tr>
<tr>
<td>P_{o}</td>
<td>1 atm</td>
</tr>
</tbody>
</table>

The experimental data reported here was provided courtesy of dPoint Technologies. The experimental setup was the same as in Figure 3.2, except a spray injection humidifier was used instead of a saturation bubbler, and a water balance technique was used to quantify the moisture content of the outlet stream rather than a dew point sensor. Pressure drop across the humidifier was measured using a digital Dwyer digital manometer (± 20 Pa accuracy).
CHAPTER 5

There are three distinctions between the analysis in Chapters 4 and 5. First, the architecture is no longer that of a single channel humidifier. In the plate and frame topology considered here, two channel walls are permeable to water as opposed to only one in the single channel study. The parameter, $M$, has been added to denote this and serve as a multiplier whenever the channel width is considered for heat and mass flux into or out of the stream. Also, the Nusselt and Sherwood numbers were modified to account for heat and mass flux occurring through opposing channel walls.

The second distinction is that under typical operating conditions, the saturated cathode exhaust entering the wet-side of the humidifier will be cooled by the dry air via sensible heat exchange through the membrane. This will cause vapour on the wet-side to condense inside the humidifier and result in two phase flow. Therefore, the fifth state variable was included—the mass flow rate of liquid water. The corresponding terms in the energy equations (Eqns.(2.4),(2.5)) for latent heat released during condensation and the thermal mass of the wet-side stream are also now included. The rate of change of liquid water is given by Eqn.(2.3).

Third, the membrane in the 5 kW humidifier is no longer Nafion, but an unknown, silica-based polyethylene membrane. The generic 2-parameter sorption curve (Eqn.(2.22)) was be used to accommodate the unknown sorption properties of this membrane.

5.3. Pressure drop estimation

The pressure drop through the device is important in the system level design. The pressure head required to flow the streams through the humidifier manifests itself as a parasitic power load via the blower or compressor. The pressure drop along the channel
was assumed to be sufficiently close to that of pure single phase flow. Under conditions with large amounts of condensate this will not be valid, but the maximum expected flow quality here is > 0.95. The single phase pressure drop in the channel was estimated from the solution according to the single phase Darcy-Weisbach equation plus channel entrance and exit losses according to [77]. Bends in the flow path were neglected. Note that pressure was not a state variable since the fluid was assumed inviscid at a constant pressure.

\[ \Delta P = \frac{1}{2} \rho_{IN} V_{IN}^2 (1 - \sigma^2 + K_e) + \int_{x=0}^{x=L} f \rho V^2 dx + \frac{1}{2} \rho_{OUT} V_{OUT}^2 (1 - \sigma^2 - K_e) \]  

(5.1)

where \( \rho \) is the density, \( V \) is mass averaged velocity, \( D_h \) is the hydraulic diameter, \( \sigma \) is the ratio of free flow to frontal area, \( K_e \) and \( K_c \) are entrance and exit loss coefficients, obtained as a function of \( \sigma \) in [77]. The laminar flow Darcy friction factor, \( f \), was found from the aspect ratio of the channel geometry, \( \alpha \), and Reynolds number of the flow [70].

\[ f \, Re = 96 \left( 1 - 1.3553 \alpha + 1.9467 \alpha^2 - 1.7012 \alpha^3 + 0.9564 \alpha^4 - 0.2537 \alpha^5 \right) \]  

(5.2)

It was assumed that Eqns.(5.1) and (5.2) are sufficient approximations despite the presence of mass transfer into or out of the channel. The friction pressure drop was obtained by integrating from channel entrance to exit in order to minimize error in these equations caused by the mass transfer. Furthermore, numerical simulations of naturally formed boundary conditions in cross flow energy recovery ventilators have shown very little variation of friction factor with vapour injection [68].

As an alternative method, the single phase pressure drop was correlated from experimental data by a flow restriction equation:
where $C_1$ is the flow restriction constant which changes with orifice cross section and fluid viscosity, and $C_2$ indicates the degree of non-linearity of the flow.

5.4. Results and discussion

5.4.1. Effect of membrane parameters

The parameter $\mu_{\text{max}}$ in Eqn.(2.22) is the maximum amount of water the material can absorb and the parameter $C$ has the effect of varying the shape of the sorption curve. This is shown in Figure 5.1. Typical values of $C$ are less than 1, equal to 1, and greater than 1 for molecular sieves, silica-based desiccant, and polymer membranes, respectively.

![Figure 5.1. Effect of parameter C on the sorption curve](image)

Figure 5.1. Effect of parameter C on the sorption curve
A higher maximum uptake of water allows for larger gradients to be established across the membrane and increase mass transfer overall. Likewise, it is evident from Eqn.(2.23) that higher diffusion coefficients and lower membrane thicknesses will also yield higher flux values. The effect of the parameter $C$, however, is not as self-evident. Figure 5.2 shows the change in latent effectiveness (LE) using different values for $C$. A higher value of $C$ was shown to result in a higher LE values.

![Figure 5.2. Simulated latent effectiveness as a function of flow rate for different $C$ values](image)

5.4.2. Channel location effects

The 5kW humidifier geometry was first considered with the wet-side inlet at a relative humidity of 65% as opposed to 100%. This provided an opportunity to observe predicted profiles of several parameters along the channel with the onset of condensation
near mid-channel. In Figure 5.3, the humid wet side stream enters at 75°C at $x/L=1$ traveling in the negative x direction. It is cooled by the dry-side flow faster than it transfers its moisture, and reaches its saturation point near $x/L=0.4$. This is indicated by the relative humidity increasing over this area until it reaches a value of 100% (Figure 5.3c). At saturation, water begins to condense and releases latent heat. The effect of this latent heat release retards the wet-side cooling rate, marked by a noticeable change in slope in Figure 5.3a. Near the same location, the amount of liquid water in the wet-side begins to increase (Figure 5.3b). Finally, looking at Figure 5.3c, the relative humidity of the dry-side plateaus near $x/L=0.6$ and further along the channel ($x/L>0.6$) despite a continued rise in dew point. This effect is caused by the temperature of the stream in this domain rising at a rate that causes the saturation vapour pressure to rise faster than the vapour pressure of water in the flow.
Figure 5.3. Simulated variation of a) temperature, b) mass flow rate of water, c) relative humidity, and d) dew point as a function of dimensionless channel location. Wet side—dashed, dry side—solid, wet side liquid—dotted. Arrows indicate direction of flow. $TD_i=25$, $TD_d=-40$, $TW_i=75$, $TD_w=65$, $Q_{wi}=Q_{di}=350$.

5.4.3. Using fitted membrane parameters

Under standard operating conditions, the membrane properties were fitted such that good correlation was achieved between experimental and simulated results. The membrane is known to be polymer-based (i.e., polyethylene), so a value of $C=5$ was selected. It is also known that silica is used as the hygroscopic agent in the membrane, so a maximum water uptake of 30-40% can be expected. A value of $D_e=1.2 \times 10^{-5}$ kg m$^{-2}$ s$^{-1}$, $C=5$, and $u_{max}=0.4$ kg kg$^{-1}$ produced the results shown in Figure 5.4.
The same data is plotted in all 3 plots of Figure 5.4, but different performance metrics are used. The effect of flow rate is similar to that observed with the single channel humidifier in Chapter 3—a higher flow rate decreases the outlet dew point. A key observation is that even small deviations between simulated and experimental results in average water flux translate into more obvious errors in outlet dew point and latent effectiveness. The maximum percent error is the same for average water flux and latent effectiveness (4.4% at 150 SLPM), but the magnitude and slope of the water flux values mask the error much better.

5.4.4. Suitability of the ERV analysis technique

In ERV literature, the membrane diffusion equation is modified so that the overall driving force for moisture transport becomes the humidity ratio (see Eqn.(2.24)). This allows inclusion of surface mass transfer resistances determined from Sherwood number correlations. This technique was applied under the current geometry and conditions with the base case membrane properties (see Table 5.1), and then applied using fitted
membrane properties. This later case resulted in a significant observation regarding the application of this technique and will be discussed below.

The base case results are shown in Figure 5.5.

![Figure 5.5. Simulated variation of a) temperature, b) mass flow rate of water, c) relative humidity, and d) dew point as a function of dimensionless channel location, including Sherwood number surface mass transfer resistances. Wet side--dashed, dry side—solid, wet side liquid—dotted. Arrows indicate direction of flow.](image)

The surface mass transfer resistances significantly reduced moisture transfer performance, evidenced by the 16.5°C dew point approach temperature (DPAT), or 38.9% latent effectiveness compared to 68% without including these effects. The sensible heat transfer remained high at 93.7% effectiveness.

Increasing the membrane diffusion coefficient to a level that would more closely match the experimental data resulted in Figure 5.6, with \( D_a = 9 \times 10^{-6} \text{ kg m}^2\text{s}^{-1} \).
CHAPTER 5

Figure 5.6. Simulated variation of a) temperature, b) mass flow rate of water, c) relative humidity, and d) dew point as a function of dimensionless channel location, including Sherwood number surface mass transfer resistances with high $D_u$. Wet side—dashed, dry side—solid, wet side liquid—dotted. Arrows indicate direction of flow.

This scenario underscores a danger in using the humidity ratio as moisture transfer driving force. Part way along the channel, the relative humidity of the dry side exceeds 1.0, which is unrealistic. The underlying cause of this phenomenon is that the humidity ratio driving force is ‘blind’ to the non-isothermal conditions across the membrane. Moisture continues to be transferred as long as the wet side humidity ratio remains higher than the dry side, regardless of whether the dry side can actually carry it. The same caution applies to partial pressure and concentration driving forces. These three are only suitable in isothermal situations. A recommendation for a more robust treatment to prevent this phenomenon is suggested in Appendix A.3.
Having established that Eqns.(2.24), (2.25), and (2.26) cannot reliably be applied to membrane fuel cell humidifiers, all other simulated results that have been reported here used Eqn.(2.23) as the mass transfer function.

5.4.5. Pressure drop

Using the Darcy friction factor pressure drop estimation (Eqns.(5.1),(5.2)) was found to substantially under predict the device pressure drops (sum of wet and dry side pressure drops). At 350 SLPM, the calculated device pressure drop was only 18% of its measured value of 1600 Pa. It is likely that a large percentage of the measured pressure drop came from losses through the fittings, manifold header, and as a result of unequal flow sharing among channels. Another possible cause for this error was that the condensate in the wet side increases pressure drop above what would be predicted by the naïve all-vapour equations employed here.

An alternative method of evaluating pressure drop is by fitting the empirical data to a flow orifice equation such as Eqn.(5.3), as suggested in [77]. A least squares regression analysis suggested appropriate parameters for the geometry of the 5kW humidifier are $C_1=3.94\times10^{-8}$ and $C_2=1.36$. The pressure drops using the fitted curves are shown in Figure 5.7.
There are at least two drawbacks to this technique. First, the maximum absolute errors can still be significant. In the current case, a maximum deviation of 19% was observed even after using a two-parameter fit over 10 data points. Second, the flow restriction equation has limited physical basis and is little more than a curve-fit. Fitted expressions from experimental testing are not desirable in a predictive model because it relies on the specific geometry of the particular humidifier and viscosity under the operating conditions. Nonetheless, the under prediction of the pressure drop along the channel suggests, as mentioned above, that either a two phase flow correlation is required or the device pressure drop is dominated by the loss through the fittings and the header.
5.4.6. The model as a design tool

Consider the case where given a fixed channel aspect ratio and number of channels, the channel length is to be optimized to suit moisture transfer and pressure drop targets. Reasonable targets for a 5kW PEMFC system at standard low temperature and pressure operating conditions are listed in Table 5.3.

<table>
<thead>
<tr>
<th>Target</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture transfer</td>
<td>Outlet dew point &gt; 60°C (DPAT &lt;= 5°C) For a cell temperature 65°C, this provides the cathode inlet a relative humidity of 80%</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>1800 Pa Assuming 3-5% of system power can be used to accommodate humidifier device pressure drop, at 350 SLPM this equals 1.6-2.6 kPa. Set target at lower end of this range.</td>
</tr>
</tbody>
</table>

Using the same number of channels and channel aspect ratio as before and standard low temperature and pressure conditions, the upper and lower limits of the design window can be determined (see Figure 5.8). The fitted membrane properties and pressure drop correlation determined above were used, and the parameter space of $L \pm 0.1$ m was considered.
Figure 5.8. Using target dew point approach temperature and device pressure drop to select a suitable channel length, calculated with fitted membrane properties

The model isolated the lengths that satisfy both moisture transfer and pressure drop targets. Here it shows that the current length, $L=0.255$ m, is near the middle of the design window as expected since the results shown in the diagram relied heavily on the fitted parameters used earlier. If one introduces a third performance metric such as humidifier volume, the lower length boundary would be preferred. Similar plots can be produced for different channel sizes and number of channels to more fully explore the parameter space. Other work that used the model as a design tool is presented in Appendix D.

5.5. Chapter summary

The predictive thermodynamic model has been applied to realistic membrane-based fuel cell humidifier conditions. A significant conclusion found in this analysis was that the membrane-based enthalpy exchanger analysis commonly used in the ERV field of technology is not suited for fuel cell humidifier application. Two justifying reasons for
this statement are (1) the fuel cell humidifier is subject to very high humidity and even two phase flow on the wet-side, and (2) using the humidity ratio as a driving parameter in the presence of temperature gradients can lead to thermodynamically impossible results.

In the absence of membrane sorption properties, the model was fit to empirical data and its use as a design tool was demonstrated.
6. Conclusions

The thrust of this thesis has been to further the understanding of moisture transfer in recuperative membrane humidifiers for PEMFC application. The motivation behind this focus is that improvements to this balance of plant component translates into increased PEM system volumetric power density and lower system cost, enabling them to compete technically and economically with other energy conversion devices such as heat engines and batteries. This final chapter summarizes the key conclusions and contributions to the field, and suggests areas where future work could be directed.

6.1. Summary

This thesis addressed the problem that there are no thermodynamically-grounded tools to aid in the development of membrane fuel cell humidifiers. Table 6.1 includes a review of the thesis contributions in the context of the specific objectives.
### Table 6.1. Review of objectives

<table>
<thead>
<tr>
<th>Objective</th>
<th>Key Result or Conclusion</th>
<th>Justification/Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Develop a thermodynamically-grounded model to aid in the development of membrane fuel cell humidifiers</td>
<td>• A numerical heat and mass transfer model was implemented, considering two parallel 1-D channels separated by a membrane.</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Experimentally collect information on the effect of flow rate and channel location on moisture transfer</td>
<td>• Effect of the wet-side air flow rate on outlet dew point is minor compared to the air flow rate of the dry-side.</td>
<td>Chapter 3</td>
</tr>
<tr>
<td>Validate model predictions for effect of flow rate and channel location on moisture transfer</td>
<td>• Limited success. The choice of diffusion coefficient correlation affected water flux by up to 86%. However, simulated trends for effect of flow rate on outlet dew point and channel location on moisture flux showed good agreement with experimental results.</td>
<td>Chapter 4</td>
</tr>
<tr>
<td>Evaluate and compare diffusion coefficient correlations from literature</td>
<td>• Nguyen and Zawodzinski diffusivity correlations provided better agreement than Fuller and Chen relations for the conditions studied. Errors caused by the large variation in diffusion coefficients found in the literature make it very difficult to predict water transport without using fitted parameters. The Nguyen relationship yielded up to 14% error in outlet dew point, 21% error in average water flux compared to experiment. • Analysis on effect of temperature on outlet dew point suggests a higher activation energy be used in Arrhenius dependency.</td>
<td>Chapter 4</td>
</tr>
<tr>
<td>Apply model to application-relevant geometry and conditions</td>
<td>• A 5 kW humidifier geometry was considered under typical low temperature and pressure conditions. Unknown membrane properties required fitted parameters to accurately predict measured values. Pressure drop estimation was also considered.</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>Evaluate suitability of modeling techniques from enthalpy exchangers in different applications</td>
<td>• Using humidity ratio as the overall mass transfer driving force across the membrane can erroneously result in relative humidities greater than 100% on the dry-side. This caution applies to non-isothermal conditions with high moisture flux values. • A more rigorous derivation of ERV-based analysis of membrane enthalpy exchangers is required before being used for PEMFC membrane humidifier modeling.</td>
<td>Chapter 5, Appendix A</td>
</tr>
</tbody>
</table>
A valuable conclusion not mentioned in Table 6.1 is that, in cases where diffusivity depends on the hydration level of the membrane, using an average membrane water content to evaluate diffusivity provides more reliable and accurate results than using the water content calculated at the average relative humidity.

This research has resulted in at least three original and useful contributions to the field of gas-to-gas PEMFC membrane humidifiers:

- Experimentally examined the effect of differential flow rate on humidifier moisture transfer performance and the effect of channel location on moisture flux
- Implemented a numerical heat and mass transfer model suitable for analyzing moisture transfer performance (and to a lesser extent, pressure drop performance)
- Assessed the applicability of existing membrane modeling techniques from other fields to PEMFC membrane humidification. Namely, the Nafion solution-diffusion technique and the ERV moisture transfer resistance technique.

In addition to these contributions, progress has been made on a novel technique to differentiate diffusion and surface desorption mass transfer resistances. The description and preliminary application of the technique is detailed in Appendix C.

6.2. Future work

Should future work be carried out with experimental single channel humidifier studies, it is recommended to reduce the channel depth, make a longer channel, or use a thinner membrane to improve the humidifier. One may encounter physical barriers, however, such as the maximum length that can be accommodated in an isothermal oven, or the minimum depth that will accommodate thermocouple probes in the channel.
Independent techniques to corroborate humidity measurement accuracy may also be worthwhile to build confidence in the data. Examples include condensing and collecting water vapour from the outlet stream or using desiccants to adsorb it.

There are numerous avenues the thermodynamic modeling can take in future research. Additional diffusion coefficient correlations from literature, alternative transport equations such as hydraulic or chemical potential, or more refined two-phase flow modeling techniques would all be worthy considerations. Alternatively, for single phase applications, one may wish to evaluate the effectiveness-NTU method in the context of heat and mass transfer in PEMFC humidifiers. It would also be useful to measure sorption data for alternative membranes to reduce the model’s dependency on fitted parameters.

The model in its current state can be used to further explore the parameter space of geometric variables and operating conditions in order to optimize humidifier designs. Pre- and post-processing modules could easily be added to include performance metrics other than moisture transport and pressure loss, such as installation volume and cost.

6.2.1. On surface mass transfer resistances

In both the single channel humidifier and 5kW humidifier, cursory examination showed that surface mass transfer resistances significantly affect mass transfer and cannot be neglected for accurate predictive modeling. Prior to this, it had been assumed that surface mass transfer resistances were negligible compared to diffusion through the membrane. Two approaches to consider these effects are (a) Sherwood number correlations for forced convection mass transfer, and (b) surface absorption and desorption parameters.
With respect to approach (a), a technique used in the ERV field of technology was considered but found to be inadequate for applications outside of common atmospheric temperatures (see Appendix A). A suggestion for improving this technique is suggested in Appendix A.3.

With respect to method (b), a technique to simultaneously determine diffusion and desorption parameters from transient experimental water flux measurements was considered (see Appendix C). Although the technique presented in Appendix C has been developed and tested, its full capabilities have not yet been realized. Gathering reliable transient experimental data for a wide range of temperatures, concentration gradients, and membrane thicknesses will allow for a more complete characterization of the surface desorption conductance and its dependencies. On the model development side, changing the Dirichlet boundary condition on the dry-side is expected to make model simulations match more closely with the experimental water flux signal.
REFERENCES


REFERENCES


REFERENCES


REFERENCES


A. Limitations of $\varepsilon$–NTU method for heat and mass transfer

This Appendix discusses the derivation and limitations of the $\varepsilon$-NTU method for heat and mass transfer in membrane humidity exchangers as proposed by L.Z. Zhang in [36]. Two key observations have been made regarding the derivation that call into question the validity of the $\varepsilon$-NTU method being applied to fuel cell humidifiers.

A.1. Use of the Clausius-Clapeyron saturation vapour pressure equation

The Clausius-Clapeyron equation is a theoretical expression for the saturation vapour pressure of most liquids:

$$P_{\text{sat}} = P_{\text{ref}} \exp \left( -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right)$$

(A.1)

The form of Clausius-Clapeyron equation used by Zhang employs a reference state of 1 atm and 298 K (25°C) and assumes a constant heat of vaporization:

$$P_{\text{sat}} = \frac{101325(10^6)}{0.622} \exp \left( -\frac{5294}{T} \right)$$

(A.2)

A result of assuming a constant heat of vaporization is that the error in the equation increases the further one gets from the reference conditions. Figure A.1 shows the percent deviation of Eqn.(A.2) compared to the Hyland Wexler equation. The well-known Goff-Gratch equation is also shown for a 3rd reference correlation.
Figure A.1. Comparison of saturated vapour pressure from three different equations

The Goff-Gratch and Hyland-Wexler equations show very little deviation from each other and are presumed to be most accurate. The percent deviation of the Clausius-Clapeyron equation, Eqn. (A.2), is within an acceptable 2% for most atmospheric temperatures, but increases rapidly at either higher or lower temperatures. The error is still less than 5% even at 70°C, but the sensitivity of the e-NTU solution to this error is yet unknown. One must be aware that using this correlation can limit the overall accuracy of the derivations that employ it.

A.2. Correlation between humidity ratio and relative humidity

From the definitions of relative humidity and humidity ratio, the following relation can be derived:
\[ \frac{\phi}{\omega} = \frac{P}{0.622 P_{sat}^{H2O}} - \frac{\phi}{0.622} \] (A.3)

where the numeric constant 0.622 is the molecular weight ratio of water to air.

Substituting in Eqn.(A.2), Zhang arrived at:

\[ \frac{\phi}{\omega} = \frac{\exp(5294/T)}{10^6} - \frac{\phi}{0.622} \] (A.4)

Zhang then neglected the second term on the right hand side on the grounds that it is generally less than 5% of the first term on the right hand side. While this is true at atmospheric pressures (~1 atm) and temperatures (20-40°C), it is not the case at the higher temperatures that are found in fuel cell humidifiers (see Figure A.2). With errors up to 20% at 60°C and 100% relative humidity, the 2\textsuperscript{nd} term on the right hand side of Eqn.(A.4) cannot be neglected.
Figure A.2. Magnitude of 2nd term compared to 1st on right hand side of Eqn.(A.4)

A.3. Recommendation

The use of the Clausius-Clapeyron equation and neglecting the $\phi/0.622$ term in Eqn.(A.4) allow Zhang to provide a simplified expression for overall moisture transfer resistance across the membrane analogous to the overall heat transfer coefficient. Without these assumptions, the problem cannot be simplified as easily. One has the following system of 3 flux equations with 5 unknowns ($J, \omega^w_{mem}, u^w_{mem}, u^D_{mem}$, and $\omega^D_{mem}$):

$$J = h^w_M \left( \omega^w - \omega^w_{mem} \right)$$

$$J = \frac{D_u}{t_{mem}} \left( u^w_{mem} - u^D_{mem} \right)$$

$$J = h^D_M \left( \omega^D_{mem} - \omega^D \right)$$

(A.5)
Introducing 2 more unknowns ($\phi^D_{\text{mem}}$ and $\phi^W_{\text{mem}}$) and 4 equations of relation close the problem:

\[
\frac{\phi^W_{\text{mem}}}{\omega^W_{\text{mem}}} = \frac{P}{0.622 P_{\text{sat},W}^{H_2O}} - \frac{\phi^W_{\text{mem}}}{0.622}
\]

\[
\frac{\phi^D_{\text{mem}}}{\omega^D_{\text{mem}}} = \frac{P}{0.622 P_{\text{sat},D}^{H_2O}} - \frac{\phi^D_{\text{mem}}}{0.622}
\]

and

\[
u^W_{\text{mem}} = \frac{u_{\text{max}}}{1 - C + C/\phi^W_{\text{mem}}}
\]

\[
u^D_{\text{mem}} = \frac{u_{\text{max}}}{1 - C + C/\phi^D_{\text{mem}}}
\]

This provides a set of 7 equations, 2 of which are non-linear. A subroutine was written in MATLAB to solve these equations in order to demonstrate an example. The parameters used and solution variables are listed Table A.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Variable</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>101325 Pa</td>
<td>$J$</td>
<td>$3.67 \times 10^{-5}$ kg m$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$T^a$</td>
<td>40°C</td>
<td>$\omega^W_{\text{mem}}$</td>
<td>0.0227 kg H$_2$O (kg air)$^{-1}$</td>
</tr>
<tr>
<td>$\omega^W$</td>
<td>0.03</td>
<td>$\phi^W_{\text{mem}}$</td>
<td>52.3 %</td>
</tr>
<tr>
<td>$\omega^D$</td>
<td>0.01</td>
<td>$\omega^D_{\text{mem}}$</td>
<td>0.0173 kg H$_2$O (kg air)$^{-1}$</td>
</tr>
<tr>
<td>$h^W$</td>
<td>0.005 kg m$^{-1}$ s$^{-1}$</td>
<td>$h^D$</td>
<td>0.005 kg m$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$D_a$</td>
<td>$2.0 \times 10^{-7}$ kg m$^{-1}$ s$^{-1}$</td>
<td>$D_{\text{mem}}$</td>
<td>1.75x10$^{-4}$ m</td>
</tr>
<tr>
<td>$l_{\text{mem}}$</td>
<td>1.75x10$^{-4}$ m</td>
<td>$C$</td>
<td>2</td>
</tr>
<tr>
<td>$u_{\text{max}}$</td>
<td>0.30</td>
<td>$u^W_{\text{mem}}$</td>
<td>0.1063 kg H$_2$O (kg mem)$^{-1}$</td>
</tr>
</tbody>
</table>

a – An isothermal condition is considered here. Eventually different temperatures could be used for the wet and dry sides.
In the model presented in this work, this set of equations should be solved at every station along the channel (in the $x$-direction). The manner in which this could be incorporated into the $\varepsilon$-NTU method has not been determined. The $\varepsilon$-NTU would eliminate the need to solve the equations at each station.
B. Derivation of energy equation differential equation

Consider the control volume in Figure B.1 in the case where only one wall is permeable to water flux:

![Figure B.1. Membrane cartridge concept](image)

Define the surface averaged heat transfer rates as:

\[ q_1 = h_{H_2O,1} \dot{m}_{H_2O,1} + h_{air,1} \dot{m}_{air} \]
\[ q_2 = h_{H_2O,2} \dot{m}_{H_2O,2} + h_{air,2} \dot{m}_{air} \]
\[ q_{surr} = U_s \Delta x (T_{surr} - T) \]
\[ q_3 = U_{mem} \Delta x (T_{ref} - T) + h_{H_2O,3} \dot{m}_{H_2O,3} \]

where the mass flow of water into the control volume can be approximated as:

\[ \dot{m}_{H_2O,3} = \left. \frac{d\dot{m}_{H_2O}}{dx} \right|_x \Delta x \]
This form assumes a constant flux value across the distance \( \Delta x \), as evaluated at the midpoint. This approximation is valid provided that \( \Delta x \) is sufficiently small, and becomes more valid as \( \Delta x \) tends to zero.

The energy equation on the control volume is written out as:

\[
\begin{align*}
&h_{air,1}m_{air} + \left( h_{H2O}m_{H2O} \right)_{x+\frac{\Delta x}{2}} + U_s' \Delta x(T_{surr} - T) + U_{mem}' \Delta x(T_{ref} - T) \\
&+ \left( h_{H2O} \frac{dm_{H2O}}{dx} \right)_{x+\frac{\Delta x}{2}} \Delta x = \left( h_{H2O}m_{H2O} \right)_{x+\frac{\Delta x}{2}} + h_{air,2}m_{air}
\end{align*}
\]

(B.3)

Perform Taylor expansions on the two terms evaluated at \( x + \Delta x/2 \):

\[
\begin{align*}
&\left( h_{H2O}m_{H2O} \right)_{x+\frac{\Delta x}{2}} = \left( h_{H2O}m_{H2O} \right)_{x} + \left( h_{H2O} \frac{dm_{H2O}}{dx} + dh_{H2O} \right) \frac{\Delta x}{2} \\
&+ \text{(2nd order terms)} \frac{(\Delta x)^2}{8}
\end{align*}
\]

(B.4)

\[
\begin{align*}
&\left( h_{H2O}m_{H2O} \right)_{x+\frac{\Delta x}{2}} = \left( h_{H2Om} \right)_{x} - \left( h_{H2O} \frac{dm_{H2O}}{dx} + dh_{H2O} \right) \frac{\Delta x}{2} \\
&+ \text{(2nd order terms)} \frac{(\Delta x)^2}{8}
\end{align*}
\]

(B.5)

Sub these 2 equations into (A.7) and simplify. Note that the zeroeth and 2nd order terms in Taylor expansions cancel out.

\[
\begin{align*}
&h_{air,1}m_{air} - \left( h_{H2O} \frac{dm_{H2O}}{dx} \right)_{x} \frac{\Delta x}{2} - \left( h_{H2O} \frac{dm_{H2O}}{dx} + dh_{H2O} \right) \frac{\Delta x}{2} + h_{air,2}m_{air} \\
&+ U_s' \Delta x(T_{surr} - T) + U_{mem}' \Delta x(T_{ref} - T) = \left( h_{H2O} \frac{dm_{H2O}}{dx} \right)_{x} \frac{\Delta x}{2} + \left( h_{H2O} \frac{dm_{H2O}}{dx} + dh_{H2O} \right) \frac{\Delta x}{2} + h_{air,2}m_{air}
\end{align*}
\]

(B.6)

Rearrange and collect terms:

\[
\begin{align*}
&- \left( \frac{dcp_{H2O}T}{dx} \right) m_{H2O} \Delta x + U_s' \Delta x(T_{surr} - T) + U_{mem}' \Delta x(T_{ref} - T) = (h_{air,2} - h_{air,1})m_{air}
\end{align*}
\]

(B.7)
Assuming constant \( c_p \) values:

\[
- \left( c_{p,H_2O} \frac{dT}{dx} \dot{m}_{H_2O} \right) \Delta x + U_s' \Delta x (T_{surr} - T) + U_{mem} \Delta x (T_{ref} - T) = c_{p,air} \frac{dT}{dx} \Delta m_{air}
\]  

Finally, the ODE can be written as:

\[
\frac{dT}{dx} = \frac{U_{mem}' (T_{ref} - T) + U_s' (T_{surr} - T)}{c_{p,air} \dot{m}_{air} + c_{p,H_2O} \dot{m}_{H_2O}}
\]  

With condensation present on the wet side, it can similarly be shown that:

\[
\frac{dT^w}{dx} = \frac{U_{mem}' (T_{ref} - T) + U_s' (T_{surr} - T) + (1 - \eta) h_{vap} \frac{d\dot{m}_{H_2O_1}}{dx}}{c_{p,air} \dot{m}_{air} + c_{p,H_2O_1} \dot{m}_{H_2O_1} + c_{p,H_2O_2} \dot{m}_{H_2O_2} + c_{p,H_2O_1} \dot{m}_{H_2O_1}}
\]

The parameter \( \eta \) is the fraction of heat released that goes into the membrane (and thus \( 1 - \eta \) goes to the wet stream). Recall that the direction of flow on the wet side is in the negative \( x \) direction, so \( \frac{d\dot{m}_{H_2O_1}}{dx} \) will usually be negative if condensation is occurring along the channel in the negative \( x \) direction.
C. On surface mass transfer resistance

Due to the length of Appendix C, a table of contents has been provided:

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C.1. Appendix overview

Understanding moisture transport through membranes is key to developing an effective membrane humidifier. The overall transport in dense, non-porous membranes is a combination of absorption on the wet side, diffusion through the bulk of the membrane, and desorption into the dry stream. Using Fick's first law and equilibrium sorption curves is valid only if the membrane interfaces have reached equilibrium with the relative humidity of the adjacent gas. This neglects surface desorption and boundary layer mass transfer resistances. Evidence has been put forward by several authors [43, 64, 65, 71, 78] suggesting that there are situations where the adsorption and desorption mechanisms cannot be overlooked as insignificant or negligible. In this case, surface mass transfer effects can become significant and only recently have a few models considered them [43, 63-65]. These models use a constant mass transfer conductance to relate the bulk gas water concentration to the water content on the membrane surface. The work of Ge [43]
goes a step further and suggests the absorption and desorption conductances have a linear dependence on water content.

Sections 4.3.6 and 5.4.4 considered the surface mass transfer effects and showed them to be an important physical process in the overall membrane transfer. This Appendix investigates the application of a mathematical analysis to transient membrane permeation data in order to differentiate and quantify diffusion and surface desorption. This study is beyond the scope of the current thesis, but is a significant step in the direction of better understanding surface desorption. Other investigators have used transient sorption data or transient permeation data to quantify the diffusion coefficient, but the desorption mass transfer resistances have, to the best of our knowledge, never been determined simultaneously from the same data. The results presented here correspond to water transport through a Nafion 115 membrane at 40°C in order to demonstrate the technique. Such parameters fitted over a wide range of conditions would not only give insight into the important processes in membrane humidifiers, but could also be used to understand water transport in operating fuel cells and be used in more complete fuel cell simulations.

C.2. Theory and calculations

![Diagram](image)

**Figure C.1. Diffusion cell experiment**
Consider the experimental situation shown in Figure C.1. Inlet fluxes of different pressure, temperature and humidification are given to two sides of a cell where they are separated by a sample of membrane. The different conditions induce a water flux across the membrane, which can be determined from the measurement of vapour concentration in the sweeping gas. The steady state and transient dependence of this water flux allows fitting of coefficients in both surface and interior membrane water transport models.

C.2.1. Experimental determination of water flux

Inlet fluxes to the chamber in Figure C.1 are given in terms of volumetric gas flow $Q$, pressure $P$, temperature $T$ and dew point $T_d$. Additional numerical subscripts refer to the two sides of the membrane. Assuming gases are ideal, the total molar inlet flow will be:

$$n = \frac{PQ}{RT}$$

(C.1)

Assuming that the water vapour and other non-condensable gases obey the ideal gas law and move at the same convective velocity, it can be show that:

$$\dot{n}_{H_2O} = \frac{P_{sat}(T_d)}{P} \dot{n}$$

(C.2)

where $\dot{n}_{H_2O}$ is the molar inlet water vapour flow and $P_{sat}(T_d)$ is the corresponding water vapour pressure at the dew point for which empirical fits are available (the Hyland and Wexler equation was used here). The rest of the inlet flux $\dot{n} - \dot{n}_{H_2O}$ is non-vapour. If there is water flux $J$ through the membrane of area $A$, and the outlet pressure is $P^*$, then the outlet water vapour pressure will be
Thus by measuring $P_{H2O}^*$ the water flux $J$ can be determined. The purpose of this work is identifying how $J$ is influenced by surface mass transfer resistance. Two assumptions have been made in this discussion:

1. $J$ does not vary across the area of the membrane in the chamber.

2. Changes in $P_{H2O}^*$ once the other side of the membrane is exposed to a different thermodynamic potential are large enough to detect accurately.

C.2.2. Membrane water transport model

Consider Figure C.1. Water flux $J_1$ enters the membrane from side 1 and $J_2$ exits from side 2 (positive $J$'s indicate flows from side 1 to side 2). The water content $\lambda(x,t)$ obeys the diffusion equation:

$$\frac{d\lambda}{dt} = \frac{1}{D(\lambda)} \frac{d}{dx} \left( D(\lambda) \frac{d\lambda}{dx} \right)$$  \hspace{1cm} (C.4)

where the diffusion coefficient, $D$, is allowed to depend on water content in general. This coefficient is also known to depend on temperature. A standard assumption is that the equilibrium membrane water content depends on the relative humidity $\phi$ of the surroundings. In this work, sorption curves from two temperatures [49, 50] based on the relative humidity of the inlet gas were linearly interpolated to correct for temperature. Under liquid equilibrated conditions, the water content was fixed at $\lambda=22$, and does not change significantly with temperature [50].

$$\lambda = \lambda_{303} + \frac{\lambda_{353} - \lambda_{303}}{50} (T - 303)$$ \hspace{1cm} (C.5)
\[ \lambda_{303} = 0.043 + 17.81\phi - 39.85\phi^2 + 36.0\phi^3 \quad \text{(C.6)} \]

\[ \lambda_{353} = 0.300 + 10.8\phi - 16.0\phi^2 + 14.1\phi^3 \quad \text{(C.7)} \]

Using the form proposed in [65], the following relationships at the membrane boundary apply:

\[ J_1 = -aD(\lambda) \frac{d\lambda}{dx} \bigg|_{x=0} = a\gamma_a (\lambda^e_i - \lambda) \bigg|_{x=0} \quad \text{(C.8)} \]

\[ J_2 = -aD(\lambda) \frac{d\lambda}{dx} \bigg|_{x=L} = a\gamma_d (\lambda) \bigg|_{x=L} - \lambda^e_2 \quad \text{(C.9)} \]

where \( a \) is the concentration of sulfonate sites in the membrane and \( \gamma_d \) and \( \gamma_a \) are desorption and absorption coefficients, respectively. Given an initial water content profile \( \lambda(x,0) \) and inlet flow parameters that determine \( \lambda^e_i \) and \( \lambda^e_2 \), \( J_1(t) \) and \( J_2(t) \) can be predicted numerically. By comparing the transient model prediction to experimental data, estimates of \( D \) and \( \gamma_a \) can be determined.

**C.2.3. Estimation of surface mass transfer effects**

To assess the magnitude of effect that surface mass transfer resistances will have, the model is linearized about the saturated vapour state. Using Springer's correlation (Eqn.(C.6)), \( \lambda \approx 14 \) at 30°C and using the fit in [42] the constant value of \( D=9.2 \times 10^{-10} \) \( m^2 s^{-1} \) is assumed in this section. In [65], an estimate of \( \gamma_d = 2.1 \times 10^{-7} \) \( ms^{-1} \) is obtained. Although this fit is primarily for desorption from a membrane with catalyst layer, this value is taken here as an estimate for a simple membrane and is used for absorption also. These assumptions are being made only to obtain a preliminary estimation of magnitudes. The standard values of \( a=1200 \text{ mol} \text{ m}^{-3} \) and thickness \( L=50 \times 10^{-6} \text{ m} \) for Nafion 112 are
used [42, 43, 65]. At steady state, the following result comes from the model after a straightforward calculation:

\[
J_1 = J_2 = aF (x_1^s - x_2^s)
\]

where

\[
F = \frac{1}{l/\gamma_d + L/D + l/\gamma_a}
\]

is in the form of a series conductance. The linear dependence of flux on the difference in equilibrium concentrations is a natural consequence of our linearization of the model. There are three things to notice about the form of \( F \):

- With only steady state measurements it is not possible to distinguish between surface \((l/\gamma_d + l/\gamma_a)\) and bulk membrane \((L/D)\) mass transfer resistances.
- With the values listed above, the surface mass transfer resistances \((4.8 \times 10^6 \text{ m}^2\text{s}^{-1})\) are two orders of magnitude larger than the diffusion resistance \((5.4 \times 10^4 \text{ m}^2\text{s}^{-1})\).
- Fitting the value of \( F \) to an effective diffusivity \( F = D_{eff} / L \) will not scale correctly with membrane thickness.

These three points are intended to stress the importance of gaining a proper understanding of mass transfer resistances at the membrane interfaces and their dependencies on other parameters.

C.2.4. An extreme case: Negligible absorption resistance

The situation is considered now where initially both sides of the chamber are exposed to non-saturated vapour and in equilibrium (i.e., no flux). The membrane interface on side 1 \((x=0)\) is suddenly exposed to liquid water and a step function in time change in water activity gradient across the membrane is established. From the
experimental time history of $J_2$ it is possible to estimate both bulk diffusion $D$ and surface desorption $\gamma_d$ parameters. In this situation adsorption from side 1 can be assumed to be very fast, so Eqn.(C.8) is replaced by

$$\lambda|_{x=0} = \lambda^e_1 \approx 22$$  \hspace{1cm} (C.12)

At steady state, fluxes are predicted by the model to be of the form of Eqn.(C.10) with

$$F = \frac{1}{1/\gamma_d + L/D}$$ \hspace{1cm} (C.13)

Experimental steady state data can be used to determine $F$ via Eqn.(C.10). Transient simulations of Eqn.(C.4) with boundary conditions Eqn.(C.9) and (C.12) were run with different values of $\gamma_d$ and $D$ that together satisfy Eqn.(C.13) (i.e., match the steady state value $F$). The values of $\gamma_d$ and $D$ are adjusted until the simulations match the transient experimental data as closely as possible. With fixed $F$, this is a one-parameter fit on an a-priori bounded interval.

In principle, it is clear that the transient data can be used to distinguish surface from bulk water transport limiting mechanisms. If $F$ above is due only to surface effects, $J_2$ will respond instantly to the step change in side 1 water content. If $F$ were due only to bulk diffusion, $J_2$ would have a delayed response. This differentiation is illustrated in Figure C.2.
C.3. **Experimental**

C.3.1. **Setup**

A two chamber cell was constructed with temperature control on either side. Figure C.3 shows the body formed by two-cylindrical stainless steel cells; the membrane holder separating both compartments (dry and wet chamber), and water jackets surrounding both chambers to control temperature. An important feature of this design is a knife-gate valve situated as close as possible to the membrane on the wet chamber side. This valve provides precise and repeatable control over the start time of the transient experiments.
Figure C.3. Assembly view of the diffusion cell showing gate-valve mechanism to control experiment start time, membrane holder, and water jackets for temperature control.

The diagram in Figure C.4 shows the complete experimental set up. A Vaisala HMT 337 sensor was used on the dry side to record the increase in water vapour partial pressure. The time response of the sensor is assumed to be negligible compared to the water transport process. The manufacturer states a 0 to 90% response time of 8s at 20°C in still air when using a grid filter. The actual response time in the experimental setup is expected to be faster because of the higher temperature and the presence of forced convective mass transfer (due to the flow of the sweep gas) as opposed to natural convective mass transfer. Temperature and dew point sensors were connected to a DAQ system to keep instantaneous record of all data.
Figure C.4. Experimental set up for transient analysis of liquid water transport

The circular 2 cm² Nafion 115 membrane samples were treated by boiling them in hydrogen peroxide, rinsing them in de-ionized water, boiling them in sulfonic acid, and finally boiling in de-ionized water again, according to Ref.[79].

C.3.2. Methodology

Transient permeation measurements for Nafion 115 were performed with liquid equilibrated membranes at 40°C and atmospheric pressure (at sea level). On the wet side, liquid water was continuously replenished by a syringe pump. Liquid water was used in order to minimize the effect of the adsorption process. The membrane was preconditioned by flowing temperature and humidity controlled carrier gas through the dry chamber to impose a relatively dry or partially hydrated membrane initial condition. The ‘dry’ condition had an inlet dew point of 16.2°C ($\phi=25\%$) and the partially humidified condition a dew point of 26.7°C ($\phi=50\%$). For application with the mathematical analysis, the membrane was partially humidified to avoid any phenomena related to dry Nafion (‘dry skin’ formation, inversion of ionic sites, etc). Helium was used as the sweeping gas at a flow rate of 100 SCCM. The supply of humid sweeping gas was done
by a saturation point bubbler humidifier. The gate valve was then lifted, exposing the membrane to the wet environment and establishing a thermodynamic potential gradient to drive the water flux.

C.4. **Model descriptions**

Two models were developed, the second building on the first. The first assumed a constant-diffusion coefficient value for the membrane and hereafter will be referred to as the Constant Diffusion Coefficient (CDC) model. The second assumed a linear dependence of diffusion coefficient on water content and will be referred to as the Varying Diffusion Coefficient (VDC) model. The VDC model is more relevant to Nafion and other membranes that are known a priori to have variable diffusion coefficient. If little is known about the membrane, however, the diffusion coefficient is generally assumed constant (see [26, 27, 29-31, 33, 39, 80] for example). In this case, the CDC model is more relevant.

C.4.1. **CDC Model**

The CDC model assumed constant diffusion and desorption coefficients. The problem becomes a linear model with two coefficients to be fitted to the experimental transient signal. Defining $G$ as the denominator in Eqn.(C.13):

$$ G = \frac{1}{G_d} + \frac{L}{D} = \frac{1}{F} $$  

(C.14)

$G$ was calculated from the steady state experimental signal, $P_{H_2O}^*$, via Eqn.(C.3), (C.10), and (C.14). A basis parameter, $\theta \in (0,1)$, was introduced which determined the respective contributions of the two terms in $G$. Two equations of relation were established:
Note that when $\theta=1$, the transport was diffusion-limited and when $\theta=0$, the transport was surface transfer limited. This parameter is nothing more than a modified form of the Biot dimensionless number for mass transfer ($Bi_M = \frac{\gamma_d L}{D} = \frac{\theta}{1-\theta}$), relating the ratio of diffusion resistance to convection resistance.

From the experimental data, the model calculated and used steady state flux to find $G$, and then simulated the time signature for a guessed value of $\theta$. A bisection method root finding technique found the $\theta$ value that minimized the least squares regression error.

**C.4.2. VDC Model**

In this model, the constant diffusion constant, $D$, was replaced by $D(w) = \delta w$, where $\delta$ is a constant. This proportionality form allowed negligible diffusivity at low water contents and increasing diffusivity with increasing water content. Several previous studies have supported a linear or monotonically increasing relationship for Nafion, such as [24], [81], and [73] (as found in [42]). We acknowledge that this is a topic of ongoing discussion, as several investigators have claimed the diffusivity passes through a maximum near $\lambda=3-4$ and then decreases [54, 72, 82, 83]. This work does not submit evidence towards a particular dependency mode, but uses a linear dependence for the purposes of the model.
Considering steady state conditions, Eqn.(C.10) was rewritten to make an expression for the minimum possible value of $\gamma_d$. Since $\lambda|_{x=L} = \lambda|_{x=0} \approx \lambda_{liq}$ would correspond to no diffusive losses (i.e., minimum $\gamma_d$),

$$\gamma_{d_{min}} = \frac{J_s}{a(\lambda_{liq} - \lambda^e)} \quad (C.17)$$

Another basis parameter was used, $\theta \in (0,1)$,

$$\gamma_d = \frac{\gamma_{d_{min}}}{\theta} \quad (C.18)$$

To determine the corresponding value of $\delta$ for a given $\theta$, one must consider the steady state flux at all points $x$ in the membrane being equal to the desorption flux:

$$J_s = -a\delta\lambda(x)\frac{d\lambda(x)}{dx} = -a\gamma_d(\lambda_2 - \lambda^e) \quad (C.19)$$

Rearranging and noting that $2\lambda \frac{d\lambda}{dx} = \frac{d(\lambda^2)}{dx}$,

$$\frac{d(\lambda^2)}{dx} = -\frac{2}{a\delta} a\gamma_d(\lambda_2 - \lambda^e) \quad (C.20)$$

Integrating both sides with respect to $x$ from 0 to $L$ with boundary conditions $\lambda(0,t)=\lambda_{liq}$ and $\lambda(L,t)=\lambda_2$ gives:

$$\lambda^2 - \lambda_{liq}^2 = -2B(\lambda_2 - \lambda^e) \quad (C.21)$$

Where by definition

$$B = \frac{L\gamma_d}{\delta} \quad (C.22)$$

Rewrite Eqn.(C.21),

$$\lambda^2 + 2B\lambda_2 - \left(\lambda_{liq}^2 + 2B\lambda^e_2\right) = 0 \quad (C.23)$$

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And finding the positive root,
\[ \lambda_2 = -B + \sqrt{B^2 + (\lambda_{iq}^2 + 2B\lambda_c^c)} \]  
(C.24)

Finally, subbing Eqn. (C.24) into (C.19) yields:
\[ J_s = a\gamma_d \left( B + \sqrt{B^2 + (\lambda_{iq}^2 + 2B\lambda_c^c)} - \lambda_c^c \right) \]  
(C.25)

With \( \gamma_d \) given via Eqn.(C.18) and \( J_s \) known from the experimental data, Eqn.(C.25) becomes an implicit equation for \( B \), which was solved with a root finding technique. With \( B \) and \( \gamma_d \) known, \( \delta \) was found from the definition of \( B \) (Eqn.(C.22)).

To summarize, for every \( \theta \in (0,1) \), values of \( \gamma_d \) and \( \delta \) were obtained that together match the steady state flux \( J_s \), just as in the linear model. The value of \( \theta \) that minimized the least squares regression error between simulation and experimental data was used to determine final \( \gamma_d \) and \( \delta \) values. For the VDC model, as opposed to the CDC model, \( \theta=0 \) refers to the diffusion-limited extreme, and \( \theta=1 \) refers to the surface-transfer-limited extreme (i.e., \( \gamma_d = \gamma_{d\text{ min}} \)).

C.5. **Results and discussion**

C.5.1. **Experimental**

Liquid-equilibrated water diffusion experiments were performed at 40°C under atmospheric pressure. An average time for the dynamic process to complete is around 3 minutes. Once equilibrium was reached, there was no further observable change in the steady state signal for at least 2 hours.

The initial water content imposed on the membrane was found to affect the response signal. Figure C.5 shows the calculated flux of water across the membrane for both 25% and 50% relative humidity initial conditions. In the initial stage of the
experiment, the flux corresponding to the drier membrane was one order of magnitude below the flux from the pre-hydrated membrane. This difference became negligible after 6 minutes when fluxes became equal. The time constants of the signals of 62 and 105s are comparable to other reported results for Nafion membranes immersed in liquid water [50, 84].

The difference caused by the initial hydration of the membrane became apparent when for the initially dry membrane, a 20 second-delay was observed before the water concentration signal began to rise, shown in Figure C.5. The two signals mimicked the trends shown in Figure C.2 for different transport limiting extremes (i.e., surface vs. diffusion-limited). Comparing the two figures confirmed our hypothesis that an initially dry membrane had a diffusion-limited transient signal while the pre-hydrated membrane showed a surface-limited transient signal. With the pre-hydrated membrane, a pre-existing hydrophilic phase interconnected pores to facilitate the transport of water after being exposed to the liquid water, accelerating the diffusion process. Since the absorption conductance on the liquid-equilibrated wet surface was large and constant the overall transport of water across the membrane was limited mostly by desorption. On the contrary, with an initially dry membrane, diffusion was observed, at least initially, to be the limiting mechanism while absorption and evaporation had a lower effect.
Figure C.5. Experimental water flux across the membrane as a function of time; comparing an initially dry membrane and pre-hydrated membrane (Nafion 115, 40°C, 1atm)

C.5.2. CDC Model

Different spatial mesh discretizations were compared to ensure solutions were not dependent on mesh size. Figure C.6 indicates that only 20 equidistant nodes in the 0.127 mm membrane were sufficient for a grid-independent solution. Since computational power was not an issue, a mesh of 100 nodes was used for all subsequent simulations. Both Matlab’s ODE45 (an explicit Runge-Kutta Dormand-Prince pair) and ODE15s (a variable order solver based on numerical differentiation formulas) [74] were used for time stepping, but no difference in solution accuracy was observed. The ODE15s solver was chosen for the rest of the simulations because it was slightly faster. The ODE solver
determines time discretization automatically. Relative and absolute error tolerances were varied from $1 \times 10^{-3}$ to $1 \times 10^{-6}$ but had no effect on the solution.

![Diagram showing grid sensitivity study for CDC model with $\theta=0.5$](image)

**Figure C.6. Grid sensitivity study for CDC model with $\theta=0.5$**

Model simulations for various $\theta$ values were compared to the data from the 40°C, liquid equilibrated water flux experiment. Values obtained for the diffusion and desorption coefficients, as well as the equivalent mass transfer resistances, are shown in Figure C.7.
The resulting transient simulations along with experimental signal are shown in Figure C.8. The $\theta$ value that best fit the experimental data was $\theta = 0.320$. Using $a=1789$ mol SO$_3^-$ m$^{-3}$ and $L=0.127$mm with Eqns. (C.11), (C.15)-(C.17) yields a diffusion coefficient of $D=5.07\times10^{-11}$ m$^2$s$^{-1}$ and a surface desorption coefficient of $\gamma_d=1.88\times10^{-7}$ m s$^{-1}$. Visual inspection of Figure C.8 indicates that the agreement remains marginal even at this $\theta$ value. The time-delay-before-rise ($t<50$s) matches the higher $\theta$ value cases, but once the signal rise begins, the fast rise time mirrors the low $\theta$ cases ($50<t<160$s). Some of the error here may be due to the time response of the sensor, which has the effect of delaying the measured signal. Other error could be attributed to the model assumptions. Namely, neglecting absorption mass transfer resistance and assuming a constant diffusion coefficient for the Nafion membrane will both cause an under-prediction in the time that is required to establish the concentration gradients. If a substantial part of the error is caused by the constant diffusion coefficient assumption, the VDC model should yield a better match in this early part of the time history.
Another observation is that the experimental signal begins to level out at lower flux values than the simulation curves ($t>160s$). This phenomenon can be explained by the Dirichlet boundary condition assigned to the model (Eqn.(C.9)). In the simulations, the dry chamber's concentration is fixed as constant at the initial condition, $\lambda_2^0$. As the experiment progresses, this value will in fact be increasing and hence the disparity between the simulation and model increases as the signal (dry-chamber water vapour concentration) increases. With these comments in mind, the $\theta = 0.320$ value mentioned above is deemed the most suitable, given the errors caused by model assumptions and experimental technique.
C.5.3. VDC Model

The non-linear VDC model was then run using the same experimental data. Recall that in the VDC model, higher $\theta$ values trend toward the surface-transfer-limited regime, as opposed to the CDC model (see section C.4.2).

![Graph showing experimental data for initially dry membrane with VDC model simulation results with $\theta$ changing from 0.1 to 0.9 in increments of 0.1.]

From Figure C.9, a $\theta$ value of 0.816 was found to minimize the least squares regression error. Using $a=1789$ mol $\text{SO}_3^-$ m$^{-3}$ and $L=0.127$ mm yields values of $\delta=4.35 \times 10^{-12}$ m$^2$ s$^{-1}$ (mol$\text{SO}_3^-$)(mol$\text{H}_2\text{O})^{-1}$ and $\gamma_d=1.57 \times 10^{-7}$ m s$^{-1}$. Just as in the CDC model, this corresponds to a regime where surface mass transfer plays a significant role. Comparing Figures C.8 and C.9, one observes that the initial time lag before the signal rises ($t<50$ s) is more accurate with the VDC model. This reveals that the error in this domain in
Figure C.8 was caused mostly by the constant diffusion coefficient assumption in the model, as opposed to the neglection of absorption mass transfer resistance or the sensor time response.

The experimental and simulated signals still diverge once the concentration reaches higher values (\( t > 120 \text{s} \)); the same phenomenon observed in the CDC case. Again, this error is suspected to be caused by the constant water concentration boundary condition imposed on the wet chamber in the mathematical model.

At the optimal \( \theta \) value, profiles of the water content and corresponding diffusion coefficient were drawn and are shown in Figure C.10.

![Simulated time progression of water content and diffusion coefficient profiles, using VDC model with \( \theta = 0.816 \).](image)

**Figure C.10.** Simulated time progression of water content and diffusion coefficient profiles, using VDC model with \( \theta = 0.816 \).
Under the given conditions, the initial equilibrium water content was calculated to be $\lambda = 2.57$. Under the model boundary conditions, this value for the dry chamber equilibrium remains constant whereas according to the experimental signal, it increases to $\lambda = 3.23$ at steady state.

Table C.1 summarizes the results obtained for both the CDC and VDC model using experimental data from an initially partially hydrated membrane. The desorption coefficients found in this work are low when compared to others found in literature that use the same form for surface mass transfer resistance. Three possible reasons for this have been identified. First, the temperature studied here was 40°C while those in literature are typically higher (~80°C). It is possible that the desorption mass transfer conductance increases at higher temperatures, allowing fast equilibration. It is possible that higher temperatures lead to faster desorption, though further investigation would be required to confirm this hypothesis. Second, the nature of mass transfer coefficients is such that it is, to some degree, geometry and flow condition dependent. The chamber geometry in this cell could be minimizing the surface desorption resistance. It is noted that other studies [43] had a gas diffusion layer applied to the membrane. Third, if the steady state experimental flux was low due to experimental error, values for both desorption and diffusion coefficient will also be low since the steady state flux is a used to calculate them.
Table C.1. Summary of results

<table>
<thead>
<tr>
<th></th>
<th>Desorption coefficient ([x10^{-7} \text{ m s}^{-1}])</th>
<th>Fickian diffusion coefficient ([\text{m}^2\text{s}^{-1}])</th>
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<td>CDC Model</td>
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<td>VDC Model</td>
<td>1.57</td>
<td>VDC Model</td>
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<td>Okada (1999) [64]</td>
<td>10-100 (^{ab})</td>
<td>Fuller (1992) [42]</td>
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<tr>
<td>Futerko (2000) [43]</td>
<td>5 (^a)</td>
<td>Nguyen (1993) [42]</td>
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<tr>
<td>Berg (2004) [65]</td>
<td>57 (^a)</td>
<td>Rivin (2001) [81]</td>
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<tr>
<td>Chen (2004) [78]</td>
<td>10-1000 (^{ab})</td>
<td>Ye (2003) [83]</td>
</tr>
<tr>
<td>Ge (2005) [43]</td>
<td>46 (^c)</td>
<td>Ge (2005) [43]</td>
</tr>
</tbody>
</table>

\(^{a}\) At higher temperatures (343-353 K)
\(^{b}\) This range was chosen for study--not measured nor determined.
\(^{c}\) Calculated at 40°C and \(\lambda_2 = 2.57\)
\(^{d}\) Calculated at 40°C and \((\lambda_1 + \lambda_2)/2 = 12.3\)

The diffusion coefficients also compare low to values found in literature. The values shown in Table C.1 were calculated at a nominal condition for comparison purposes and it can be seen that results vary by 2 orders of magnitude. Reasons that the values determined in this study are on the lower end of the spectrum could be attributed to a low measured steady state flux value due to experimental error. This would also have explained the low desorption coefficient values, as mentioned above. Another reason for this deviation could be caused by an inaccurate parameter fit stemming from the marginal correlation between simulation and experimental at high flux values. Figure C.7 indicates that near \(\theta = 0.320\) (the best-fit value established above), the diffusion coefficient is quite susceptible to change in \(\theta\) (a tangent slope of \(1.54 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{theta}^{-1}\)).

C.6. Appendix summary

Two 1D transient mathematical models were implemented and used with experimental transient time-lag data to differentiate the diffusion and surface desorption water transport mechanisms. The first model, assuming a constant diffusion coefficient, yielded a desorption mass transfer coefficient of \(1.88 \times 10^{-7} \text{ ms}^{-1}\) and a diffusion
coefficient of $5.07 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ at $40^\circ\text{C}$. The second model, assuming a linear dependence of diffusion coefficient on water content, resulted in a similar desorption coefficient of $1.57 \times 10^{-7} \text{ m} \text{s}^{-1}$ and the expression for diffusion coefficient $D = 4.35 \times 10^{-12} \lambda$, where $\lambda$ is the number of water molecules per sulfonate site in the membrane. The linear dependence of diffusion coefficient on water content (VDC) model provided a better prediction of the experimental signal at small times ($t<50$s), but both models deviated from the experimental signal as the flux increased, presumably due to Dirichlet boundary conditions on the dry side. Both models indicated that the mass transfer resistance across the gas-membrane interface was significant. If in the application of a membrane fuel cell humidifier a similar membrane and temperature are used, the surface mass transport effects cannot be neglected.
D. Folded Membrane Architecture: Prototype Development

Current membrane-based humidifier topologies are derived from compact heat exchanger technology, such as the shell-and-tube or plate-and-frame technologies. A novel architecture used proposed by dPoint Technologies by folding the membrane into a membrane cartridge and then flowing the process streams through the folds of the membrane on opposite sides, as shown in Figure D.1.

Figure D.1. Membrane cartridge concept

D.1. Product specifications

In industry, the customer (fuel cell stack and/or system design company) will typically specify design operating conditions and required performance specifications. Target specifications presented here are what are believed to be a typical scenario for a 1 kW fuel cell stack. Based on a stoichiometry of 2 and cell voltage of 0.6 V, an air flow rate of 60 SLPM can be expected. If the parasitic loss caused by fluid friction through the device is limited to 1% of the system pressure, then at 60 SLPM the maximum allowable device pressure drop is 8.4 kPa. Typical flow conditions are with the wet side inlet to be fully saturated at 65°C and the dry side inlet to be 25°C and dry. Humidification performance will be measured in terms of dew point approach temperature, which is the
difference between the wet side inlet dew point and the dry side outlet dew point. An acceptable dew point approach temperature for the stated design conditions would be less than 5°C (derived from a desired outlet condition of 80% relative humidity at 65°C).

D.2. Changes to thermodynamic model

To account for the two phase pressure drop through a plastic extruded mesh that will be found in the 1 kW prototype, the Sato/Ergmunson equation was used. This correlation was originally developed to describe two phase pressure drop through chemical beds of porous fibrous meshes – similar to the plastic extruded meshes used in the 1 kW prototype. The two phase pressure drop, $P_{lg}$, is found from:

$$\log \left[ \frac{P_{lg}}{P_g + P_f} \right] = \frac{0.7}{\left[ \log \left( \frac{X}{1.2} \right) \right]^2 + 1}$$  \hspace{1cm} (D.1)

where $X = \left( \frac{P_f}{P_g} \right)^{0.5}$ \hspace{1cm} (valid for $0.1 < X < 20$)

The single phase pressure drops $P_g$ and $P_f$ are found from:

$$P = 10^{-6} \left[ \mu \nu S^2 \left[ \frac{k(1-e)^2}{e^3} \right] \right]$$  \hspace{1cm} (D.2)

Where $e$ is the porosity and $k$ is the Kozeny constant:

$$k = 3.6 \left[ \frac{e^3}{(1-e)^{0.5}} \right] \left[ 1 + 57(1-e)^3 \right] \hspace{1cm} (valid \ for \ 0.68 < e < 0.96)$$  \hspace{1cm} (D.3)

D.3. Development

Plastic extruded meshes were used to ensure even spacing between the membrane folds. The pressure drop across different extruded meshes was measured experimentally
in order to select a mesh that would minimize the device pressure drop. Note that the effect of these meshes on mass transfer was neglected in the model.

![Figure D.2. Pressure drop vs. mass flux for dry air at 25°C](image)

The large variation in pressure drop in Figure D.2 indicates that material selection for membrane spacing can significantly affect device pressure drop.
D.4. **Final performance**

The moisture transfer performance of the 1 kW prototype is shown in Figure D.3. The dew point approach temperature is 3.4°C, within the target maximum of 5°C. The pressure drop at rated flow, 60 SLPM, was measured as 1.6 kPa across the dry side and 5.2 kPa across the wet side (+/- 0.2 kPa for both sides). The total device pressure drop then is 6.8 kPa, which is higher than would be predicted from Eqns. (D.1) to (D.3), but still lower than the target maximum of 8.4 kPa. The discrepancy between pressure drop predictions and measured values is most likely due to condensation on the wet side of the humidifier. The condensation is caused because the wet side stream temperature drops faster than the dew point.