PEM FUEL CELL LOW FLOW RATE

DIAGNOSTICS

by

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Abstract

Efficient, reliable, and durable operation of Polymer Electrolyte Membrane (PEM) fuel cells are key requirements for their successful commercialization. One way to achieve this is to use diagnostic tools that can be used during product development and operation to satisfy these requirements. Such diagnostic tools are introduced in this thesis.

We introduce the ratio between call voltage and cathode output pressure oscillations as a diagnostic tool for the PEM fuel cell cathode. We show that for our system, these oscillations have similar frequency. Therefore, we propose using the amplitude ratio and phase difference between these oscillations to understand fundamental processes in PEM fuel cells.

We use the measure introduced above to design a signal based Fault Detection & Isolation (FDI) algorithm to isolate anode and cathode low flow induced faults during operation. We show that cathode flooding corresponds with an increase in the amplitude of voltage oscillations. Cathode starvation occurs at a cathode stoichiometry that is a second order function of the fuel cell current density for our system, while anode starvation occurs at a fixed anode stoichiometry. We use these measures to design diagnostic residuals, along with a boolean diagnostic logic, to isolate the low flow induced faults. We then examine the robustness of the proposed algorithm to changes in current, pressure, temperature, and humidity operating conditions.

Finally, we introduce a sensory vessel capable of measuring the two phase flow as it exits the fuel cell. Using this vessel, we detect two different modes of liquid water retention from the cathode. The first mode is periodic and imposes similar oscillations on the fuel cell voltage, while the second mode corresponds with a spike in the cell
voltage. We conclude that the source of the first liquid water is in the Gas Diffusion Layer (GDL) and catalyst pores, while the second sources is in the cathode flow field.

The pressure-voltage oscillations and sensory vessel are diagnostic tools that can be used to provide fundamental understanding of processes in PEM fuel cells, while the FDI algorithm can be used during operation to improve system performance, reliability, and lifetime.
To my lovely wife, Maryam.
Make everything as simple as possible, but not simpler.

Albert Einstein
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# Nomenclature

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<th>Description</th>
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<tbody>
<tr>
<td>$a$</td>
<td>Activity</td>
</tr>
<tr>
<td>$\bar{c}$</td>
<td>Molar heat capacity, JgK/mol</td>
</tr>
<tr>
<td>$e$</td>
<td>Electron charge, $1.602 \times 10^{19}$ Coulombs</td>
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<tr>
<td>$e$</td>
<td>Error</td>
</tr>
<tr>
<td>$E$</td>
<td>Electromotive force, V</td>
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<tr>
<td>$E^0$</td>
<td>Electromotive force at standard pressure, V</td>
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<td>$f$</td>
<td>System fault</td>
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<tr>
<td>$F$</td>
<td>Faraday constant, 96500 Coulombs</td>
</tr>
<tr>
<td>$F$</td>
<td>Volumetric flow rate, slpm</td>
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<tr>
<td>$\bar{g}$</td>
<td>Molar Gibbs free energy, J/mol</td>
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<td>$\bar{h}$</td>
<td>Molar Enthalpy, J/mol</td>
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<tr>
<td>$H$</td>
<td>Heater control signal</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density, mA/cm²</td>
</tr>
<tr>
<td>$i_0$</td>
<td>Exchange current density, mA/cm²</td>
</tr>
<tr>
<td>$i_L$</td>
<td>Limiting current density, mA/cm²</td>
</tr>
<tr>
<td>$i_n$</td>
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<td>$m$</td>
<td>Empirical value for concentration loss, V</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>Mass Flow rate, kg/s</td>
</tr>
</tbody>
</table>
\(n\)  empirical value for concentration loss, \(\text{cm}^2/\text{mA}\)

\(n\)  Window size

\(\dot{n}\)  Molar flow rate, \(\text{mol/s}\)

\(N\)  Avogadro number, \(6.022 \times 10^{23}\)

\(P\)  Pressure, Pa

\(P^0\)  Standard pressure, 100 kPa

\(q\)  Total electric charge, Coulombs

\(r\)  Specific resistance, \(\text{k}\omega/\text{cm}^2\)

\(r\)  Residual

\(R\)  Universal gas constant, 8.314 J/K

\(s\)  Molar entropy, JK/mol

\(S\)  Solenoid valve signal

\(t\)  Time, s

\(T\)  Temperature, \(^\circ\text{C}\)

\(u\)  System input

\(v\)  Measured Voltage, V

\(V\)  Voltage, V

\(W_e\)  Electric work, J

\(y\)  System output

\(Z_p\)  Pressure-Voltage oscillations ratio, V/Pa

**Greek**

\(\alpha\)  Charge transfer coefficient

\(\delta\)  Difference

\(\lambda\)  Stoichiometry

\(\omega\)  Frequency, \(\text{s}^{-1}\)

\(\sigma^2\)  Variance

\(\zeta\)  Electrode potential, V
Subscript

\( a \) Anode

\( act \) Activation loss

\( c \) Cathode

\( cell \) Fuel cell

\( con \) Concentration loss

\( conv \) Convective

\( D \) Differential coefficient

\( dp \) Dew point

\( evap \) Evaporation

\( I \) Integral coefficient

\( in \) Input

\( int \) Internal current loss

\( liq \) Liquid

\( ohm \) Ohmic loss

\( out \) Output

\( P \) Proportional coefficient

\( prod \) Produced

\( ref \) Reference

\( s \) Sampled data

\( total \) Total

\( use \) Consumed reactant

\( v \) Voltage

\( vap \) Vapor

\( w \) Water
Chapter 1

Introduction

Fuel cells are electrochemical cells that convert the chemical energy of a fuel into electricity. The power delivered by a fuel cell is proportional to its electrochemical active area, while the total deliverable energy is determined by the size of its fuel container. Therefore, it is possible to scale fuel cell power and energy independently. This allows fuel cells to satisfy power and energy requirements of a wide range of applications; from portable electronics to transportation and stationary power generation. Their successful commercialization, however, requires fuel cells to compete with their mature rival technologies, i.e., batteries and Internal Combustion Engines (ICEs).

Fuel cells have several advantages compared to batteries and ICEs. Batteries store the chemical energy internally and consume it when required. This limits the amount of energy supplied by batteries to their internally stored materials. Fuel cells on the other hand, do not consume their internal materials, and allow for separate storage of chemical fuel. This allows them to have higher energy densities as well as fast recharging compared to batteries.

ICEs convert chemical energy of the fuel to thermal energy, and then use the thermal energy to generate mechanical energy. As a result, the total efficiency of conversion is limited by the Carnot Cycle [31]. In addition, the mechanical energy conversion has many moving parts which contribute to the losses. Fuel cells on the other hand, do not have the intermediate thermal conversion and therefore are not
subject to Carnot Cycle limitations. In addition, they have fewer moving parts compared to ICEs, and therefore less friction losses. These result in higher conversion efficiencies for fuel cells compared to ICEs.

An alternative motive for using fuel cells is the fact that they can use hydrogen as their fuel. Hydrogen is the most abundant element on earth, and can be produced from reforming hydrocarbon fuels, as well as electrolysis of water. Natural gas is currently the primary source of hydrogen that is used in many industries such as agriculture (fertilizers) and semiconductor manufacturing (prevents oxidation). Hydrogen is also produced as a byproduct in many chemical plants, which can be used for use in fuel cells. Other than these conventional hydrogen production methods, heavier hydrocarbons such as propane (LPG) and methanol can also be used as a fuel for fuel cells, either directly or through fuel reformers that extract the hydrogen.

Electrolysis of water is an alternative method for producing hydrogen. The significance of electrolysis lies in the fact that the required electrical energy can be produced using renewable energy sources such as wind and solar, and stored as chemical energy of hydrogen by electrolysis of water. Fuel cells are then used to transform the chemical energy of hydrogen back into electricity when needed. Note that conventional energy storage devices such as batteries and capacitors have a low energy density, and can not be used efficiently for storage of large quantities of electrical energy.

From the above discussion, we can see that hydrogen production, unlike fossil based fuels, does not rely on a single energy source, and can be produced from conventional fossil fuels as well as renewable resources. Therefore, a hydrogen based economy would benefit from a geographically distributed hydrogen production network, which is tailored to tap into local energy resources, conventional or renewable. This in turn reduces global dependence on concentrated fossil based resources, and has significant social, economical, and political effects world wide. This vision has been the main driving force behind building a hydrogen based economy.
1.1 Motivation

Despite the drivers mentioned above that promote a hydrogen based economy, fuel cells have to pass rigorous cost, performance, durability, and reliability targets, before they can compete with mature rival energy conversion devices, i.e., batteries and ICEs. Diagnostic tools are used at different stages of product life cycle to meet these targets [41]:

1. **Product development**: In this phase, diagnostic tools are required to provide understanding of the fundamental processes in the fuel cell, as well as characterization of component performance. These tools need to be accurate, reproducible, and robust to variations in operating conditions. Cost and complexity of the diagnostic tool is not a barrier at this stage.

2. **Manufacturing**: In this phase, diagnostic tools are needed to detect failures in fuel cell components as well as the fully integrated system. Timely detection of failures during mass production is a key requirement for the diagnostic tools developed for this purpose.

3. **Operation**: During operation, diagnostic tools are needed to detect faults that occur during operation such as drying, flooding, starvation, and CO poisoning [3] in real time, preferably before they fully develop. This would allow the control system to take compensatory actions in order to mitigate from the faulty modes of operation. These diagnostic tools need to be cost effective and they should not add significantly to the system weight and size.

Among different fuel cell types, Polymer Electrolyte Membrane (PEM) fuel cells are specifically suitable for portable and transportation applications. PEM fuel cells use a proton conductive polymer membrane as their electrolyte. The polymer membrane is mechanically stable and can be made very thin (50-175 microns), increasing the PEM fuel cell volumetric power density. The solid membrane allows them to operate in different directions, which is specifically important for mobile applications. Furthermore, they work at relatively low temperature (50-100°C), allowing for quick
startup. As a result, PEM fuel cells are the focus of many scientific research and engineering developments in this field.

In this thesis, the objective is to develop a cost effective diagnostic algorithm that is capable of diagnosing faults in an operational PEM fuel cell in real time (stage 3 above). Such algorithm would allow reliable operation of PEM fuel cells with improved performance and lifetime; which is key to their successful commercialization.

1.2 Problem Formulation

Many commercial PEM fuel cells consume hydrogen at their anode and oxygen from air at their cathode to produce electricity. Anode and cathode flow rates are controlled such that they satisfy flow requirements at different operating conditions. However, if the control system does not provide the required flow rates at different operating conditions, or system flow requirements change due to aging, low flow rates in the anode or cathode could occur. This in turn could result in flooding or starvation in the electrodes, hindering PEM fuel cell performance and lifetime [26, 28, 36]. Timely detection and correction of these faults is key to improving system performance and lifetime.

The objective in this thesis is to design a diagnostic algorithm capable of early diagnosis of PEM fuel cell flooding and starvation in real time. The algorithm should use available sensory information in the fuel cell to avoid an increase in system cost. Furthermore, the diagnostic algorithm needs to be robust to changes in fuel cell operating conditions, not to signal false alarms. Different diagnostic tools and approaches reported in the literature for this purpose are discussed next.

1.3 Literature Review

Fault detection algorithms work based on creating a redundancy in the system, and use that redundancy to make a decision regarding the presence or absence of a fault. Process fault detection algorithms can be classified based on the type of redundancy they create as [77]:
• **Model-based approach**: In this approach, a quantitative or qualitative model of the system is used to create redundancy for fault detection, e.g., replication system output given system input parameters [16]. When a good model for the system is available, this method is very powerful for early detection of faults as well as dealing with transients. However, the shortcoming of this method lies within modeling inaccuracies that arise from simplifying assumption that are made to allow modeling complex systems. This could result in false alarms in the system.

• **Signal-based approach**: In this approach, symptoms of the system are extracted that carry information about the faults of interest. Such symptoms could be measures such as magnitude, phase, mean, or variance of the signal. The symptoms are then used during system operation to evaluate the presence of the fault. Signal-based methods are widely used in practice.

To detect faults in PEM fuel cell, authors in [54] and [20] used a model based approach. In [54], Riascos et al. modeled faults in air fan, cooling fan, fuel cross over, and hydrogen pressure. Using the model, they built a data base of the effect of these faults on parameters that can be measured, i.e., voltage, current, humidity, pressure, and temperature. They used a Bayesian network fault detection system to calculate the probability of the fault from the symptoms. In [55], they used this algorithm for supervisory detection of faults in an operational fuel cell system.

Hissel et al. [20] built a fuzzy model of the fuel cell polarization curve (voltage-current relationship). They experimentally showed that the fuel cell voltage dropped faster in the case of flooding compared to drying, and used that to isolate flooding from drying.

The problem with using model-based approaches is that there is a high degree of simplification and uncertainty in the models built for fuel cell system. This is partially due to the large variations of characteristic lengths and time constants in the fuel cell system, which limits modeling accuracy. For example, the characteristic length of catalyst pores is the order of few nano-meters, while that of flow fields is in the order of meters.
Another complication with modeling efforts with PEM fuel cells arises from the ambiguity surrounding Nafion membrane dynamical behavior. While it has been established that the conductivity of the membrane is a function of its water content [63], the transport mechanisms of water in the membrane is still not well understood. Adding to this the two phase flow of water in liquid and gas phases significantly limits the accuracy of first principle models for PEM fuel cells. As a result, empirical models are used to describe the dynamical behavior of fuel cells. However, these models can not fully capture the many possible variations in fuel cell operating conditions. These limitations are inherited by model-based fuel cell diagnostic algorithms, which limits their reliability.

Limitations in model-methods has resulted in increased attention to signal-based methods. Authors in [43] and [15] used the fuel cell polarization curve to detect a fault in the fuel cell, by means of a change in the cell voltage from its reference value. The short come of this method is that voltage drop is common to almost all fuel cell faults. Therefore, measures other than the polarization curve is required to diagnose a specific fault in the fuel cell system.

Authors in [38], [19], and [5] proposed using pressure drop fluctuations as a diagnostic tool to detect flooding in the PEM fuel cell cathode. The complication with using pressure drop for real time flooding diagnostics remains in the fact that the pressure drop is also affected by changes in operating conditions. For example, pressure drop changes with variations in the flow rate [5] and temperature [19]. Therefore, to construct a robust diagnostic algorithm, one should compensate for the effect of changes in operating conditions on pressure drop.

Impedance measurement is a powerful technique for PEM fuel cell diagnostics [78]. Authors in [10] and [41] proposed using cell impedance to diagnose faults in PEM fuel cells. Le Canut et al. [10] reproduced dehydration, flooding, and CO poisoning, and showed that during dehydration, the fuel cell impedance magnitude and phase increases at all frequencies. However, flooding caused an increase in the cell impedance only at frequencies below 10Hz, and a decrease in phase at frequencies below 100Hz. Anode CO poisoning on the other hand, caused an increase in the impedance magnitude at 100-300Hz, with a maximum phase shift around 20 Hz.
Mérida et al. [41] showed that two high and low frequency measurements of the cell impedance would suffice to diagnose flooding and drying. They showed that while dehydration resulted in impedance variations at both high and low frequencies, flooding corresponded to variations only at the lower frequency.

Despite its rich information content, one limitation with impedance measurement for fault detection is the steady state requirement which limits its performance for real time fault diagnosis. In addition, the active excitation required for impedance measurement increases the system cost and complexity, and is not suitable for use during operation.

The stoichiometry ratio (ratio between the supplied and used reactants) is an alternative measure that can be used to detect fuel cell faults. Authors in [65] and [73] used a fixed air stoichiometry set point as a measure for detecting and mitigating from cathode starvation. We show later in this work that for our system, the air stoichiometry at which cathode starves is a function of the fuel cell current, therefore, a fixed stoichiometry set point can not accurately capture cathode starvation at all operating conditions. The relationship between the air stoichiometry at which cathode starvation occurs and fuel cell operating conditions should be understood in order to design a reliable fault detection algorithm. We have presented a summary of the signatures proposed in the literature for isolating fuel cell faults in Table 1.3.

From the above literature review, it is clear that there is a need for a cost-effective and reliable diagnostic algorithm that can detect PEM fuel cell flooding and starvation in real time. The development of such algorithm is critical for reliable operation of fuel cell and the subject of this work.

1.4 Contributions of this Thesis

Improving PEM fuel cell performance, durability, and reliability are key challenges facing the industry [64]. One way to achieve these goals is by designing cost effective Fault Detection and Isolation (FDI) algorithms that can be integrated into the system and allow early diagnosis of faults in real time. In this thesis, we first reproduce the anode and cathode low flow regions, in order to extract measures that can be used to
### Table 1.1: Summary of measures proposed in the literature to detect and isolate anode and cathode flooding and starvation.

<table>
<thead>
<tr>
<th>Measure</th>
<th>Reference</th>
<th>Fault</th>
<th>Strength</th>
<th>Weakness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average voltage</td>
<td>[20, 43, 15]</td>
<td>all</td>
<td>signal available</td>
<td>can't isolate a specific fault</td>
</tr>
<tr>
<td>Voltage drop rate</td>
<td>[20]</td>
<td>flood, dry</td>
<td>signal available</td>
<td>can't expand to other faults</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>[38, 19, 5]</td>
<td>flood</td>
<td>signal available</td>
<td>effected by operating conditions</td>
</tr>
<tr>
<td>Impedance</td>
<td>[10, 41]</td>
<td>flood, dry, CO</td>
<td>rich information content</td>
<td>expensive, require steady state</td>
</tr>
<tr>
<td>Cathode stoich</td>
<td>[65, 73]</td>
<td>cathode starve</td>
<td>real time calculation</td>
<td>change with operating conditions</td>
</tr>
</tbody>
</table>
design diagnostic residuals that capture PEM fuel cell faults. As a result:

- We introduce a variable cathode stoichiometry polarization curve. We show that for our system, it results in higher voltage at high current densities, and higher reactant utilization at low current densities, compared to a fixed cathode stoichiometry polarization curve.

- We introduce the cell voltage variance as a measure that can be used to detect the onset of the cathode flooding region. We show that a fixed reference value for the cell voltage variance can be used to identify the flooding region at all operating conditions examined.

- We show that a fixed cathode stoichiometry set point proposed in the literature for detecting cathode starvation would result in false alarms [65], [73]. For our system, the stoichiometry at which cathode starvation occurs depends on the fuel cell current density, and can be described as by second order equation.

- We show that cell voltage is not affected by changes in the anode pressure for the operating conditions examined in this thesis. Therefore, the model based method proposed in the literature for detecting anode starvation from the cell voltage and anode pressure would not be effective for our operating conditions and system configuration [2]. We show that for our system, anode starvation occurs at a fixed stoichiometry, independent of fuel cell current density.

We use the above measures to design a diagnostic algorithm that can isolate cathode flooding, cathode starvation, and anode starvation in real time. To achieve this, we design diagnostic residuals that capture fault symptoms from the measurements. We then use these residuals in a decision logic to detect and isolate fuel cell faults, i.e.:

1. We introduce four diagnostic residuals that can capture fault, cathode flooding, cathode starvation, and anode starvation in PEM fuel cells, i.e.:

   - **Voltage residual**: Difference between the cell voltage and reference value.
CHAPTER 1. INTRODUCTION

- **Voltage variance residual**: Difference between the cell voltage variance and a reference value.
- **Cathode stoichiometry residual**: Difference between the cathode stoichiometry and reference value.
- **Anode stoichiometry residual**: Difference between anode stoichiometry and reference value.

2. Using the above residuals, we introduce a diagnostic logic that can isolate cathode flooding, cathode starvation, and anode starvation in real time.

3. We examine the effect of changes in current, pressure, temperature, and humidity operating conditions. We show that the algorithm is robust to changes in current and humidity operating condition, however, correction terms are required to make the algorithm robust to cell temperature and pressure variations.

Finally, to achieve better insight into water transport mechanisms that cause flooding in the PEM fuel cell cathode, we introduce two diagnostic tools that provide fundamental understanding of these mechanisms:

- **Pressure-voltage oscillations**: We show that for our system, the cathode output pressure and cell voltage oscillations have the same characteristic frequency. We propose using the amplitude and phase of the cathode output pressure and voltage oscillations, similar to that used in impedance measurement with voltage and current, as a diagnostic tool for detecting operating conditions in the PEM fuel cell cathode. Using this tool, we present a hypothesis regarding the water vapor and liquid boundary conditions in the pores of the PEM fuel cell cathode catalyst.

- **Liquid water measurement system**: We introduce a sensory system capable of measuring two-phase water flow as it exits the fuel cell. From the correlation between the cell voltage and the temporal measurement of liquid water leaving the fuel cell cathode, we identify two distinct modes of liquid water transport
in the fuel cell. To my knowledge, this is the first time that water vapor and liquid water have been measured separately in real time.

1.5 Thesis Outline

The rest of this thesis is presented as follows: In chapter 2, we first explain the operating principals of PEM fuel cells and the sources of loss. We then present the specific fuel cell we use to carry experiments in this thesis. Next, we explain the subsystems used to control the fuel cell operating parameters, i.e., current, flow, pressure, temperature, and humidity. We finally introduce the sensory system that we have designed to measure two-phase flow of water as it exits the fuel cell.

In chapter 3, we use the experimental setup introduced in chapter 2 to carry experiments in order to characterize the cathode low flow region, and introduce measures that can capture it in real time. We then introduce pressure-voltage oscillations as a measure that can be used for better understanding of PEM fuel cell cathode dynamics. In the rest of chapter 3, we present experimental results to examine the characteristics of the anode low flow region, and use that to introduce measures that can capture it in real time.

In chapter 4, we use the measures introduced in the previous chapter to design four diagnostic residuals and their reference values for fault detection. Next, we introduce a boolean decision logic using these residuals to detect and isolate cathode flooding, cathode starvation, anode starvation, and anode starvation warning in real time. We then examine the robustness of the algorithm to changes in current, temperature, pressure, and humidity operating conditions.

In the last part of chapter 4, we further analyze the effect of humidity in PEM fuel cells. We review the available methods in the literature for studying water transport in PEM fuel cells, and show that there is a need for a sensory system capable of measuring liquid water as it exits the fuel cell in real time. We derive the equations required to use the sensory system introduced, present the results obtained by placing this sensor at the PEM fuel cell cathode output during membrane humidification.

Finally, we conclude the results obtained in this thesis in chapter 5 and make
CHAPTER 1. INTRODUCTION

suggestions for future work in this field.
Chapter 2

PEM Fuel Cell System

A Polymer Electrolyte Membrane/Proton Exchange Membrane (PEM) fuel cell system consists of two main components (Figure 2.1)

1. Fuel cell stack
2. Control system

![Figure 2.1: PEM fuel cell system block diagram.](image)

The PEM fuel cell is where the electrochemical reactions take place, i.e., hydrogen and oxygen combine to produce water, heat, and electricity. The control system
supplies the anode and cathode with reactants at desired temperature, pressure, flow rate, and humidity, and controls the fuel cell stack temperature and load.

In this chapter, we first explain the operating principles of PEM fuel cells, followed by a description of the fuel cell specifications used in this work. We then discuss the test station control subsystems used to control and monitor the PEM fuel cell operating conditions.

2.1 PEM Fuel Cell

A PEM fuel cell consists of the following main components (Figure 2.2):

- Membrane Electrode Assembly (MEA)
  - Polymer Electrolyte Membrane (PEM)
  - Electrodes
    * Gas Diffusion Layer (GDL)
    * Catalyst
- Flow fields

The MEA consists of two electrodes separated by a PEM. The PEM is a good proton conductor, with low gas permeability and electron conductivity. A typical PEM material, such as Nafion™, is a poly-perfluorosulfonic acid consisting of three regions [68]:

1. The hydrophobic fluorocarbon backbone, made of repeating \(-\text{CF}_2 - \text{CF} - \text{CF}_2-\) units

2. The \(-\text{O} - \text{CF}_2 - \text{CF(CF}_3) - \text{O} - \text{CF}_2 - \text{CF}_2-\) side chains, which connects the backbone to the sulfonic acid ions

3. The hydrophilic sulfonic acid ions, \(\text{SO}_3\text{H}^+\)
Figure 2.2: PEM fuel cell schematic diagram.

When the polymer membrane becomes hydrated, water molecules bond to hydrogen ions on the sulfonic acid. This results in their protons to come mobile and hop from one sulfonic acid cluster to another, making the PEM proton conductive.

The electrodes are electrically conductive and have a porous structure that is permeable to liquids and gasses. They consists of a Gas Diffusion Layer (GDL) that is typically made of carbon cloth or carbon fibre paper, bonded by a hydrophobic agent, such as Teflon. A thin layer of carbon supported platinum particles (e.g. 0.2 mg Pt/cm$^{-2}$) is dispersed between the GDL and the PEM as catalyst, in order to enhance electrochemical reaction rates.

Flow fields are typically made of graphite plates. Anode and cathode flow fields sandwich the MEA, deliver reactants to the electrodes, and remove the produced heat, water, and electricity. Gaskets are placed between the flow field plates and PEM to seal the electrodes (not shown in Figure 2.2).

During operation, hydrogen and oxygen are supplied through the anode and cathode flow fields to the GDL, from which point they diffuse to the anode and cathode catalyst layers, respectively. At the anode catalyst sites, hydrogen is split into electrons and protons. Protons are transported from the anode to the cathode catalyst
sites through the PEM. Electrons are transported through the anode GDL and flow field plates to the external circuit to power the load. They arrive through the cathode flow field and GDL to the cathode catalyst cites, at which point they combine with protons and oxygen to produce water. Therefore, the anode and cathode reactions in a PEM fuel cell are as follows:

\[
\text{Anode : } \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \tag{2.1}
\]

\[
\text{Cathode : } 2\text{H}^+ + 2e^- + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \tag{2.2}
\]

In the rest of this section, we derive equations for the fuel cell Electromotive Force (EMF) or reversible (no loss) Open Circuit Voltage (OCV), followed by the sources of loss in an operational fuel cell.

### 2.1.1 Electromotive Force

We can see from reaction 2.1 that for each molecule of hydrogen, 2 electrons pass through the external circuit. Therefore, for one mole of hydrogen \(2N\) electrons pass through the external circuit, with \(N\) being the Avogadro number (\(6.022 \times 10^{23}\)). The total charge of electrons, \(q\), that flow through the external circuit for one mole of hydrogen consumed would then be:

\[
q = -2Ne = -2F \text{ Coulombs} \tag{2.3}
\]

with \(-e\) being the charge of one electron (\(1.602 \times 10^{-19}\) Coulombs) and \(F\) the Faraday constant, or the charge of one mole of electrons (96,485 Coulombs). If we denote the fuel cell voltage by \(E\), the electrical work done by the charge transfer of one mole of hydrogen, \(W_e\) in Joules, is:

\[
W_e = qE = -2FE \text{ joules} \tag{2.4}
\]

For a reversible (no loss) electrochemical system, this electrical work is equal to the changes in the molar Gibbs free energy of formation, \(\Delta\bar{g}\) in J mol\(^{-1}\), i.e:
\[ \Delta \bar{g} = W_e \]  

(2.5)

Therefore, the cell potential can be calculated from equations 2.5 and 2.4 as:

\[ E = -\frac{\Delta \bar{g}}{2F} \text{ volts} \]  

(2.6)

Equation 2.6 gives the Electromotive Force (EMF) for the hydrogen fuel cell reaction:

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \]  

(2.7)

The value of \( \Delta \bar{g} \) depends on the temperature, pressure, and state (liquid or gas) of the reactants and products. At Standard Temperature and Pressure (STP) conditions (25°C and 0.1 MPa), this value is equal to -237.2 kJmol\(^{-1}\), resulting in a cell voltage of 1.23 V from equation (2.6). The effect of changes in temperature, pressure, and reactant state on the Gibbs free energy is discussed next.

**Temperature Effects**

The molar Gibbs free energy of a system is defined in terms of the molar enthalpy, \( \bar{h} \), and molar entropy, \( \bar{s} \), as:

\[ \bar{g} = \bar{h} - T\bar{s} \]  

(2.8)

The energy released in a reaction depends on the initial and final state of the reactants and products. Assuming a constant temperature for the fuel cell, we can say that:

\[ \Delta \bar{g} = \Delta \bar{h} - T\Delta \bar{s} \]  

(2.9)

with \( \Delta \bar{h} \) the changes in molar enthalpy of formation in J mol, \( \Delta \bar{s} \) the changes in molar entropy in J mol\(^{-1}\) K, and \( T \) the cell temperature in Kelvin. The value of \( \Delta \bar{h} \) is the difference between the molar enthalpy of products and reactants in reaction 2.7.
Similarly, the value for $\Delta \bar{s}$ is the difference between the molar entropy of products and reactants in the fuel cell reaction 2.7, i.e.:

$$
\Delta \bar{h} = \bar{h}_{\text{H}_2\text{O}} - \bar{h}_{\text{H}_2} - \frac{1}{2} \bar{h}_{\text{O}_2}
$$

$$
\Delta \bar{s} = \bar{s}_{\text{H}_2\text{O}} - \bar{s}_{\text{H}_2} - \frac{1}{2} \bar{s}_{\text{O}_2}
$$

The values of $\bar{h}_x$ and $\bar{s}_x$, $x = \{\text{H}_2, \text{O}_2, \text{H}_2\text{O}\}$, depend on the temperature, and can be calculated using the below equations [31]:

$$
\bar{h}_x = \bar{h}_{298.15,x} - \int_{298.15}^{T} \bar{c}_x dT,
$$

$$
\bar{s}_x = \bar{s}_{298.15,x} - \int_{298.15}^{T} \frac{1}{T} \bar{c}_x dT,
$$

The values for $\bar{h}_{298.15}$ and $\bar{s}_{298.15}$, the molar enthalpy and entropy at standard temperature and pressure conditions (298.15 K and 100,000 Pa) is given in Table 2.1. The value for $\bar{c}$, the molar heat capacity at constant pressure in J g mol$^{-1}$ K, can be calculated using the following empirical equations:

$$
\bar{c}_{\text{H}_2\text{O}} = 143.05 - 58.04T^{0.25} + 8.2751T^{0.5} - 0.036989T
$$

$$
\bar{c}_{\text{H}_2} = 56.505 - 22222.6T^{-0.75} + 116500T^{-1} - 560700T^{-1.5}
$$

$$
\bar{c}_{\text{O}_2} = 37.432 + 2.0102 \times 10^{-5}T^{1.5} - 178570T^{-1.5} + 2368800T^{-2}
$$

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\bar{h}_{298.15,x}$</th>
<th>$\bar{s}_{298.15,x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O(liquid)</td>
<td>-285.838</td>
<td>70.05</td>
</tr>
<tr>
<td>H$_2$O(steam)</td>
<td>-241.827</td>
<td>188.83</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>130.59</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0</td>
<td>205.14</td>
</tr>
</tbody>
</table>
By substituting the values for $\bar{h}_{298.15,x}$, $\bar{s}_{298.15,x}$, and $\bar{c}_x$ in equations 2.12 and 2.13, the functions can be integrated and evaluated at temperature $T$, in order to result the values for $\bar{h}_x$ and $\bar{s}_x$, for steam, hydrogen, and oxygen ($x = \{H_2, O_2, H_2O\}$). In the case of liquid water, standard values from Table 2.1 are used for $\bar{h}_x$ and $\bar{s}_x$. These values are used in equations 2.10 and 2.11 to calculate $\Delta\bar{h}$ and $\Delta\bar{s}$. The changes in Gibbs free energy, $\Delta\bar{g}$, is calculated by submitting these values into equation (2.9). Finally, the cell voltage, $E$, can be calculated from equation (2.6).

**Pressure Effects**

In a chemical reaction, the activity of species, $a$, determines their tendency to participate in the reaction. The activity of liquids is close to one. The activity of ideal gases can be calculated as the ratio between their partial pressure, $P$, and standard pressure, $P^0$, i.e.:

$$a = \frac{P}{P^0} \quad (2.17)$$

The activity of the reactants and products in the fuel cell chemical reaction 2.7, modifies the changes in the Gibbs free energy according to the following equation [31]:

$$\Delta\bar{g} = \Delta\bar{g}^0 - RT \ln \left( \frac{a_{H_2}a_{\frac{1}{2}O_2}}{a_{H_2O}} \right) \quad (2.18)$$

with $R$ being the universal gas constant $(8.314 \text{ J K}^{-1})$. If we substitute equation (2.18) into equation (2.6), we have:

$$E = E^0 + \frac{RT}{2F} \ln \left( \frac{a_{H_2}a_{\frac{1}{2}O_2}}{a_{H_2O}} \right) \quad (2.19)$$

where $E^0$ is the EMF at standard pressure. Equation 2.19 is called the Nernst equation, and allows calculating the equilibrium cell voltage in terms of the reactant activities.

If we use bar as the unit for pressure, then the standard pressure would be 1 bar (0.1Mpa). In this case, the activity of the reactants from equation (2.17) would be
equal to their partial pressure in bar. Also assuming that liquid water is produced in the cathode, its activity can be assumed equal to one. In this case, the Nernst equation simplifies to:

\[ E = E^0 + \frac{RT}{2F} \ln(P_{H_2}, P_{O_2}^{0.5}) \]  

(2.20)

Using equation (2.20), it is possible to calculate the effect of changes in the reactant pressure on the ideal fuel cell voltage. However, the measured voltage is always below this value due to the losses that occur in the cell. The sources of these losses in PEM fuel cells are discussed next.

### 2.1.2 Activation Losses

Activation losses occur due to the energy required to drive the electrochemical reactions in the anode and cathode of the PEM fuel cells, as a result of slow reaction rates. For the anode and cathode reactions of 2.1 and 2.2, activation losses can be calculated using the Tafel equation as [31]:

\[ V_{act} = \frac{RT}{2\alpha F} \ln \left( \frac{i}{i_0} \right), \quad i > i_0 \]  

(2.21)

with \( i \) being the fuel cell current density, and \( i_0 \) the exchange current density, in mA/cm². The exchange current density is a measure for the electrode activity. The charge transfer coefficient, \( \alpha \), has a value between 0 and 1, and represents the amount of electrical energy that is applied to change the rate of electrochemical reaction. In PEM fuel cells running on hydrogen and oxygen, the value of the exchange current density is about \( 10^5 \) higher for the anode compared to the cathode [31]. Therefore, the anode activation losses are negligible and the exchange current density in fact represents cathode activation losses.

Activation losses can be reduced by using catalysts and rough electrodes that increase the reaction surface area. An increase in cell temperature would also reduce activation losses. Note that while the Tafel equation suggests that activation losses increases with temperature, the increase in exchange current density with temperature far exceeds the proportional temperature term in equation (2.21).
One way to directly measure the activation potential is by current interrupt methods \[32\]. In this method, the fuel cell current is suddenly disconnected, resulting in sudden drop in the load current and voltage. However, the activation potential in this case recovers gradually, i.e., until reactions reach equilibrium. The total amount of this voltage increase represents the activation loss.

The Tafel equation (2.21) represents voltage losses when current is drawn from the fuel cell. However, even if no current is drawn, the cell voltage would be lower than that calculated from equation (2.20). The source of this voltage drop is explained next.

### 2.1.3 Internal Currents

Although the polymer membrane is designed to selectively conduct protons, it would always have small electron conductivity. In addition, while the membrane is designed to be permeable to reactant gasses, small hydrogen molecules can still pass and react with oxygen in presence of catalyst on the cathode side. The effect of internal currents and fuel crossover is equivalent to wasting electrons (one hydrogen molecule passing is equivalent to two electrons). This results in nonzero cell currents, even at OCV. This can be captured using the internal current density, \(i_n\) in mA/cm\(^2\), with equation (2.21) as:

\[
V_{act+int} = \frac{RT}{2\alpha F} \ln \left( \frac{i + i_n}{i_0} \right), \quad i > i_0
\]  (2.22)

we can see that at no load conditions, \(i_n\) results in cell voltage drop. Note that in equation (2.22), we have assumed that the effects of anode activation losses are negligible compared to the cathode side.

Internal currents cannot be measured directly. However, the effect of internal currents and fuel cross over is the same, both resulting in fuel consumption at no load conditions. Therefore, one way to measure the internal currents is by measuring the amount of reactants used at OCV. However, small consumption rates do not allow the use of regular flow meters, and special hardware will be required \[31\].
2.1.4 Ohmic losses

Ohmic losses are due to the protonic resistance of the polymer membrane electrolyte and the electronic resistances of the electrodes. We can write the ohmic loss, $V_{ohm}$ as:

$$V_{ohm} = ir \quad (2.23)$$

with $r$ being the area specific resistance in kΩ/cm$^2$. The electronic losses is predominantly due to the contact resistances between the catalyst, GDL, flow fields, and end plates. The protonic resistance of the membrane depends on to the membrane thickness, temperature, and water content [63].

One way to measure ohmic losses in fuel cells is by current interrupt. Ohmic losses respond immediately to changes in current. Therefore, immediate changes in voltage resulting from current interrupt could be associated with ohmic losses, while gradual changes represent the activation losses [32].

2.1.5 Concentration Losses

As reactants pass through the anode and cathode flow fields, they are consumed proportional to the current taken from the fuel cell. This results in a reduction in concentration and therefore partial pressure of reactants along the flow field channel. The reduction in reactant partial pressure results in a reduction in cell voltage, known as mass transport or concentration losses, $V_{con}$. Analytic modeling of concentration losses is very complicated due to the non uniform distribution of reactants and potentials along the flow field channel. One approach is to define a limiting current density, $i_L$, at which all the supplied fuel is consumed. At this current density, the fuel pressure would drop to zero. Assuming that fuel pressure drops linearly with current density from its value at zero current, $P_{H_2}$, then the fuel cell pressure, $P$ can be calculated using the following relationship:

$$P = P_{H_2} \left( 1 - \frac{i}{i_L} \right) \quad (2.24)$$

Using equation (2.20), we can easily calculate the concentration losses as:
\[ V_{\text{con}} = E2 - E1 = \frac{RT}{2F} \ln \left( 1 - \frac{i}{i_L} \right) \] (2.25)

Note that the above equation is calculated for the anode side. On the cathode, the term \( \frac{RT}{2F} \) should be replaced by \( \frac{RT}{4F} \) (due to the 0.5 exponent in the Nernst equation). However, there are problems with the above derivation: In most practical application, air is supplied instead of oxygen. In addition, the derivation does not account for the buildup and transport of water out of the cathode. As a result, empirical equations are proposed to capture the fuel cell behavior at high current densities. One such equation uses two empirical values, \( m \) in volts and \( n \) in cm\(^2\)/mA, to capture the exponential drop that occurs at high current densities [25]:

\[ V_{\text{con}} = me^{ni} \] (2.26)

If we subtract activation, crossover, ohmic, and concentration losses captured by equations 2.22, 2.23, and 2.26 from the fuel cell ideal voltage described by equation (2.20) at a given temperature and pressure, it results in the fuel cell terminal voltage, \( V \) in volts, as:

\[ V = E - \frac{RT}{2\alpha F} \ln \left( \frac{i + i_n}{i_0} \right) - ir - me^{ni} \] (2.27)

Equation 2.27 describes the fuel cell current-voltage relationship at steady state. In the next section, we obtain the polarization relationship of a single 49 cm\(^2\) PEM fuel cell, and use that to find one realization for the parameters of equations 2.27, using nominal values published in the literature as initial conditions.

### 2.1.6 Fuel Cell Specification

We used a commercially available 12 series ETEK (www.etek-inc.com) MEA with an active area of 49 cm\(^2\) for our experiment. It consists of a Nafion 112 membrane with carbon supported anode and cathode platinum loading of 0.1 and 0.4 mgPt/cm\(^2\), respectively. A 200 micron thick Toray carbon paper is used as both anode and cathode GDLs. We have shown the worn MEA in Figure 2.3.
Figure 2.3: A commercially available ETEK MEA. The GDL has been removed on the upper left corner to make the catalyst visible.
The square black section in the middle of Figure 2.3 is the GDL. We can see that the top right corner of the GDL has been torn, and the black catalyst below it has become visible. We can also see that the membrane is wrinkled and exceeded the GDL perimeter. The wrinkle is due to the water uptake of the membrane which increases its length. When the membrane is dried out, it does not return to its initial conditions. In fact, initial conditioning of the membrane impacts its lifetime. The part of the membrane that exceeds the GDL is used to seal the electrodes and manifolds, and prevent the anode and cathode graphite plates from electric short. The anode and cathode flow fields and seals used in our experiment are shown in Figure 2.4.

![Figure 2.4: Anode (left) and cathode (right) graphite plates. Flow field is engraved on the graphite plate, equal to the MEA active area. Sealing rubber is placed around the MEA and manifolds.](image)

We can see in Figure 2.4 that when the graphite plates are placed on both sides of an MEA, they result in cross flow fields (perpendicular on the anode and cathode sides). The anode flow fields have 38 passes with a cross section of $1 \times 1$ mm, and the cathode flow field has 36 passes with a cross section of $1.5 \times 1$ mm. We can also see the reactant manifolds as through holes at the edge of the graphite plates in Figure 2.4. These manifolds are connected to the beginning and end of the flow fields using
through holes that are drilled from the side of the graphite plate. The first part of the hole connects the manifold to the outside, and the rest of it connects the manifold to the flow field. The part that connects the manifold to the outside is later closed with sealant. The inner part is used to supply reactants to the electrodes and remove the excess reactants as well as products.

In order to heat the fuel cell to the desired temperature, hot water flow fields are placed on the back side of the anode and cathode flow fields (the side that is not in contact with the MEA). Two gold plated current collectors are then placed on the other side of the heating graphite plates. Finally, a compression system is used to compress the stack of current collectors, graphite plates, and MEA, as shown in Figure 2.5.

The fuel cell of Figure 2.5 was built as a joint effort between the University of British Columbia Clean Energy Research Center (UBC CERC) and Tandem Technologies Ltd (www.tandemtech.ca). These cells are commercially available from Tandem as model TP50.

In Figure 2.5, we can see three fittings on the side of the fuel cell. These three, along with three other on the other side (not shown) connect to hydrogen, air, and water input and output manifolds on the graphite plates.

The compression system in Figure 2.5 uses four adjustable bolts to align the stack and the top compression plate. The compression plate has a build in piston that is actuated using compressed gas. The hose on top of the stack is used to supply the pressurized gas to the piston. We used nitrogen at a pressure of 120 psi for this purpose.

We operated the above fuel cell at a temperature of 80°C, with humidified hydrogen and air at 30 psi. At a fixed hydrogen and air stoichiometry (ratio of supplied to used reactants) of 1.5 and 2, we increased the fuel cell current density from zero in increments of 70 mA/cm², until the cell voltage reached near zero volts. The result of this experiment is shown in Figure 2.6.

In Figure 2.6, we have also graphed the fuel cell no loss voltage at 80°C and 30 psi, using equation (2.20) \( E = 1.18 \) volts. Next, we used the nominal values for the parameters in equation (2.27) as initial conditions [31], and fitted the parameters such
Figure 2.5: Assembled Tandem Technologies TP50 fuel cell stack. The two inner graphite plates that sandwich the membrane contain the anode and cathode flow fields. The two outer graphite plates that are in contact with the gold plated current collectors contain the cell heating flow fields.
that the resulting polarization curve matches the measured one (Table 2.2). Using the fitted parameters, we have graphed the activation, ohmic, and concentration losses separately. We can see in Figure 2.6 that activation losses dominate low current densities (below 70mA/cm\(^2\)), while concentration losses become more critical at high current densities (above 560mA/cm\(^2\)). Ohmic losses dominate the range between these two higher and lower values.

From a control perspective, the region of the polarization curve that concentration losses dominate is to be mitigated. This is because the voltage drop in this region reduces system performance. In addition, degradation rates are higher in this region [28]. As we show later in this work, cathode stoichiometry highly affects PEM fuel cell behavior in this region. Real time detection of this region is the subject of the work done in this thesis, and discussed further in the following chapters.

In the next section, we explain the test station used to control and monitor the operating conditions of the PEM fuel cell explained earlier.
Table 2.2: Fuel Cell fitted parameters using equation (2.27).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (V)</td>
<td>1.18</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.5</td>
</tr>
<tr>
<td>$i_n$ (mA/cm$^2$)</td>
<td>1</td>
</tr>
<tr>
<td>$i_0$ (mA/cm$^2$)</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$r$ (kΩcm$^2$)</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$m$ (V)</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>$n$ (V)</td>
<td>$1.5 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

2.2 PEM Fuel Cell Control System

A PEM fuel cell control system consists of four major subsystems [74]:

- Flow control subsystem
- Humidification subsystem
- Cell temperature subsystem
- Load subsystem

The flow subsystem controls the anode and cathode output pressure, $P_{out,a}$ and $P_{out,c}$, input flow rate, $F_{in,a}$ and $F_{in,c}$, and input temperature, $T_{in,a}$ and $T_{in,c}$, at the pressure reference $P_{ref,a}$ and $P_{ref,c}$, flow reference $F_{ref,a}$ and $F_{ref,c}$, and temperature reference values $T_{ref,a}$ and $T_{ref,c}$, respectively. The humidity subsystem controls the anode and cathode saturation temperature, $T_{dp,a}$ and $T_{dp,c}$, at their reference values, $T_{ref,dp,a}$ and $T_{ref,dp,c}$, respectively. The temperature subsystem controls the fuel cell temperature, $T_{cell}$, at its reference value, $T_{ref,cell}$. Also the load subsystem controls the fuel cell current, $I$, at its reference values $I_{ref}$. The output of these subsystems are the input to the fuel cell, at which it produces a voltage, $V$. This is shown schematically in Figure 2.7.

The reference values used for controlling the reactant temperature, pressure, and humidity are usually fixed, and a function of the system design parameters. The
reference values used in our experiment are presented in Table 2.3. These values are remained constant in the rest of this work, unless mentioned otherwise.

The fuel cell reference current, $I_{\text{ref}}$, is set based on application demand. The anode and cathode reference flow rates, $F_{\text{ref,a}}$ and $F_{\text{ref,c}}$, are set based on the cell current demand. The complication arises from the fact that when increasing the current, the flow should precede the current, in order to have sufficient reactant to drive the reactions. This could be addressed by a combination of system design, control algorithm, and fast dynamical response of the flow control system.

In this work, the system design and dynamical response of the flow control system are dictated by the test station used. However, an algorithm for calculating the reference flow value is discussed. Usually, a fixed stoichiometry ratio, i.e., the ratio between supplied to consumed reactants, is used to calculate the flow reference value [50], [9]. We show in the next chapter that such a scheme would not result in an optimal flow rate for the cathode, and propose an optimal scheme for calculating $F_{\text{ref,c}}$. 

![Figure 2.7: Fuel cell system block diagram.](image)
Table 2.3: Fuel cell temperature, pressure, and humidity reference values for the experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{ref,cell}}$ ($^\circ$C)</td>
<td>80</td>
</tr>
<tr>
<td>$T_{\text{ref,a}}$ ($^\circ$C)</td>
<td>80</td>
</tr>
<tr>
<td>$T_{\text{ref,c}}$ ($^\circ$C)</td>
<td>80</td>
</tr>
<tr>
<td>$T_{\text{ref,dp,a}}$ ($^\circ$C)</td>
<td>70</td>
</tr>
<tr>
<td>$T_{\text{ref,dp,c}}$ ($^\circ$C)</td>
<td>70</td>
</tr>
<tr>
<td>$P_{\text{ref,a}}$ (psi)</td>
<td>30</td>
</tr>
<tr>
<td>$P_{\text{ref,c}}$ (psi)</td>
<td>30</td>
</tr>
</tbody>
</table>

In the rest of this chapter, we discuss the control subsystems used in this work to control the fuel cell inputs in further detail.

2.2.1 Flow Subsystem

The flow subsystem controls and monitors anode and cathode reactants temperature, pressure, and flow rate. We have shown the instrumentation diagram for this system in Fig 2.8. Note that since the system is similar for both the anode and the cathode, we have omitted their subscripts for simplicity.

The input control valve, $S_{\text{in}}$, controls the fuel cell input flow rate using the mass flow sensor $F_{\text{in}}$. The reactant heater, $H_{\text{in}}$, controls the reactant input temperature from temperature reading $T_{\text{in}}$. The output control valve, $S_{\text{out}}$, controls the fuel cell output pressure using the pressure sensor, $P_{\text{in}}$. Three PID control loops are used to control the valves and heat actuators such that:

\[
S_{\text{in}} = K_{P,F} \cdot e_F + K_{I,F} \int e_F dt + K_{D,F} \frac{de_F}{dt} \tag{2.28}
\]
\[
H_{\text{in}} = K_{P,T} \cdot e_T + K_{I,T} \int e_T dt + K_{D,T} \frac{de_T}{dt} \tag{2.29}
\]
\[
S_{\text{out}} = K_{P,P} \cdot e_P + K_{I,P} \int e_P dt + K_{D,P} \frac{de_P}{dt} \tag{2.30}
\]

with $K_{P,x}$, $K_{I,x}$, and $K_{D,x}$ being the proportional, integral, and differential control
Figure 2.8: Anode and cathode flow subsystem. $P_0$ is the hydrogen and air tanks mechanical pressure regulator. $S_{in}$ and $S_{out}$ are the input and output solenoid valves. $F_{in}$ and $P_{out}$ are the input flow and output pressure measurements. $H_{in}$ is the reactant heater and $T_{in}$ is the reactant input temperature measurement.
variables for the flow, temperature, and pressure PID control systems ($x = \{F, T, P\}$). $e_F$, $e_T$, and $e_P$ are the flow, temperature, and pressure errors, respectively. They are calculated as the difference between the measured and reference values, i.e.:

\begin{align*}
    e_F &= F_{\text{in}} - F_{\text{ref}} \\
    e_T &= T_{\text{in}} - T_{\text{ref}} \\
    e_P &= P_{\text{out}} - P_{\text{ref}}
\end{align*}

with $F_{\text{ref}}$, $T_{\text{ref}}$, and $P_{\text{ref}}$ being the flow, temperature, and pressure reference values, respectively.

For our system, the flow rates are controlled using Brooks model 5850E mass flow controllers with a maximum flow rate of 1 and 2 slpm for the anode and cathode, with an error of ±1% of full scale. The anode and cathode pressure control loop consists of a GO model BP3-1A11D5G11H pneumatic pressure regulator, and a Measurement Specialties Inc. model MSI-US671 pressure sensor with a maximum reading of 50 psig, and accuracy of ±75% of full scale. The temperature control loop consists of a 200 W tape heater, with a temperature limit of 232°C for both anode and cathode sides. An Omega K-type thermocouple is used to measure the reactant temperature with ±1.1°C. A high pressure hydrogen and air tank at 120 psi is used on anode and cathode side to supply the reactants. Note that in practical applications, most fuel cell systems are built using air compressor instead of air/oxygen tank for the cathode supply [4], [74], [69]. This is due to the higher cost and size of tanks compared to air compressors. However, the lifetime of a tank far exceeds that of an air compressor. Therefore, with a proper financial model, it could have a higher economic value compared to an air compressor. In addition, compressors impose a parasitic loss on the cell voltage, while air/oxygen tanks allow operating the fuel cell at higher pressures, hence increasing fuel cell system performance. Therefore, is size constraints of the application allows, use of air/oxygen tanks could become attractive.

The dynamic behavior of the flow, temperature, and pressure control loops are quite different. The flow control loop has a relatively shorter time constant and reaches steady state in the order of few seconds, while the temperature and pressure
loops have a time constant in the order of minutes. Furthermore, the time constant for the anode and cathode control loops are also different. This is specifically important for the pressure control loop during startup, as one electrode could build up pressure faster, resulting in a pressure gradient across the MEA beyond its tolerance.

2.2.2 Humidification Subsystem

Reactant humidification is achieved by placing a humidifier between $F_{in}$ and $H_{in}$, the flow sensor and the heater, in Figure 2.8. The humidifier operates by passing the input stream through tank that is fully saturated with water vapor. The dew point temperature of the vapor in the tank is controlled by heating the water at the bottom of the tank using a 1000 W heater, $H_{dp}$, to the reference dew point temperature, $T_{ref,dp}$, using a PID controller as follow (anode and cathode subscripts are eliminated for simplicity):

\[
H_{dp} = K_{P,dp} \cdot e_{dp} + K_{I,dp} \int e_{dp} dt + K_{D,dp} \frac{de_{dp}}{dt}
\]

\[
e_{dp} = T_{dp} - T_{ref,dp}
\]

with $K_{x,dp}$, $x = \{P, I, D\}$ being the humidifier control loop PID parameters, and $T_{dp}$ the temperature reading of the liquid water in the humidifier tank.

When the reactant flows through the humidifier tank, it dilutes the humidified reactant inside the tank, therefore reducing its humidity. In order to reduce the effect of this dilution, large humidification tanks are used. This also reduces the effect of the cold water that is added to compensate for the water vapor that leaves the humidifier. However, the large volume of humidification tanks along with the high heat capacity of water results in very slow dynamics for such humidifiers. For our system, when started from cold, it takes in the order of tens of minutes for the humidifier to reach the desired steady state dew point temperature. At steady state, the dew point temperature reading remains steady within $\pm 3^\circ$C of the $T_{ref,dp}$ set point.

While the humidification system integrated with the test station is able to control the reactant dew point temperatures entering the few cell, the test station lacks a
reliable way for measuring the fuel cell output humidity. Since this information is critical in understanding the effects of water on the fuel cell, we designed a humidity sensory vessel capable of separately measuring the water vapor and liquid leaving the fuel cell. This is explained next.

**Humidity Measurement**

There are various methods used in the literature for humidity measurement. One way is to cool the stream in order to condensate the water vapor in the stream. Next, the volume or weight of the liquid water is used to measure the total water content of the reactant. The shortfall of this method is that the mass/volume of the water is small, therefore, measurement of the water content reveals only average values over time and can not produce reliable real time readings.

An alternative method is to use laser diode and sensors, in order to measure the water content of the stream from the diffraction of light. As humidity in the reactant stream increases, so does the diffraction rate, therefore less light reaches the laser diode. While this method results in fast and reliable reading for the dew point temperature, it can not measure the amount of liquid water in the stream.

An alternative method is to use solid state humidity sensors to measure the humidity of the reactant stream. These sensors measure humidity from the temperature and the electric charge capacitive effect of the reactants. We used a Sensirion model SHT75 humidity sensor, with an error of ±1.8% and response time smaller than 8 seconds, inside a heated vessel. To mount the sensor in the vessel, we passed a wire through a T like opening in the vessel, connected the sensor to the wire, and placed it inside the vessel, as shown in Figure 4.18.

Similar to optical methods, humidity sensors can only measure the dew point temperature of the gas stream, and not the liquid water content. In fact, if water condensates on these sensors, it results in unreliable readings. Therefore, to avoid water condensation on the humidity sensor, we heated the vessel to a temperature above that of the stream to avoid condensation. For this purpose, we wrapped a 1 m long tubing with a 1 cm diameter around the vessel, and circulated hot water using a
CHAPTER 2. PEM FUEL CELL SYSTEM

2.2. Temperature Subsystem

Since the fuel cell consists of only one cell, the cell needed to be heated to reach the desired temperature. For this purpose, we used a Haake model DC10-P5 open circulation hot water bath. It uses a PID control system to control the cell temperature,
The temperature of the cell, \( T_{\text{cell}} \), at the reference value, \( T_{\text{ref,cell}} \), with an error of \( \pm 0.2^\circ\text{C} \). The circulation pump circulates the hot water to the fuel cell, using the water flow fields on the outer side of the anode and cathode graphite plates (top and bottom graphite plates in Figure 2.5).

Due to the high heat capacity of water, the temperature control subsystem has slow dynamics. For our system, it takes in the order of tens of minutes for the hot water to reach steady state.

### 2.2.4 Load Subsystem

The reference load current, \( I_{\text{ref}} \), is set replicating application power requirements. A solid state electronic load is used by the load subsystem to control the cell current, \( I \), at the reference value. The solid state switch changes the duty cycle of a Pulse Width Modulated (PWM) signal that controls an active load to sink the desired current from the fuel cell. A capacitor bank is used to reduce the load ripple. The electronic load used in our experiment is capable of drawing 100 Amps DC at 10 Volts.

In this chapter, we introduced the PEM fuel cell and control system that we used to carry out experiments. In the next chapter, we use this setup to reproduce PEM fuel cell anode and cathode low flow regions. Using these experimental results, we introduce measures that can capture low anode and cathode induced faults in real time.
Chapter 3

PEM Fuel Cell Low Flow Induced Faults

The PEM fuel cell cathode stream supplies oxygen and removes the produced water. Low flow rates in the cathode could result in water accumulation as well as low oxygen concentration, causing cathode flooding and oxygen starvation. These faults result in lower fuel cell performance and lifetime. The anode stream supplies the required hydrogen for reaction, and therefore low anode flow rates would also result in anode starvation. This would also affect PEM fuel cell performance and lifetime. In this chapter, we propose measures that can be used to design a diagnostic algorithm that can detect and isolate these faults in real time. The algorithm itself is presented in the next chapter.

This chapter proceeds as following: we first analyze diagnostic measures proposed in the literature for detecting cathode flooding and starvation. We then reproduce these faults, and use the experiment results to propose measures that can be used to design algorithms that can detect and isolate these faults in real time. Following that, we analyze diagnostic tools used in the literature to detect anode starvation. We then reproduce anode starvation, and use that to propose measures for reliable isolation of anode starvation from other possible sources of fault examined in real time.
3.1 Cathode Low Flow Induced Faults

Low flow rates on the cathode side could result in erratic cell voltage that correspond to cathode flooding [10, 38]. Also when cathode stoichiometry reaches very low values, not enough reactant is available for reaction, and the cathode starves from oxygen [36]. These regimes reduce fuel cell performance and lifetime, due to lower average cell voltage and faster degradation rates [28]. As a result, it is desired to detect these regimes as early as possible, in order to take correcting action. This has been the subject of many works in this field, as explained below.  

A drop in cell average voltage is common to almost all fuel cell faults, therefore it can not be used to uniquely identify a specific fault in the cathode. As a result, authors have proposed different methods to isolate cathode flooding and starvation from other possible sources of fault in PEM fuel cells. These faults include membrane drying/dehydration, anode starvation, and CO poisoning.

One way to isolate flooding is by looking at the fuel cell impedance at different current/voltage excitation frequencies. At different operating regimes, the dominant processes in fuel cell change, which often have different characteristic frequency. Therefore, by looking at the fuel cell dynamic response at different frequencies, it is possible to isolate these operating regimes/faults.

Le Canut et al. [10] reproduced dehydration, flooding, and CO poisoning in a Hydrogenics Series 500 stack with 4-20 cells, and reported cell voltage drop with all three faults. They proposed using the cell impedance as a signature to distinguish between these faults. They showed that during dehydration, the fuel cell impedance magnitude and phase increases at all frequencies. However, flooding caused an increase in the cell impedance only at frequencies below 10Hz, and a decrease in phase at frequencies below 100Hz. Anode CO poisoning on the other hand, caused an increase in the impedance magnitude at 100-300Hz, with a maximum phase shift around 20 Hz.

Mérida et al. [41] showed that two high and low frequency measurements of the cell impedance would suffice to diagnose flooding and drying. They imposed drying

\footnote{A comprehensive literature review of the effect of flow rate on fuel cell performance is presented in Appendix A.}
CHAPTER 3. PEM FUEL CELL LOW FLOW INDUCED FAULTS

and flooding conditions on a 4 cell stack, and measured the impedance at frequencies between 0.1-2×10^5 Hz. They showed that while dehydration resulted in impedance variations at both high (f>10^3 Hz) and low frequencies, flooding corresponded to variations only at the lower frequency.

We can conclude from the above works that impedance measurement can be used to detect flooding in the PEM fuel cell cathode. However, the active excitation requirement makes this method expensive and not suitable for real time fault detection in fuel cell end use applications. In addition, the steady state requirement for measuring the cell impedance in an additional constraint that limits its performance.

A more cost effective algorithm was proposed by Hissel et al. [20]. They used the rate at which the cell voltage declines in order to distinguish between dehydration and flooding. They carried experiments with a 20 cell stack, and observed that voltage drop was in the order of 10 times faster during flooding than drying. They used this signature to construct a diagnostic algorithm that could distinguish between flooding and dehydration in real time. The advantage of their method is its simplicity; only voltage and current measurements were used to distinguish between drying and flooding. However, one shortcoming of this algorithm is that other faults can also produce similar voltage drops, resulting in false alarms. For example, it can be seen from the work of authors in [10] that 50 ppm of CO in the anode causes slow decay of the cell voltage (in the order of 10 minutes), while 100ppm causes a rapid voltage drop, hence, the algorithm would detect low CO poisoning as drying, and high CO poisoning as flooding.

An alternative tool proposed in the literature is using the pressure drop across cathode to detect and isolate PEM fuel cell cathode flooding [38, 19, 5]. Ma et al. [38] used a transparent cathode and showed that the discharge of water droplets corresponds to reduction in the cathode pressure drop. They also observed erratic pressure drop at low flow rates, due to water accumulation and discharge from the cathode, i.e., flow field flooding.

He et al. [19] also proposed using the cathode pressure drop as a diagnostic tool to monitor electrode flooding in PEM fuel cells. They used a PEM fuel cell with interdigitated flow field, and showed that the cathode pressure drop increases
significantly in the mass transport limiting region of the polarization curve. They also examined the effect of temperature on cathode pressure drop, and showed that with an increase in the cell temperature, the pressure drop decreased. They associated this to the higher water vapor pressure at higher temperature, higher volumetric flow rate of air at elevated temperatures, and reduced water surface tension and viscosity at higher temperatures.

Barbir et al. [5] proposed using the cathode pressure drop and cell resistance to isolate flooding and drying in a fuel cell stack. They flooded the cathode of a three cell stack by setting the stack temperature below the air dew point temperature. They observed erratic behavior in cell voltage, with an increase in pressure drop and no changes in the cell resistance. They increased the cell temperature above that of the humidification temperature, and observed reduction in the pressure drop, along with less erratic behavior of the cell voltage. To reproduce drying, they reduced the cathode dew point temperature to about 20°C below the stack temperature of 75°C. They observed drop in the cell voltage, along with a reduction in the cathode pressure drop and increase in the cell resistance. When they increased the cathode dew point temperature to levels equal to that of the cell temperature, the cell voltage increased, corresponding with an increase in the pressure drop, and reduction in the cell resistance was decreased.

The complication with using pressure drop for real time flooding diagnostics remains in the fact that the pressure drop is also affected by changes in operating conditions. For example, pressure drop changes linearly with the flow rate[5]. He et al. [19] also showed that the pressure drop across the cathode is also a function of temperature. Therefore, in order to construct a robust diagnostic algorithm to detect cathode flooding, one should compensate for the effect of operating conditions on the pressure drop, in order to obtain the contribution of water. The uncertainties associated with such compensation algorithms makes pressure drop not a suitable measure for real time flooding diagnostic.

Cathode stoichiometry is an alternative measure that can be used to detect operating regimes in the cathode. Sun et al. [65] used a fixed reference cathode stoichiometry to prevent the PEM fuel cell from cathode starvation. To achieve this, they used a
fixed cathode stoichiometry of 2 to calculate a limit for the PEM fuel cell current. Using this limit, they designed a load governor that constrained the load current to protect the fuel cell from cathode starvation. Similarly, Vahidi et al. [73] used a fixed cathode stoichiometry ratio to prevent a PEM fuel cell from cathode starvation. Instead of limiting the current by a load governor, they used an ultra-capacitor to supply additional current in order to ensure that the stoichiometry requirement was satisfied.

The cathode stoichiometry can be effectively used for early detection and prevention on cathode starvation. However, for our system, a fixed cathode stoichiometry would not represent cathode starvation at all operating conditions examined. As we show in the next section, the stoichiometry at which cathode starvation happens is itself a function of the load current.

From the above literature review we can conclude that there is a need for measures that can be used to reliably detect and isolate cathode flooding and starvation in real time. In the next section, we reproduce these regimes, and use the experiment results to propose measures that can be used for real time FDI. We then use these measures in the next chapter to design real time FDI algorithms.

### 3.1.1 Cathode Low Flow Fault Region

In order to reproduce the cathode low flow region, we operated the fuel cell described in chapter 2 at operating conditions of Table 2.3, and a nominal fixed current density of 500 mA/cm$^2$. We fixed the anode stoichiometry at 1.3, while reducing the cathode stoichiometry from 2.4 with steps of 0.1, until the cell voltage reaches zero volts. We calculated the stoichiometries as the ratio between the supplied reactants, measured using mass flow meters, and the used reactants, calculated from the fuel cell current density (see equations (4.5) and (4.9)). The result of this experiment is shown in Figure 3.1.

We can see in Figure 3.1.a that when the cathode stoichiometry is reduced below 1.5, the cell voltage reaches zero volts, corresponding to cathode starvation as shown in Figure 3.1.b. This suggests that the cathode stoichiometry can be used to detect
Figure 3.1: Cell voltage at a fixed current density of 500 mA/cm². a) Cell voltage and cathode stoichiometries versus time. b) Voltage mean and voltage variance at each stoichiometry examined. Cathode flooding corresponds with high voltage oscillations. Cathode starvation corresponds with zero volts caused by low cathode stoichiometry.
cathode starvation. However, the cathode stoichiometry at which cathode starvation occurs depends on the fuel cell current density. To show this, we operated the fuel cell at current densities of 100, 200, 300, 400, 500, and 600 mA/cm², with an anode stoichiometry of 1.3 and other operating conditions as in Table 2.3. We increased the cathode stoichiometry to a high stoichiometry beyond which the cell average voltage did not increase, and reduced it to a low stoichiometry at which the cell voltage reached zero volts. The result of this experiment is shown in Figure 3.2.

Figure 3.2: Cell average voltage versus cathode stoichiometry at different current densities.

We can see in Fig 3.2 that for our system, with an increase in the fuel cell current from 100 to 600 mA/cm², the stoichiometry at which cathode starvation occurs (cell voltage drops to zero), is increased from 1 to 1.7. Therefore, a fixed cathode stoichiometry cannot be used to effectively detect cathode starvation over a wide range of load conditions, as suggested by authors in [65, 73]. We propose storing the stoichiometry value at each current density which cathode starvation occurs as \textit{a priori} information for real time cathode starvation diagnostics. We present the corresponding algorithm in section 4.1, and analyze its sensitivity to variations in operating conditions in section 4.2.
If we revisit Figure 3.1.a, we can see that before cathode starvation occurs, reducing cathode stoichiometry at a fixed current density corresponds to an increase in cell voltage oscillations caused by flooding [10]. This suggests that the amplitude of voltage oscillations can be used to detect flooding. One way to quantify the amplitude of cell voltage oscillations is by the cell voltage variance. In Figure 3.1.b, we have graphed the cell voltage variance (see equation (4.3)) at the cathode stoichiometries examined. We can see in Figure 3.1.b that the voltage variance exhibits exponential growth in the flooding region. In order to verify that at all current densities, the cell voltage variance grows in amplitude with a reduction in cathode stoichiometry, we have graphed the cell voltage variance along with the cell voltage for experiment of Figure 3.2 in Figure 4.4. Note that we have graphed the voltage variance on logarithmic scale.

![Figure 3.3: Cell average voltage and voltage variance versus cathode stoichiometry at current densities of 100 to 600 mA/cm².](image)

We can see in Fig 4.4 that at all current densities examined, cell voltage variance...
grows with reducing stoichiometry and dropping cell average voltage. Therefore, we propose using the cell voltage variance as a measure that can be used to detect cathode flooding in real time. We present the corresponding algorithm in sections 4.1, and analyze its sensitivity to variations in operating conditions in section 4.2.

Although the high oscillation region is called flooding, the fundamental processes that result in such behavior are still not well understood. Reducing the cathode stoichiometry at a fixed pressure, not only reduces the water carrying capacity of the cathode stream, but also reduces the oxygen concentration at the cathode output. The cumulative effect of these changes in operating conditions result in a growth in cell voltage oscillation. In the next section, we study the characteristic frequency of cell voltage oscillations in order to gain better understanding of the origin of these oscillations in PEM fuel cells. This understanding is useful for designing both better fuel cell system as well as diagnostic algorithms that are robust to variations in cathode stoichiometry.

3.1.2 Pressure-Voltage Oscillations

To explain the origin of cell voltage oscillation at low flow rates, Kulikovsky et al. [29] carried experiments at which they operated the fuel cell at a current density of 300 mA/cm², with cathode stoichiometries of 1.3 and 2.6. They reported voltage oscillations at the lower stoichiometry, but not at the higher stoichiometry. They also modeled the fuel cell polarization curve along the flow filed channel, taking into account changes in channel oxygen concentration, oxygen transport trough GDL, and electrochemical activation losses. They showed that at low stoichiometry ratios, non-uniform oxygen concentration in the cathode flow field results in different possible voltages at a fixed current density (steady state multiplicity). As a result, the cell voltage could exhibit oscillation between these values. However, higher flow rates provide more uniform oxygen concentrations along the channel, which result in a unique voltage-current relationship, extinguishing voltage oscillations.

Schneider et al. in [59] and [61] showed that when an ac current is superimposed on the fuel cell load at frequencies below 10 Hz for impedance measurement, it results
in oscillations of the oxygen concentration in the cathode flow field channel. In [59], authors fed the cathode output of a 200 cm$^2$ segmented fuel cell to the cathode input of a 30 cm$^2$ sensor cell. They operated both cells at the same dc voltage, while imposing a sinusoidal current excitation on the primary cell for impedance measurement purposes. Using air at frequencies below 10 Hz, they observed similar oscillations in the voltage of the sensory cell. They concluded that the sinusoidal current excitation in the primary cell has caused oscillations in oxygen concentration in the gas channel. Since the sensory cell is coupled to the primary cell through the cathode, forced convection of the concentration oscillation causes voltage oscillations in the sensory cell. In [61], they used mathematical modeling to superimpose the effect of ac current excitation and oxygen concentration oscillation caused by upstream oscillatory oxygen consumption along the channel of a segmented fuel cell. They showed that the difference between the amplitude and phase of these two sources of oscillation could explain the variations of impedance spectrum along the channel of PEM fuel cells.

In Figure 3.1.a, we can see that the fuel cell voltage is not constant and oscillates at all cathode flow rates examined. We can also see that the amplitude of these oscillations increase with decreasing cathode flow rate. To better understand the origin of these oscillations, we have graphed 50 seconds of the cell voltage of Figure 3.1.a at low, medium, and high stoichiometries, as well as cathode input and output pressures in Figure 3.4.

We can see in Figure 3.4 that the characteristic frequency, $\omega$, of cell voltage oscillations and cathode output pressure are the same, and around 0.14 Hz for our system. This suggest that the amplitude ratio and the phase difference between the two signals can be used as a diagnostic tool for detecting operating conditions in the cathode, similar to that used by voltage and current in impedance measurement. We define the voltage-pressure oscillation ratio, $Z_P(\omega)$, as:

$$Z_P(\omega) = \frac{V(\omega)}{P(\omega)} \text{ (VPa}^{-1})$$

(3.1)

with $\omega$ being the oscillation frequency, $V$ the cell voltage, and $P$ the cell output pressure. We then calculate the amplitude and phase of voltage-pressure oscillations
Figure 3.4: Cell voltage and output pressure of Figure 3.1.a versus time. a) high, b) medium, c) low cathode stoichiometries.
ratio, $|Z_P|$ and $\angle Z_P$, using the following relationship:

\begin{align}
|Z_P| &= \frac{|V|}{|P|} \\
\angle Z_P &= \angle V - \angle P
\end{align}

(3.2) \hspace{1cm} (3.3)

with $|.|$ being the amplitude, $\angle$ the phase, and $\omega$ the frequency of oscillations. The voltage-pressure oscillations amplitude and phase can be used to understand dynamical behavior of the fuel cell cathode. For example, in our system, we can see that the output pressure and cell voltage are out of phase at all cathode flow rates examined. This is a counter intuitive result, as one would expect that an increase in pressure result in higher cell voltages due to higher concentrations, as explained by the Nernst equation (2.20). However, the dynamic response of the fuel cell voltage to pressure oscillations can be dominated by changes in the water liquid-vapor boundary conditions in the catalyst pores. Berg et al. in [8] showed that the active catalyst sites are located inside the catalyst wetted region. Eikerling in [14] used an agglomerate geometry for the cathode catalyst layer and showed that during normal operation, the liquid-gas boundary exists in the nano pores inside the agglomerates. Gradients in the output pressure could result changes in the liquid-gas boundary conditions in the agglomerates. A drop in the output pressure would result the liquid-gas boundary to advance towards larger pores, hence replacing gas phase by water. This would in turn increase the number of active catalyst sites, resulting in a higher cell voltage. Alternatively, an increase in output pressure would push back the water into the smaller pores, reducing the number of active catalyst sites, and hence lowering the cell voltage. Substantiating this hypothesis however, requires a systematic study that is outside the scope of this thesis.

In this section, we experimentally produced the cathode low flow region and used that to propose diagnostic measures that can be used to isolate cathode flooding and starvation in real time. In the next section, we perform similar experiments to produce the anode low flow region. We then use that to propose measures for detecting anode starvation in real time.
3.2 Anode Low Flow Induced Fault

The PEM fuel cell anode stream supplies the hydrogen required for reaction. Low anode flow rates could result in anode starvation and permanent damages to fuel cell performance and lifetime [26, 66]. Therefore, it is desired to detect anode starvation as early as possible, in order to take correcting actions to mitigate from it during operation.

To detect anode starvation, Arcak et al. [2] designed a nonlinear observer for estimating the hydrogen partial pressure at the anode exit from the cell voltage. Assuming that the oxygen partial pressure in the cathode was known, they related changes in cell voltage caused by changes in hydrogen partial pressure using the Nernst equation (2.20). However, the problem with this observer is that voltage losses in PEM fuel cells are dominated by losses on the cathode side. Therefore, changes in the hydrogen partial pressure can not be observed by the cell voltage. For our system, we show this experimentally in the next section.

3.2.1 Anode Low Flow Fault Region

In order to show the anode low flow region, we operated the fuel cell at a the operating conditions of Table 2.3 and a nominal current density of 500 mA/cm$^2$. We fixed the cathode stoichiometry at 2.8 (max value in Figure 3.2 at 500 mA/cm$^2$), while reducing the anode stoichiometry from 1.7 with steps of 0.1 until the cell voltage reaches zero. The result of this experiment is shown in Figure 3.5.

We can see in Figure 3.5 that a reduction in the anode stoichiometry does not have an effect on the fuel cell voltage until the anode stoichiometry reaches a value around 1.1, from which point the cell voltage drops to zero volts, corresponding to anode starvation. We can also see that the fuel cell voltage is not affected by reduction in the hydrogen stoichiometries, until an excess ratio close to unity is reached. At this point, the supplied reactant is not sufficient for the reaction, therefore the cell voltage drops to zero. This suggests that unlike the cathode side, the anode stoichiometry at which starvation occurs is solely driven by the rate of hydrogen consumption, and occurs at stoichiometry close to one. To verify this, we operated the fuel cell at current densities
of 100, 200, 300, 400, 500, and 600 mA/cm². We fixed the cathode stoichiometry at its maximum value in Figure 3.2, and reduced the anode stoichiometry from a high value until the cell voltage reached zero volts. The result of this experiment is shown in Figure 3.6.

We can see in Figure 3.6 that when the anode stoichiometry reaches 1.1, the cell voltage drops to zero, independent of the current density examined. Therefore, we propose using the anode stoichiometry as a measure that can be used to detect anode starvation in real time. We present the corresponding real time fault detection algorithm in section 4.1.

### 3.3 Conclusions

In this chapter, we reproduced anode and cathode low flow regions. We showed that cathode flooding corresponds with an increase in the amplitude of cell voltage oscillations, and proposed using the cell voltage variance as a measure that can be used to isolate cathode flooding in real time. We showed that cathode starvation
occurs when the cathode stoichiometry drops below a value that depends on the fuel cell current density, and proposed using this signature to isolate cathode starvation. We also showed that anode starvation occurs when the anode stoichiometry drops below a fixed value, independent of the current density. We proposed using the anode stoichiometry to detect anode starvation in real time.

In the next chapter, we use the measures introduced in this chapter to design a diagnostic algorithm that can isolating low flow induced faults in real time.
Chapter 4

PEM Fuel Cell Low Flow FDI

We showed in the previous chapter that low flow rates in the anode and cathode of PEM fuel cell could result in anode starvation, cathode flooding, and cathode starvation. In this chapter, we present a Fault Detection & Isolation (FDI) algorithm that can isolate these faults in an operational PEM fuel cell in real time. To achieve this, we use the experimental results presented in the previous chapter to design diagnostic residuals that can capture these faults. We then use these residuals in a diagnostics algorithm that can isolate these faults in real time. Finally, we examine the robustness of the proposed algorithm to changes in load, temperature, pressure, and humidity operating conditions.

4.1 Fault Detection & Isolation

In the FDI context, a fault is defined as an unexpected change in the system function that tends to degrade the system performance, while a failure suggests complete breakdown of the system. There are various classifications by which faults can be categorized. One way is to classify them based on their evolution with time [24], i.e.:

- **Incipient**: A fault is called incipient if it is developed slowly and continuously.
- **Abrupt**: A fault is called abrupt if its effect on the system is sudden and brings the system close to the limit of acceptable behavior.
• **Intermittent**: A fault is called intermittent if it effects the system for discontinuous periods of time.

Inciipient faults are relatively difficult to detect early, since they progress slowly. In the fuel cell context, cathode flooding shown in Figure 3.1.a is an incipient fault. Abrupt faults develop are relatively easier to detect, however, they have more critical effect on the system. Anode starvation shown in Figure 3.5 is an abrupt fault.

An alternative classification for faults is based on the location of the fault. A fault can occur in the following system components:

• Process
• Sensors
• Actuators
• Control algorithm

The focus of this work is detecting and isolating process faults, represented by a PEM fuel cell. Fault diagnostic algorithms used to detect process faults consist of two main stages [11]:

• **Residual generation**: Residual generation extracts fault symptoms from the system, using available input and output information.

• **Residual evaluation**: Residual evaluation examines the generated residuals to decide if a fault is present in the system and isolate specific faults.

A fault tolerant control system can use the information regarding faults to take corrective actions [46]. The block diagram of such a fault detection and correction system is shown in Figure 4.1.

For our diagnostic system, the variables in Figure 4.1 are as follows:

\[
y = \begin{bmatrix} V \\ I \\ \dot{m}_{a,in} \\ \dot{m}_{c,in} \end{bmatrix}, \quad r = \begin{bmatrix} r_v \\ r_{a^2} \\ r_c \\ r_a \end{bmatrix}, \quad f = \begin{bmatrix} \text{Fault} \\ \text{Cathode Flooding} \\ \text{Cathode Starvation} \\ \text{Anode Starvation Warning} \\ \text{Anode Starvation} \end{bmatrix}
\]
with \( I \) being the fuel cell current, \( V \) the fuel cell voltage, \( \dot{m}_{a,in} \) the anode input mass flow rate, \( \dot{m}_{c,in} \) the cathode input mass flow rate, \( r_v \) the voltage residual, \( r_{\sigma^2} \) the voltage variance residual, \( r_c \) the cathode stoichiometry residual, and \( r_a \) the anode stoichiometry residual. These residuals are used to declare the faults in the fuel cell as defined by vector \( f \).

The faults defined in this work by vector \( f \) are in fact process faults, as opposed to sensor and actuator faults. There are many methods developed in the literature for process fault diagnosis. These methods can be classified in three main categories [77]:

- **Analytic model-based methods**: These methods use measurements along with the system model to create analytic redundancy [17]. This analytic redundancy is used to detect and isolate faults in the system. Parity space approach [12], observer based approach [56], and parameter estimation [23] are different approaches that use an analytic model of the system for fault detection. Model-based methods are very effective when a proper model of the system is available.
• **Qualitative model-based methods**: These methods use heuristic symptoms produced by qualitative models or human operators to detect a fault in the system. Artificial intelligence, expert systems, and fuzzy logic techniques can be used for diagnostic reasoning strategies [16]. These methods are more effective than analytic model based methods when the system can not be accurately modeled, is too complex, and/or human knowledge of the process is available.

• **Signal-based methods**: These methods extract symptoms from the measured signals such as mean, variance, envelope, correlation coefficient, covariance, etc, to detect faults in the system. These methods are used widely in practice, however, they have limitation for early detection of faults where the symptoms have not been fully developed, and for faults that occur during system transients [77].

As we mentioned in chapter one, For PEM fuel cell fault detection, the shortcoming with analytic model-based methods is the many processes, different characteristic lengths, and complicated dynamics that results in model uncertainty. To deal with these uncertainties, authors in [55] use a statistical approach to assign a probability to the system fault, and use that for supervisory monitoring of the system.

Compared to analytic methods, qualitative models are more powerful for PEM fuel cell fault detection. This is due the fact that the model uncertainties can be captured by the fuzzy model. In addition, human knowledge of the system behavior can be used for reasoning in these method. In [20], authors use a fuzzy model of the PEM fuel cell to isolate two faults in the system.

Signal based methods are the most simple, practical, and widely used method for fault detection. In this approach, PEM fuel cell faults are reproduced and their symptoms are captured. These symptoms are then used during operation to detect and isolate the fault of interest. In this chapter, we introduce a signal based approach capable of detecting low anode and cathode flow rate induced faults in a PEM fuel cell. We first introduce four diagnostic residuals that can capture the effect of anode and cathode low flow rates. We then use this residuals in an FDI logic to isolate the faults.
4.1.1 Voltage Residual

Previous authors have showed that a drop in the cell voltage is common to almost all fuel cell faults [10, 20]. Therefore, presence of a fault in the fuel cell system is detectable by monitoring the cell voltage. In order to detect a fault, we define the voltage residual, $r_v$, as:

$$ r_v = v_s - v_{ref} $$

with $v_{ref}$ being the cell reference voltage, and $v_s$ the cell sampled voltage. A negative value for $r_v$ represents a drop in the cell voltage from reference value, pointing to the presence of a fault in the system.

Reference Voltage

The reference voltage, $v_{ref}$, is obtained from a reference polarization curve, given the fuel cell current density. To obtain the reference polarization curve, we use the cathode stoichiometry-voltage relationship shown in Figure 3.2. In this Figure, at each current density examined, we have increased the cathode stoichiometry until the cell voltage shows no further increase. Therefore, the last two data points with the highest cathode stoichiometry result in the highest cell voltage. However, among these points, the one with lower cathode stoichiometry would result in lower air utilization. Therefore, we use this cell voltage and stoichiometry to obtain the reference polarization curve for our fuel cell, as shown in Fig 4.2. Note that we have also graphed the fuel cell polarization curve using a fixed cathode stoichiometry of 2, as used in fuel cell literature for comparison [9, 50, 57].

We can see in Figure 4.2 that for stoichiometries larger than 2, the reference polarization curve results in a higher voltage compared to the standard polarization curve obtained using a fixed cathode stoichiometry of 2. This results in higher performance for the fuel cell. At stoichiometries below 2, the reference polarization curve results in the same voltage as the standard polarization curve, however, at a lower air flow rate. This improves the reactant utilization on the cathode side. Therefore, we conclude that for our system, the variable cathode stoichiometry polarization curve results in
lower flow rates at low current densities, and higher voltage at high current densities, compared to a fixed cathode stoichiometry polarization curve. Therefore, we use this polarization curve to obtain the reference voltage at each current density.

In order to calculate the reference voltage at different current densities in real time, we fit the variable stoichiometry polarization curve to equation (2.27), to get the fitted parameters of table 4.1. We use these fitted parameters in equation (2.27), along with the cell current to obtain the reference voltage in real time.

4.1.2 Voltage Variance Residual

If we revisit Figure 3.1.a, we can see that as we reduce the cathode flow rates, cell voltage oscillations grow in amplitude. This suggests that the amplitude of the cell voltage oscillations can be used to detect the beginning of the cathode low flow region. In Figure 3.1.b, we can see that the variance of the cell voltage is increased exponentially when the fuel cell enters the flooding region. Therefore, to detect flooding, we
Table 4.1: Fuel Cell fitted parameters for the variable stoichiometry polarization curve using equation (2.27).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$(V)</td>
<td>1.18</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.5</td>
</tr>
<tr>
<td>$i_n$(mA/cm²)</td>
<td>1</td>
</tr>
<tr>
<td>$i_0$(mA/cm²)</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$r$(kΩcm²)</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$m$(V)</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>$n$(V)</td>
<td>$1.35 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

define the voltage variance residual, $r_\sigma$, as:

$$r_\sigma^2 = \sigma_v^2 - \sigma_{ref}^2$$ (4.2)

with $\sigma_{ref}^2$ being the reference voltage variance and $\sigma_v^2$ the real time voltage variance.

**Voltage Variance**

The cell voltage variance at each point in time is calculated over the last $n$ samples of the cell voltage, $v_s$, i.e.:

$$\sigma_v^2 = \frac{1}{n} \sum_{i=1}^{n} (\bar{v} - v_s)^2$$ (4.3)

with $\bar{v}$ being the cell average voltage over the same window of $n$ samples. In Figure 4.3, we have graphed the cell voltage variance with window lengths of 30, 60, and 120 seconds. We can see in Figure 4.3 that the variance becomes smoother with increasing window length, reducing the residual fluctuations. However, a too large window size reduces the sensitivity and response time of the algorithm. Therefore, in order to balance between sensitivity and smoothness, we choose a window length of 60 seconds in order to calculate the voltage variance in real time.
Figure 4.3: Voltage variance and cathode stoichiometry of Figure 3.1 versus time, for three window lengths of 30, 60, and 120 seconds.

Reference Voltage Variance

The reference voltage variance, $\sigma_{ref}^2$, is the voltage variance that identifies the beginning of the growth in cell voltage oscillations, i.e., flooding region. In order to measure this value at different current densities, we have graphed the cell average voltage and voltage variance of Figure 3.2 in Figure 4.4. Note that in Fig. 4.4, we have eliminated the lowest stoichiometry data point of Figure 3.2, which corresponds with a cell voltage of zero volts.

We can see in Figure 4.4 that a fixed reference variance of $10^{-6}$ corresponds with the beginning of the voltage drop at all current densities examined. Therefore, we use this fixed value as the reference voltage variance to detect cathode flooding in real time.

4.1.3 Cathode Stoichiometry Residual

We showed in Figure 3.2 that at each current density, there exist a stoichiometry at which the cell voltage drops to zero. This voltage drop is due to cathode starvation...
Figure 4.4: Cell average voltage and voltage variance versus cathode stoichiometry at current densities of 100 to 600 mA/cm$^2$. The horizontal arrowed lines correspond to the voltage variance at the beginning of the flooding region, and the vertical arrowed lines show its corresponding cell average voltage. Note that the voltage variance is graphed on a logarithmic scale.
caused by low air stoichiometry. Therefore, to detect cathode starvation, we generate the cathode stoichiometry residual, \( r_c \) as:

\[
 r_c = \lambda_c - \lambda_{c,ref} \tag{4.4}
\]

with \( \lambda_{c,ref} \) being the cathode starvation reference stoichiometry and \( \lambda_c \) the real time cathode stoichiometry.

**Cathode Stoichiometry**

In order to calculate the cathode stoichiometry, \( \lambda_c \), in real time, we use the following relationship:

\[
 \lambda_c = \frac{\dot{m}_{c,in}}{\dot{m}_{c,use}} \tag{4.5}
\]

with \( \dot{m}_{c,in} \) being the cathode input air flow rate, measured using mass flow sensors. The consumed air flow rate, \( \dot{m}_{c,use} \), in equation (4.5) is calculated from the cell current, \( I \) in amps, using the following relationship (see [31] for derivation):

\[
 \dot{m}_{c,use} = 3.57 \times 10^{-7} I \text{ (kg/s)} \tag{4.6}
\]

**Cathode Starvation Reference Stoichiometry**

In Figure 3.2, we reduced the cathode stoichiometry until the cell voltage reached zero, causing cathode starvation. We set the cathode starvation reference stoichiometry at each current density at the point which the cell voltage drops to zero. We have shown this in Figure 4.5.

In order to calculate the cathode starvation reference stoichiometry, \( \lambda_{c,ref} \), at different current densities in real time, we fit a second order equation to Figure 4.5, i.e:

\[
 \lambda_{c,ref} = 3.3i^2 - i + 1.07 \tag{4.7}
\]

with \( i \) being the cell current density in A/cm\(^2\). Note that the cell current density in Figure 4.5 is expressed in mA/cm\(^2\).
4.1.4 Anode Stoichiometry Residual

We showed in Figure 3.6 that when the anode stoichiometry drops below 1.2, the cell voltage drops to zero. This voltage drop is due to anode starvation caused by low hydrogen stoichiometry. Therefore, in order to detect anode starvation, we generate the anode stoichiometry residual, $r_a$, as:

$$r_a = \lambda_a - \lambda_{a,ref}$$  \hspace{1cm} (4.8)

with $\lambda_{a,ref}$ being the anode starvation reference stoichiometry and $\lambda_a$ the anode stoichiometry in real time.

Anode Stoichiometry

To calculate the anode stoichiometry, $\lambda_a$, in real time, we use the following relationship:

$$\lambda_a = \frac{\dot{m}_{a,in}}{\dot{m}_{a,use}}$$  \hspace{1cm} (4.9)
with $\dot{m}_{a,\text{in}}$ being the supplied hydrogen flow rate, measured using mass flow sensors. $\dot{m}_{a,\text{use}}$ is the consumed hydrogen flow rate and is calculated from the cell current, $I$ in amps, using the following relationship (see [31] for derivation):

$$
\dot{m}_{a,\text{use}} = 1.05 \times 10^{-8} I \text{ (kg/s)}
$$

(4.10)

**Anode Reference Stoichiometry**

We showed in Figure 3.6 that at any current density, when the anode stoichiometry drops below a fixed value of 1.2, anode starvation occurs, causing the cell voltage drops to zero. Therefore, we use this fixed value as the anode starvation reference stoichiometry.

If we revisit Figure 3.5, we can see that the cell voltage drops shortly after the anode stoichiometry drops below 1.2. We use this delay to announce an anode starvation warning before the anode actually starves.

In the next section, we use the residuals constructed above to build a diagnostics algorithm that can isolate cathode flooding, cathode starvation, and anode starvation in real time.

### 4.1.5 Residual Evaluation Logic

We use the residuals presented above to detect and isolate low flow induced faults in the PEM fuel cell. To achieve this, we use a thresholds for the residual, along with a boolean logic, to detect a fault in the fuel cell, and isolate cathode flooding, cathode starvation, and anode starvation. This is explained below.

**Fault**

In section 4.1.1, we noted that in PEM fuel cells, a fault is associated with a drop in the cell voltage. We defined the voltage residual, $r_v$, as the difference between the cell actual voltage and the reference voltage. Based on the two sets of data that we obtained, we declare a fault in the fuel cell system, if the cell average voltage drops over 3% below the reference value, i.e.:
In rule 4.11, we average the voltage residual over a window in order to filter out fluctuations in cell voltage. A too large window would cause algorithm in the algorithm response time, while a too small window would not filter out voltage fluctuations. A window of $n = 15$ samples is the smallest window resulting in a stable fault signal.

We have shown the Fault signal for the cathode stoichiometry sweep of Figure 3.1.a. in Figure r1:

![Figure 4.6: Cell voltage and fault signal versus time, for the stoichiometry sweep of Figure 3.1.a.](image)

We can see in Figure 4.6 that the Fault signal jumps to one when the cell voltage drops to low values, signaling the presence of a fault in the fuel cell. While it is useful to know the presence of a fault in the system, the control system can not take any actions, until a specific fault is isolated. This is the subject of the following sections.
CHAPTER 4. PEM FUEL CELL LOW FLOW FDI

Cathode Flooding

We showed in section 3.1.1 that cathode flooding corresponds with an increase in the cell voltage oscillations. In section 4.1.2, we introduced the voltage variance residual, $r_{\sigma^2}$, as a measure that can capture these voltage oscillations. We use this characteristic to isolate cathode flooding (see Figure ??) from other possible faults examined, i.e.:

$$\text{Fault} \& (r_{\sigma^2} > 0) \& (r_a > 0) \rightarrow \text{Cathode Flooding}$$ (4.12)

We can see in rule 4.12 that in addition to the voltage variance, we have also set the presence of a fault, as well as a positive anode stoichiometry residual as conditions for flooding. This is because changes in fuel cell current cause voltage variations in the fuel cell voltage, which in turn results in a high voltage variance residual and false flooding alarm. By adding the fault condition, the algorithm would not declare flooding unless the cell average voltage has also dropped below its reference value, eliminating such false alarms. In addition, when anode starvation occurs, the cell voltage drops, causing an increase in the cell voltage variance and false flooding alarm. The anode stoichiometry residual condition eliminates such false alarm. In Figure 4.7, we have graphed the cathode flooding fault signal for the stoichiometry sweep of Figure 3.1.a.

We can see in Figure 4.7 that the cathode flooding signal is set when the cell voltage oscillations grow in amplitude. However, we can see that the fault signal fluctuates when the amplitude of the cell voltage oscillations reaches boundary values defined to isolate cathode flooding. This is because cathode flooding is an incipient fault and develops gradually, causing an oscillation in the fault signal. The cathode flooding signal can be used by the control system to increase the cathode air flow rate during operation.

Cathode Starvation

We showed in section 3.1.1 that when the cathode stoichiometry drops to very low values, the cell voltage reaches zero. We defined this region as cathode starvation.
Figure 4.7: Cell voltage and cathode flooding signal versus time, applied to stoichiometry sweep of Figure 3.1.a.

In section 4.1.3, we generated the cathode stoichiometry residual, \( r_c \), such that it captures this effect. Therefore, we introduce the following rule to isolate cathode starvation from other possible faults examined:

\[
\text{Fault} \& \left( \sum_{n} \frac{r_c}{n} < 0.2 \right) \rightarrow \text{Cathode Starvation} \tag{4.13}
\]

We can see in rule 4.13 that in addition to the cathode stoichiometry condition, we have also set the presence of a fault in the system as a condition for cathode starvation. This is because in the absence of the fault condition, while a temporary drop in cathode stoichiometry or spike in the cell current would not result in cathode starvation, it would reduce the cathode stoichiometry residual and hence a false cathode starvation signal. By adding the fault condition, the algorithm would not declare starvation unless the cell voltage has in fact dropped below the reference value. This would improve the algorithm reliability. The average cathode stoichiometry residual is also calculated for similar reason, i.e., filter out spikes in the cathode stoichiometry. A window of \( n = 7 \) seven samples was used for this purpose.
We can also see in rule 4.13 that we have used a threshold of 0.2 for the cathode stoichiometry residual to declare starvation. This is to isolate cathode starvation early before it fully develops, in order to allow the control system to take compensatory actions.

In Figure 4.8, we have graphed the cathode starvation signal for the cell voltage of Figure 3.1.a. We can see that the cathode starvation rule based is set before the cell voltage reaches zero volts. On the control side, this residual should be used to set a constraint on the current drawn from the fuel cell, in order to mitigate from losses that occur during cathode starvation.

![Figure 4.8: Cell voltage and cathode starvation signal versus time, for the cathode stoichiometry sweep of Figure 3.1.a.](image)

**Anode Starvation**

We showed in section 3.2.1 that when the anode stoichiometry drops below a fixed value, the cell voltage reaches zero. We defined this region as anode starvation. In section 4.1.4, we generated the anode stoichiometry residual, $r_a$, such that it reaches zero values when anode starvation occurs.
CHAPTER 4. PEM FUEL CELL LOW FLOW FDI

If we revisit Fig. 3.5, we can see that when the stoichiometry is reduced to 1.1, the cell voltage remain constant for about 10 seconds, before it drops to zero at a rate of about 1 mV/sec. The constant voltage during the low stoichiometry could be explained by the extra hydrogen available in the flow field and manifolds, acting as a reservoir, similar to that proposed by Liu et al. [36]. We use the delay between cell voltage drop and low hydrogen stoichiometry to generate an anode starvation warning before anode starvation occurs. If, in addition to the anode stoichiometry drop, fault is also present in the fuel cell system, we set the anode starvation signal, i.e.:

\[(r_a < 0.1) \rightarrow \text{Anode Starvation Warning} \quad (4.14)\]
\[\text{Fault } \& (r_a < 0.1) \rightarrow \text{Anode Starvation} \quad (4.15)\]

In Figure 4.9, we have graphed the anode starvation warning and anode starvation signal for the data set of Figure 3.5. We can see that when the anode stoichiometry drops to very low levels, the anode stoichiometry warning signals to one. This signal can be used by the control system to increase the anode flow rate. However, if the anode stoichiometry remains at low levels, the cell voltage also drop to low level, setting the anode starvation fault signal. We can also see that anode starvation in an abrupt fault, resulting in a stable fault signal. This signal can be used by the control system to set a limit on the current drawn from the fuel cell, in order to mitigate from losses that occur during anode starvation.

In this section, we introduced diagnostic residuals and logic to detect low flow induced faults on the anode and cathode of a PEM fuel cell. We showed that cathode starvation depends on the current density at which the fuel cell operates. We also observed that cathode flooding was incipient, and developed gradually with changes in cathode stoichiometry. Because of the correlation of cathode faults on operating conditions, we analyze the effect of changes in cell load, temperature, pressure, and humidity operating conditions on cathode flooding and starvation in the next section.
Figure 4.9: Anode stoichiometry, cell voltage, and a) anode starvation warning and b) anode starvation variables, $R_4$ and $R_5$, versus time, calculated for the stoichiometry sweep of Figure 3.5.
4.2 Robustness

The control system is responsible for maintaining the PEM fuel cell operating conditions at desired set points. However, variations in these conditions can result in false alarms by the fuel cell diagnostic algorithm. The different time constant and the reciprocal effect of these parameters makes it very challenging to isolate failures associated with the fuel cell, from those that correspond to the control system. In this section, we analyze the robustness of cathode flooding and starvation signals to variations in the fuel cell operating current, pressure, temperature, and humidity. When required, we propose terms that can be used to compensate for such changes, in order to mitigate from false alarms.

4.2.1 Current Effects

Changes in the fuel cell load current effects the cell voltage immediately. To examine the effects of changes in cell current on the diagnostic algorithm, we used the polarization data of Figure 2.6. We obtained this polarization curve with an anode and cathode stoichiometry of 1.5 and 2, respectively. We increased the cell current density from zero with steps of 70 mA/cm$^2$, until the cell voltage reaches zero volts. We have presented the resulting voltage, as well cathode flooding and cathode starvation signals in Figure 4.10.

We can see in Figure 4.10 that the cathode flooding signal is set when the amplitude of the voltage oscillations grow in amplitude. We can also see that the increase in current results in an abrupt flooding region to develop, resulting in a stable cathode flooding signal. In Figure 4.10, the cathode starvation signal is also set before the cell voltage reaches zero values. Therefore, we conclude that rules 4.12 and 4.13 are robust to changes in fuel cell current density for the operating conditions examined.

4.2.2 Pressure Effects

We explained in section 2.2.1 that the cell pressure has slow dynamics, in the order of few minutes. Therefore, we analyze the effect of pressure variations on the diagnostic
Figure 4.10: a) Cathode flooding and b) cathode starvation signals, graphed for the polarization data of Figure 2.6.
algorithm when pressure steady state conditions change.

We showed in section 2.1.1 that the effect of pressure on fuel cell voltage at equilibrium can be explained using the Nernst equation (2.20). However, at non equilibrium, the Butler-Volmer equation can be used to capture this effect. At a fixed current density, $i$, the cell voltage and pressure are related by the Butler-Volmer equation as [44]:

$$i = i_0 \frac{P}{P_0} \exp \left( \frac{\alpha F \zeta}{RT} \right) \text{ (mA/cm}^2\text{)}$$

(4.16)

with $\alpha$ being the charge transfer coefficient, $\zeta$ the electrode potential, $P$ the average pressure, $P_0$ the standard pressure, and $i_0$ the exchange current density. If the pressure changes from $P_1$ to $P_2$ at a constant current, the electrode potential, and hence cell voltage would change according to:

$$\Delta V = \frac{RT}{\alpha F} \ln \left( \frac{P_2}{P_1} \right) \text{ (volts)}$$

(4.17)

with $\Delta V$ being the change in cell voltage that results from pressure variations.

To examine the effect of pressure variations, we varied the anode and cathode pressure from 30 psi by $\pm 15$ psi at a current density of 500 mA/cm$^2$, while keeping other conditions similar to that of Table 2.3. We have plotted the cell average voltage and voltage variance at each stoichiometry in Figure 4.11.

We can see in Figure 4.11 that changes in the cell operating pressure from 30 psi results in the cell average voltage to shift by a relatively constant amount at various cathode stoichiometries. If we calculate the ratio between voltage change and the logarithmic pressure change from Figure 4.11, it results in a value about 0.057. This is in good agreement with the $\frac{RT}{\alpha F}$ coefficient being around 0.06 at a cell temperature of 80°C and transfer coefficient of 0.5 (Table 4.1). Therefore, we propose updating the reference voltage, $v_{ref}$, for changes in pressure using equation (4.17).

We can also see in Figure 4.11 that a fixed reference voltage variance corresponds to the beginning of the growth in voltage oscillations for all the three pressure cases. We can also see that the cathode reference stoichiometry, $\lambda_{ref}$, corresponds to the beginning of the sharp voltage drop for all three scenarios. These suggest that the
Figure 4.11: Cell average voltage and voltage variance versus cathode stoichiometry at cell pressure of 15, 30, and 45 psi. The reference variance, $\sigma^2_{ref}$, is shown by a right to left arrow. The cathode reference stoichiometry, $\lambda_{c,ref}$, is taken from Figure 4.5, and is shown by a bottom to top arrow.

reference voltage variance and the cathode reference stoichiometry are independent of the cell operating pressure. We have graphed cathode flooding and starvation signals in Figure 4.12.

We can see in Figure 4.12 that for the three pressure scenarios, the flooding signal is set when the voltage oscillations grow in amplitude, as a result of lower cathode stoichiometries. The cathode starvation signal is also set before the cell voltage reaches zero volts. Therefore, we conclude that using a voltage correction term for pressure variations, the cathode flooding and starvation signals can be made robust for the operating conditions examined.

### 4.2.3 Temperature Effects

We explained in section 2.2.3 that the cell temperature has slow dynamics, in the order of few ten minutes. Therefore, we analyze the effect of cell temperature variations on the diagnostic algorithm at steady state conditions.
Figure 4.12: Cathode flooding and starvation signals versus time, for three cell pressures of 15, 30, and 45 psi.
To examine the robustness of our diagnostic algorithm to different cell temperature, we varied the cell temperature by ±10°C around the 80°C operating point, while maintaining other conditions similar to Table 2.3. We have graphed the cell average voltage and voltage variance versus the cathode stoichiometry for this experiment in Figure 4.13.

Figure 4.13: Cell average voltage and voltage variance versus cathode stoichiometry at cell temperature of 70, 80, and 90°C. The reference variance, $\sigma_{ref}^2$, is shown by a right to left arrow. The cathode reference stoichiometry, $\lambda_{c,ref}$, is taken from Figure 4.5, and shown by a bottom to top arrow.

We can see in Figure 4.13 that the cell average voltage is proportional to the cell temperature, i.e., an increase in the cell temperature results in an increase in the cell voltage for the operating conditions examined. As we explained in section 2.2.3, variations in cell temperature affects the dynamics of all processes in the cell, including thermodynamic equilibrium, activation, ohmic, and mass transport losses. These results analytic modeling of temperature effects on cell voltage to become relatively complicated, and therefore not practical for real time diagnostic applications.

An alternative approach is to compensate for the variations in the cell temperature by experimental methods. A polarization curve similar to that of Figure 4.2 can be
obtained at several cell temperatures. The reference cell voltage can then be derived from those polarization curves at different cell temperatures. In this work, we use the measured cell voltage at the highest cathode stoichiometry examined as the reference voltage.

We can also see in Figure 4.13 that a fixed reference voltage variance corresponds to the beginning of the voltage drop caused by low cathode stoichiometry at the cell temperatures examined. However, the cathode stoichiometry at which the cell voltage drops to zero is higher at elevated temperature. One way to calculate the reference cathode stoichiometry for different temperatures is to store its value at different cell temperatures. Using this approach, we have graphed cathode flooding and starvation signals in Figure 4.14.

We can see in Figure 4.14 that the cathode flooding signal is set when the voltage oscillations grow in amplitude. Therefore, we conclude that rule 4.12 is robust to changes in cell temperature. In Figure 4.14, the cathode starvation signal is also set before the cell voltage reaches zero values. However, the cathode starvation reference stoichiometry, \( \lambda_{c,\text{ref}} \), needs to be adjusted for temperature variations before the rule 4.13 can correctly be used to isolate cathode starvation.

### 4.2.4 Humidity Effects

We explained in section 2.2.2 that the humidification system has slow dynamics, in the order of tens of minutes. Therefore, we also analyze changes in the cell humidity on the diagnostic algorithm at steady state conditions.

In order to examine the effect of different cathode humidities on our diagnostic algorithm, we changed the cathode dew point temperature from 70°C by ±20°C, while keeping other operating conditions similar to that of Table 2.3. In Figure 4.15, we have graphed the cell average voltage and voltage variance versus cathode stoichiometry for the above conditions.

We can see in Figure 4.15 that changes in the humidity has little effect on the fuel cell voltage and voltage variance at the operating conditions examined. In Figure 4.16, we have graphed cathode flooding starvation signals for the three cathode input
Figure 4.14: Cathode flooding and starvation signals versus time, for the three cell temperatures of 70, 80, and 90°C.
Figure 4.15: Cell average voltage and voltage variance versus cathode stoichiometry at humidification temperature of 50, 70, and 90°C. The reference variance, $\sigma_{ref}^2$, is shown by a right to left arrow. The cathode reference stoichiometry, $\lambda_{c,ref}$, is taken from Figure 4.5 and shown by a bottom to top arrow.

dew point temperature of 50, 70, and 90°C examined.

We can see in Figure 4.16 that for the three dew point temperatures examined, the cathode flooding signal is set when the voltage oscillations grow in amplitude. Also the cathode starvation signal is set before the cell voltage reaches zero volts. Therefore, we conclude that rules 4.12 and 4.13 are robust to changes in the cathode dew point temperature under the examined conditions.

Our observation in Figure 4.15 that changes in the cathode inlet dew point temperature has little impact on the cell voltage is counter intuitive. In fact, one would expect that the dew point temperature effect humidity conditions inside the cathode, and hence the cell voltage. One explanation for this could be that the cathode stream is cooled below the dew point temperature of 50°C, before entering the fuel cell cathode, e.g. in the manifolds, causing water condensation. Therefore, the inlet humidity conditions at the cathode inlet is constant with three dew point temperatures examined. This can explain the voltage insensitivity to variations in the cathode dew point
Figure 4.16: Cathode flooding and starvation signals versus time, graphed for three humidification temperature of 50, 70, and 90°C.
temperature. In order to verify this effect, we changed our manifold design to reduce the temperature drop. However, to date, we have not yet repeated the experiment with the new manifold. This is the subject of future work.

An alternative explanation for the invariance of the cell average voltage to cathode humidity conditions could arise from a well humidified membrane. At all humidity conditions examined, the water produced in the cathode could result in a fully saturated cathode stream. Therefore, membrane drying would not occur in any of the cases. If the additional accumulated water is removed from the cathode, its effect on cell voltage would be relatively small.

In the next section, we calculate the rate of water transport in the cathode by evaporation and convection for the operating conditions of Figure 4.15 using steady state analysis. Next, we use a sensory system that is capable of measuring the evaporative and convective water transport mechanisms separately. We use this as a diagnostic tool to study water accumulation and discharge processes in the cathode.

Cathode Water Transport

In many commercial fuel stacks, the anode and cathode streams are well humidified before entering the fuel cell, in order to improve humidification conditions of the membrane. This results in the amount of water transported out of the cell through evaporation to be less than the produced water. Assuming that the net water flux across the membrane is zero, this residual liquid water is transported out of the cathode through convection. This liquid water is then transported out of the cell using convective forces. Therefore, water transport exhibits a two phase flow in the cathode of PEM fuel cells, i.e., in vapor and liquid phases.

The evaporative water transport component in the cathode, \( \dot{n}_{w,\text{evap}} \), can be calculated as the difference between the cathode input and output water vapor molar flow rates, \( \dot{n}_{w,\text{in}} \) and \( \dot{n}_{w,\text{out}} \), respectively. Assuming that air and water vapor behave as ideal gasses, the molar flow rate of water at the cathode input, \( \dot{n}_{w,\text{in}} \), can be calculated from the cathode input air flow rate, \( \dot{n}_{c,\text{in}} \), cathode input air pressure, \( P_{c,\text{in}} \), and water vapor partial pressure at the cathode input, \( P_{w,\text{in}} \), using the following relationship (see
Appendix B for derivation):

\[
\dot{n}_{w,\text{in}} = \frac{P_{w,\text{in}} \dot{n}_{c,\text{in}}}{P_{c,\text{in}}} \text{ (mol/s)}
\] (4.18)

The cathode input air flow rate and pressure in equation (4.18) are measured at the cathode input using mass flow and pressure sensors, respectively. The water partial pressure, \(P_w\), at the cathode input can be calculated from the cathode dew point temperature, \(T_{dp}\) in degrees Celsius, using the following empirical relationship [63]:

\[
P_w = 10^{(-3.18+0.03T_{dp}-9.18\times10^{-5}T_{dp}^2+1.45\times10^{-7}T_{dp}^3)} \text{ (Pa)}
\] (4.19)

The cathode dew point temperature in our experiment was controlled at 50, 70, and 90\(^\circ\)C using a bubbling humidifier. By substituting these values in equation (4.19), the water vapor partial pressure at the cathode input can be calculated. This would allow us to calculate the molar flow rate of water at the cathode input using equation (4.18).

Similarly, the molar flow rate of water at the cathode output, \(\dot{n}_{w,\text{out}}\), can be calculated from the cathode output air flow rate, \(\dot{n}_{c,\text{out}}\), cathode output air pressure, \(P_{c,\text{out}}\), and water vapor partial pressure at the cathode output, \(P_{w,\text{out}}\), using the following relationship (see Appendix B for derivation):

\[
\dot{n}_{w,\text{out}} = \frac{P_{w,\text{out}} \dot{n}_{c,\text{out}}}{P_{c,\text{out}}} \text{ (mol/s)}
\] (4.20)

The partial pressure of air at the cathode output was measured using a pressure sensor at the output of the condenser. The air flow rate at the cathode output can be calculated from the input air flow rate and the consumed oxygen, calculated from the fuel cell current [31], i.e.:

\[
\dot{n}_{c,\text{out}} = \dot{n}_{c,\text{in}} - \frac{I}{4F} \text{ (mol/s)}
\] (4.21)
The dew point temperature of the cathode output stream was measured using the solid state humidity sensor explained in section 2.2.2. By substituting the dew point temperature in equation (4.19), we calculate the partial pressure of water at the cathode output. We then use this in equation (4.20) to calculate the molar floe rate of water vapor exiting the cathode. Finally, the evaporative water flow rate in the cathode, $\dot{n}_{w,\text{evap}}$, can be calculated as the difference between the cathode input and output water vapor flow rates, i.e.:

$$\dot{n}_{w,\text{evap}} = \dot{n}_{w,\text{out}} - \dot{n}_{w,\text{in}} \text{ (mol/s)}$$ (4.22)

The net rate of water production in the cathode, $\dot{n}_{w,\text{prod}}$, can be calculated from the fuel cell current, $I$, using the following relationship [31]:

$$\dot{n}_{w,\text{prod}} = \frac{I}{2F} \text{ (mol/s)}$$ (4.23)

Finally, if we deduct the rate of water produced in the cathode from the rate of water evaporated, it results in the rate of water transported out of the cathode through convection, $\dot{n}_{w,\text{conv}}$, i.e.:

$$\dot{n}_{w,\text{conv}} = \dot{n}_{w,\text{prod}} - \dot{n}_{w,\text{evap}} \text{ (mol/s)}$$ (4.24)

Using these equations, in Figure 4.17, we have graphed the rate of water production, evaporation, and convection in the cathode for the three cathode dew point temperatures of Figure 4.15.

We can see in Figure 4.17 that at the cathode dew point temperatures examined, the rate of water transported through convection is higher than the water transported through evaporation. Therefore, the convective water transport is dominant compared to the evaporative component at the high humidification conditions examined. The convective water transport however depends primarily on the water droplet size and pressure drop across the droplets [35]. As the droplets grow in size, the convective force that drives them increases due to their bigger surface area. This results the droplets to detach from the cathode GDL and flow field when they reach a critical size. This critical size is a function of the GDL and flow field material, as well as
the pressure drop across the droplet. However, both the material properties as well as pressure drop remain constant with changes in humidity conditions. This could explain the similar response observed at different cathode humidification levels.

The above explanation reveals one problem with the calculations presented in Figure 4.17. In these calculation, we have assumed steady state conditions for both the evaporative and convective water transport components. However, previous authors showed that water convection is rather instantaneous than continuous [35]. Therefore, a steady state analysis of the convective component can not fully reveal its dynamics. An alternative approach would be to measure the liquid water content of the cathode as it exits the fuel cell. Such diagnostic tool would provide additional insight into the dynamics of the convective water transport in the fuel cell cathode, and can be used to validate models and optimize fuel cell design.

In the next section, we first review different techniques reported in the literature to study the two-phase flow in PEM fuel cells. We analyze the strengths and limitations of each technique, and identify the need for a sensory system capable of temporal
measurement of liquid water as it exits the fuel cell. We then introduce a sensory system capable of performing such measurement. We finally demonstrate its capability by using it to study convective water transport dynamics in the PEM fuel cell cathode during membrane humidification.

**Liquid Water Measurement Systems**

To understand the behavior of water transport in PEM fuel cells, many authors have modeled the two-phase flow [75, 34, 1, 81, 22, 14, 52, 33]. These models are validated using the measurements from the fuel cell operating parameters. However, the many degrees of freedom and parameters used to capture the transport properties in the fuel cell result in an ill-posed parameter fitting problem. Therefore, increasing the dimension of the measurement space would result in more reliable solutions. When modeling the two phase flow in PEM fuel cells, measurement of liquid water is critical for validation. Following is an overview of the techniques reported in the literature to measure liquid water transport in PEM fuel cells.

Previous authors used various techniques to study the dynamical behavior of the two phase flow in PEM fuel cells. One approach is to use a transparent cathode to observe the transport of liquid water in the GDL and flow fields [76, 82, 18, 71, 62, 35, 45]. The visualization technique provides insight into the mechanical behavior of water transport in the cathode, however, they have limited capability in terms of quantifying the amount of liquid water in the fuel cell. In addition, building the transparent cathode requires use of special materials, which have different heat transfer and surface tension properties than the fuel cell flow field. This in turn results in distortion in the observed water transport behavior.

An alternative technique that is used to visualize spatial water accumulation and distribution in PEM fuel cells is neutron imaging [72, 21, 27, 83, 60, 70, 47]. In this method, a neutron source and detector is placed on both sides of a PEM fuel cell anode and cathode flow fields. The neutron intensity measured by the detector changes proportional to the amount of water present in the fuel cell, revealing the spatial accumulation and transport of water in the fuel cell. In addition, the measured data
can be calibrated to quantify the total amount of water. One shortfall of this method is that it can only measure the total amount of water in the cathode and anode, rather than separate measurements for the two electrodes. In addition, the measurement would represent the total amount of water in both vapor and liquid phases, not distinguishing between the two. Finally, neutron imaging requires expensive hardware and challenging to calibrate for reliable data quantification.

MRI (Magnetic Resonance Imaging) is an alternative technique for studying spatial water distribution in PEM fuel cells [13, 84, 7, 67]. In this method, an array of RF transmitters and receivers are used to provide slices of two and a half dimensional images from the volume of interest. The high spatial resolution of MRI makes it an excellent tool for studying water profiles in the fuel cell membrane. The main short fall of this technique when applied to PEM fuel cells arises from the fact that the magnetic inductive properties of carbon limits acquiring useful data from GDL and flow fields, unless alternative materials are used. Also similar to neutron imaging, MRI requires expensive hardware and is challenging to calibrate in order to quantify the amount of water in the fuel cell.

The transparent flow field, neutron imaging, and MRI techniques explained above are more useful for phenomenological study of water transport in fuel cells, rather than quantifying the amount of water transported in the fuel cell. Other techniques are used to quantify the amount of water at the fuel cell input and output, in order to calculate the water balance PEM fuel cells [51, 6, 48, 37, 39, 80, 79, 58, 42, 8]. In these techniques, the fuel cell is supplied with reactants at a known humidity level, and the water content of the output stream is measured. The difference between the input and output water contents in the anode and cathode is used to study the water transport mechanisms in the fuel cell. Since the stream leaving the fuel cell consists of a two-phase flow, measuring the vapor and liquid water components is one challenge with water balance measurement. Following is a summary of different techniques used in the literature to measure water balance in PEM fuel cells.

Laser absorption spectroscopy is one of the methods used to measure the water vapor partial pressure in the fuel cells [51, 6, 48]. In this method, a laser source and detector are used. As the water vapor partial pressure changes, so does the absorption
rate of laser passing through the stream. This property changes the laser intensity at the detector, which allows quantifying the partial pressure of water vapor. This method can also be integrated into the fuel cell to obtain spatial distribution of water vapor pressure within the cell. However, the short come of this method is that it cannot measure the amount of liquid water in the stream.

Gas chromatography is an alternative technique used to measure the gas concentration in PEM fuel cells [37, 39, 80]. In this method, a relatively small sample of the gas is taken from the fuel cell, and directed to the chromatograph for species concentration measurement. This method can too be integrated into the fuel cell to obtain spatial measurement of species concentration in the fuel cell, however, its limit also resides in the fact that it can only handle gas phase species, therefore, liquid water concentration can not be measured using gas chromatography.

Another method used to measure the water content of the fuel cell output stream is condense the liquid water and measure the weight or volume of the condensed water [79, 58]. This method results in the total amount of water leaving the cell. Therefore, in combination with other techniques that measure the water vapor pressure, e.g. laser absorption spectroscopy, it is possible to quantify amount of water leaving the fuel cell in vapor and liquid phases. The shortfall of this method is that the mass/volume of the condensed water is relatively small. As a result, measurement of the weight/volume is obtained over long periods of time in order for the measurement to fall within resolution of the measurement devices. This in turn limits the temporal resolution of the measured data, which is essential for studying liquid water depletion from the cell, with exhibits a rather instantaneous behavior [35].

Solid state humidity sensors are an alternative device used to measure the relative humidity of the PEM fuel cell anode and cathode output streams [42, 8]. These sensors measure changes in a capacitor dielectric constant to quantify the RH (Relative Humidity) of the stream. By simultaneous measurement of temperature, they calculate the water vapor saturation pressure. From the saturation pressure and the relative humidity, they then calculate the water vapor partial pressure and dew point temperature. Similar to laser absorption chromatography and gas chromatography,
RH sensors can only measure water in the gas phase. In fact, when used with a saturated stream, water condensation on these sensors is one source of unreliable reading. We have summarized the different methods used to measure water content in the fuel cell stream in Table 4.2.4.

**Sensory Vessel**

In order to measure the amount of liquid water leaving the fuel cell cathode, we placed a stainless steel vessel with a diameter larger than the cathode output tubing at the fuel cell output (Fig. 4.18). Therefore, the bursts of liquid water exiting the cathode accumulated inside this vessel. To measure the amount of accumulated water in the vessel, we heated the vessel to a temperature above that of the cathode output stream. This vaporized the accumulated liquid water into the cathode stream that was passing through the vessel. By measuring the dew point temperature of the stream exiting the vessel using a Sensirion SHT75 solid state humidity sensor, we are able to calculate the amount of liquid water that was accumulated in the vessel.

We can see in Figure 4.18 that we have positioned the humidity sensor slightly below the vessel output opening. This is because if the total amount of water entering the vessel is larger than its storage capacity, the vessel would flood and the liquid water would directly exit the vessel without being evaporated. This would result in the dew point temperature of the vessel output not to measure the total amount of water leaving the vessel. However, the humidity sensor is sensitive to liquid water, and would signal an error if in contact with liquid water. Placing the humidity sensor below the sensor exit opening would allow us to detect vessel flooding, increasing the reliability of the measurement system.

To heat the vessel, we circulated hot water in a tubing around the vessel. The large thermal mass of water resulted in a relatively constant vessel temperature, even when liquid water was depleted into the vessel. However, an electric heater was used to heat the tubing. Due to the short residence time of liquid water in the tubing, and low thermal conductivity of the plastic tubing, the thermal mass of the liquid water did not affect the tubing temperature.
Table 4.2: Analysis of different water measurement methodologies reported in the literature.

<table>
<thead>
<tr>
<th>Methodology</th>
<th>Reference</th>
<th>Strength</th>
<th>Weakness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparent Cathode</td>
<td>[76, 82, 18, 71]</td>
<td>phenomenological study</td>
<td>limited quantification</td>
</tr>
<tr>
<td>Neutron imaging</td>
<td>[72, 21, 27, 83]</td>
<td>non intrusive, spatial distribution</td>
<td>cumulative anode &amp; cathode reading limited accuracy, expensive</td>
</tr>
<tr>
<td>MRI</td>
<td>[13, 84, 7, 67]</td>
<td>membrane water distribution</td>
<td>not carbon compatible, expensive</td>
</tr>
<tr>
<td>Laser Spectroscopy</td>
<td>[51, 6, 48]</td>
<td>spatial distribution</td>
<td>can’t measure liquid water</td>
</tr>
<tr>
<td>Gas Chromatography</td>
<td>[37, 39, 80]</td>
<td>spatial species distribution</td>
<td>can’t measure liquid water</td>
</tr>
<tr>
<td>Condensation</td>
<td>[79, 58]</td>
<td>total water balance</td>
<td>small temporal resolution</td>
</tr>
<tr>
<td>Humidity sensor</td>
<td>[42, 8]</td>
<td>accurate, cheap</td>
<td>can’t measure liquid water</td>
</tr>
</tbody>
</table>
Figure 4.18: Schematic of the sensory vessel for measurement of water content of the PEM fuel cell output. The pressure sensor, P, measures the total pressure in the vessel, $P_v$. The humidity sensor, RH, measures the temperature and dew point temperature inside the vessel, $T_v$ and $T_{dp}$, respectively. The vessel is heated to evaporate the liquid water, and tubing is heated to avoid water vapor condensation. The vessel input flow stream contains air, $\dot{n}_{v,in}$, water vapor, $\dot{n}_{w,vap}$, and liquid water, $\dot{n}_{w,liq}$. The vessel output stream also contains air, $\dot{n}_{v,out}$, and water vapor equal to the total amount of water entered the vessel, $\dot{n}_{w,total}$. 
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If we take the vessel as the control volume, the liquid water entering the vessel in moles, $n_{w,liq}$, between two fully liquid water depleted vessel time, $t_1$ and $t_2$, can be calculated from the total water vapor leaving the vessel, $\dot{n}_{w,total}$, and the water vapor entering the vessel, $\dot{n}_{w,vap}$, using the following relationship:

$$n_{w,liq} = \int_{t_1}^{t_2} (\dot{n}_{w,total} - \dot{n}_{w,vap}) dt \text{ (moles)} \quad (4.25)$$

In equation (4.25), the molar flow rate of water vapor at the vessel input, $\dot{n}_{w,vap}$, is equal to the molar flow rate of water vapor at the cathode output, $\dot{n}_{w,out}$, when there is no liquid water in the cathode output. When this condition is satisfied, $\dot{n}_{c,out}$ can be calculated from the cathode output dew point temperature, pressure, and air flow rate using equation (4.20).

In equation (4.25), the molar flow rate of water vapor exiting the vessel, $\dot{n}_{w,total}$, can be calculated from the vessel output pressure, flow rate, and dew point temperature, similar to that calculated for the cathode output water vapor flow rate in equation (4.20), using the following relationship (see Appendix B for derivation):

$$\dot{n}_{w,total} = \frac{P_{w,total}}{P_{v,out}} \dot{n}_{v,out} \text{ (mol/s)} \quad (4.26)$$

In equation (4.26), the vessel output pressure, $P_{v,out}$, is directly measured using pressure sensor. At steady state conditions, the molar flow rate of air existing the vessel, $\dot{n}_{v,out}$, is equal to the molar flow rate of air entering the vessel, $\dot{n}_{v,in}$, and equal to the molar flow rate of air exiting the fuel cell cathode, $\dot{n}_{c,out}$, which can be calculated from the cathode input flow rate and cell current using equation (4.21). Finally, the water vapor partial pressure at the vessel output, $P_{w,total}$, is calculated from the vessel dew point temperature using equation (4.19), assuming steady state and uniform water vapor partial pressure in the vessel. By substituting these values in equation (4.26), the molar flow rate of water vapor at the vessel output, $\dot{n}_{w,total}$, can be calculated. Substituting this into equation (4.25) results in the amount of liquid water entering the vessel between fully depleted vessel times $t_1$ and $t_2$.

To demonstrate the capability of this system, we measured liquid water transport in the PEM fuel cell cathode during membrane humidification. We set the fuel cell
operating parameters at a temperature of 80°C, anode and cathode pressure at 20 psi, dew point temperature of 40°C, and input temperatures of 50°C (Table 4.2.4). We operated a not fully humidified membrane at a current density of 100 mA/cm², with anode and cathode stoichiometries of 1.5 and 1.8, respectively. We have shown the resulting fuel cell voltage in Figure 4.19.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{cell}$ (°C)</td>
<td>80</td>
</tr>
<tr>
<td>$T_a$ (°C)</td>
<td>50</td>
</tr>
<tr>
<td>$T_c$ (°C)</td>
<td>50</td>
</tr>
<tr>
<td>$T_{dp,a}$ (°C)</td>
<td>40</td>
</tr>
<tr>
<td>$T_{dp,c}$ (°C)</td>
<td>40</td>
</tr>
<tr>
<td>$P_a$ (psi)</td>
<td>20</td>
</tr>
<tr>
<td>$P_c$ (psi)</td>
<td>20</td>
</tr>
<tr>
<td>$\lambda_a$</td>
<td>1.5</td>
</tr>
<tr>
<td>$\lambda_c$</td>
<td>1.8</td>
</tr>
</tbody>
</table>

We can see in Figure 4.19 that for our system, even a small load on a not fully humidified membrane results in zero fuel cell voltage. As water is produced on the cathode side, it humidifies the membrane and the cell voltage increases to a steady state voltage of about 0.8 volts. To study the dynamics of liquid water during this process, we placed the sensory vessel of Figure 4.18 at the output of the fuel cell cathode. We heated the vessel to 90°C, in order to evaporate the liquid water that exits the fuel cell and accumulates in the vessel into the stream. In Figure 4.20.a, we have graphed the vessel humidity sensor temperature and dew point measurements, $T_v$ and $T_{dp}$, from 500 seconds after imposing load on the fuel cell. We have also marked the right axis of Figure 4.20.a with the molar flow rate of water vapor exiting the vessel, $\dot{n}_{w,total}$, calculated from the air flow rate, pressure, and vessel dew point temperature using equation (4.26). In Figure 4.20.b, we have graphed the fuel cell voltage for the same period. Note that the fuel cell voltage oscillations observed in Figure 4.20.b is not seen in Figure 4.19 due to the large voltage scale. Focusing on
the steady state region which occurs from 500 seconds onwards allows studying the small amplitude voltage oscillations as discussed below.

We can see in Figure 4.20.a that there are two steady state levels for the dew point temperature, one around 70°C and the other around 85°C. The lower steady state corresponds to a depleted vessel from liquid water, representing the saturation level of the air stream exiting the cathode. The higher steady state corresponds to liquid water present in the vessel, resulting in a higher vessel dew point temperature.

Points A, B, C, and D in Figure 4.20.a correspond to the time at which liquid water is depleted from the cathode into the vessel, causing a jump in the vessel dew point temperature. In Figure 4.20.b, points A, B, and C correspond with the peak of cell voltage oscillations, while point D corresponds with a spike in the cell voltage. This suggest that the source of liquid water leaving the fuel cell cathode at points A,
Figure 4.20: Dew point temperature and stream temperature of the cathode stream in the humidity sensing vessel (top), and cell voltage (bottom) versus time. The point A, B, C, and D on the top and bottom graphs correspond to the same moment in time. The difference in time observed is due to the accuracy of the different data acquisition systems used to measure the data on the top and bottom graphs. The horizontally and vertically hashed lines correspond to two convective water transport mechanisms by the cathode stream. The output water flow rate on the top graph is calculated from the vessel dew point temperature reading.
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B, and C, is similar, and different from that of point D.

We can see in Figure 4.20.b that the cell voltage has a decaying periodic oscillation with a characteristic period about 1070 seconds (BC). The slow dynamics of the cell voltage oscillations suggest that it corresponds to changes in membrane humidification conditions. The decreasing amplitude of the low frequency voltage oscillations could also result from a better humidified membrane, being less affected by the liquid water leaving the cathode.

Depletion of liquid water from the cathode means that the rate of water production in the cathode is higher than evaporation, which results in a fully saturated cathode stream. Therefore, the presence of liquid water in the cathode should not affect the partial pressure of water vapor in the cathode. The fact that liquid water leaving the cathode at points A, B, and C deteriorates membrane humidification conditions suggest that the liquid water is in direct contact with the membrane in the cathode, i.e., at the catalyst/GDL. This hypothesis is in line with the observation of authors in [51, 6].

The amount of liquid water depleted in the cathode between two depleted vessel instances, e.g., B and C in Figure 4.20.a, can be calculated from equation (4.25), with points B and C representing times $t_1$ and $t_2$, respectively. We have shown this amount of liquid water in Figure 4.20.a by the horizontally hashed area. If we calculate the area of this region using the left vertical axis (molar flow rate of water vapor exiting the cathode) and the horizontal axis (time), it results in a total amount of liquid water about $10^{-2}$ moles, or equivalently 0.18 cm$^3$. Assuming that all this water is in the GDL, with a cell area of 49 cm$^2$ and GDL porosity of 50%, this volume would fill an average depth of 73 microns. This is comparable with the GDL thickness around 170 microns. Therefore, it is feasible for the periodic liquid water that affects the membrane humidification conditions to originate from the GDL. We can also see in Figure 4.20.a that the amount of liquid water depleted from the cathode at points A, B, and C are almost equal. This suggest that when the liquid water at the membrane/GDL interface reaches a critical mass, the convective forces dominate the forces attaching the water droplets to the GDL, resulting in their detachment.

The net rate of water production in the fuel cell cathode at 100 mA/cm$^2$ is
2.54 × 10^{-5} \text{ (mol/s)}. The net rate of water evaporation in the cathode can also be calculated from the cathode input and output dew point temperatures and flow rates using equation (4.22) to be 1.62 × 10^{-5} \text{ (mol/s)}. This results in an average liquid water accumulation in the cathode of about 0.92 × 10^{-5} \text{ (mol/s)}. The periodic liquid water that is released from the cathode has an average value about 0.95 × 10^{-5} \text{ (mol/s)}, well in agreement with the calculated amount.

We can also see in Figure 4.20.b that at point D, liquid water removal out of the cathode result in a transient spike in the cell voltage. This suggests that the liquid water released at point D originates from the flow field and manifolds, creating a suction that temporarily opens that GDL pores from liquid water, allowing more oxygen to reach the reaction sites and therefore a spike in cell voltage. This is in line with the observation of authors in [35], that showed a sudden voltage jump could result from depletion of water from the cathode flow field. Note that the total amount of liquid water that is released at point D is shown in Figure 4.20.a by the vertically hashed area, and is about 10^{-2} moles, or equivalently 0.18 cm^3, which is well within the range of the cathode and manifold volume of about 6 cm^3.

4.3 Conclusions

In this chapter, we presented a diagnostics algorithm capable of isolating cathode flooding, cathode starvation, and anode starvation in real time. We examined the robustness of the algorithm to changes in current, temperature, pressure, and humidity operating conditions. Cathode flooding was robust to changes in all operating conditions examined, while cathode starvation required correction terms for cell temperature and pressure variations.

We also introduced a sensory system that can used as a diagnostic tool to study two phase water transport in PEM fuel cells. We used the sensory system to measure water vapor and liquid as it exits the PEM fuel cell cathode. From these measurements, we identified two distinguish modes of liquid water transport in the PEM fuel cathode: one originating from the cathode catalyst/GDL, and the other from the cathode flow field.
Chapter 5

Conclusions

Diagnostic tools are used at different stages of product life cycle to improve their performance and reliability. In this work, we introduced two diagnostic tools, i.e., the ratio between the voltage-pressure oscillations, and a sensory vessel, that can be used as a diagnostic tool to provide fundamental understanding of processes in PEM fuel cells.

We used the pressure-voltage oscillation diagnostic measure and designed a diagnostic algorithm that can detect and isolate low flow rates in the anode and cathode of PEM fuel cells in real time using available sensory information. This diagnostic algorithm can be used to detect low flow induced faults in an operational fuel cell.

Pressure-Voltage Oscillations

We showed that the frequency of the cell voltage oscillations is equal to that of the cathode output pressure. We proposed using the amplitude and phase of the pressure and voltage oscillations as a diagnostic tool for detecting operating conditions in the fuel cell, similar to that used for impedance measurement with current and voltage. We also showed that the voltage-pressure oscillations amplitude depends on the cathode stoichiometry, while the phase is constant at 180°.
Fault Measures

We showed that at each cell current density, there exist a cathode stoichiometry beyond which the cell voltage would not increase. We defined this stoichiometry as the operating stoichiometry, and used it to obtain a reference polarization curve. We showed that calculating the cathode flow rate using the operating stoichiometry instead of a fixed stoichiometry, results in higher efficiency at low current densities, and higher performance at high currents. We defined a fault in the fuel cell as a drop in the cell average voltage from the reference polarization curve.

We showed that for our system, when the cathode flow rate is reduced from a high to low value at a fixed current density, the cell voltage oscillations grow in amplitude, resulting in a lower cell average voltage. We called this mode of system operation flooding, and proposed using the cell voltage variance as a measure for detecting it. We showed that a fixed voltage variance set point can be used to detect the onset of this region, independent of the cell current density.

We showed that if the cathode flow rate is reduced further than the flooding region (high voltage oscillations), the cell voltage drops to zero. We called this cathode starvation, and showed that for our system, the cathode stoichiometry at which this occurs depends on the cell current density. We showed that with an increase in the cell current, this stoichiometry increased in value, with higher growth at higher current densities. We proposed measuring and storing these stoichiometries over the dynamic range of cell current a priori, in order to detect cathode starvation in real time.

We showed that on the anode side, the cell voltage does not change for a large dynamic range of anode stoichiometries. In our system, if the anode stoichiometry dropped below a fixed low value of about 1.2, independent of the cell current density, the cell voltage dropped to zero. We defined this regime as anode starvation, and proposed using the anode stoichiometry and a fixed a priori calibrated set point to detect it.
Residual Generation & Evaluation

We designed our diagnostic algorithm to detect a fault and isolate cathode flooding, cathode starvation, anode starvation warning, and anode starvation. We defined the voltage residual as the difference between the reference average voltage and the cell voltage. We obtained the reference voltage ay each current density in real time by curve fitting the reference polarization curve. We defined a fault in the system when the average voltage residual over a window of 15 seconds dropped over 3% below the reference voltage.

We defined the voltage variance residual as the difference between a reference value and the voltage variance calculated over a fixed window in real time. We examined various window sizes for the variance, and showed that a window size of 60 seconds balanced smoothness and sensitivity. For the reference voltage variance, we showed that a fixed value of $10^{-6}$ corresponded to the beginning of the flooding region independent of the current density. In order to isolate flooding from other possible sources of fault, we added fault and anode stoichiometry residual as conditions to declare cathode flooding. The fault signal would prevented false alarms resulting from an increased cell voltage variance caused by changes in fuel cell current, and hence changes in cell average voltage. The anode stoichiometry residual also prevents false alarms that could result from an increased voltage variance caused by cell voltage drop during anode starvation.

We defined the cathode starvation residual as the difference between a reference value and the cathode stoichiometry in real time. We calculated the real time cathode stoichiometry from the measured cell current and cathode flow rate. We defined the cathode starvation reference stoichiometry as the stoichiometry at each each current density which resulted the cell voltage to drop to zero volts. We fitted a second order polynomial to obtain the cathode starvation reference stoichiometry at each current density in real time. To prevent the fuel cell from cathode starvation, we declared cathode cathode starvation when the cathode starvation residual reached within 0.2 of the cathode starvation reference stoichiometry. To prevent false cathode starvation alarms caused by spikes in the cell current, we added the presence of a fault as a
CHAPTER 5. CONCLUSIONS

condition for cathode starvation.

We defined the anode stoichiometry residual as the difference between the actual anode stoichiometry, calculated from the measured cell current and anode flow rate, and a fixed reference anode stoichiometry of 1.2, i.e., the anode stoichiometry below which the cell voltage dropped to zero. We showed that for the operating conditions examined, there existed a delay between the time that the anode stoichiometry dropped below the reference value and the time that the cell voltage dropped to zero, associated with the additional reactant available in the anode flow field and manifold. The algorithm signaled anode starvation warning, when the anode stoichiometry dropped below the anode reference stoichiometry. However, if the fault was also present in the system, the algorithm signaled anode starvation.

Robustness

We examined the robustness of the cathode flooding and starvation signals explained above to variations in current, pressure, temperature, and humidity conditions. We changed the cell current density from OCV with steps of 70 mA/cm$^2$ and calculated the fault signals. We showed that cathode flooding was set when the cell voltage oscillations grew in amplitude, and the cathode starvation was set before the cell voltage reach zero volts. Therefore, we concluded that the algorithm is robust to changes in cell current.

We changed the anode and cathode pressure around a 30 psi operating point by ±15 psi. At each point, we varied the cathode stoichiometry from a high to low value, until the cell voltage hit zero volts. We showed that for our system, pressure changes cause the cell average voltage to shift by an almost constant value over the entire range of stoichiometries examined. In order to adapt the reference voltage to this voltage shift, we proposed using the voltage correction term, $\Delta V = \frac{R T}{\alpha F} \ln \left( \frac{P_2}{P_1} \right)$, and showed that it is in agreement with our measured data. We showed that the cathode flooding signal became robust to changes in cell pressure using this correction term. Also, cathode starvation was not affected by pressure variations. Therefore, with the correction term introduced, the algorithm became robust to changes in cell pressure...
for the operating conditions examined.

To examine the robustness of the algorithm to temperature variations, we changed the cell temperature around a 80°C operating point by ±10°C. At each cell temperature, we varied the cathode stoichiometry from a high to low value, until the cell voltage hit zero volts. Data showed that the cell average voltage shift with temperature variations. We argued that since temperature variations effect dynamical response of all transport mechanisms, it was not practical to accurately model temperature effects. We proposed measuring the reference polarization curve at different cell temperatures \textit{a priori} of operation, and use that as the correction factor to make the algorithm robust to variations in cell temperature.

We finally examined the effect of changes in the cathode input dew point temperature from a 70°C operating point by ±20°C. At each cathode dew point, we varied the cathode stoichiometry from a high to low value, until the cell voltage reached zero volts. At all stoichiometries examined, data revealed little difference in cell voltage for the three cases, resulting in robust cathode flooding and starvation signals.

The above observation that humidity conditions had little effect on the cell voltage is not intuitive, as one expects humidity conditions to affect the water carrying capacity of the cathode and therefore flooding conditions. We hypothesized that convective transport of liquid water was the dominant process for transporting water out of the cathode, rather than water evaporation into the cathode stream. Assuming steady state conditions, we calculated the two phase flow components, and showed that in fact liquid water flow rate out of the cathode was higher than the water vapor component at all operating conditions examined.

**Liquid Water Transport**

To better understand liquid water transport in the cathode, we introduced a sensory vessel capable of measuring water vapor and liquid separately. Using this vessel, we detected two different modes of liquid water retention from the fuel cell cathode. The first mode was periodic, and correspond with a periodic oscillation in the fuel cell voltage of about 0.001 Hz. We associated the slow dynamics of cell voltage oscillations
to changes in the humidity conditions of the MEA. Therefore, we concluded that the liquid water source was in the GDL and catalyst pores. The second mode of liquid water removal from the cathode corresponded with a spike in the cell voltage. We associated this with water removal from the flow field.

**Future Work**

The diagnostic tools introduced in this work can be used in future works to provide fundamental understanding of processes in PEM fuel cells:

A systematic approach need to be developed in order to understand the results obtained by the pressure-voltage oscillations diagnostic tool. We can see in Figure 3.4.c that while the amplitude of the cathode output pressure oscillation is about 0.6%, the cell voltage oscillation amplitude is over 50%. This result can not be explained by the Butler-Volmer equation, and other effects should be responsible for that. We postulated that the pressure oscillations impose a similar oscillation on the liquid water in the catalyst/GDL pores, which effects catalyst utilization. This hypothesis needs to be substantiated.

The sensory vessel introduced in this work can be used to understand liquid water transport at various operating conditions in PEM fuel cells. However, the design of this sensor needs to be modified before it can measure water produced at higher current densities. The water carrying capacity of the current sensor is limited by the maximum temperature that it can be heated, which is about 100°C, as imposed by the solid state humidity sensor. However, if an additional stream of dry reactant is circulated in the vessel, it would increase the flow rate exiting the vessel, and hence would increase its water carrying capacity. Using a pair of these sensors at the anode and cathode output would allow quantitative study of two phase water flow in PEM fuel cells.

Finally, the diagnostic algorithm introduced in this work can be expanded to include more faults. Faults such as dehydration and CO poisoning can be reproduced, and measures can be defined to isolate them from the low flow induced faults studied in this work.
Appendix A

PEM Fuel Cell Flow Dynamics

A.1 Cathode Flow Dynamics

Losses occurring in the PEM fuel cell cathode are more significant compared to those on the anode side [31]. This is because reaction rates are in the order of $10^{-5}$ times lower on the cathode side compared to that on the anode side. In addition, in practical applications, air is usually used instead of pure oxygen, further affecting reaction rates in the cathode. Furthermore, the water produced on the cathode side needs to be removed, causing mass transport limitation especially at high current densities. As a result, many approaches have been used in the literature to study cathode dynamics in PEM fuel cells. Below, we present a review of these methods, their strengths and weaknesses, and highlight the results obtained. This review is aimed to provide better understanding of fundamental processes in PEM fuel cells, which is key to designing more efficient and reliable control and diagnostic systems.

Authors in [76], [82], [18], [71], [62], [35], and [45] used a PEM fuel cell with a transparent cathode to study water accumulation in the cathode. They all reported liquid water accumulation at low cathode flow rates, with improved water removal at higher flow rates.

In [76], Weng et al. operated a 100 cm$^2$ PEM fuel cell with a transparent cathode at three current densities of 300, 500, and 700 mA/cm$^2$, and various oxygen stoichiometries. They showed that the cell power became unstable when the cathode
stoichiometries dropped below 20, 4, and 4, for the three examined current densities, respectively. They observed enhanced water removal in the cathode at higher stoichiometries. They argued that higher velocity of oxygen at higher stoichiometries enhance liquid water removal capabilities of the oxygen stream. They associated the high oxygen stoichiometry requirement at low current densities to low oxygen velocity at low current densities. At the medium and high current densities, they argued that higher velocities resulted in lower oxygen stoichiometry requirements.

Zhang et al. [82] operated a 14 cm$^2$ PEM fuel cell with a transparent cathode at a current density of 800 mA/cm$^2$ and observed the modes of water distribution and transport in the cathode flow field and GDL. At an anode and cathode stoichiometry of 2, they observed liquid droplets on the GDL surface, with annular liquid water flow at the corners of the flow field. With an increase in the amount of liquid water, they observed that the corner flow grows to a water film on the channel surface, until it reaches a critical thickness that triggers an unstable regime. At this point, the flow regime transitions to a slug flow, clogging the gas flow channel. This corresponded with high amplitude oscillations in the cell pressure drop and voltage. They increased the stoichiometries to 10, and observed no water droplets in the GDL. They suggested that water droplets were removed by the shear force of gas flow from the GDL surface, following by a mist flow of tiny water droplets traveling in the gas stream at a speed near to that of the gas. They also obtained the polarization curve at the two stoichiometries examined, and observed an improvement in the mass transport limiting current density at the higher stoichiometry.

To better understand water transport mechanisms, Zhang et al. [82] also observed the GDL and catalyst Micro Porous Layer (MPL) using Environmental Scanning Electron Microscopy (ESEM). They showed that liquid water beads up on the GDL carbon fibres with a diameter between 10 to 20 µm. With a more hydrophobic MPL surface, they reported droplets as small as 2 µm. They concluded that water produced at the catalyst layer is transported to the GDL by capillary forces, and emerges to the GDL surface due its hydrophobicity.

In [18], Hakenjos et al. operated a PEM fuel cell with a 49 segment anode, along
with infrared thermography and digital photography on the cathode to achieve simultaneous data on current, temperature, and water distribution in the fuel cell simultaneously. They operated the fuel cell at three current densities of 190, 235, and 275 mA/cm$^2$, with stoichiometry of 4, 6.4, and 8.2, respectively. At low current, the segment cell was active mainly at the beginning of the flow field channel channel. Water was accumulated at the middle of the cell, corresponding with higher temperatures. At the mid current, the segment cell area become more active, with less water accumulation and high temperatures in the middle section. At the high current density, the cell area was highly active, with no water and no hot regions observed. They explained the correlation between water and high temperature by the enthalpy of water condensation. They also observed rise in cell voltage with increased flow rate. They associated the improvement to higher water drag out of the cell.

In [45], Ous and Arcoumanis operated a 25 cm$^2$ PEM fuel cell at ambient temperature, and photographed liquid water formation at the bend and central locations of the cathode flow field channel, with changes in cathode relative humidity, air flow rate, and load. With a load of 1.3 Ω (current density of 8.8 mA/cm$^2$), dry cathode (RH of 20%), and flow rate of 12.1 mL/min (stoichiometry of 3.1), they observed no water droplet formation at the channel bends. They associated this with higher air velocity at these locations. In the central location, they observed two types of droplets: those who contacted the flow field wall (land touching,) and those who solely appeared on the GDL surface and did not contact the channel walls (non-land touching). With the above operating conditions, they observed the first droplet on the GDL surface after 25 minutes (non-land touching). They attributes this delay to the time required for water to permeate through the gas diffusion layer and appear on the GDL surface. They reported the size of a non-land touching droplet between 0.1 to 0.6 mm in diameter, with an instantaneous increase in size, however, they also reported that the land touching droplets increased in size gradually and faster than the non touching ones.

Above authors also examined the time at which the first droplet appeared with humidified air (RH of 80%), load of 1.3 Ω (current density about 8 mA/cm$^2$), and different cathode flow rates. They observed that the droplet appearing time increased
with an increase in the air flow rate, until it reached 219 mL/min (stoichiometry of 62). At this point, no droplet formation was observed. They concluded that at high flow rates, humidity did not have a significant contribution on droplet formation and that high flow rates were capable of preventing the cell to flood. They also operated the cathode at a fixed flow rate of 24 mL/min, while changing the load from 0.6 to 10 Ω. They observed that with the larger load, the first droplet appeared on the surface in about 43 minutes later than the smaller load. They argued that a smaller load resulted in a higher current and therefore higher rate of water production, resulting in the first water droplets to appear on the surface earlier. They also investigated the effect of air velocity on droplet detachment for different droplet sizes, and concluded that the air velocity required to detach a droplet from the surface is inversely proportional to the droplet size.

In [62], Spernjak et al. investigated the effect of GDL materials on cathode water removal using a 10cm$^2$ transparent cell. They observed lower water content in the flow field channel with untreated GDL. They attributed this to the inability of the GDL to push water out, resulting in its pores saturated with liquid water, therefore reducing its gas transport performance. With hydrophobic GDLs, water droplets were expelled into the flow field, leaving the pores open for gas transport. They also showed that adding a MPL (Micro Porous Layer) to the hydrophobic GDL increased the pressure barrier, resulting in a well humidified membrane. When the current density was exceeded above 500 mA/cm$^2$, the observed liquid water at the exit of the anode flow field. They attributed this to the pressure barrier of the MPL, pushing the water produced in the cathode to the anode side.

Liu et al. [35] studied water transport in parallel, interdigitated, and cascade flow fields of a 5cm$^2$ PEM fuel cell using a transparent cathode. They observed that liquid water accumulation in the flow channels reduces the cell performance. They reported that interdigitated and cascade channels had a better water removal and performance, compared to parallel ones. They attributed this to enhance mass transfer in the interdigitated and cascade flow field channels. They also observed less condensation of liquid water in the flow field at high temperatures, compared to lower temperatures. At low temperatures, the observed a lot of liquid water in the flow field
APPENDIX A. PEM FUEL CELL FLOW DYNAMICS

channels, hindering mass transfer. They also reported enhanced water removal from the flow field at higher flow rates, however, with too high flow rates (stoichiometry of about 42.9 for oxygen), the fuel cell performance decreased dramatically. They attributed this to membrane drying, reducing its proton conductivity and hence cell performance.

In [71], Tüber et al. operated a 4cm² transparent PEM fuel cell with humidity sensors at the anode and cathode input and output streams. They used mathematic modeling, and calculated a stoichiometry requirement of 29 to keep the cathode output fully saturated. To verify this, they fixed the cell voltage at 0.5 V, and changed the cathode flow rate to 150, 225, and 450 mL/min, resulting in a current of 193, 200, and 178 mA/cm² (stoichiometries of 12, 17, and 38, respectively). At the two lower flow rates, they observed water accumulation in the cathode flow field with saturated cathode outlet stream, resulting in two phase flow. However, at the high flow rate, which resulted in a stoichiometry above 29, they observed no water accumulation in the flow field and the cathode output was not saturated with water, resulting in a single phase flow.

Authors in [72], [21], [27], [83], [60], [70], and [47] used neutron imaging techniques to study spatial water accumulation and distribution in the cathode. For this purpose, a neutron source and detector are placed on both sides of the fuel cell. The neutron intensity as measured by the detector changes proportional to the amount of water present along its path way. When the source and detector are placed opposite the the anode and cathode flow fields, the readings would be proportional to the water present under the flow field and its landings. If they are placed along the MEA plane, the water gradient across the cell is measured. Compared to optical methods, neutron imaging can be calibrated to measure the total amount of water in the cell, however, lack of reliable reference data imposes a limit on the accuracy of this method.

In [72], Turhan et al. used neutron imaging to measure the mass of water in a 14.5 cm² PEM fuel cell at a current density of 350 mA/cm² and cell temperature of 80°C. They operated the cell with two anode/cathode stoichiometries of 2/2 and 5/5, and showed that the total amount of liquid water in the cell is reduced with higher stoichiometries. They also masked the flow field and landings in different experiments,
and showed that the amount of water under the landings (in the GDL), was greater than the amount of water in the flow field for both stoichiometries examined. With an increase in the stoichiometry, they observed reduction in both locations, however, the water in the flow field reduced as much as three times more than the water under landings. They concluded that water accumulates easily under the landings, and is difficult to remove using parallel flow fields.

Above authors also examined the effect of anode and cathode pressure changes on the water accumulation in the cell. They measured the total amount of water in the cell with an anode and cathode equal pressures of 1, 1.5, and 2 MPa, and anode and cathode dew point temperatures of 90 and 80°C, and equal stoichiometries of 1.5. They observed higher water accumulation at lower cell pressures. They calculated the partial pressure of water using the ideal gas law, and showed that at the over-humidified conditions examined, decreasing the cell pressure favors water accumulation due to higher partial pressure of water in the input stream.

Turhan et al. also operated the cell with three anode and cathode dew point temperatures of 50, 60, and 70°C, and at each humidification level, examined three stoichiometries of 1.5, 2, and 3. They observed that with different humidification levels, changes in the the total amount of liquid water in the cell at steady state was so small that they were unable to identify a trend, however, the cell voltage showed significant performance loss with decreasing humidity. In addition, they observed higher performance loss at higher stoichiometries with decreasing humidification. They calculated the total amount of water uptake by the membrane and showed that it was equivalent to a 8 µm liquid water thickness, however, the minimum amount of liquid water thickness detectable by their neutron imaging setup was 12.7 µm. Therefore, they concluded that while higher flow rates and lower humidification results in membrane drying and a drop in cell performance, the total amount of liquid water in the cell seemed unchanged, due to the fact that variations in the membrane humidification levels were not detectable by their setup.

In [21], Hussey et al. used neutron imaging to distinguish between the water at the anode, cathode, and membrane of a 10 cm² PEM fuel cell. They operated the cell at current densities of 20, 50, 100, and 200 mA/cm², with air stoichiometries of 440,
191, 98, and 49, respectively. The used low current and high stoichiometry in order to avoid water accumulation in the channels. They reported that membrane swelling caused influenced the calibration of their data set, neutron imaging still showed higher water thickness on the cathode side at higher current densities.

Kowal et al. [27], used a 12.5 cm$^2$ PEM fuel cell with neutron imaging and compared the performance of carbon cloth and carbon paper as GDL. They obtained polarization curves with a fixed anode/cathode flow rate of 436/1040 sccm. They showed that at this flow rate, when carbon paper was used, the fuel cell flooded and the cell voltage dropped significantly at a current density above 500 mA/cm$^2$. However, the carbon cloth continued to perform until a current density of 1700 mA/cm$^2$. They compared neutron imaging results for the two GDLs, and showed that on a normalized volumetric basis, the carbon paper accumulated 174% more water under landing compared to the carbon cloth, therefore flooding the cell more easily. They also performed transient experiments, and showed that the time for accumulation of significant amounts of liquid water was in the order of tens of seconds to minutes.

In [83], Zhang et al. operated a 100 cm$^2$ PEM fuel cell with neutron imaging, and compared water accumulation in graphite and gold coated aluminum flow fields at a current density of 400 mA/cm$^2$, with anode and cathode stoichiometries of 1.5, and a cathode relative humidity of 50%. Neutron radiography of the gold coated aluminum flow field revealed liquid water clusters that stretched over the width of the flow field channel, however, the graphite plates inhibited smaller droplets. They explained this by the hydrophilic gold coated surfaces attracting water droplets upon contact, forming a layer of liquid water at the flow field wall, therefore reducing the liquid water contact cross section with the cathode flow. However, in the case of graphite plates, they argued that liquid clusters grow inside the graphite plates, and removed by the pressure drop and/or flow speed.

Above authors also obtained the polarization curve with an increasing and decreasing current, at a relative humidity of 80% and stoichiometry of 1.5 and 2.5 for hydrogen and air, respectively. They observed hysteresis in the water accumulation level: the water level increased with an increase in current density to a maximum level, but not returned to initial values when current was reduced. They explained
this by the dependence of the rate of droplet removal on its size. When large water clusters are shaped at high current densities due to high rate of water production, reducing the flow rate would not bring it back to original levels. They also observed hysteresis in the cell voltage, with a slightly higher voltage on the return path, i.e., the water accumulated in the flow field did not hinder cell performance. They attributed the enhanced cell performance to the reduced ohmic resistance of the membrane due to better humidification conditions. They also presented two alternative explanations for the additional water not being detrimental to cell performance: first that the clogged channels could result in the gas to flow convectively through the GDL; increasing oxygen concentration at reaction sites. Alternatively, they argued that the observed liquid water could be on the flow field walls, freeing the GDL surface from liquid, therefore not effecting the path for oxygen reaching reaction sites.

Schneider et al. [60] used neutron radiography along with impedance measurement on a nine segment 29.2 cm² PEM fuel cell, and studied cell local performance and limiting precesses. For this purpose, they operated the cell at current density of 500 mA/cm² with humidified hydrogen at a relative humidity of 40% and dry oxygen in co-flow mode, both at a stoichiometry of 1.5. They observed that the segment current densities increased along the flow field channel from a minimum at segment one, to a maximum at segment 7, with lower current densities at segments 8 and 9. Neutron imaging also revealed high water accumulation along the channel end, hence, they attributed the drop in current density of segments 8 and 9 to flooding. In addition, impedance measurements along the flow field channel showed a decrease in the high frequency component from segments 1 to 7. They corresponded this to better membrane humidification along the channel due to the produced water in the cathode. However, they observed no changes in the high frequency component of the impedance spectrum for segments 8 and 9, with an increase in the magnitude of the low frequency component. They attributed the constant high frequency component to the saturation conditions in the last three segments, and the increase in the low frequency component to flooding conditions in segments 8 and 9.

In [70], Trabold et al. used a 50 cm² cell with neutron radiography to investigate water transport in PEM fuel cells. They operated the cell at three current densities of
100, 500, and 1000 mA/cm², with fully humidified hydrogen and air at a stoichiometry of 2 and 1.3, respectively. They observed that the overall quantity of water retained in the flow fields was reduced with an increase in current density. They associated this to the higher gas velocity at higher current densities, resulting from a fixed stoichiometry, which removes the additional water produced in the cell. In addition, unlike the work of authors in [45] that reported no water accumulation at the channel bends, they reported water accumulation at the bends at all conditions. They associated this to the decreasing channel to channel pressure gradient as the flow approaches the bend, therefore reducing the liquid water driving force through the GDL or along the flow field channel.

Above authors also operated the cell at a high current density of 1000 mA/cm², and examined three cathode stoichiometries of 1.3, 1.4, and 2, while keeping the anode stoichiometry fixed at 2. They observed a large voltage gain (around 35 mV) over the range of increased cathode stoichiometries, with small changes in the amount of water this is accumulated in the cell. They concluded that if there was a beneficial effect of water removal with higher stoichiometries, it should have been in the GDL under the flow field landings, which was masked and hence not measured in the course of the experiment.

Pekula et al. [47] used neutron imaging to calculate the speed of water droplets in a 50 cm² PEM fuel cell at 1 A/cm², and compared it with that of the anode and cathode flow velocity. They showed that the droplet velocity was an order of magnitude slower than the gas, and concluded that no-slip boundary conditions for water-gas interface was not appropriate when modeling two-phase flow. They also showed that water tends to accumulate more at the channel bends and flow field walls, and associated this with a decrease in gas velocity at these locations.

Authors in [6], [79], [37], and [8] measured the anode and cathode water balance (input and output), in order to understand water transport in the cell. In [6], Basu et al. measured the water vapor partial pressure along two gas channels on the input and output of a PEM fuel cell cathode, using laser absorption spectroscopy. They operated the cell at two cathode relative humidities of 22.6 and 40%, at a cell temperature of 65 and 80°C, respectively. They showed that the cell output water vapor partial
pressures was higher than the input, with both input and output partial pressures increasing linearly with current density. They also calculated the water produced from the electrochemical reaction, assuming that it was produced homogeneously along the channel, and showed that it fully accounted for the measured water partial pressure difference in the cathode input and output. Therefore, they concluded that water transport by electro-osmotic drag was not significant at the operating conditions examined. Note that they did not account for the effect of water back diffusion from the cathode to the anode in their water balance calculations.

In [37], Lu et al. used a 10 segment, 6 cm² PEM fuel cell with gas chromatography for each segment, in order to measure current and species distribution simultaneously along the flow field channel. They connected the 10 segments to a 10 channel potentiostat and operated each segment at 0.5 V, with hydrogen and air at flow rates equivalent to a stoichiometries of 2 at 1 A/cm², pressure of 2 atm, dew point temperature of 60°C, and cell temperature of 80°C. They measured the segment current densities along the channel, and showed that it was reduced from the input to the output, until two third of the cathode flow field, from which point it increased. They measured oxygen concentration along the channel using gas chromatography, which proved reduction in cathode oxygen concentration from the input to the output. Therefore, they attributed the reduction in current density at the beginning of the cell to the reduced oxygen concentration along the channel. They also measured water concentration in the cathode and anode using the same technique, and used that to calculate the net water transport through the membrane along the flow field channel. They showed that the net water transport was from the anode to the cathode until the middle of the cell, from which point it reversed from the cathode to the anode. They explained this by the difference between the electro-osmotic water drag from the anode to the cathode, and water back diffusion from the cathode to the anode. They hypothesized that while the electro-osmotic drag was a function of current density and hence relatively constant along the flow field, the back diffusion was a function of water concentration difference on both sides of the membrane. Therefore, the increase in water concentration on the cathode side along the flow field channel, resulting from the water production on the cathode side, increase the back diffusion of water from the
cathode to the anode; changing the net rate of water transport across the membrane. They associated this net water transport from the cathode to the anode towards the end of the flow field to better membrane humidification, justifying the higher current densities observed towards the cell end.

Yan et al. [79] used a U-shaped drying tube with Dryerite in order to condense and trap the water leaving the anode and cathode of a 25 cm\(^2\) PEM fuel cell. They operated the cell at current densities between 100 and 700 mA/cm\(^2\), with fully humidified hydrogen and air at relative humidities between 10 and 100\%, anode and cathode stoichiometries of 2, and a cell temperature of 80\(^\circ\)C. They showed that the net electro-osmotic drag from the anode to the cathode was reduced with an increase in current density, and/or increase is cathode relative humidity. They attributed this to the additional water concentration on the cathode in both cases, resulting in an increase in water back diffusion from the cathode to the anode side, hence a lower net electro-osmotic drag.

Above authors also obtained the polarization curve with the mentioned conditions, and anode relative humidities between 60 and 100\%. They showed that at medium and high air relative humidities, changes in the anode humidity has little or no effects on the cell voltage (RH of 70\% and above). They attributed this to sufficient back diffusion at high cathode humidities that keeps the membrane well hydrated, therefore, further humidification of the anode does not result in significant improvements in the cell performance. We should note that from their polarization curve data, it could be seen that the highest cell performance occurs with an anode and cathode relative humidities of 90 and 50\%. This is because while the high anode humidity maintains the membrane well hydrated, the lower cathode humidity results in a higher limiting current density.

In [8], Berg et al. used a customized Ballard 16 segment cell with RH sensors to measure the anode and cathode input and output water contents. In order to get accurate reading from the RH sensor at the outputs, they added sufficient amount of dry gas to the output stream such that its relative humidity was reduced below 100\%. They also developed a 2-D mathematical model, assuming that the oxygen diffuses through the water present in the membrane to reach the active catalyst sites.
They fitted four model parameters to match the data sets obtained: cathode exchange current density, oxygen and water mass transfer coefficients, and average membrane conductivity. Their experimental setup and mathematical model showed that at a cell current density of 1 A/cm², cell temperature of 80°C, anode dew point of 63°C, and counter-flow configuration, the local current density had a blip at the beginning of the cathode channel, if the air relative humidity dropped below 50%. They repeated the experiment with co-flow conditions, and observed the blip even with high cathode relative humidities. They calculated the anode inlet relative humidity and membrane water content with both co-flow and counter-flow conditions, and showed that they were appreciably lower in the co-flow mode, even with higher cathode humidities, causing a drop in the cell current density. They concluded that the counter-flow configuration has a substantial benefit to even out the water balance across the membrane, with the saturated end of one gas humidifying the dry inlet of the opposite stream.

In order to verify their conjecture that the active sites were predominantly in the membrane, above authors calculated the effective oxygen diffusivity from the fitted value of oxygen mass transfer coefficient, and showed that it was an order of magnitude lower than the binary diffusivity of oxygen in nitrogen. They also replaced nitrogen with helium to change the diffusivity of oxygen by a factor of three, however, the runs showed little change in the cell performance. They concluded that diffusion of the dissolved oxygen in the membrane water plays a significant role in mass transport limitations in the cathode. They also calculated the diffusive length for oxygen, and showed that it was about 35 nm, an order of magnitude larger than the catalyst particles.

Authors [14], [52], [30], and [28] also used mathematical modeling to explain transport phenomena in the PEM fuel cell cathode. In [14], Eikerling modeled the cathode catalyst layer with an agglomerate geometry, consisting of primary pores between 3-10 nm inside the agglomerate, and secondary pores of 10-50 nm between them. Eikerling calculated the rate of evaporation in the two pores, and showed that the rate was in the order of 10 times faster in the primary pores compared to the secondary pores. He showed that in the optimal mode, the primary pores contain liquid water, with
the liquid-gas boundary in the primary pores. He also showed that when the primary pores are not flooded, evaporation rates are high, hence drying the cathode. In contrast, during flooding, the large pores between the agglomerates are also filled with liquid water.

In a two series paper, [53] and [52], Rho et al. examined the effect of changes in oxygen concentration on mass transport limitation in the PEM fuel cell cathode. In [53], they obtained the polarization curves for a 50 cm$^2$ cell with cathode stoichiometry of 1.5 and oxygen concentration of 5 to 100%. They observed that with an increase in oxygen concentration, the open circuit voltage increased, as a result of thermodynamic and electrode kinetic effects. With an increase in the cell current density, the cell voltage dropped, with the drop being more significant for low oxygen concentrations, due to increased mass transport limitations. In [52], they used mathematic modeling to interpret the effect of the observed mass transport limitations on cathode performance. They explained the rapid fall off at the end of the mass transport limiting region due to a reduction in the diffusion coefficient in the GDL. They attributed the reduction in the diffusion coefficient to presence of water droplets or film in the GDL pores.

In [30], Kulikovsky modeled the fuel cell polarization curve, taking into account oxygen concentration along the channel, oxygen transport through the GDL, and electrochemical activation losses. He showed that increasing the oxygen stoichiometry increases the fuel cell limiting current density. He also showed that at low stoichiometry ratios, most of the oxygen is consumed at the beginning of the flow field channel, starving the channel end.

A.2 Anode Flow Dynamics

The PEM fuel cell anode stream supplies hydrogen and humidifies the membrane. Compared to the cathode, potential losses on this electrode are negligible. This is because reaction kinetics are about 5 order of magnitude faster in the anode compared to the cathode [31]. In addition, no water is produced on the anode side, therefore, mass transport limitations do not occur at high current densities. As a result, less
work has been focused on the anode side compared to the cathode.

To understand the dynamics of PEM fuel cell at low anode stoichiometries, Liu et al. [36] operated a 12 segment 30 cm$^2$ at a constant anode flow rate of 76 sccm, equivalent to a stoichiometry of 1 at a current density of 350 mA/cm$^2$, with a high cathode flow rate of 380 sccm. They obtained the polarization curve using a potentiostatic load, such that the cell voltage was reduced from open circuit at a rate of 1 mV/sec. They showed that during anode starvation, the polarization curve had a hump, i.e., the current density passed about 100 mA/cm$^2$ beyond the 350 mA/cm$^2$ theoretical limit imposed by a unity anode stoichiometry. By further reduction of cell voltage, they observed that the cell current returned and remained at the 350 mA/cm$^2$ theoretical limit. They explained this hump by the hydrogen stored in the pipes and flow channels, acting as a reservoir. During starvation, they observed a vacuum effect at the output of the anode. They concluded that the vacuum effect in the anode pulls the additional hydrogen from the reservoir to take part in the reaction, therefore the cell current could go beyond a unity stoichiometry. However, when the extra hydrogen is consumed, the cell current returns to the 350 mA/cm$^2$ theoretical limit.

In [26], Knights et al. presented full anode starvation results from a Ballard PEM fuel cell stack. They reproduced anode starvation by replacing hydrogen with humidified nitrogen. They showed that with applying a small load, the cell voltage drops due to negative values. They attributed this to an increase in the anode potential, to levels required for water oxidation. They confirmed this by measuring oxygen at the anode output using gas chromatography. They explained that in the presence of platinum, the resulting high electrode potentials would be sufficient to oxidize carbon particles that support the platinum particles, and suggested that this could result in loss of catalyst particles from the electrode, hence reducing the cell performance.

Above authors measured the robustness of the catalyst layer at a current density of 200 mA/cm$^2$, using the time it took for the cell voltage to reach -2 volts, resulting in anode full starvation. They showed that it took less than 5 minutes for the standard catalyst to reach -2 volts. They added PTFE (Polytetrafluoroethylene) to the catalyst, in order to enhanced water retention capabilities of the anode, and showed an increase
in the full starvation time to about 20 minutes. Next, they added ruthenium to the PTFE supported catalyst to reduce the required anode potential for water electrolysis, hence reducing the rate of carbon oxidation. They observed that the time for anode starvation was increased to over 30 minutes. Finally, they added graphitic carbon to enhance the platinum support, and showed that full starvation was delayed to about 70 minutes.

In [66], Taniguchi et al. studied the effect of anode starvation on a platinum-ruthenium anode catalyst. They operated a 10 cm$^2$ circular cell at a current density of 345 mA/cm$^2$ and anode stoichiometry of 1, and measured the anode and cathode potentials separately using a reference electrode. They showed that at the low stoichiometry examined, anode potential jumped from near zero values to 1.5 volts, causing a negative cell voltage about -0.5 V. They returned the cell to normal conditions after three minutes of anode starvation, and showed performance loss by comparing the polarization curves before and after the experiment. They measured the ruthenium and platinum content of the catalyst after anode starvation using energy dispersive X-ray (EDX), which revealed ruthenium dissolution from the anode catalyst particles.
Appendix B

Calculation of Water Molar Flow Rates

Assuming that water vapor and air behave as ideal gas, we can write the following equations at the cathode input:

\[ \begin{align*}
P_{w,in}V_{w,in} &= n_{w,in}RT \\ 
P_{c,in}V_{c,in} &= n_{c,in}RT
\end{align*} \] (B.1) (B.2)

with \( P_{w,in} \) and \( P_{c,in} \) the water vapor and air partial pressure at the input, \( V_{w,in} \) and \( V_{c,in} \) the water vapor and air volume at the input, \( n_{w,in} \) and \( n_{c,in} \) the number of moles of water vapor and air at the inlet, and \( R \) and \( T \) the gas constant and input stream temperature, respectively. If we take the derivative of both sides of equations (B.1) and (B.2), we have:

\[ \begin{align*}
P_{w,in}\dot{V}_{w,in} &= \dot{n}_{w,in}RT \\ 
P_{c,in}\dot{V}_{c,in} &= \dot{n}_{c,in}RT
\end{align*} \] (B.3) (B.4)

with \( \dot{n}_{w,in} \) and \( \dot{n}_{c,in} \) being the molar flow rate of water vapor and air at the input, respectively. \( \dot{V}_{w,in} \) and \( \dot{V}_{c,in} \), the volumetric flow rate of water vapor and air at the cathode input, are equal. Therefore, if we divide equations (B.3) and (B.4), we have:
\[
\frac{P_{w,in}}{P_{c,in}} = \frac{\dot{n}_{w,in}}{\dot{n}_{c,in}} \quad (B.5)
\]

Similarly, at the cathode output we have:

\[
\frac{P_{w,out}}{P_{c,out}} = \frac{\dot{n}_{w,out}}{\dot{n}_{c,out}} \quad (B.6)
\]
Bibliography


BIBLIOGRAPHY


