Non-isothermal two-phase transport in the polymer electrolyte membrane fuel cell microporous layer

by

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Abstract

This thesis investigates the water transport mechanisms in the crack-free microporous layer (MPL) of a polymer electrolyte membrane (PEM) fuel cell. Synchrotron X-ray radiography was used to visualize and quantify the in situ liquid water in the gas diffusion layers (GDLs) of an operating fuel cell. A methodology was developed to correct the artefact of imaging sample movement. Furthermore, to address inaccuracies due to the scattering effect and higher harmonics at the synchrotron beamline, a calibration technique was introduced in order to experimentally determine the liquid water X-ray attenuation coefficient. Through in situ radiography, liquid water breakthrough events were observed in the MPL, and measured water thicknesses were used as inputs into a one-dimensional (1D) heat and mass transport model. The 1D model was used to describe the coupled relationship between liquid and vapour transport through the cathode MPL and the temperature distributions in the operating fuel cell.
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### Abbreviations

<table>
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<th>Description</th>
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<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>CCM</td>
<td>Catalyst-coated membrane electrode assembly</td>
</tr>
<tr>
<td>CL</td>
<td>Catalyst layer</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>MPL</td>
<td>Microporous layer</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PEM</td>
<td>Polymer electrolyte membrane</td>
</tr>
<tr>
<td>PEN</td>
<td>Polyethylene naphthalate</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>µCT</td>
<td>Microscale computed tomography</td>
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</table>
Nomenclature

\( C \): Vapour concentration \( \text{mol/m}^3 \)

\( D^{\text{eff}} \): Effective diffusion coefficient \( \text{m}^2/\text{s} \)

\( D_{\text{vap}} \): Diffusivity for water vapour \( \text{m}^2/\text{s} \)

\( E \): Measured fuel cell voltage \( \text{V} \)

\( E_{\text{ref}} \): Reference voltage \( \text{V} \)

\( F \): Faraday constant, 96487 \( \text{C/mol} \)

\( f \): Correction factor

\( I \): Attenuated beam intensity

\( I_0 \): Incident beam intensity

\( I_{\text{cr}} \): Corrected pixel intensity

\( I_a \): Averaged pixel noise intensity

\( I_{\text{dry}} \): Pixel intensity of the reference dry state image

\( I_m \): Measured intensity at the scintillator

\( I_{\text{nf}} \): Noise-free pixel intensity

\( I_{\text{raw}} \): Measured pixel intensity of the raw image

\( I_{\text{wet}} \): Pixel intensity of the target wet state image

\( \bar{I} \): Mean pixel intensity

\( i \): Current density of the fuel cell \( \text{A/m}^2 \)

\( k \): Thermal conductivity of the dry fuel cell material \( \text{W/m/°C} \)

\( k^{\text{eff}} \): Effective thermal conductivity with consideration of liquid water \( \text{W/m/°C} \)

\( l \): Length of active area \( \text{cm} \)

\( L \): Through-plane length \( \text{m} \)

\( L_f \): Specific latent heat for water condensation, 4.06E4 \( \text{J/mol} \)

\( N \) (Chapter 3): Molar flux of water \( \text{mol/m}^2/\text{s} \)

\( N \) (Chapter 4): Number of images in the stack
\( n: \) Image number

\( n_d: \) Electro-osmotic drag coefficient

\( P_{sat}: \) Saturation water vapour pressure \( \text{Pa} \)

\( r_{pc}: \) Volumetric phase change rate \( \text{mol/m}^3/\text{s} \)

\( R: \) Gas constant, 8.314 \( \text{J/°C/mol} \)

\( R_{1,2,\ldots,6}: \) Region names for calibration device

\( s: \) Water saturation

\( \bar{s}: \) Mean water saturation

\( T: \) Temperature \( °C \)

\( x: \) Through-plane position in the cathode GDL \( \text{m} \)

\( x_0: \) The through-plane position of boundary between the flow field and anode GDL \( \text{m} \)

\( X: \) Material thickness along the beam direction \( \text{cm} \)

\( X_w: \) Measured water thickness \( \text{cm} \)

\( \varepsilon: \) Porosity

\( \phi: \) Heat flux \( \text{W/m}^2 \)

\( \mu: \) Material attenuation coefficient \( 1/\text{cm} \)

**Superscript**

\( a: \) Anode GDL

\( c: \) Cathode GDL

\( n: \) Image number

**Subscript**

\( att: \) Attenuation
\( c: \) Calibrated
\( ch: \) Flow field
\( \text{diff}: \) Diffusive flux
\( gdl: \) Gas diffusion layer
\( j: \) GDL material: MPL or substrate
\( m: \) Membrane
\( mpl: \) Microporous layer
\( NIST: \) NIST reference value
\( pc: \) Phase change
\( sub: \) Carbon fibre substrate
\( tot: \) Total
\( w: \) Liquid water
Chapter 1: Introduction

1.1 Preamble

The polymer electrolyte membrane (PEM) fuel cell produces electricity from the electro-chemical reaction of hydrogen and oxygen. It is able to provide clean energy to automobile applications, and is particularly attractive for its high efficiency. Yet, the high cost of this technology remains as a major barrier to widespread adoption [1]. High current density operation of the PEM fuel cell is one solution to overcome this cost challenge, as higher current densities result in higher power densities and more effective use of the catalyst [2]. However, high current densities lead to large rates of water generation at the cathode. The presence of water is critical for ensuring membrane hydration, which is required for achieving the necessary levels of ionic conductivity in the membrane [3]. Yet, excess water tends to condense and accumulate in the cathode catalyst layer (CL) and in the pores of the gas diffusion layer (GDL), thereby hindering oxygen transport to the reaction sites. Severe water saturation causes cathode flooding, and the fuel cell performance suffers from mass transfer polarization (losses). Hence, it is critical to design fuel cell components that will facilitate effective water management and allow for high current density operation.

In a PEM fuel cell, water is produced as a by-product at the cathode CL. Figure 1-1 shows a schematic of a PEM fuel cell and the fuel cell components. Hydrogen and oxygen are delivered to the anode and cathode flow fields, respectively. The reactant gases diffuse through the GDLs to the anode and cathode CLs at the catalyst-coated membrane electrode assembly (CCM),
driven by concentration differences. At the anode, the hydrogen is oxidized to form protons according to the following reaction:

\[ 2H_2 \rightarrow 4H^+ + 4e^- \]  (1.1)

The electrons are conducted to the anode flow field and travel to the cathode CL through a connected circuit, generating the electrical current. The protons travel through the ionically conductive membrane to the cathode CL. At the cathode CL, the reduction of oxygen occurs as per the following reaction:

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  (1.2)

The overall reaction is given by:

\[ 2H_2 + O_2 \rightarrow 2H_2O \]  (1.3)

Additionally, water is also introduced into the fuel cell through the humidification of the reactant gases. Water is also transported from the anode to the cathode by electro-osmotic drag, where the water molecules move through the membrane facilitating proton transport [4]. At typical operating temperatures between 20 - 90°C [5], the combination of high water flux and high humidity leads to the increased water vapour pressure at the cathode CL and its adjacent GDL. When the water vapour pressure reaches the saturation water vapour pressure, \( P_{sat} \), any additional water flux leads to the presence of liquid water.

A microporous layer (MPL), as a part of the GDL, is implemented between the carbon fibre substrate and the CCM to mitigate the flooding and improve the fuel cell performance at high current operation [6–13]. The water at the cathode CL is mainly transported towards the cathode
flow field through the MPL. Therefore, the study of water transport mechanisms in the MPL is critical for advancing water managements for the PEM fuel cell.

1.2 Motivation and objectives

Successful high current density operation is vital for PEM fuel cells to compete with other technologies. High current operation requires that the fuel cell components must be designed for effective water management. Hence, understanding the two-phase water transport mechanism in the PEM fuel cell MPL is of great interest to fuel cell manufacturers.

Synchrotron X-ray radiographic visualization has been proven to be a useful tool to concurrently track and quantify the liquid water in an operating fuel cell [7,14–24]. During the visualization process, the inaccuracies from the sample movement, scattering, and higher harmonics poses significant challenges for fuel cell diagnostics. Hence, one objective of this thesis is to develop an image processing technique to address the aforementioned sources of inaccuracy.

The feasibility of combining the experimentally measured water content with a numerical model is explored in this thesis. The implementation of the concurrent liquid water distribution as a key input to the developed numerical model allows for the accurate simulation of the water transport mechanisms and temperature distribution in the MPL. Using this method, the other objectives of investigating the non-isothermal two-phase water transport in the MPL are achieved.
1.3 Contributions

The work presented in this thesis has led to the following first authored-research contributions:


It is noteworthy that this work was performed in close collaboration with Nissan Motor Co., Ltd. (T. Kotaka and Y. Tabuchi), who co-developed the polymer electrolyte membrane (PEM) test fuel cell as well as the custom material components.

1.4 Co-authorship

Synchrotron X-ray imaging is a large team effort within this research group, and the work presented in this thesis has been vital for conducting a variety of studies. Therefore, the work presented in this thesis has been core to several other co-authored publications, which are listed below:


1.5 Organization of thesis

This thesis is divided into 5 chapters. Chapter 1 includes a description of the need for water management in the PEM fuel cell, along with the motivation, objectives, and contributions of this thesis. In Chapter 2, the role of MPL in water management is described. A literature review of the MPL water transport mechanisms is presented. The background of the synchrotron X-ray radiography as a visualization tool in PEM fuel cell research is introduced. The sources of inaccuracies of this application are discussed. Chapter 3 provides the details of the image processing technique, which accounts for sample movement during in situ PEM fuel cell investigations of liquid water transport. A method for calibrating the liquid water attenuation coefficient used in liquid water quantification of synchrotron X-ray imaging is presented. In Chapter 4, the water transport mechanism in the crack-free MPL of a PEM fuel cell is investigated through an in situ experiment with synchrotron X-ray radiography. A one-dimensional (1D) heat and mass transport model is developed to determine the through-plane temperature distribution and water fluxes across the cathode region of the fuel cell. The simulation and visualization results are combined to study the coupled relationship between the liquid and vapour transport, and the effect of temperature on the water transport in the cathode MPL. Chapter 5 presents the conclusions and future works to this thesis.
Figure 1-1 Schematic of PEM fuel cell and the fuel cell components.
Chapter 2: Background

2.1 Introduction

This chapter presents the background literature for this thesis. A thorough literature search has been performed resulting in the objectives of this work. The role of the microporous layer (MPL), a key component in water management, is described in detail. The two water transport mechanisms in the MPL are explained: the liquid- and vapour-phase transport. Synchrotron X-ray radiography is introduced as a tool for imaging polymer electrolyte membrane (PEM) fuel cell and PEM fuel cell materials, particularly for tracking liquid water transport behaviour. Sources of erroneous water detection in the radiographs, such as sample movement and attenuation coefficient inaccuracy are also discussed.

2.2 Water transport in the MPL

2.2.1 Roles of MPL in water management

The MPL, made of carbon black particles and polytetrafluoroethylene (PTFE), is highly hydrophobic compared to the carbon fibre substrate. The MPL has pore sizes of ~100 nm [25] compared to 10 - 30 µm in the substrate [26]. Figure 2-1 shows microscale computed tomography (µCT) images of the carbon fibre substrate and a crack-free MPL. With the applied µCT spatial resolution of 2.88 µm, the pores in carbon fibre substrate (Figure 2-1(a)) can be clearly observed. By comparison, the pores in the MPL image is not visible in Figure 2-1(b). The small pore size and the hydrophobic composition of the MPL create a capillary barrier to prevent
condensed water in the substrate from flowing to catalyst layer (CL), thus reducing the liquid water coverage of the catalyst [12].

The MPL has been studied extensively for developing an understanding of its influence on water management. Weber and Newman [10] suggested that the mechanism whereby MPL reduces the liquid water content at the cathode CL is through forcing water across the membrane to the anode. Through electrochemical impedance spectroscopy (EIS) and synchrotron X-ray radiography, Antonacci et al. [21] found that thicker MPLs led to decreased oxygen transport resistance due to decreased water content in the cathode gas diffusion layer (GDL). Thomas et al. [27] measured the water flux in the cathode and anode at various temperature settings. They concluded that the MPL led to the reduction of liquid water accumulation at the cathode CL, and a thermal gradient across the membrane induced a water flux that hydrated the anode catalyst layer ionomer. Multiple studies [8,28,29] have shown that the MPL constrains the number of liquid water injection points to the substrate, and this leads to the reduction of substrate water saturation.

2.2.2 Liquid-phase water transport in MPL

Understanding the water transport mechanisms in the MPL has been sought after in the literature through extensive studies focussed specifically on the dominance of the liquid- and vapour-phase transport. In one proposed mechanism, liquid water travels across the MPL along continuous pathways as the liquid-phase pressure increases [6,30,31]. In this mechanism, high levels of liquid water saturation occur near the CL-MPL interface [6,32], as shown in Figure 2-2(a). When the resulting liquid-phase pressure overcomes the threshold capillary pressure of an adjacent
pore, liquid water penetrates and saturates this pore. This process is termed \textit{invasion percolation}. At the moment of \textit{breakthrough}, liquid water reaches the opposite side of the MPL to form a continuous pathway through the porous media. After the breakthrough event, all subsequent liquid water introduced at the CL travels via this established pathway, whereby the saturation level in the MPL is no longer influenced by the production of liquid water [33,34]. The saturation trend in Figure 2-2(a) was experimentally confirmed through the synchrotron visualization results reported by Lee et al. [6].

In general, liquid water preferentially occupies larger and more hydrophilic pores [5]; hence, MPL cracks provide primary pathways for liquid transport. Using visualization tools, several research groups [8,35,36] observed that MPL cracks facilitate liquid water transport at high current densities. However, cracks lead to poor mechanical durability of the MPL, so in practice crack-free MPLs have been preferred [37]. In addition, temperature has proven to have an impact on the capillary pressure [38–41]; however, there is a lack of information about how the temperature distribution within the GDL affects the nature of liquid transport in the MPL.

2.2.3 Vapour-phase water transport in the MPL

In another proposed mechanism for water transport in the MPL, vapour-phase diffusion across the MPL is driven by the water vapour concentration gradient (Figure 2-2(b)), which has also been referred to as the heat-pipe effect [42]. In this mechanism, a concentration gradient is caused by a temperature gradient from the cathode CL to the flow field [42,43] due to the heat generated from the electrochemical reaction at the CL and condensation at the MPL-substrate interface. This temperature gradient induces water vapour transport toward the substrate, and
condensation occurs as a result of the decreased vapour pressure in the MPL. Several authors [44,45] have reported that the addition of the MPL to the GDL leads to a decrease in thermal conductivity, increased temperatures at the catalyst coated membrane (CCM), and enhanced vapour transport. Yet, the addition of the MPL is accompanied by an unavoidable increase in the diffusion path length for water vapour across the cathode, which in turn, acts to decrease the diffusive flux [46].

Contrary to the previously discussed liquid-phase transport mechanism, multiple studies have demonstrated that even at high current densities, all the water travelling across the MPL can be attributed to the vapour-phase. Kandlikar [47] and Kandlikar and Lu [48] predicted that all produced water is transported through the MPL in vapour phase and condenses outside the MPL. They explained that water vapour is less likely to condense in the MPL due to its smaller pore sizes compared to the substrate, and thus a condensation front would be expected in the substrate near the MPL-substrate interface. Using an ex situ experiment and a diffusion model, Xu et al. [49] observed that all product water could be removed from the CL via vapour diffusion through the MPL-coated GDL. Owejan et al. [50] measured the water vapour diffusion across the GDL, and they demonstrated that all product water is expected to exit the GDL via vapour diffusion alone. The aforementioned literature includes clearly observed, yet opposing transport mechanisms for liquid water transport in the MPL.

Numerical models have been used to understand the two-phase water transport in the cathode GDL [12,13,51–57]. In numerical modeling, the vapour-phase transport is dependent on the liquid water distribution in the GDL [58]. However, existent models have not utilized the high resolution distribution of liquid water that are obtained during in operando experiments with visualization tools.
2.3 Synchrotron X-ray radiography visualization

At a synchrotron facility, electrons are accelerated to nearly the speed of light and boosted to high energies. The electrons are contained while circulating in the storage ring. Around the storage ring, a wide spectrum of light is generated when the electron path is redirected by magnets. X-rays produced from a synchrotron source exhibit a high photon flux, and this feature significantly reduces the radiography imaging time that would otherwise be needed with conventional X-ray sources, providing the unique opportunity to conduct in situ experiments [59]. The synchrotron X-ray spectra can also be isolated to a desired energy level through the use of a monochromator [60]. Hence, quantitative analysis can be performed with precisely controlled and stable beam characteristics, including X-ray attenuation and penetration [61].

Recently, synchrotron X-ray radiography has been developed as a tool for imaging PEM fuel cells and PEM fuel cell materials, particularly to track liquid water transport behaviour [7,14–24]. Manke et al. [14] studied the development of liquid water in the GDL with a spatial resolution of 3-7 µm, and observed cathode channel water droplets migrating from the GDL region under the land. Later, Hartnig et al. [15] visualized the water distribution in the through-plane direction and explained that liquid water clusters in the GDL result from repeated Haines jumps and capillary pressure differences in the pores, defined as choke-off effects. Using synchrotron imaging, the roles of GDL structures, such as cracks in MPL [62], carbon fibre orientation [63], and perforated holes on the GDLs [18,64,65] in water management were studied. While synchrotron radiography is a powerful tool for visualizing liquid water in the
PEM fuel cell, radiation was reported to degrade the fuel cell performance [17,66] by damaging the fuel cell materials [67] and so must be applied with care.

2.3.1 The Beer-Lambert law

The Beer-Lambert law is commonly employed for post-processing synchrotron X-ray images [19,68,69]. This law describes the relationship between the incident beam intensity and the attenuated beam intensity, as shown in Figure 2-3(a), based on the attenuation coefficient and the length of the path traversed by the X-ray beam:

\[ I = I_o \exp(-\mu X) \]  

(2.1)

where \( I \) is the attenuated beam intensity, \( I_o \) is the incident beam intensity, \( \mu \) is the attenuation coefficient of the material, and \( X \) is the material thickness along the beam direction [70]. Lee et al. [68] presented an image normalization technique, which was derived from Equation 2.1, to quantify the water thickness in the through-plane direction of the GDL. This technique requires a reference image in the absence of liquid water, termed the dry state image in this thesis, in order to determine the water content in the image that contains liquid water, termed the wet state image in this thesis, using the following equation:

\[ X_w = \frac{1}{\mu_w} \ln \left( \frac{I_{dry}}{I_{wet}} \right) \]  

(2.2)

where \( X_w \) is the cumulative water thickness along the X-ray path, \( \mu_w \) is the attenuation coefficient of liquid water as a function of photon energy level, \( I_{dry} \) is pixel intensity of the reference dry state image (as shown in Figure 2-3(b)), and \( I_{wet} \) is the pixel intensity of the target wet state image (as shown in Figure 2-3(c)). By using Equation 2.2, Hinebaugh et al. [71]
developed an image processing routine to quantify liquid water with the goal of increasing the accuracy of the measured liquid water thickness by compensating for vertical oscillations of the beam position.

2.3.2 Attenuation coefficient of liquid water

While synchrotron radiography has already proven to be a powerful tool for visualizing PEM fuel cells, special attention should be made during the stages of image processing and analysis in order to obtain highly accurate results. A reference value for the attenuation coefficient has been published by the National Institute of Standards and Technology (NIST) [72]; however, in Equations 2.1 and 2.2 the attenuation coefficient is a direct function of the material and photon energy level. The liquid water content calculation is highly dependent on the attenuation coefficient of liquid water, yet this attenuation coefficient is not typically calibrated (or reported) in the literature.

Directly applying the reference attenuation coefficient (from NIST) can result in inaccurate image interpretation if one experiences scattering effects or if the incident beam contains harmonic frequencies in addition to the intended frequency. The scattering effect is the process in which a portion of incident photons are redirected from its original path by the sample material [61,73], as illustrated in Figure 2-3(a). The scatter angle, which describes the travel direction of a scattered photon with respect to the incident beam direction, is unpredictable [61]. Hence in practice, the scattered photons can be unintentionally measured at the scintillator, unfortunately contributing to the pixel intensity of the collected image.

Higher harmonics contamination is the phenomenon whereby a portion of the incident photons from the double-crystal monochromator exhibit undesired higher energy levels, which are integer
multiples of the fundamental (prescribed) energy level [74,75]. The attenuation coefficient of the sample is lower for the high-energy photon beam, compared to that for the fundamental energy level. By applying the reference attenuation coefficient of the fundamental energy level, an error is introduced when quantifying the liquid water via the Beer-Lambert law. Therefore, an experimentally calibrated attenuation coefficient is vitally needed in order to account for scattering and higher harmonic effects.

2.3.3 Artefact from sample movement

Sample movement at the micron scale during in operando imaging can also be a significant source of image artefacts. The image normalization technique based on Equation 2.2 was established upon the condition that the sample does not move during the imaging process. The normalization calculation relies on the pixel intensity change to be solely caused by the presence of liquid water. However, if the sample moves during the imaging process, false water thicknesses will be observed. For example, as shown in Figure 2-4, a normalized imaged processed solely using the technique by Hinebaugh et al. [71] results in false water thicknesses including negative and positive values at the anode channel edges (where liquid water was not expected based on the experimental conditions used). Movement artefacts decrease the accuracy of liquid water measurements, and without properly addressing sample movement, synchrotron radiography-based imaging could be rendered unusable.
2.4 Figures

Figure 2-1 µCT images of (a) carbon fibre substrate and (b) crack-free MPL. The length bars represent 0.4 mm.
Figure 2-2 Water transport mechanisms in the MPL: (a) liquid-phase transport and (b) vapour-phase transport.
Figure 2-3 Schematics illustrating: (a) the interaction between the incident, parallel X-ray beam and the sample before the camera measures the detected signal, (b) the attenuation process of the imaging sample with absence of water, and (c) the attenuation process of the imaging sample with presence of water.
Figure 2-4 Example processed image obtained from synchrotron X-ray radiography of an operating PEM fuel cell before the movement correction was applied. The appearance of false water thicknesses is highlighted and the length bar represents 0.5 mm.
Chapter 3: Visualizing liquid water distribution in a PEM fuel cell with synchrotron X-ray radiographic imaging

3.1 Introduction

The micrometer-scale movement of the sample poses a significant challenge to synchrotron-based imaging for polymer electrolyte membrane (PEM) fuel cell diagnostics. At a photon energy level of 20 keV, a maximum movement of 7.5 µm resulted in a false water thickness of 0.93 cm (9% higher than the maximum amount of water the experimental apparatus could contain). In this chapter, a methodology for artefact correction that involves artefact calibration (correlation between the artefact and distance moved by the sample) and image translation was presented, the implementation of which led to a significant reduction in false water thickness to values of ~0.04 cm. Furthermore, to account for inaccuracies in pixel intensities due to the scattering effect and higher harmonics, a calibration technique was introduced for the liquid water X-ray attenuation coefficient, which was found to be 0.657±0.018 cm\(^{-1}\) at 20 keV. The work presented in this chapter provides valuable tools for artefact compensation and accuracy improvements for dynamic synchrotron X-ray imaging of fuel cells. The work presented in this chapter was submitted as a journal manuscript\(^1\).

\(^1\) Ge, N., Chevalier, S., Hinebaugh, J., Yip, R., Lee, J., Antonacci, P., Kotaka, T., Tabuchi, Y, and Bazylak, A. “Calibrating the X-ray attenuation of liquid water and correcting sample movement artefacts during in operando synchrotron X-ray radiographic imaging of polymer electrolyte membrane fuel cells.” Journal of Synchrotron Radiation. (Accepted)
3.2 Methodology

3.2.1 Fuel cell hardware and control

The PEM fuel cell considered in this study consisted of cathode and anode flow fields, gas diffusion layers (GDLs) and catalyst-coated membrane electrode assembly (CCM) as shown in the radiograph in Figure 3-1. The channels of the flow fields had a width of 0.2 mm and a depth of 0.5 mm. The GDL is herein defined as the combined carbon paper substrate and microporous layer (MPL). The TGP-H-60 (Toray Industries) carbon paper substrate was used for the in operando experiment described in this chapter. The GDL was compressed to 85% of its original thickness using polyethylene naphthalate (PEN) spacers. The active area had a width of 0.80 cm and a length of 0.85 cm, where the length coincided with the distance traversed by the X-ray beam. For complete details of our fuel cell design, the reader is referred to the following work: Chevalier et al. [22] and Lee et al.[6].

The PEM fuel cell was mounted to the sample stage using four stainless steel bolts and was controlled using a Scribner 850e fuel cell test station (Scribner Associates Inc.). During the experiments, gaseous hydrogen and air were set to a relative humidity (RH) of 100% and a temperature of 60°C at both the cathode and anode. The inlet flow rate was set to 1 slpm at a pressure of 2 atm (absolute). The operating temperature of the fuel cell was set to 60°C and controlled with a water-cooling system (Figure 3-1). The low operating temperature and high reactant RH were chosen to promote the accumulation of liquid water in order to impose the saturated conditions that are unfavourable in practical applications. In addition, high current density operation was constrained to a short period of time in order to avoid cathode flooding
and the back diffusion of water to the anode. As a result, liquid water transport was restricted to the cathode side during the experiments.

3.2.2 Synchrotron imaging

The images presented in this chapter were obtained from in operando PEM fuel cell imaging work conducted at the Biomedical Imaging and Therapy Bending Magnet (BMIT-BM) 05B1-1 beamline at the Canadian Light Source (CLS) synchrotron facility in Saskatoon, Canada [76]. The photon energy level of the beam was set to 20 keV. A Hamamatsu ORCAII-ERG camera (Hamamatsu Photonics K.K.) was used, and in order to obtain a high signal-to-noise ratio, the camera was set to the high-precision readout mode. At this setting, the dynamic range of the charge-coupled device (CCD) camera was 4625:1, based on a readout noise of 4 electrons and a full well capacity (maximum amount of charge that each pixel can hold before saturating) of 18500 electrons. A 14-bit analog-to-digital converter was used, which resulted in a pixel intensity range of 0-16383. The exposure time was set to 1.7 s, and every image was obtained from 4 integrated sequential frames from the camera. The resulting temporal resolution (time duration between two consecutive images) was 8.3 s. A pixel resolution of 4.4 µm/pixel was obtained.

3.2.3 Experimental protocol

The primary purpose of using synchrotron radiography with in situ PEM fuel cell diagnostics was to accurately measure the liquid water content in the cathode GDL, specifically the water
thickness (or equivalent saturation) distribution. The water thickness is defined as the summation of liquid water content accumulated in the in-plane direction traversed by the X-ray beam. In this study, the term *normalized image* refers to the image obtained using Equation 2.2, and the water thickness corresponds to the pixel brightness in the normalized image.

During the fuel cell experiment, three sets of images were captured in the following sequence: 1) 10 dark field images, 2) 5 dry state images, and 3) wet state images (of the in operando fuel cell experiment). In this study, the term *image stack* refers to the sequence of images of the dry state and wet state collected in situ. The first dry state image occurred at time $t = 0$, and the location of the fuel cell in this image is the *reference location* for the image stack. An image number (frame number), $n$, depending on the collection time was assigned to each image in an image stack. For example at time $t = 0$, the first dry state image was prescribed an image number $n = 1$.

The dark field image was obtained without the application of the incident X-ray beam, and the purpose of the dark field image was to measure the background noise of the camera. The pixel intensities in the dark field images ranged from ~2100 to ~2300. Any non-zero pixel intensities detected in the dark field image were the result of the dark current noise generated from the electron thermal excitation in the CCD camera [77]. Minimizing dark current noise was ideal for obtaining accurate water thickness measurements.

The dry state images were obtained at open circuit voltage (OCV) with the incident X-ray beam. During OCV conditions, the membrane was humidified with fully moisturized reactant gases (100% RH). Steady state OCV conditions were used to ensure that any pixel intensity changes (especially near the interfaces of CCM and GDLs) were not caused by membrane swelling due to changes in humidity [78].
The wet state images were collected during cell operation in the presence of electrochemically produced water. The pixel intensity of the cathode region in the wet state images was lower than that in the dry state images due to the attenuation of the X-rays by liquid water. During the operation, the fuel cell was set to current densities typically ranging from 0 to 3.0 A/cm². The fuel cell was held at each current density for at least 5 min in order to reach a steady state. Hence, the duration of each in situ fuel cell experiment was between 1 - 2 hours.

3.2.4 Attenuation coefficient calibration

To account for the unique scattering effect and higher harmonics of the beam (in comparison to conditions of the National Institute of Standards and Technology (NIST)), a calibration technique was created to experimentally determine the attenuation coefficient for liquid water at the beamline. Because of scattering and higher harmonics (discussed in Chapter 2), the measured intensity at the scintillator was higher than the attenuated intensity. Hence, we anticipated that our attenuation coefficient would be lower than the NIST reference value (0.810 cm⁻¹ at 20 keV [72]).

A custom-made calibration device containing a single liquid water reservoir was developed, as shown in Figure 3-2(a). The device held six known thicknesses of water ($X_{water}$) in distinct regions ($R_1, R_2, \ldots, R_6$) ranging from 0 to 1.6 cm (Table 3-1). The expected accuracy level of this device is ±0.02 cm accounting for machining and assembly tolerances. This device was composed of polycarbonate (PC), which was chosen specifically to simulate the scattering and attenuation effects due to the higher harmonics that would occur during in operando fuel cell imaging. The material attenuation coefficient of the PC (~0.620 cm⁻¹ at 20 keV [72]) was
comparable to the carbon-based GDL (0.995 cm$^{-1}$ at 20 keV [72]) and the PEN spacer (~0.747 cm$^{-1}$ at 20 keV, estimated based on information provided by the Center for X-ray Optics [79] and the NIST [72]). A critical feature of this device is the constant solid material thickness ($X_{pc}$ on Figure 3-2(a)) adjacent to each prescribed water thickness region. Thus, while the liquid water induced attenuation should change with varying $X_{water}$, the beam attenuation induced by the solid material of the device itself should remain constant.

During the calibration experiment, a sequence of images consisting of 10 dry state images, 10 dark field images, and 10 wet state images were obtained. The dry state images were collected when the water compartment of the calibration device was free of water; the wet state images for this device were collected when the water compartment was filled with water. The calibration experiment was conducted over a period of 5 minutes.

3.2.5 Image processing

This section includes the explanation of the four steps that constitute the image processing methodology for obtaining water thickness distributions: 1) dark current noise elimination, 2) water attenuation coefficient measurement, 3) beam intensity correction, and 4) sample movement correction. In particular, the description of steps 2) and 4) are the most recent developments in our group’s image processing methodology.
3.2.5.1 Dark current noise elimination

The dark current noise signal is pixel-dependent and fluctuates as a function of time. Therefore, the 10 dark field images were averaged in order to quantify the average noise at each pixel. Then, the average dark field image was subtracted from the each dry state and wet state image using the following equation [77]:

\[ I_{nf} = I_{raw} - I_d \]  \hspace{1cm} (3.1)

where \( I_{nf} \) is the noise-free pixel intensity, \( I_{raw} \) is the measured pixel intensity of the raw image, and \( I_d \) is the averaged pixel noise intensity. The noise-free images in this thesis describes the best estimation for the ground true images. This noise elimination process was performed for both image stacks collected from the fuel cell experiment and the calibration experiment.

3.2.5.2 Water attenuation coefficient measurement

The noise-free dry state and wet state images from the calibration experiment were used to determine the attenuation coefficient of liquid water. Based on Equation 2.2, the attenuation coefficient can be determined using linear regression. Hence, the water thickness of each region in the calibration device (in Table 3-1) was obtained based on the prior knowledge of the device dimensions, and the natural logarithm of the ratio of the dry state intensity to the wet state intensity, i.e. \( \ln \left( \frac{I_{dry}}{I_{wet}} \right) \), for each region was determined based on the noise-free images from the calibration experiment.

Each noise-free dry state and wet state image was obtained from an average of 10 sequential images. The pixel intensity in this dry state image was denoted by \( I_{dry,c} \), and the pixel intensity
in the wet state image was denoted by \( I_{\text{wet},c} \). The subscript, \( c \), indicates that a calibration image was used. Accordingly, \( \ln \left( \frac{I_{\text{dry},c}}{I_{\text{wet},c}} \right) \) was calculated for each region (shown in Figure 3-2(b)).

The value of \( \ln \left( \frac{I_{\text{dry},c}}{I_{\text{wet},c}} \right) \) as a function of the water thickness produced a linear relationship (shown in Figure 3-2(b)), the slope of which was the water attenuation coefficient (\( \mu_{w,c} = 0.657 \pm 0.018 \text{ cm}^{-1} \), using the least-squares regression method). The value has a confidence interval of 90%, calculated using the Student’s \( t \) distribution [80].

3.2.5.3 Beam intensity correction

The incident beam intensity at a synchrotron facility can decrease with time due to the current loss of the electron beam in the storage ring [71], particularly in the case when top-up is not available. In this case, even over short time periods this intensity change can be almost linear, which can be observed by monitoring the beam current. The duration of an in situ fuel cell experiment was typically more than one hour; therefore, the beam intensity dependence on time was an important factor in our analysis. However, a critical assumption of Equation 2.2 is that the change in pixel intensity occurs strictly due to the attenuation of liquid water. Therefore, a linear intensity correction was required.

For each image, a beam intensity correction factor was first obtained, and then this factor was applied to all the pixels of the corresponding image. It was important that the region selected for determining the correction factor did not contain liquid water for the duration of the experiment, so that we could strictly attribute the intensity change to a loss in beam intensity. The correction
factor was calculated from our analysis of the top side of the cathode bipolar plate (shown in Figure 3-3(a)). The correction factor was determined as follows:

\[ f^n = 1 - \left( \frac{n - 1}{N - 1} \right) \times \frac{I_1 - I_{\text{end}}}{I_1} \]  

where \( n \) is the image number, \( I_1 \) and \( I_{\text{end}} \) are the mean intensity of the selected region in the first and last noise-free images of the stack, and \( N \) is the number of images in the stack. The corrected pixel intensity, \( I^n_{cr} \), was determined using the factor, \( f^n \), and the noise-free pixel intensity, \( I^n_{nf} \):

\[ I^n_{cr} = \frac{1}{f^n} \cdot I^n_{nf} \]  

### 3.2.5.3 Sample movement correction

During the in situ experiment, sample movement occurred. One possible explanation for the movement is that the mounting bolts on the fuel cell might have become loose over time due to the mechanical stress from the rigid pipes of the inlets, outlets, and coolant. In this section, the cause of false water thickness due to sample movement is explained, and the steps used for image correction are presented.

**Cause of false water thickness**

Figure 3-3(b) is an image of the fuel cell during operation that was normalized through Equation 2.2 using the first dry state image, i.e. \( I^n_{cr} \) and the wet state image of Figure 3-3(a). Region 1
highlights the selected anode flow channel used for determining the appropriate movement correction, and this region is also noted in Figure 3-3(a). Region 1 is located in the centre region of this image where the beam intensity is the highest, helping to ensure that the artefact value of the false water thickness was measured with the optimal degree of precision. Since liquid water was not expected in Region 1 (due to the imposed operating conditions), the pixel intensities in Region 1 are expected to be 0. However in Figure 3-3(b), a thin band of negative values and a bright band of positive values can be observed at the two vertical channel edges of Region 1 (left and right, respectively). These false water thickness values were attributed to sample movement.

Figure 3-4 provides an illustration of how sample movement leads to the determination of false water thicknesses. We define $x_0$ as the horizontal reference location of the dry state image. During the experiment, the fuel cell moved to the left (in the negative $x$ direction), causing a phenomenon described as pixel material mismatch, whereby the location of a pixel in one image represents a different position of the sample in a subsequently obtained image. Hence, as a result of Equation 2.2, false water thicknesses at the channel edges were observed in the normalized image. The value of false water thickness was influenced by the distance moved by the sample in the wet state image with respect to the reference location. On Figure 3-4, a line across the vertical channel edge with a height of a single pixel (marked on the inset of the figure) was selected to explain this relationship. The pixel intensities of this line in both the dry state and the wet state images were presented. The pixel intensity has a value of ~1700 at the land, increasing to a value of ~3000 at the channel where the beam is attenuated by less material. The pixel intensity of the region between the land and the channel has a gradual and close-to-linear change. This region is termed the edge transition region in this thesis, and the width of the edge transition region is dependent on the angle (yaw) alignment of the fuel cell with the X-ray beam.
and the spatial resolution available at the beamline facilities. In this example, the movement of ~2 µm caused a maximum false water thickness of -0.25 cm. Increasing distances moved by the sample correspond to larger intensity differences at the edge transition region. Therefore, based on Equation 2.2, the artefact value of false water thickness corresponds to the magnitude of the distance moved.

**Artefact calibration**

Motivated by the cause of the false water thickness, a two-step correction method was developed. In this section, we translated an image over a large range of distances moved to produce all the possible false water thickness values. By image translation, the sample movement was artificially simulated in order to determine the relationship between the false water thickness and the distance moved.

The selected anode channel region as shown in Figure 3-3(a) from the first image, i.e. \(n = 1\), was used to calibrate the movement. To simulate the horizontal sample movement during the experiment, this region was translated in the horizontal direction within a ±2 pixel range in increments of 0.01 pixels. As a result, 400 translated images were produced, and each image corresponded to a prescribed distance moved. To determine the false water thickness associated with each distance moved, the translated images were normalized to the original, untranslated image using Equation 2.2. For each of the 400 normalized images (each of which correspond to a distinct distance moved), the false water thickness with the largest absolute value along Edge 1 (Figure 3-3(b)) was assigned as the corresponding negative water thickness.
To obtain the relationship between the false water thickness and vertical distance moved, the selected anode channel region (shown in Figure 3-3(a)) was translated in the vertical direction within a ±2 pixel range in increments of 0.01 pixels. The same procedure described above for calibrating the horizontal distance movement was also employed here for calibrating the vertical distance moved. For each of the 400 normalized images (each of which corresponded to a distinct vertical distance moved), the false water thickness with the largest absolute value along Edge 2 (Figure 3-3(b)) was assigned as the corresponding false water thickness. The calibration curves for horizontal and vertical distances moved are shown in Figures 3-5(a) and (b), respectively.

**Calculation of distances moved and image translation**

Based on the calibration relationships presented in Figure 3-5, the distances moved within each image from the image stack (of the in situ fuel cell experiment) were determined using the respective normalized image prior to the application of movement correction. Each in situ image was normalized to the first dry state image using Equation 2.2. The horizontal movement for each image distance was determined by correlating the false water thickness along Edge 1 (reference location shown in Figure 3-3(b)) to the corresponding horizontal distance moved in the calibration curve (Figure 3-5(a)). For example, the largest measured false water thickness relating to a horizontal movement was -0.93 cm, and according to the calibration curve (Figure 3-5(a)), the sample moved 1.7 pixels (or 7.5 µm) to the left of the reference location during the experiment. The vertical movement was also determined by applying the same analysis to Edge 2.
With the determination of the horizontal and vertical sample movements, each original raw image was translated to the ideal reference location (same as the location of the fuel cell at time $t = 0$) so that corrected water thicknesses could be determined. The 5 corrected dry state images were combined and averaged to produce a single dry state image used to account for the fluctuation and instabilities of the beam. Each subsequent wet state image (raw and corrected for sample movement) was then normalized to this averaged dry state image using Equation 2.2. The final, corrected water thickness values were then determined from the corrected images, an example of which is shown in Figure 3-6.

### 3.3 Results and discussion

In this section, the experimentally measured attenuation coefficient for liquid water is compared with the reference value from the NIST X-ray database. The improved accuracy of the water thickness measurements due to the movement correction technique is also discussed.

#### 3.3.1 Attenuation coefficient measurement

The measured attenuation coefficient for liquid water at 20 keV, $0.657 \text{ cm}^{-1}$, is 23.3% lower than the value from the NIST database, $0.810 \text{ cm}^{-1}$. This expected result was caused by higher-than-expected intensities that resulted from the scattering effect and higher harmonics.

To explain the difference between the attenuation coefficients, consider the imaging sample (in Figure 2-4(a)) as a quantity of liquid water with a uniform thickness of $X_w$ in the direction of the
traversing X-ray beam. \( I_0 \) is the incident beam intensity, and \( I_{\text{att}} \) is the attenuated beam intensity. Thus, the liquid water thickness at 20 keV can be determined with Equation 2.1:

\[
X_w = \frac{1}{\mu_{w,NIST}} \ln \left( \frac{I_0}{I_{\text{att}}} \right)
\]

(3.4)

where \( \mu_{w,NIST} \) is the reference attenuation coefficient of water.

However, the measured intensity at the scintillator, \( I_m \), consists of two other sources in addition to \( I_{\text{att}} \): the scattered intensity and the attenuated beam with energy levels higher than 20 keV (the higher harmonics). As a result, the reference attenuation coefficient at 20 keV, \( \mu_{w,NIST} \), cannot accurately determine the water thickness. Hence, the following equation was modified from Equation 3.5 to calculate the water thickness based on the measured intensity at the scintillator:

\[
X_w = \frac{1}{\mu_{w,c}} \ln \left( \frac{I_0}{I_m} \right)
\]

(3.5)

where \( \mu_{w,c} \) is the attenuation coefficient of liquid water with the consideration of scattering radiation and higher harmonics. Based on Equations 3.4 and 3.5, the experimentally calibrated \( \mu_{w,c} \) is expected to be lower than the reference \( \mu_{w,NIST} \) because the ideal attenuated intensity, \( I_{\text{att}} \), is lower than the measured intensity at the scintillator, \( I_m \). If the reference value from NIST was directly applied, the water content would have been underestimated by 18.9%. As the water content (or equivalent saturation) directly influences the cell performance, the attenuation coefficient calibration is critical for imaging PEM fuel cells using synchrotron X-ray facilities [81].
3.3.2 Water thickness at the anode channel region

Figure 3-7 illustrates the calculated water thickness values as a function of horizontal position along the \( x \) axis for the anode channel region (Region 1 of Figure 3-6) before and after movement correction was applied. At each \( x \) position, the average water thickness was determined by averaging over all pixels in the \( y \) axis within Region 1 of Figure 3-6. Before the movement correction, the calculated water thicknesses reached extreme values of \(-0.193 \text{ cm}\) and \(0.216 \text{ cm}\). After applying the movement correction technique, the range of calculated water thicknesses in this region significantly dropped to \(\pm 0.04 \text{ cm}\). The residual water thickness values visible in Figure 3-7 in the case where the movement correction has been applied is thought to be due to two sources of error: water attenuation and image instability. Thin films of water was likely to form on the anode channel walls because the imposed RH of 100% may have facilitated water condensation.

There are some limitations to the correction technique that should be noted. The development of our technique was highly influenced by the specifications of the bipolar plate, the through-plane field of view, and the experimental operating conditions. Particularly, the sharp vertical and horizontal channel edges facilitated a reliable correlation between the artefact value and the distance moved. Additionally, the water-free anode was a critical prerequisite for the calibration. Any water signal at the anode channel edge region will affect the perceived artefact value. In future experiments, one could address these concerns by pre-emptively designing an additional channel-like structure on the bipolar plates that is outside the active area, yet within the field of view. The X-ray path that traverses these edges would be free of liquid water throughout the entire course of the experiment. Hence, the correction technique (calibration and application) could be performed even on experiments which involve the presence of liquid water in the
anode. Furthermore in order to apply this technique for both in-plane and through-plane imaging, the edges for movement correction should be designed such that the normal direction to their corresponding surfaces are perfectly perpendicular to the beam direction.

3.3.3 Water thickness at the cathode GDL region

An example single cathode channel/land region is shown in the inset of Figure 3-8, which was cropped from Region 2 in Figure 3-6. This figure includes the GDL below the channel and land of the cathode flow field. The water thicknesses for the highlighted area (white line whose height is a single pixel) are presented in this figure. Before the movement correction procedure was applied, significant negative water artefacts could be seen between $x = 45$ to $75 \, \mu m$. The authors attributed this to the horizontal movement of the cell. Specifically, the GDL material was shifted out of this region in the wet state image, so during the image normalization, negative water thickness values were produced. After applying the image movement correction, the calculated water thickness profile became more homogeneous, and under the land region the largest measured water thickness was $0.30 \, \text{cm}$.

The uneven distribution of water near the flow field observed in Figure 3-8 can be attributed to the tendency for water to condense near the cold bipolar plate [82–85]. The raw image in Figure 3-6 was obtained when the fuel cell was operating at a high current density of $2.5 \, \text{A/cm}^2$. In the cathode GDL, saturated water vapour diffused from the cathode catalyst layer towards the cathode flow field. The catalyst layer was at a higher temperature than the flow field ($60^\circ\text{C}$). Hence, water tended to condense in the GDL underneath the land region of the bipolar plate.
3.4 Section summary

In this chapter, we determined the primary cause of false water thicknesses measured during our synchrotron X-ray radiographic images of PEM fuel cells. We presented a procedure to obtain an experimental-specific attenuation coefficient for liquid water, and we presented our image processing technique to correct for sample movement during synchrotron radiography.

A calibration experiment for the liquid water attenuation coefficient was conducted with a custom-made device which contained a water reservoir, which provided multiple, parallel X-ray beam pathways, each with distinct pathway lengths for enabling a precise calibration for liquid water attenuation. The attenuation coefficient of liquid water was determined to be 0.657±0.018 cm\(^{-1}\) with a confidence level of 90%. The difference between the reference and experimentally calibrated attenuation coefficient values was attributed to the X-ray scattering effect and higher harmonics present during our experiments. The determination and application of our attenuation coefficient prevented the underestimation of liquid water by 18.9%.

The false water thickness artefacts caused by sample movement was found to produce a liquid water thickness error of up to 0.93 cm. It also was demonstrated that the calculated water content in the GDL, with a height of 1 pixel, was significantly affected by the movement despite the misleading impression of a seemingly accurate global water distribution. With the newly proposed correction methods, the negative water thickness error was reduced to ±0.04 cm, which has a magnitude comparable to that of the experimental background noise. The sample movement correction has been found to be a crucial step needed before applying the Beer-Lambert law calculation.
3.5 Tables

Table 3-1 The water thickness for each of the regions, R, for the calibration device shown in Figure 3-2.

<table>
<thead>
<tr>
<th>Region Name</th>
<th>Water thickness (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>0</td>
</tr>
<tr>
<td>R₂</td>
<td>0.33</td>
</tr>
<tr>
<td>R₃</td>
<td>0.63</td>
</tr>
<tr>
<td>R₄</td>
<td>0.96</td>
</tr>
<tr>
<td>R₅</td>
<td>1.27</td>
</tr>
<tr>
<td>R₆</td>
<td>1.60</td>
</tr>
</tbody>
</table>
Figure 3-1 Schematic showing the orientation of the fuel cell apparatus and the incident beam during synchrotron X-ray radiographic imaging. Top inset illustrates fuel cell components in the obtained radiograph and the length bar represents 0.4 mm.
Figure 3-2 Illustration of the liquid water attenuation coefficient calibration: (a) Top view of the calibration device. (b) Determination of the attenuation coefficient, and the inset illustrates the processed image of $\ln \left( \frac{I_{dry,c}}{I_{wet,c}} \right)$ for each region.
Figure 3-3 Example synchrotron X-ray radiographic images of an operating PEM fuel cell: (a) Raw, wet state image, and (b) normalized image prior to movement correction. The length bar represents 0.4 mm.
Figure 3-4 Calculated false water thickness caused by the sample movement. Pixel intensities in the dry state and moved wet state images and the calculated water thickness were taken over the white line in the inset.
**Figure 3-5** Calibration curves relating false water thicknesses to distance moved due to sample movement: (a) horizontal direction and (b) vertical direction.
Figure 3-6 Example synchrotron X-ray radiograph after movement correction has been applied. The two regions highlighted were instrumental in the determination of the false water thickness artefact and the correction of it. The length bar represents 0.4 mm.
Figure 3-7 Calculated water thickness values as a function of horizontal position along the x axis for the anode channel region (Region 1 of Figure 3-6) before and after movement correction was applied.
**Figure 3-8** Calculated water thickness values along a selected region (white line) from the Region 2 of Figure 3-6, illustrating the impact of applying the movement correction.
Chapter 4: Two-phase water transport in the PEM fuel cell microporous layer

4.1 Introduction

In this chapter, liquid water breakthrough events were observed in microporous layers (MPLs) of operating polymer electrolyte membrane (PEM) fuel cells through in situ synchrotron X-ray radiography, and measured water thicknesses were used as inputs into a one-dimensional (1D) heat and mass transport model. This 1D model was developed in order to describe the coupled relationship between liquid and vapour transport through the cathode gas diffusion layer (GDL), and the temperature distributions in the fuel cell that accompany the in operando measurements. The current density was increased from 1.4 - 2.4 A/cm², during which MPL breakthrough was observed. Immediately following MPL breakthrough events, the fraction of vapour-phase transport in the total water flux in the MPL increased by up to 6%. Post MPL breakthrough, further increases in current density resulted in increases in thermal and water vapour concentration gradients in the MPL and enhanced this vapour transport. A temperature gradient at the cathode catalyst layer (CL)-MPL interface resulted in a decrease in threshold capillary pressures, and as a result higher liquid water saturations were observed near this interface. The work presented in this chapter is in preparation for submission as a journal manuscript².

4.2 Methodology

4.2.1 Fuel cell hardware and experimental protocol

The PEM fuel cell (used in the study of this chapter) was same as that presented in Section 3.2.1 except for the GDLs. The GDLs in this study consisted of a commercial carbon paper substrate (TGP-H-060, Toray Industries) and a custom, stand-alone crack-free MPL (100 μm-thick). Each GDL was compressed to 85% of its original thickness using polyethylene naphthalate (PEN) spacers.

The PEM fuel cell was controlled using a Scribner 850e fuel cell test station (Scribner Associates Inc.). Hydrogen and air were delivered to the anode and cathode, respectively, at a flow rate of 1 slpm at a backpressure of 2 atm (absolute). A constant-temperature water bath was used to circulate the coolant through both the anode and cathode endplates. Two operating temperatures (60°C and 40°C) were applied so that the effect of operating temperature could be observed. The reactant gases (hydrogen and air) had a RH of 100% at the same temperature as the operating temperature. At 60°C, current densities from 0 to 2.4 A/cm² were applied, and at 40°C current densities from 0 to 1.8 A/cm² were applied. The upper bound of the current densities discussed in this chapter were the upper limits of the fuel cell operation. Each operational set point was held for 5 min before steady state was reached.

4.2.2 Synchrotron visualization and liquid water content

The raw images of the in operando PEM fuel cell were obtained at the Biomedical Imaging and Therapy Bending Magnet (BMIT-BM) 05B1-1 beamline at the Canadian Light Source (CLS)
synchrotron facility in Saskatoon, Canada [76]. Synchrotron X-rays with a photon energy level of 24 keV were applied. A Hamamatsu C11440-22CU charge-coupled device (CCD) camera was employed to achieve a pixel resolution of 6.5 µm/pixel and a temporal resolution of 3 s/frame. Figure 4-1(a) illustrates an example raw radiograph.

The raw images were processed using an image processing technique presented in Chapter 3 to determine the water content in the fuel cell. In the processed image of Figure 4-1(b), the pixel brightness corresponds to the presence of liquid water, and the contour corresponds to the quantity of water traversed by the X-ray beam. Figure 4-1(c) illustrates the through-plane liquid water distribution in the cathode GDL, starting from the cathode CL-MPL interface (through-plane position of the cathode GDL domain = 0 µm) to the cathode flow field (through-plane position of the cathode GDL domain = 240.5 µm). The water thickness at each through-plane position, $X_w$, was calculated by averaging the water thickness in the processed image along the $y$ axis in Figure 4-1(b). As shown in Figure 4-1(c), the MPL region (97.5 µm-thick) and carbon fibre substrate region (143 µm-thick) have been highlighted, where their boundaries were defined based on their observed through-plane thicknesses in the radiographic images.

The measured water thickness was used to calculate the liquid water saturation in each through-plane position. The through-plane porosity of the GDL is presented in Figure 4-1(c). The MPL porosity, $\varepsilon_{mpt}$, was 0.54 for the custom material used in this chapter [86]. The porosity of the substrate, $\varepsilon_{sub}$, was obtained from microscale computed tomography (µCT) image analysis of the compressed GDL [87]. The water saturation was calculated using the following equation:

$$s_f(x) = \frac{X_w(x)}{\varepsilon_f(x) \cdot l}$$

(4.1)
where $s_j$ is the local saturation, $\varepsilon_j$ is the local porosity, $l$ is the length of the active area traversed by the X-ray beam, and $x$ is the position in the through-plane direction. The subscript $j = [1, 2]$, where 1 denotes the MPL, and 2 denotes the substrate. The mean water saturations in the cathode MPL, $s_{mpl}$, and substrate, $s_{sub}$, were calculated by averaging the water saturation values (obtained from Equation 4.1) in the MPL and substrate regions respectively.

4.2.3 Heat and mass transport model

A schematic of the geometry considered for the numerical model is shown in Figure 4-2. The model consists of 3 domains: the anode GDL, membrane, and cathode GDL. Each GDL is composed of an MPL and a substrate.

A 1D heat and mass transport model was developed to predict:

(i) $N_{gdl}^c(x)$, the water vapour diffusion flux at the cathode GDL as a function of through-plane position,

(ii) $N_{pc}^c(x)$, the flux of liquid water and water vapour as a function of through-plane position that was introduced to the cathode GDL through condensation and evaporation, respectively,

(iii) $N_{tot}^c$, the total water flux at the cathode CL-MPL interface, and

(iv) $T_{mpl}^c(x)$, the temperature distribution across the cathode MPL.

This model was used in combination with the X-ray based liquid water measurements to provide a complete description of the two-phase transport behaviour in the MPL.
The following experimentally measured values were used as direct inputs to the 1D model:

(i) Liquid water thicknesses calculated from radiographic images,

(ii) Fuel cell voltage,

(iii) Current density, and

(iv) Operating temperature of the fuel cell.

Values used in this model are presented in Table 4-1. The following assumptions were used:

(i) Fully saturated gases were assumed in all the domains.

(ii) The CL was considered as an interface (of zero thickness) between the membrane and GDL [54].

(iii) The overpotential was converted into thermal energy and introduced at the cathode CL [50].

(iv) The thermal energy related to the phase change of water was only considered in the cathode GDL, since an insignificant amount of liquid water was experimentally measured in the anode.

\[ \phi^a_j (x) = -k_j \frac{dT^a_j (x)}{dx} \]  

(4.2)

where \( \phi^a_j \) is the heat flux \([W/m^2]\), \( T^a_j \) is the local temperature \([^\circ C]\), and \( k_j \) is the thermal conductivity \([W/m/^\circ C]\). The superscript \( a \) denotes the anode GDL. The subscript \( j = [1, 2] \), where 1 denotes the MPL, and 2 denotes the substrate.
The heat flux through the membrane was calculated with the Fourier conduction equation:

$$
\phi_m(x) = -k_m \frac{dT_m(x)}{dx}
$$

(4.3)

where $\phi_m$ is the heat flux [W/m$^2$], $T_m$ is the local temperature [°C], and $k_m$ is the thermal conductivity of the membrane [W/m/°C]. The subscript $m$ denotes the membrane.

The heat flux through the cathode GDL was calculated with the Fourier heat conduction equation:

$$
\phi^c_j(x) = -k^{eff}_j(x) \frac{dT^c_j(x)}{dx}
$$

(4.4)

where $\phi^c_j$ is the heat flux [W/m$^2$], $T^c_j$ is the local temperature [°C], and $k^{eff}_j$ is the effective thermal conductivity [W/m/°C]. The superscript $c$ denotes the cathode GDL.

The effective thermal conductivity of the cathode GDL was calculated using the following equation, which was based on the conductivities of water and the GDL materials [49]:

$$
k^{eff}_j(x) = k_j + s_j(x) \cdot \epsilon_j(x) \cdot k_w
$$

(4.5)

where $s_j$ is the measured saturation (based on our experimental observations and calculated with Equation 4.1), and $k_w$ is the thermal conductivity of liquid water [W/m/°C].

The conservation of energy in the anode GDL can be written as

$$
\frac{d\phi^a_j(x)}{dx} = 0
$$

(4.6)

In the membrane, the conservation of energy can be written as
\[
\frac{d\phi_m(x)}{dx} = 0
\]  

(4.7)

In the cathode GDL, the conservation of energy relation was:

\[
\frac{d\phi_f^c(x)}{dx} = -L_f \cdot r_{pc}(x)
\]  

(4.8)

where \(L_f\) is the specific latent heat for water condensation and evaporation [J/mol], and \(r_{pc}\) is volumetric rate for water phase change [mol/m\(^3\)/s], which is calculated based on the conservation of water vapour (Equation 4.19).

The following are the boundary conditions applied to the anode GDL:

\[
T_j^a(x = x_0) = T_{ch}
\]  

(4.9)

\[
T_j^a(x = x_{gdt}^a) = T_m(x = x_{gdt}^a)
\]  

(4.10)

\[
\phi_j^a(x = x_{gdt}^a) = \phi_m(x = x_{gdt}^a)
\]  

(4.11)

where \(T_{ch}\) is temperature at the flow field (the operating temperature of the fuel cell).

The following conditions were applied to the membrane-cathode GDL boundary:

\[
T_m(x = x_m) = T_j^c(x = x_m)
\]  

(4.12)
\[ \phi_m(x = x_m) = \phi_j^c(x = x_m) + i \cdot (E_{ref} - E) + L_f \cdot (N_{tot}^c - N_{gdt}^c(x = x_m)) \] (4.13)

where \( i \) is the measured current density \([\text{A/m}^2]\), \( E \) is the measured voltage \([\text{V}]\), \( E_{ref} \) is the reference electrical potential \([\text{V}]\), \( N_{tot}^c \) is the total water flux at the cathode CL traveling towards the cathode flow field \([\text{mol/m}^2/\text{s}]\), and \( N_{gdt}^c(x = x_m) \) is the water vapour flux due to diffusion at the cathode CL \([\text{mol/m}^2/\text{s}]\). In Equation 4.13, the second term on the right-hand side represents the heat generated due to the electrochemical reactions at the CL, and the third term represents the heat generation from water condensation at the cathode CL-MPL interface.

The following condition was applied to the cathode GDL-flow field boundary:

\[ T_{gdt}^c(x = x_{gdt}) = T_{ch} \] (4.14)

4.2.3.2 Water transfer calculation

In the cathode GDL, the 1D molar flux for water vapour diffusion, \( N_{gdt}^c \) \([\text{mol/m}^2/\text{s}]\), was given by Fick’s first law of diffusion as

\[ N_{gdt}^c(x) = -D_{eff}^c(x) \frac{dC(x)}{dx} \] (4.15)

where \( D_{eff}^c \) is the effective diffusion coefficient for water vapour \([\text{m}^2/\text{s}]\), \( C \) is the molar concentration of water vapour \([\text{mol/m}^3]\). The effective diffusion coefficient was calculated with the Bruggeman equation as follows [54,88]:

53
\[ D^{\text{eff}}(x) = D_{vap} \cdot [\varepsilon(x) \cdot (1 - s(x))]^n \]  

(4.16)

where \( D_{vap} \) is the bulk diffusion coefficient for water vapour in air [m\(^2\)/s], and \( n = 1.5 \). Several authors [46,53,83,89–92] have reported that the Bruggeman equation overestimates the diffusion of gaseous species in the GDL when applying the Bruggeman equation to the whole GDL based on the species concentrations on both sides of the GDL. However, Equations 4.15 and 4.16 were applied locally over a material thickness of 6.5 \( \mu \text{m} \), the same value as the radiograph pixel size. The Bruggeman equation was verified based on a GDL material thickness of 10 \( \mu \text{m} \) using our pore network model, OpenPNM [93].

The concentration of water vapour, \( C \) [mol/m\(^3\)], can be expressed using the ideal gas law as follows [49]:

\[ C(x) = \frac{P_{\text{sat}}(T)}{R \cdot (T(x) + 273)} \]  

(4.17)

where \( R \) is the gas constant [8.314 J/°C/mol], and \( P_{\text{sat}} \) is the saturation water vapour pressure [Pa]. The saturation water vapour pressure was calculated using the Clausius-Clapeyron [94] as follows:

\[ P_{\text{sat}}(T) = 1.013 \times 10^5 \times \exp \left[ 0.018 \times 2.26 \times 10^6 \times \left( \frac{1}{373} - \frac{1}{T(x) + 273} \right) \right] \]  

(4.18)

The volumetric rate of phase change (evaporation or condensation) introduced in Equation 4.8 was calculated based on the conservation of water vapour, using the following equation [95]:

\[ r_{pc}(x) = \frac{dN_{g\text{at}}(x)}{dx} \]  

(4.19)
where negative values indicate that condensation takes place, and positive values indicate that evaporation takes place. The water flux due to phase change, \( N_{pc}^c \) [mol/m\(^2\)/s], was the water vapour diffusion between two adjacent through-plane positions, calculated as follows:

\[
N_{pc}^c(x) = N_{gdl}^c(x + \Delta x) - N_{gdl}^c(x)
\]  

(4.20)

where \( \Delta x \) is 6.5 \( \mu \)m in the work presented in this chapter, which is the same value as the radiograph pixel size.

The total water flux at the cathode CL, \( N_{tot}^c \), for Equation 4.13 was determined based on the mass balance of the electro-osmotic drag, water produced by the electrochemical reaction, and vapour diffusion across the membrane [5]:

\[
N_{tot}^c = n_d \frac{i}{F} + \frac{i}{2F} \left( C(x_{gdl}^a) - C(x_m) \right) \frac{D_m}{L_m}
\]  

(4.21)

where \( n_d \) is the electro-osmotic drag coefficient, \( F \) is the Faraday constant [96487 C/mol], \( C(x_{gdl}^a) \) [mol/m\(^3\)] is the water vapour concentration at the anode CL, and \( C(x_m) \) [mol/m\(^3\)] is the water vapour concentration at the cathode CL. The water vapour diffusion coefficient in the membrane, \( D_m \) [m\(^2\)/s], was calculated using [96,97]

\[
D_m = 4.17 \times 10^{-8} \left[ 1 + 161 \exp (-\lambda) \right] \exp \left( \frac{-2436 \times 2}{T(x_{gdl}^a) + T(x_m) + 546} \right)
\]  

(4.22)

where \( \lambda \) is the water-uptake (14 with the RH of 100% [98,99]), \( T(x_{gdl}^a) \) [°C] is the temperature at the anode CL, and \( T(x_m) \) [°C] is the temperature at the cathode CL.
4.2.3.3 Model resolution

The flow chart diagram used to solve the model is presented in Figure 4-3. An absence of water phase changes was assumed for the initial condition of the model \( r_{pc} = 0 \) in Equation 4.8 and \( N_{tot}^C - N_{gdt}^C(x = x_m) = 0 \) in Equation 4.13). For each iteration Equations 4.2 to 4.22 were solved, and the computed water flux due to condensation at the cathode CL, \( N_{tot}^C - N_{gdt}^C(x = x_m) \), was compared to the initial value used at the beginning of the iteration as the convergence criterion. The convergence criterion was set such that the computed value fell within 0.5% of the initial value. This procedure was repeated until convergence was achieved.

4.3 Results and discussion

4.3.1 Evidence of liquid transport in the MPL from measured radiographs

The steady state mean water saturations in the cathode MPL, \( \bar{s}_{mpl} \), and substrate, \( \bar{s}_{sub} \), measured through X-ray radiography are presented in Figure 4-4 as a function of current density. As shown in Figure 4-4, the MPL saturation increased with the current density, and the MPL saturation stabilized at 1.4 A/cm\(^2\) and 0.3 A/cm\(^2\) for 60°C and 40°C, respectively. For both operating temperatures, this liquid water saturation stabilization provided an indication that breakthrough events had occurred in the MPL, and these breakthrough events coincided with the current density associated with the onset of the liquid water stabilization (1.4 A/cm\(^2\) and 0.3 A/cm\(^2\) for 60°C and 40°C, respectively) \([6,32–34]\). These breakthrough events understandably occurred at different current densities (1.4 A/cm\(^2\) and 0.3 A/cm\(^2\)) due to the vast difference in operating temperatures (60°C and 40°C, respectively). The observation of breakthrough events themselves
is highly significant as they provide support for the presence of liquid water transport pathways in the MPL, thereby enabling liquid water to travel from the CL-MPL interface to the MPL-substrate interface on the cathode side.

The measured liquid water saturation in the substrate also increased during MPL breakthrough events (Figure 4-4). At 60°C, the liquid water saturation in the substrate increased from 0.1 to 0.21 over the period in which MPL breakthrough was taking place and the stabilization of liquid water saturation in the MPL. Likewise, at 40°C the liquid water saturation in the substrate increased from 0.2 to 0.25 during and after MPL breakthrough. This increase in liquid water in the substrate is attributed to the liquid water that traveled from the CL-MPL interface across the MPL breakthrough pattern and released into the substrate at the MPL-substrate interface.

4.3.2 Analysis of MPL liquid water distributions

4.3.2.1 Experimental: liquid water distribution in the MPL from measured radiographs

In Figure 4-5, the distribution of measured liquid water in the MPL is shown as liquid water thickness as a function of through-plane position and current density. This liquid water thickness increases across the through-plane position with increasing current density. There was a significant difference between the water thickness at the CL-MPL interface at breakthrough for 60°C (0.19 cm) and at 40 °C (0.13 cm). Overall, the liquid water content was uniformly higher for 60°C compared to 40°C between $x = 0 - 30$ µm. The impact on CL-MPL liquid water thickness at breakthrough and the content near the CL-MPL interface illustrates the strong influence of operating temperature on liquid water transport on the MPL. It is also noteworthy
that relatively higher amounts of liquid water were observed in the MPL at the MPL-substrate interface in the GDL. In the next section, the numerical results from the transport model were used to predict the transport mechanisms that would have led to these measured liquid water distributions shown in Figure 4-5.

4.3.2.2 Numerical: quantification of water flux due to phase change

The 1D numerical heat and mass transport model presented in Section 4.2.3 was used to predict the water flux of phase change (evaporation or condensation), \( N_{pc}^C(x) \), that would take place at each through-plane position in the MPL. The water flux of phase change is presented in Figure 4-6 (left-hand side y axis), whereby negative values correspond to a rate of liquid water flux introduced via condensation, and positive values correspond to a rate of water vapour flux introduced via evaporation. At the cathode CL-MPL interface, liquid water flux due to condensation was determined to be \( N_{pc}^C(x = 0 \mu m) = -0.175 \text{ mol/m}^2/\text{s} \) for 60°C and \( N_{pc}^C(x = 0 \mu m) = -0.042 \text{ mol/m}^2/\text{s} \) at 40°C, which are condensation induced water fluxes that exceed those at other areas in the MPL by 1 order of magnitude.

The large quantity of water flux due to condensation at the CL-MPL interface indicates that a large portion of the total water flux at the cathode CL, \( N^C_{tot} \) (calculated using Equation 4.21) was introduced into the MPL as liquid water. In other words, a large quantity of water introduced at the CL-MPL interface immediately condensed close to the CL layer, and this condensed water blocked transport pathways for water vapour diffusion (Equation 4.16). At the lower operating temperature, these blocked pathways exacerbated the conditions that encouraged condensation, including the lower relative temperature and low porosity. Therefore, the cathode CL-MPL
interface was dominated by condensation compared to the other regions of the MPL, and this relatively heavily saturated region acted as the inlet for liquid water entering the cathode MPL.

In the region of the MPL between 5 - 60 µm, there are two key observations that can be seen when comparing Figures 4-5 and 4-6. The first observation in this region is that the measured local liquid water content (as shown in Figure 4-5) is increasing with increasing current density, even though water condensation is not predicted (Figure 4-6). Therefore, it can be concluded that liquid water transport from the CL-MPL interface resulted in the accumulation of liquid water in this region. The second observation is that the local water vapour diffusion flux (Figure 4-6, 5 - 60 µm) was greater than the water vapour diffusion flux introduced at the CL-MPL interface. This increase in local water vapour flux can be attributed to the evaporation of local liquid water (Figure 4-6) present in this region (Figure 4-5, between 5 - 60 µm).

Condensation was prevalent in the final region of the MPL nearest the MPL-substrate interface (60 - 90 µm), as shown in Figure 4-6. This condensation can be attributed to the lower relative temperature compared to the bulk of the MPL, which was expected due to the thermal contact resistance between the MPL and carbon substrate [100]. This accumulating liquid water in this region served as a potential inlet to the substrate, where droplets would have tended to migrate towards the relatively larger pores of the substrate [5,50].
4.3.3 Coupled liquid phase and vapour phase transport

4.3.3.1 Effect of temperature on vapour-phase transport

The total water flux at the cathode CL-MPL interface, $N_{tot}^c$ defined by Equation 4.21 and the water vapour diffusion flux at the cathode MPL-substrate interface, $N_{diff,mpl-sub}^c$ defined by Equation 4.15, are presented as a function of current density in Figure 4-7. The difference between these two values is the quantity of liquid water flux across the MPL. The ratio of vapour diffusion flux to the total water flux, $N_{diff,mpl-sub}^c/N_{tot}^c$, is also presented in Figure 4-7 (right-hand side y axis). As can be seen in Figure 4-7, a maximum of 27% more vapour transported across the MPL at 60°C compared to 40°C. This observation was expected, as the water vapour diffusion coefficient increases with increasing temperature [101].

4.3.3.2 Relationship between vapour and liquid phase transport in the MPL

As shown in Figure 4-7, approximately 40% of the total water flux in the MPL transported in the vapour phase at current densities between 0.1 - 0.8 A/cm$^2$ at 60°C, with the remainder in liquid phase. Prior to breakthrough at these current densities, the presence of liquid water can be attributed strictly to condensation. The fraction of vapour phase transport decreased from 34% to 17% between current densities 0.8 to 1.4 A/cm$^2$ (60°C), as shown in Figure 4-7. This decrease in vapour diffusion flux coincides with the increase in MPL liquid water saturation from 0.9 to 0.19 (shown in Figure 4-5).

The fraction of vapour-phase transport increased to 23% as the current density increased from 1.4 to 2.4 A/cm$^2$ (60°C) (Figure 4-7). Post breakthrough, the liquid water saturation does not
experience any significant change, even when the current density increases (Figure 4-4). At 1.4 A/cm$^2$ (60°C), the water vapour concentration gradient at the MPL-substrate interface was calculated to be 6.9 mol/m$^3$/mm, which led to a vapour diffusion flux of 0.037 mol/m$^2$/s. By comparison, at 2.4 A/cm$^2$ (60°C) the water vapour concentration gradient increased to 16.1 mol/m$^3$/mm due to the increased local temperature. This concentration gradient at 2.4 A/cm$^2$ resulted in a vapour diffusion flux of 0.085 mol/m$^2$/s, which was 130% higher than that at 1.4 A/cm$^2$. Table 4-2 presents a summary of the temperature, water vapour concentration gradient, and the resulting vapour diffusion flux at the MPL-substrate interface. Hence, increases in current density post breakthrough are accompanied by an increase in water vapour flux. Therefore, the establishment of a breakthrough event facilitates an increase in vapour phase transport.

4.3.3.3 Effect of temperature on the liquid-phase transport

The average water saturation distributions in the cathode MPL at breakthrough densities, 1.4 A/cm$^2$ for 60°C and 0.3 A/cm$^2$ for 40°C, are shown in Figure 4-8. A maximum difference in saturation (0.11) was observed between the distributions for 60°C and 40°C. Since the same fuel cell hardware and materials were used, this result illustrates the influence of temperature on the saturation distribution. The spatial distribution of temperature is also shown on Figure 4-8 (right-hand side y axis), and the higher temperatures at the CL-MPL interface would also be expected to facilitate relatively higher saturations since capillary pressure decreases with increasing temperature [40,41]. At the through-plane position of 60 μm, a capillary barrier was observed at both operating temperatures where the saturation was ~0.06. This can be accounted for by the
presence of a critical MPL pore size encountered by the invading liquid water. At this capillary barrier, a large capillary pressure would be required for liquid water to overcome the threshold capillary pressure and invade the region beyond 60 µm. Once the liquid water reached the critical threshold capillary pressure required to penetrate the capillary barrier, the remainder of the MPL would have been invaded.

4.4 Section summary

In this chapter, in operando, in situ synchrotron X-ray radiographic analysis was combined with a 1D heat and transport model to determine the interplay between water transport mechanisms in a crack-free MPL. Operating temperatures of 60°C and 40°C were selected so that distinctive two-phase transport behaviours could be identified across the MPL. By analyzing the relationship between the vapour phase and liquid phase transport in the MPL, it was found that the liquid-phase water transport dominated the cathode MPL with up to 83% of the total water transport at 60°C and 92% at 40°C. Furthermore, MPL breakthrough was found to facilitate the increase in vapour-phase transport with increasing current density.

At breakthrough, the mean saturations at the cathode MPL were measured to be 0.19 and 0.17 at operating temperatures of 60°C and 40°C, respectively. The variance was attributed to the distinctive temperature distributions at the MPL. Specifically at 60°C, the elevated temperature near the cathode CL-MPL interface decreased the local capillary pressure, which led to a higher liquid water content. Hence, the large temperature gradient in the MPL resulted in the more flooded cathode MPL at 60°C compared to 40°C.
4.5 Tables

**Table 4-1** Numerical modelling parameters.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
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</thead>
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<tr>
<td>Geometry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_{mpl}$</td>
<td>Porosity of MPL [86]</td>
<td>-</td>
<td>0.54</td>
</tr>
<tr>
<td>$l$</td>
<td>Length of active area</td>
<td>cm</td>
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<td>$L_{m}$</td>
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<td>$X_w$</td>
<td>Measured water thickness</td>
<td>cm</td>
<td>-</td>
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</tr>
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<td>W/m°C</td>
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<td>Diffusion</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>Diffusivity for water vapour in air [101]</td>
<td>m²/s</td>
<td>3.15E-5 (60°C), 2.77E-5 (40°C)</td>
</tr>
</tbody>
</table>
Table 4-2 Calculated temperature, water vapour concentration gradient, and vapour diffusion flux at the cathode MPL-substrate interface.

<table>
<thead>
<tr>
<th>Operating temperature, °C</th>
<th>Current density, A/cm²</th>
<th>( T^c_{mpl-sub} ), °C</th>
<th>( \frac{dc^c_{mpl-sub}}{dx} ), mol/m³/mm</th>
<th>( N^c_{diff, mpl-sub} ), mol/m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.4</td>
<td>61.3</td>
<td>6.9</td>
<td>0.037</td>
</tr>
<tr>
<td>60</td>
<td>2.4</td>
<td>62.9</td>
<td>16.1</td>
<td>0.085</td>
</tr>
<tr>
<td>40</td>
<td>0.3</td>
<td>40.3</td>
<td>0.7</td>
<td>0.004</td>
</tr>
<tr>
<td>40</td>
<td>1.8</td>
<td>41.9</td>
<td>5.2</td>
<td>0.028</td>
</tr>
</tbody>
</table>
Figure 4-1 Water content measurement at 0.3 A/cm$^2$ (40°C): (a) raw image obtained from synchrotron X-ray radiograph, (b) processed image, and (c) water thickness profile and porosity of the cathode GDL. The length bar in (a) represents 0.4 mm.
Figure 4-2 Schematic of the 1D heat and mass transport model in the fuel cell.
Input $X_w, E, i, T_{ch}, r_{pc} = 0$ and $N_{tot}^c - N_{gdt}^c(x = x_m) = 0$

Solve heat flux

Solve temperature profile

Solve water transfer flux

Solve water phase change rate

Check convergence: $N_{tot}^c - N_{gdt}^c(x = x_m)$

No

Yes

Output results

**Figure 4-3** Flow chart diagram illustrating the model calculation process.
Figure 4-4 Measured mean water saturations in the cathode MPL and substrate.
Figure 4-5 Measured water thickness at the cathode MPL as a function of current density for the following operating temperatures: (a) 60°C and (b) 40°C.
Figure 4-6 Simulated water fluxes of water phase change and vapour diffusion at the cathode MPL at the following operating temperatures: (a) 60°C and (b) 40°C. The solid line represents the water flux of phase change and the dashed line represents the water flux of vapour diffusion.
Figure 4-7 Calculated vapour diffusion flux and total water flux at the cathode CL-MPL interface (left-hand side y axis), and the percentage of vapour diffusion with respect to the total water flux (right-hand side y axis)
**Figure 4-8** Measured water saturation and the calculated temperature distributions at the cathode MPL at breakthrough.
Chapter 5: Conclusions

5.1 Summary of findings

In this thesis, the two-phase water transport mechanism in a custom-made crack-free MPL was investigated through in situ polymer electrolyte membrane (PEM) fuel cell experiment. Synchrotron X-ray radiography was used to visualize and quantify the concurrent liquid water. A literature review on the role of microporous layer (MPL) in water management and the transport mechanisms whereby water moves through the MPL was conducted. Besides, the sources of inaccuracies from the synchrotron X-ray imaging was surveyed.

In Chapter 3, the imaging technique developed to obtain high-resolution water distribution during the in situ PEM fuel cell experiment was introduced. This technique consisted of a calibration experiment and an advanced image processing technique. The calibration aimed to experimentally determine the attenuation coefficient for liquid water at a synchrotron beamline to account for the effects of scattering and higher harmonics. The image processing technique addressed the image artefacts due to the sample movement. The findings and the results of the measured water content were summarized as follow:

• The attenuation coefficient of liquid water was experimentally determined to be $0.657\pm0.018 \, \text{cm}^{-1}$ at 20 keV, which prevented an underestimation of liquid water by 18.9%.

• The fuel cell was found to move from its original location by up to 7.5 µm (1.7 pixels) in both the horizontal and vertical directions. The movement produced a false water
thickness error of up to 0.93 cm, 9% higher than the maximum amount water that the apparatus could contain.

- False water thickness error of negative values was detected with the cathode gas diffusion layer (GDL), which was attributed to horizontal movement. Without proper correction, the water thickness results is useable despite the misleading impression of a seemingly accurate global water distribution.

- With the movement correction methods developed, the false water thickness error was reduced to ±0.04 cm, which has a magnitude comparable to that of the experimental background noise.

In Chapter 4, the two-phase water transport mechanism was studied through an in situ PEM fuel cell experiment with synchrotron X-ray radiography visualization. A one-dimensional (1D) heat and mass transport model was developed. The model used the measured liquid water distribution and the monitored performance data as inputs, and the model was designed to simulate the water vapour diffusion and temperature distribution. The interplay between the liquid and vapour transport mechanisms in the crack-free MPL was observed and analyzed. The effect of temperature on the water transport in the MPL was reported. The findings and conclusions were presented as follow:

- The liquid-phase water transport dominated the cathode MPL with up to 83% of the total water transport at 60°C and 92% at 40°C.

- The MPL breakthrough of liquid water was found to facilitate the increase in vapour-phase transport with increasing current density.
• At breakthrough, a large temperature gradient in the MPL (2.1°C) was measured at the operating temperature of 60°C compared to that at 40°C (0.4°C). This large temperature gradient led to the high liquid water saturation in the cathode catalyst layer (CL)-MPL interface at 60°C (0.40) compared to that at 40°C (0.29).

The work presented in Chapter 3 has provided valuable insight into the impact of microscale sample movement on false water thickness detection for PEM fuel cell researchers using synchrotron X-ray facilities. This work also provides a useful tool for synchrotron researchers to address image movement and the scattering and higher harmonics that can lead to artefacts in a broader array of applications that may be the focus of X-ray imaging. In Chapter 4, the findings suggested that the temperature gradient should be introduced in two-phase flow modeling and pore network modeling due to its impact on liquid water distributions. The observations provide valuable insight into the inlet conditions that are experienced by the GDL substrate at the onset of liquid water accumulation.

5.2 Future works

The following suggestions and recommended works are provided from this thesis:

(i) Design the fuel cell component for movement correction during synchrotron X-ray imaging:

A metal (such as aluminum) rectangular block is suggested to be implanted into the graphite bipolar plate of a PEM fuel cell. This metal block would be located in the field of view during the imaging process. The metal component would result in a low-intensity
shape with sharp edges in the collected radiographic images due to its high attenuation coefficient compared to water and the fuel cell materials [72]. Hence, with these edges present in the image, the micrometer-scale movement can be tracked without the impact of liquid water production during the experiment.

(ii) Determine the attenuation coefficient at various energy levels:

X-ray radiography with energy levels ranging from 2 - 24 keV has been reported to be used to visualize water in the PEM fuel cell [6,17,22,66,104–106]. Based on this thesis, calibration experiment is required for accurate quantification of liquid water. Hence, calibration experiments of the attenuation coefficient at the aforementioned energy levels is recommended. The results would provide valuable insight on the energy level selection for synchrotron-based imaging for PEM fuel cell diagnostics.

(iii) Investigate the effect of temperature gradient on the liquid water distribution in MPL:

This thesis demonstrated that the temperature gradient impacted the liquid water distribution in the MPL by affecting the capillary pressure. The elevated temperature has been shown to produce two countering effects on the liquid water accumulation: reducing liquid water content by enhancing vapour-phase transport and increasing liquid water content by causing a lower capillary pressure near the CL-MPL interface. The optimal temperature gradient in the MPL for mitigating the liquid water accumulation is recommended.
References


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