Investigation of Surface Properties and Heterogeneity in Gas Diffusion Layers for Polymer Electrolyte Membrane Fuel Cells

by

J. Zachary Fishman

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Mechanical and Industrial Engineering
University of Toronto

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Abstract

The development of improved water management strategies for the polymer electrolyte membrane fuel cell (PEMFC) could stand to benefit from an improved understanding of the surface and internal structure of the gas diffusion layer (GDL). The GDL is a fibrous porous material enabling mass transport between the PEMFC catalyst layer and flow fields. Fluorescence-based visualizations of liquid water droplet evaporation on GDL surfaces were performed to investigate water droplet pinning behaviours. The heterogeneous in-plane and through-plane porosity distributions of untreated GDLs were studied using computed tomography visualizations. The through-plane porosity distributions were utilized to calculate heterogeneous local tortuosity, relative diffusivity, and permeability distributions. Finally, the heterogeneous through-plane porosity distributions of GDLs treated for increased hydrophobicity were investigated. This work provides new insight into GDL material properties to better inform future PEMFC models.
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### Abbreviations & Nomenclature

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<tr>
<td>$D_{\text{eff}}$</td>
<td>Effective diffusivity</td>
</tr>
<tr>
<td>$D_{AB}$</td>
<td>Binary diffusivity</td>
</tr>
<tr>
<td>$\Delta f(\epsilon)_{\text{avg}}$</td>
<td>$f(\epsilon)<em>{\text{bulk,avg}} - f(\epsilon)</em>{\text{core,avg}}$</td>
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<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>IP</td>
<td>In-plane</td>
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<td>$K$</td>
<td>Permeability</td>
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<tr>
<td>$\Delta K_{\text{avg}}$</td>
<td>$K_{\text{bulk,avg}} - K_{\text{core,avg}}$</td>
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<tr>
<td>MIP</td>
<td>Mercury intrusion porosimetry</td>
</tr>
<tr>
<td>MPL</td>
<td>Micro-porous layer</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer electrolyte membrane fuel cell</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>$r_f$</td>
<td>Carbon fibre radius</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>TP</td>
<td>Through-plane</td>
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<tr>
<td>$t_0$</td>
<td>Uncompressed thickness</td>
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### Greek Letters

<table>
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<tr>
<td>$\alpha$</td>
<td>TS model exponent</td>
</tr>
<tr>
<td>$\Delta \epsilon_{\text{avg}}$</td>
<td>$\epsilon_{\text{bulk,avg}} - \epsilon_{\text{core,avg}}$</td>
</tr>
<tr>
<td>$\Delta \tau_{\text{avg}}$</td>
<td>$\tau_{\text{bulk,avg}} - \tau_{\text{core,avg}}$</td>
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<tr>
<td>$\epsilon$</td>
<td>Porosity</td>
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<tr>
<td>$\epsilon_p$</td>
<td>Percolation threshold porosity</td>
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<tr>
<td>$\tau$</td>
<td>Tortuosity</td>
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<td>$\mu$CT</td>
<td>Microscale computed tomography</td>
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### Subscripts

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<tr>
<td>slope</td>
<td>Slope of the transitional surface region</td>
</tr>
<tr>
<td>bulk, avg</td>
<td>Average over the entire bulk volume</td>
</tr>
<tr>
<td>core, avg</td>
<td>Average in the core region</td>
</tr>
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1.0 Introduction

1.1 General background & motivation
The hydrogen polymer electrolyte membrane fuel cell (PEMFC) is an emerging energy conversion technology that only releases heat and water as by-products. Product water, as well as water from humidified inlet gases, must be carefully managed for improving the performance and lifetime of the PEMFC. An insufficient amount of water in the fuel cell can lead to membrane dehydration and ionic conductivity losses; however, excess liquid water in the gas channels and gas diffusion layer (GDL) can inhibit the transport of oxygen to the catalyst layer reaction sites. Liquid water flooding especially inhibits transport at high current densities [1]. As shown in the schematic of the PEMFC cathode (Fig. 1.1), liquid water travels through the GDL until droplets emerge in the gas channel on the GDL. Even though the GDL is typically treated with polytetrafluoroethylene (PTFE) to increase its hydrophobicity for the enhancement of water removal, in practice, cathodic flooding still occurs [1].

The GDL is an electronically conductive and porous material composed of an arrangement of carbon fibres approximately 7-10μm in diameter [2]. Scanning electron microscopy (SEM) images help to illustrate the topographical distinctions between the three main categories of commercially available GDLs: paper (Fig. 1.2 (a)), non-woven felt (Fig. 1.2 (b)), and woven cloth (Fig. 1.2 (c)). The paper GDL consists of a quasi-random dispersion of straight carbon fibres with an overall alignment in a single machine direction caused by the manufacturing step in which fibres are drawn and deposited.

The non-woven felt GDL, alternatively known as a fleece mat, also consists of randomly dispersed fibres at the microscale with an overall machine direction at the macroscale. However, in contrast to paper GDL, the felt carbon fibres exhibit a highly tortuous orientation. This is the result of the hydro-entanglement process used in manufacturing, where fine water jets are employed to bend the fibres into the through-plane direction of the GDL [2].

The woven cloth GDL is a textile consisting of approximately 200-300 carbon fibres bundled per yarn [3]. Each individual yarn is twisted and doubled with another yarn for added strength in weaving [2]. The cloth GDL is a plain weave, which is composed of yarns that are regularly
interlaced at right angles [4]. Cloth GDL exhibits surface features with longer length scales compared to the surface features of paper or felt GDL, which are composed of individual fibres. The reader is referred to Mathias et al. [2] for a detailed overview of GDL manufacturing processes and available characterization methods.

1.2 Organization of the Thesis
The focus of this thesis is to investigate the surface and internal structure of the GDL to inform the development of improved water management strategies and numerical models. This thesis is organized into 5 chapters. The background, motivation, and an overview of the contributions of the thesis are presented in this Chapter 1. Chapter 2 describes an investigation of water droplet pinning behaviour on the surfaces of the different GDL microstructures. In Chapter 3, microscale computed tomography is utilized to examine the in-plane and through-plane local porosity distributions of untreated paper, felt, and cloth GDL. A model is applied to the through-plane porosity distributions of paper and felt GDL in Chapter 4 to determine the corresponding through-plane local tortuosity, relative diffusivity, and permeability distributions. Changes in the local porosity distribution of paper GDLs with hydrophobic treatment are determined Chapter 5. Finally, conclusions and possibilities for future research are presented. In this work, the figures and tables are provided together at the end of each chapter.

1.3 Objective
The objective of this work is to investigate the microstructural properties of the PEMFC GDL, including the effect of the surface structure on droplet pinning and the through-plane (TP) heterogeneity. The scope of this work includes uncompressed GDLs. Initially, the surface roughness, porosity distributions, and transport properties of untreated GDLs are investigated. PTFE treated GDLs are studied to investigate their variations in porosity distributions. The effects of the micro-porous layer (MPL) are not investigated in this work. It is also important to note that an emphasis is placed on the TP direction of the GDL is this work.

1.4 Contributions
The specific contributions are summarized in the following list:

Water droplet pinning on GDL surfaces
- Observed side view images of the liquid-gas-solid interface during liquid water droplet evaporation on various untreated GDLs
-Measured the change in contact diameter as a function of evaporative volume loss to quantify the unpinning rates of droplets
-Correlated the contact diameter pinning behaviour to the material roughness, which is measured with profilometry
-Found that the carbon fibre paper exhibits the smallest average roughness, compared to felt and cloth yarn, and the strongest degree of pinning
-Found that GDL materials exhibit Cassie-Baxter wetting behaviour, and reduced GDL roughness promotes water shedding

**Heterogeneous in-plane and through-plane porosity distributions of untreated GDLs**
- Made a first comparison of the in-plane and through-plane heterogeneous porosity distributions of paper, felt, and cloth GDLs
-Presented a methodology to analyze the through-plane and in-plane porosities of various materials
-Identified high porosity transitional surface regions and core regions for each GDL
-Provided insight into the manufacturing process employed for GDLs

**Heterogeneous local tortuosity, relative diffusivity, and permeability distributions**
- Applied a model to the through-plane porosity distributions of paper and felt GDL
-Calculated the local distributions of tortuosity ($\tau$), relative diffusivity ($f(\phi)$), and single phase permeability ($K$)
-Determined that the heterogeneous distributions of relative diffusivity and permeability strongly correspond to measured heterogeneous porosity distributions, exhibiting transitional surface and core regions
-Found reasonable agreement between the average transport properties of the GDL core region with bulk values from literature

**Heterogeneous through-plane porosity distributions of PTFE treated GDLs**
-Measured the through-plane porosity distributions of PTFE-treated paper GDLs from high resolution microscale computed tomography visualizations
-Compared PTFE-treated porosity distributions to untreated GDL porosity distributions to determine the location of PTFE in the GDL and its effect on the structure
• Found that PTFE resulted in decreased local porosities near the surface regions and non-uniform distributions of PTFE throughout the material
• Provided insight that more attention should be given to the shape of through-plane porosity distribution, rather than the average bulk porosities, due to the observed variations attributed to batch-specific manufacturing

The work presented in this thesis resulted in two publications [5,6], one submitted manuscript [7], and one manuscript in preparation [8] investigating the surface and internal structure of the GDL.
Fig. 1.1. Schematic of a hydrogen PEMFC cathode cross-section with a water droplet in the gas channel (not to scale). The GDL carbon fibres in this schematic are represented with an SEM image cross-section of cloth GDL.
Fig. 1.2. SEM images of GDL materials: (a) Toray TGP-H-120 paper, (b) SGL Sigracet 10AA felt, (c) AvCarb 1071HCB cloth.
2.0 Droplet pinning by PEM fuel cell GDL surfaces

2.1 Introduction
In addition to understanding the mass transport behaviour within the GDL [9,10], an understanding of how the GDL surface affects droplet pinning is also required for predictive modeling and design. The GDL is an electronically conductive and porous material, which is typically treated with poly(tetrafluoroethylene) (PTFE) to increase its hydrophobicity for the enhancement of water removal [1]. Several researchers have investigated liquid water droplet detachment behaviour in a flow field through modelling [11,12] and experimental studies [11-15]. Droplets on the surface of the GDL initially begin with liquid water emerging from a preferential pore to form a growing droplet. Once the droplet reaches a critical size, it detaches from the surface and flows downstream [16,17]. Droplets may also grow until they are wicked to a channel wall and slowly removed through film flow. The most undesirable scenario for PEMFC operation is when droplets coalesce to form water slugs that completely block the gas channel [17]. Increased air flow rates are required for purging droplets and slugs from the flow field, resulting in additional parasitic power losses. Water droplets that pin strongly to the GDL are less likely to detach and be removed during gaseous purges. These pinned droplets will result in the coalescence of liquid water droplets in a channel, thereby increasing the presence of slugs and flooding of the PEMFC cathode [13].

Previous studies in literature have been conducted to compare material property response [1,2,9,18,19], water transport behaviour [1,2,9-18,20-28], and resulting fuel cell performance [1,2,11,16,17,20-23] of various GDL materials. Bazylak [29] provided a review of liquid water visualization in PEMFCs. Theodorakakos et al. [11] investigated droplet detachment in an air flow on paper and cloth GDLs with numerical and experimental analysis, and they found that droplets detached more readily from cloth than paper GDL. Water droplet transport and detachment due to air flow has been investigated through experimental [14] and numerical [30] studies with various GDL microstructures. Zhu et al. [30] developed a volume of fluid 3D computational fluid dynamics model that explored the variation of the droplet contact angle, channel air velocity, water injection velocity, and water inlet pore size. Kumbur et al. [14] developed a force balance analysis of a droplet with air flow, and they incorporated this force balance with characteristic channel and droplet parameters, such as channel height and droplet
contact angle hysteresis of droplets in motion. However, in [31], little difference was observed between the advancing and receding contact angles for droplets forming in the presence of air flow in an air-breathing PEMFC.

Spernjak et al. [22] compared the employment of various GDL microstructures in an optically transparent PEMFC and found that performance improved with the use of untreated cloth compared to untreated paper. While their polarization curves provided information about mass transport losses at high current densities, direct correlations between droplet-specific water transport behaviour and GDL microstructure were not presented. In-situ water build-up is also investigated by Ous and Arcoumanis [31] with a dual camera system to capture droplets from both the top and side views in a custom-made flow channel plate under various operating conditions. Adjusting the reactant stoichiometries was found to have a large impact on droplet aggregation and current density, and increasing the operating temperature was found to be effective for droplet removal [31]. In-situ observations of water transport in the PEMFC flow channel were also achieved with neutron radiography-based visualizations [32-34], in which liquid water slug formation was correlated to performance degradation.

When a droplet does not easily detach from the GDL surface, the contact line along the liquid water-GDL interface is consider pinned [13,24]. Sinha & Wang [24] attributed pinning of the contact line to the liquid water interaction on a GDL with mixed wettability, where the non-homogeneous wettability was attributed to uneven PTFE application. The authors reported that a droplet experiences pinning when it is in contact with a hydrophilic region surrounded by hydrophobic surfaces. For droplets on a solid surface, pinning of the contact line was attributed to physical defects or kinks, such as microscopic scratches [35,36] on the inherently rough GDL material. Ous and Arcoumanis [31] also observed the unpinning of droplet three phase boundary points on a GDL material in a transparent PEMFC during droplet emergence. A deeper understanding of how the microstructure of the GDL affects droplet pinning in the absence of chemical hydrophobic treatments is required.

Kumbur et al. [14] estimated that the GDL surface roughness features only affect contact angle measurements by ±2%. Theodorakakos et al. [11] measured the surface roughness of GDL materials, but concluded that the GDL could be considered a smooth surface due to low surface roughness measurements. However, when investigating the porosity of various GDL materials
with mercury droplet intrusion, Gostick et al. [9] derived and utilized roughness factors with the Cassie-Baxter equation [37,38] to correct the observed contact angle due to surface roughness features. Nam and Kaviany [18] also used a form of the Cassie-Baxter equation to estimate the contact angle for their water saturation distribution model of the GDL. Gurau et al. [25] noted that surface roughness is required to explain the large contact angle of a sessile droplet on a GDL. In light of this discrepancy, further investigation is needed to understand the surface roughness effects on liquid water transport.

Previous authors have studied Cassie-Baxter state wetting for non-GDL materials [39-41]. In these studies, which are of a fundamental nature, the authors observed contact line movement for liquid droplets increasing and decreasing in volume. Droplet volume was controlled with a syringe inserted directly into the centre of the droplet. Alternatively, contact line movement during droplet volume reduction was visualized by droplet evaporation [40]. For a droplet evaporating in the Cassie-Baxter state, the contact line was observed to jump across the roughness features in discrete steps [41]. Through numerical modeling, Girard et al. explored the effects of substrate temperature and relative humidity on evaporating pinned droplets [42,43]. They reported that increasing substrate temperature results in decreased droplet evaporation time, and they provided an empirical relationship between temperature and evaporation time. As well, smaller droplet contact lines resulted in a reduction of the evaporation time [42]. Girard et al. [42] found that the relative humidity only affects a pinned evaporating droplet for a substrate temperature less than 50°C, above which the droplet evaporation time is independent of humidity. Ous and Arcoumanis [23] visualized water droplets in a PEMFC channel on a paper GDL, while the operating temperature was increased from 30°C to 60°C at 70% relative humidity. They determined that the visible water droplets in the channel evaporated by the time 60°C was reached.

In this chapter, we present a simplified ex-situ experiment to investigate the ability of the rough GDL surface to pin water droplets. By removing the inlet air flow and channel wall effects, we attempted to isolate the influence of the GDL topography on droplet pinning. Focusing on the GDL topography, we studied the contact diameter progression of an evaporating droplet placed on the surface of various commercially available GDL materials. We employed a slow evaporation mode to systematically model the pinning/unpinning behaviour of the drop contact
diameter with respect to topologically different GDL materials. The provided results are useful for selecting the GDL material for the lowest ability to pin water droplets.

2.2 Experiment

We employ an ex-situ apparatus to observe contact diameter pinning during water droplet evaporation on the surface of various commercially available GDL materials. Single sessile water droplets (~1µL) are dispensed with a micro pipette (Finnpipette) on the following untreated GDLs: Toray TGP-H-030 paper, SGL Sigracet 10AA felt and AvCarb 1071HCB cloth GDLs. Untreated GDL materials are selected in order to isolate the pinning effects due to topography differences from those due to the chemical non-homogeneity of PTFE treatments. It is noteworthy that the droplets employed in this work are approximately double the maximum volume of a spherical droplet that could reside in a 1mm x 1mm flow field before being wicked to the channel wall [16]. Nonetheless, a 1µL droplet volume is chosen to facilitate the repeatable initial conditions that the evaporation process begins with a spherical cap droplet shape. The bond number (the ratio of surface energy to gravity force) of a 1µL droplet is such that the gravitational body force on the droplet can be considered negligible. Smaller droplets are expected to have similar droplet pinning behaviour as the larger 1µL droplets.

The visualization of water evaporation on the GDL surface can be challenging because of the transparency of water and the reflectivity of carbon fibres. To overcome this obstacle, we tag the liquid phase with a dilute solution of fluorescein dye (~1 mM) and employ florescence microscopy (Leica Z16 APO) to elucidate the gas-liquid-solid interfaces, as implemented by previous authors [13,26-28].

Each droplet is observed during the evaporation process in ambient air (25°C, 21% relative humidity) from the side view with a 3mm x 3mm right angle prism (Westport Micro Optics), as shown in Fig. 2.1. Images are captured with a 12 bit CCD camera (PCO Pixelfly), and the recorded evaporation sequences are processed with software developed in-house using Matlab to locate and track the droplet boundary profiles. Multiple experiments are conducted to verify repeatability, and similar droplet pinning trends are observed for all droplets analyzed.

To characterize the topography of the GDLs, we employ non-contact profilometry (Micro Photonics Nanovea ST400) based on a chromatic aberration technique. Profilometry
measurements capture the heights of the peaks and troughs of the GDL surface features. The through-plane heights and depths are utilized to calculate the average material surface roughness \((S_a)\), defined as:

\[
S_a = \frac{1}{mn} \sum_{i=1}^{m} \sum_{j=1}^{n} |z_{i,j}|
\]  

(2.1)

where \(n\) and \(m\) are the spatial coordinates of the roughness feature, and \(z\) is the height of the roughness feature [44]. The datum utilized to calculate \(S_a\) is located at the centre line average of the height data for each sample.

2.3 Results
2.3.1 Material Roughness
Profilometry is employed to compare the topographical features of paper, felt and cloth GDL (Fig. 2.2). The average surface roughness for felt GDL, \(S_{a,\text{felt}}\), is approximately 30µm, whereas the average surface roughness of paper GDL, \(S_{a,\text{paper}}\), is approximately 15µm. The \(S_{a,\text{paper}}\) corresponds approximately to the height of two fibres. It is interesting to note that the \(S_{a,\text{paper}}\) found here is significantly larger than the 8µm stated by manufacturer specifications for Toray TGP-H-030. Low roughness specification values may contribute to the underestimation of surface roughness effects on droplet behaviour found in literature. The average surface roughness of cloth GDL, \(S_{a,\text{cloth}}\), is approximately 270-350µm, while the average roughness of an individual yarn is approximately 32µm.

2.3.2 Contact diameter pinning
During evaporation, pinning is evaluated by the change in droplet contact diameter \((\Delta CD)\), defined as the change in distance between the three phase boundary points on each side of the droplet [41]. As shown in Fig. 2.3 (a), the contact diameter of the droplet on the Toray-H-030 paper GDL remains relatively constant during evaporation while the contact angle gradually decreases. This behaviour matches the ‘sticky’ state described by Kulinich & Farzaneh [40], whereby the water droplet experiences strong pinning to a nanostructured surface. We attribute the strong pinning exhibited by the paper GDL to its moderate roughness, in contrast to felt GDL and cloth surfaces.
The side view of the droplet evaporation on untreated felt GDL is shown in Fig. 2.3 (b). In contrast to paper GDL, the droplet only experiences partial pinning. Although the contact angle also decreases during evaporation, the marked decrease in contact diameter indicates weaker pinning behaviour compared to the paper GDL. After the third profile, the boundary points slip inwards on the left hand (LH) and right hand (RH) sides, with stronger pinning on the RH side. As the droplet continues to evaporate, the RH side recedes inwards but not as quickly as the LH side. It is noteworthy that by the eighth profile (t ≈ 10 min), it is evident that the asymmetrical pinning causes unequal contact angles for this sessile droplet.

During droplet evaporation on the felt GDL, droplets experience faster rates of unpinning compared to the paper GDL depending on the local surface features. In comparison to the paper GDL, the rougher topography of felt GDL results in differing contact angles and less consistent contact diameter progression throughout the evaporation of any given droplet. Irregular fibres protruding out of the felt GDL surface are also commonly observed (not shown here). These fibres are likely caused by the hydro-entanglement process during manufacturing.

Fig. 2.3 (c) shows that the contact diameter of a water droplet resting on cloth GDL evolves quite differently than on paper GDL, with similar qualities to contact diameter evolution on the felt GDL. Here, the contact diameter readily decreases due to the relatively facile unpinning behaviour of the contact line during evaporative volume loss. Droplets on the cloth GDL exhibit the weakest pinning behaviour, as shown by the significant decreases in contact diameter; however, the droplet still experiences pinning on the cloth GDL. A droplet that experiences absolutely no pinning would have a constant contact angle during chord length decreases [40].

The change in contact diameter as a function of evaporative volume loss is illustrated in Fig. 2.4 for droplets evaporating on the paper, cloth, and felt GDL. For each GDL material, a range of unpinning rates (ΔCD as a function of ΔV) are measured and outlined by the shaded regions in Fig. 2.4. Several droplet evaporation experiments were conducted, and similar pinning behaviours were observed. A representative droplet is shown for each GDL (Fig. 2.4). As can be seen, a non-zero ΔCD is measured for all materials; however, paper GDL exhibits the slowest average unpinning rate of 0.13mm/μL. Felt and cloth GDLs exhibit average unpinning rates of 0.21mm/μL and 0.19mm/μL, respectively, with felt exhibiting the widest range of unpinning rates (Fig. 2.4 (c)). It was generally observed that initially droplets experienced similar unpinning
rates, but after approximately 0.3μL of evaporative volume loss, the unpinning rates for felt and cloth GDL significantly diverged from that of paper GDL. This can be seen in the representative data presented in Fig. 2.4.

2.4 Discussion

Droplet interaction with a rough surface is commonly classified as being in a Wenzel [45] or Cassie-Baxter state [37,38]. The Wenzel state describes homogeneous wetting, with full water droplet immersion into the surface roughness features for complete interfacial contact. The Cassie-Baxter state describes the water droplet resting on air in between the liquid water and the rough surface. For both models, roughness correction factors, based on the material topography, are employed to relate the apparent contact angle to the actual contact angle utilized in surface energy balance calculations.

We attribute droplet pinning on the GDL to the extent of wetting in the Cassie-Baxter state. Complete homogenous wetting (Wenzel state) is not observed. Initial Cassie-Baxter states are identified from non-penetrating liquid interfaces along visible surface roughness features of the GDL. Fig. 2.5 is a schematic illustrating the liquid water-carbon fibre contact behaviour for (a) moderately rough and (b) highly rough surfaces. These results indicate that water droplets experience more immersion on moderately rough surfaces, which provide more liquid-solid contact areas for adhesion and, in turn, induce stronger pinning effects. The increased water-carbon fibre contact on a moderately rough surface would also result in more menisci along the interface. Since most evaporation occurs at the meniscus region [46], droplet evaporation rates are slightly higher for paper than for felt GDL (~10% increase in evaporation rate).

Untreated GDLs are investigated in this work to isolate the morphological surface feature effects of pinning from chemical effects. While binder is not employed during the manufacture of felt and cloth GDL, residual binder from the paper GDL manufacturing process may have induced regions of mixed chemical wettability. Although we attribute droplet pinning to the GDL topography, the presence of mixed wettability may also be a factor in pinning, as proposed by Sinha and Wang [24].

It is also noteworthy that we observed droplets which strongly adhere to protruding fibres, in addition to surface roughness induced pinning. Surface defects may play an important role in
channel flooding in a PEMFC. These irregular fibres would extend far into the gas channel, exacerbating GDL intrusion into the air flow as reported by Kandlikar [19].

2.5 Conclusions
In this chapter, a simplified experimental apparatus is employed to observe the ex-situ evaporation of water droplets on paper, felt, and cloth GDL to study the effect of the GDL topography on liquid droplet pinning behaviour. Untreated GDL materials are employed to isolate the effects of GDL topography on droplet pinning from the effects of hydrophobic chemical treatments (PTFE). Non-contact profilometry is also employed to measure the surface roughness of these materials. We find that paper GDL exhibits a lower average roughness compared to felt and cloth GDL. Throughout droplet evaporation, the contact diameter is tracked as a function of time to gain insight into the droplet pinning behaviour with respect to varying GDL topographies. The paper GDL, which is found to have the smallest average roughness (15µm), exhibits the strongest degree of pinning (unpinnning rate of 0.13 mm/µL). Similar average surface roughnesses for felt (30µm) and cloth yarn (32µm) result in similar unpinning rates, 0.21 mm/µL and 0.19 mm/µL, respectively. This correlation between the topographical roughness features and strength of pinning is attributed to the extent of wetting in the Cassie-Baxter state. From the perspective of facile droplet detachment in a PEMFC flow field, it is important to consider the effect of GDL topology on droplet pinning.
Fig. 2.1. A schematic of the experimental apparatus employed to investigate droplet evaporation on GDL surfaces. Fluorescence microscopy is employed, and the side view is obtained through the use of right angle prism. Light paths are shown with arrows.
Fig. 2.2. Profilometry results of paper GDL Toray TGP-H-030 (a), felt GDL SGL Sigracet 10AA (b), and cloth GDL AvCarb 1071HCB (c). The colour scale represents fibre height. The white region on (b) indicates heights greater than 80µm due to the out of plane fibre protrusions. The black background color is the reference datum. The scale bar represents 200µm.
Fig. 2.3. Side view of droplet evaporation on: (a) Toray TGP-H-030 carbon fibre paper, (b) SGL Sigracet 10AA carbon fibre felt, and (c) AvCarb 1071HCB carbon fibre cloth. The progression of the liquid-gas interface is outlined in red, labeled in increasing order with time. Observation of the three phase contact points during evaporation is used to determine the degree of contact diameter pinning. The scale bar represents 400μm. The time elapsed between each profile is 75s.
Fig. 2.4. Evolution of the change in contact diameter ($\Delta CD$) versus change in droplet volume ($\Delta V$) for paper (X), cloth (■), and felt (▼) GDL. The shaded regions outline the range of best fit lines for several droplet evaporation observations on (a) paper, (b) cloth, and (c) felt GDL.
Fig. 2.5. Schematic demonstrating the effect of roughness on contact line pinning. Blue represents liquid water, and black circles represent carbon fibres. Water droplet wetting is more conformal to the topography on a fibre arrangement that is moderately rough (a) compared to a surface with higher roughness features (b). Increased water-carbon fibre contact surfaces shown in (a) result in stronger pinning. Likewise, fewer water-carbon fibre contact surfaces result in weaker pinning. The liquid water in (a) and (b) depict a range of wetting for two droplets, both in the Cassie-Baxter state.
3.0 Heterogeneous porosity distributions by microscale tomography

3.1 Introduction
An important fundamental material property of the GDL is the pore structure, including the pore size and porosity. The GDL pore structure is important because it directly impacts key transport properties, including tortuosity, diffusivity, and permeability. PEMFC models [47,48] elucidate that the GDL porosity is especially influential to the polarization performance for high current densities, where a less porous GDL performs less favourably compared to a more porous GDL [47]. This is due to the reduced number of transport pathways for reactant oxygen transfer and product water removal. This study contributes to an improved understanding of the GDL porosity in order to provide better input data for modelling of multiphase transport within the material.

The porosity of the GDL is typically evaluated over the entire bulk volume, resulting in a bulk porosity measurement. The most common technique for evaluating the GDL porosity is mercury intrusion porosimetry (MIP) [49-53], while other fluids are also utilized to verify MIP [50,52]. Table 3.1 provides a review of bulk porosity values that are measured in literature for GDL materials. The porosities presented in Table 3.1 are determined with a variety of different measuring techniques. Gostick et al. [52] observed a maximum deviation of 5.1% for their measured porosity values for different types of GDL materials. Despite the abundance of reported bulk average porosity measurement values [50,52,54], more detailed information about the internal pore structure of this complex porous material is still required. A greater understanding of the internal pore structure of the GDL would be beneficial for informing microscale and macroscale PEMFC numerical models for advanced fuel cell design and performance.

The complexity of the GDL is partly due to the high degree of anisotropy associated with the microstructure [50,55]. Specifically, the GDL carbon fibres form a thin layer of stacked cylinders that extend far into the in-plane (IP) direction compared to the through-plane (TP) direction. Pasaogullari et al. investigated the anisotropy of heat and water transport in the GDL through the numerical determination of diffusion, permeability, thermal conductivity, and electrical conductivity [56]; however, diffusivity and permeability values are typically based on average
bulk porosity values [50,53,56-58]. Even though the GDL diffusivity and permeability are observed to be anisotropic and functions of porosity, the underlying anisotropy of GDL porosity has yet to be studied.

In investigations related to the GDL for PEMFCs, there are a few indications [51,59,60] that the GDL porosity may be non-uniform. Surface pore sizes have been reported to be significantly larger than the internal pore sizes, which are typically about 20µm in diameter [2,50,61-63] and occupy most of the GDL volume. When investigating the surface features of the GDL, Berejnov et al. [59] measured approximately 100µm-deep pores using an optical profilometry technique. With confocal microscopy, Gao et al. [60] reported large surface pore sizes of two GDLs: one made by Toray with a 30µm pore diameter and another made by SGL with an 80µm pore diameter. Likewise, Chou et al. [51] reported average pore diameters of 61.4µm and macropores up to 400µm in an SGL product calculated from MIP. This large variance in pore size within the literature points towards a local heterogeneous porosity within the GDL. In a review of water flooding issues in the PEMFC, Li et al. [1] noted that most modelling studies are based on the assumption of a uniform and constant porosity for simplicity. Proposed PEMFC models with a gradient in GDL porosity [48,64-66] account for liquid water clogging in the pores but do not include the actual GDL heterogeneity that is explored in this work. It is necessary to understand the local porosity variation that is intrinsic to GDLs.

Microscale computed tomography (µCT) enables the direct calculation of the GDL porosity, without the assistance of an intruding fluid. This technology, regularly applied in the medical field, can provide great insight into the local GDL material microstructure with non-destructive cross-sectional imaging. Ostadi et al. [55,67,68] employed nanoscale CT imaging (680nm resolution) on a GDL and provided a detailed overview of the tomography analysis process. Compared to higher resolution tomography imaging [55,69], µCT scanning is financially and computationally less expensive, enabling many more GDL materials to be compared and analyzed.

To the authors’ best knowledge, Büchi et al. [70] are the only previous authors that reported the heterogeneous porosity of the GDL. Their ex-situ µCT visualizations, with a 1µm resolution, successfully captured the TP porosity of a Toray TGP-H-060 GDL with 20 wt. % PTFE. The non-uniform TP porosity is correlated with water saturation distributions, where the high local
porosity value in the centre of a Toray TGP-H-060 GDL retains liquid water between low porosity regions near the surfaces. Ostadi et al. presented nanoscale CT imaging of the GDL, and calculated the porosity as a single volume-averaged uniform value [55]. CT data is also used when investigating the diffusivity and permeability of the GDL in the IP and TP directions [55,71]. In the work of Becker et al. [71], the authors employed µCT imaging to investigate the variation of GDL transport properties under compression. Porosity values were shown to decrease with compressed GDL thicknesses, beginning with initially uncompressed bulk porosity. These authors noted that the distribution of fibres and binder in the GDL was not homogeneous. Sinha et al. [69] utilized µCT imaging, with a spatial resolution of 10µm, to show the TP liquid water saturation along the thickness of a Toray GDL. Their work provided important insight into the saturation behaviour in the central region of the GDL. The µCT imaging used in these previous studies has provided powerful methods to determine bulk porosity [55], transport parameters [55,71], and behaviour of liquid water transport within the GDL [69]. Although Büchi et al. [70] reported a TP porosity distribution, only one material microstructure was analyzed and no quantification of the heterogeneous regions is provided. A comprehensive investigation is required to quantify the porosity distribution of GDL materials with varying thicknesses and manufacturing styles in order to provide accurate input data for fuel cell models.

In this chapter, the first comparison of measured local IP and TP porosity distributions for various commercially available GDL materials is presented. µCT imaging is performed to characterize the IP and TP porosity distributions for various uncompressed carbon fibre paper, felt, and cloth GDL materials. It will be shown here that every GDL tested has a non-uniform pore structure prior to compression.

3.2 Experimental
The GDL materials studied in this work do not contain microporous layers (MPLs) or polytetrafluoroethylene (PTFE) treatments. It is necessary to systematically characterize the intrinsic GDL substrate transport properties prior to the addition of the MPL and PTFE in order to properly evaluate the effect of the MPL and PTFE on the PEMFC electrode in future work. The GDLs investigated with a paper microstructure are Toray TGP-H-030, TGP-H-060, TGP-H-090 and TGP-H-120. The GDLs investigated with a felt microstructure are SGL Sigracet 10AA and Freudenberg H2315. The GDL investigated with a cloth microstructure is AvCarb
X-ray based µCT imaging is performed (40kV, 177µA, Skyscan 1172, Belgium) to obtain cross-sections of the GDLs mentioned above. In addition, a single Toray TGP-H-090 GDL sample is imaged with nanoscale resolution CT imaging (40kV, 200µA, Skyscan 2011, Belgium). The initial µCT data reconstruction is performed using the SkyScan NRECON software associated with the imaging device. This software automates the removal of ring artifacts from the raw image data by neighbourhood pixel averaging. The GDL cross-sections are combined to form a three-dimensional reconstruction of the GDL with a custom image analysis program, using Fiji image analysis and Matlab. The µCT reconstruction is then re-sliced in orthogonal planes to visualize the GDL from three directions: two sets of TP slices traversing the length and width of the GDL sample and IP slices across the thickness of the GDL.

Each greyscale image of the GDL stack is converted into a binary image to identify voxels of material and void space. The different stages of the analysis process are elucidated in Fig. 3.1: (a) raw greyscale, (b) greyscale with median filter, (c) binary image (d) final binary image with unconnected noise filter. Similar to the analysis performed by Becker et al. [71], a three part process is performed, starting with a median filter that is applied to the greyscale image (Fig. 3.1(a)) to remove noise, resulting in Fig. 3.1(b). The median filter slightly reduces the edge sharpness of the carbon fibre material, but without significant impact. A median filter has been successfully utilized by previous authors for µCT reconstruction of the GDL [71], for non-GDL materials [72], as well as for neutron radiography [73] and x-ray [74] imaging analysis of the PEMFC.

A histogram of a typical GDL IP cross-section (Fig. 3.2(a)) does not contain well-defined minima and maxima, from which one would intuitively define a threshold value. Fig. 3.2(b) illustrates a profile of the greyscale values across a line of the image. The profile further demonstrates that the distinction between material and void space is not trivial. Therefore, Otsu's method [75] is utilized to evaluate an appropriate threshold value for image processing (Fig. 3.1(c)). Rather than calibrate the greyscale to binary segmentation threshold to a previously determined porosity value from MIP, Otsu’s method provides an independent statistical determination of the porosity directly from the image data. This algorithm determines the
greyscale cut-off threshold by calculating the minimum of the sum of weighted variances of the greyscale values. The algorithm is applied to every TP greyscale image in the stack to provide an array of threshold values. The mode value of this threshold array is applied to the entire stack for consistent binary segmentation. In the case of Toray TGP-H-060 shown in Fig. 3.1 and 3.2, the threshold level is a greyscale value of 50 for the 8 bit image. It is important to note that although some low greyscale pixels associated with fibres may be removed during Otsu’s method (Fig. 3.1 (c)), these fibres are accounted for in adjacent cross-sections, where they are more pronounced.

Ostadi et al. [68] described the importance of a threshold level to segment the voxels for GDL μCT analysis. They also reported that a change of threshold cut-off by 1 greyscale value will result in a variation of porosity by approximately 0.43%. Similarly, in this work, a threshold variation of 1 greyscale value resulted in only a 0.36% porosity change.

The 3D binary structure is filtered again to remove any additional noise after phase contrast, which are identified by unconnected non-fibrous voxels (Fig. 3.1(d)). This filter utilizes 3D connectedness; therefore, any remaining material in a single slice is connected to larger material clusters in neighbouring slices. To determine the bulk GDL envelope volume for the volume averaged porosity, the stack of images is cropped so that the GDL fills the entire length and width of the data matrix. The thickness of the GDL is defined such that each IP slice contains at least 1% material, which captures the entire surface region except the outermost frayed surface fibres.

The spatial resolution for most of the μCT data gathered is 2.44μm, where 1 voxel = 2.44 x 2.44 x 2.44 μm³. The spatial resolution for the cloth GDL μCT data is 3.05μm/voxel. Although the voxel size is expected to lead to some segmentation error, we consider the net change of structure due to segmentation to be negligible, as our porosity distribution of Toray TGP-H-060 closely agrees with the measurement performed by Büchi et al. (1μm/voxel) [70]. The spatial resolution of the nanoCT data is 390nm/voxel. The GDL voxels of each binary μCT slice are counted to compute the local slice porosity, defined as:

\[
\varepsilon = 1 - \frac{\text{Material voxels}}{\text{Total GDL voxels}}. \tag{3.1}
\]

The material voxels are the number of voxels representing carbon fibres and binder. The total
GDL voxels are all the voxels in a slice (material and void). Equation 3.1 is applied to every image slice, in all three orthogonal directions. The two sets of TP slices are analyzed to provide two corresponding IP porosity distributions traversing across the GDL length and width. Likewise, the IP slices are analyzed to provide a TP porosity distribution traversing across the GDL thickness. GDL samples analyzed with µCT are approximately 5mm wide x 5mm long (see Tables 3.2, 3.3 and 3.4 for uncompressed thicknesses, t₀). From a sample size sensitivity analysis performed on paper, felt, and cloth GDLs, a minimum 1mm x 1mm sample size is recommended to obtain a repeatable TP porosity distribution of the GDL with less than a 4% difference in distribution shape change. The distribution shape change is measured as the average difference between porosity distributions. In order to capture the high resolution (390nm) nanoCT data, a reduced sample size is required. The sample size of the nanoCT data is 475µm x 274µm, which is below the minimum sensitivity size to obtain a consistent TP porosity distribution.

3.3 Results

3.3.1 Paper GDL

With the µCT images obtained, the interior GDL pore space is directly visible. The µCT resolution provides images of the GDL with visible carbon fibres as shown in Fig. 3.3, which is a representative binary GDL µCT image of the IP and TP slices of Toray TGP-H-060. Although the spatial resolution is close to that of the carbon fibre diameter [2,53], approximately 7-10µm, the resolution employed here is sufficient to gather structural information about the GDL. The 2.44µm and 3.05µm sized voxels enable our observation of the expected carbon fibres in the IP cross section (Fig. 3.3). The appearance of discontinuous fibres is attributed to resolution limits and fibres lying in more than one distinct plane of the GDL. The sensitivity of the µCT equipment in this work is incapable of distinguishing between the carbon fibres and the binder material present in the GDL, so the structure of the binder itself could not be analyzed separately. The binder material is visible as clusters in the IP view of Fig. 3.3. The GDL microstructure shown in the IP and TP slices from the µCT reconstruction is in agreement with previously reported tomography images [55,70,71,76].

The anisotropy of the GDL is evident from the porosity distributions in the TP and IP directions, with a typical set of paper GDL distributions shown in Fig. 3.4 for Toray TGP-H-060. As expected, the average bulk porosity (εbulk_avg) is the same value when calculated from all plane directions, independently. This effective porosity value (Fig. 3.4, red) corresponds to the porosity
value measured by other porosimetry techniques as shown in Table 3.1 \([50,54,77]\). The TP porosity distribution is distinct for each paper GDL material. The TP porosity distributions are typically divisible into three segments: two transitional surface regions and a core region, as shown in Fig. 3.4(a). Each face of the GDL consists of a transitional surface porosity, which changes from open space outside the material (100\% porosity) to the core of the material due to the unevenness and surface roughness of the porous fibrous GDL. For the surface region, the porosity transitions approximately linearly into the core region of the GDL (Fig. 3.4(a), green). The slopes of the transitional surface regions \((\epsilon_{\text{slope}})\) are dependent on the GDL microstructure and are presented in Tables 3.2 and 3.3. The change from surface pore region to the core pore region is marked by local minima of porosity at each side, which are especially evident for the paper GDL microstructure.

The TP GDL core is defined as the region of GDL in between the two transitional surface regions. As with the surfaces, the core region is dependent on the particular GDL microstructure. For each GDL core, the average core porosity \((\epsilon_{\text{core, avg}})\) is the mean value of the TP porosity distribution of the GDL core (Fig. 3.4(a), dashed line). Fig. 3.4 illustrates that \(\epsilon_{\text{core, avg}}\) is less than \(\epsilon_{\text{bulk, avg}}\) for a GDL. The difference between the average bulk and average core porosities is defined as:

$$\Delta \epsilon_{\text{avg}} = \epsilon_{\text{bulk, avg}} - \epsilon_{\text{core, avg}}. \quad (3.2)$$

The TP porosity distribution (Fig. 3.4(a)) has well defined peaks and valleys, whereas the IP porosity distributions of paper GDL (Fig. 3.4(b), 4(c)) fluctuate randomly. The IP porosity distributions do not appear to have any pattern corresponding to material manufacturing. There is also no apparent IP porosity behaviour to correspond to the machine and cross-machine directions. The IP porosities assist to clarify that \(\epsilon_{\text{bulk, avg}}\) of the GDL is the mean value of the entire porosity distribution in any orthogonal plane.

The heterogeneous TP porosity distributions for various Toray TGP-H GDLs are shown in Fig. 3.5. Toray TGP-H-030 (Fig. 3.5(a)) is the thinnest of the Toray family of GDLs. Based on the porosity distribution, Toray TGP-H-030 consists of a single ply layer with a core region approximately 40\(\mu\)m thick. Approximately two-thirds (66\%) of the TGP-H-030 thickness
consists of its transitional surface regions. Toray TGP-H-060 (Fig. 3.5(b)) possesses a well-defined core porosity that is more distinct from its two surfaces. The core region porosity of TGP-H-060 increases steadily towards the centre of the material. Similarly, the TP porosity distributions for Toray TGP-H-090 (Fig. 3.5(c)) and TGP-H-120 (Fig. 3.5(d)) exhibit distinct surface pore regions with local minima at each side. The core region porosity of these thicker Toray GDLs consists of 2 peaks and 3 troughs. The thickness of each core region is proportional to the overall material thickness and can be calculated as the distance between the surface minima.

There is an average 2.6% decrease between $\varepsilon_{\text{bulk, avg}}$ and $\varepsilon_{\text{core, avg}}$ for Toray TGP-H paper GDLs, excluding TGP-H-030 (See Table 3.2). Toray TGP-H-030 has a larger $\Delta\varepsilon_{\text{avg}}$ than the other Toray paper GDLs because its core region is relatively small. The Toray GDL transitional surface porosities are calculated with a linear regression; all of the GDLs with paper microstructure possess a similar slope, which is approximately 0.7%/µm. The transition from surface to core porosity for Toray GDLs usually occurs at a distance of approximately 50µm from the material edge (See Table 3.2). The surface regions contribute approximately 45%, 33%, and 28% for Toray TGP-H-030, 060, and 090, respectively, as a percentage of the thickness of the paper GDLs.

The paper GDL Toray TGP-H-090 investigated with nanoCT imaging provides a detailed high resolution 3D reconstruction measuring 475µm x 274µm (Fig. 3.6). This nanoCT GDL sample size is below the sensitivity size to characterize the TP porosity distribution but can still provide a useful bulk average porosity to evaluate the µCT scan quality. The high resolution nanoCT scan of the Toray TGP-H-090 can be taken as the best obtainable data for comparison, where 0.39µm sized voxels capture ~10µm carbon fibre features. To properly compare the $\varepsilon_{\text{bulk, avg}}$ of the two scans, the µCT data is divided into many subsections, each with a volume approximately equal to the volume of the nanoCT data. The µCT scan data subsections had an average $\varepsilon_{\text{bulk, avg}}$ of 82.6% (same as for the entire sample) with a standard deviation of 1.3%. The nanoCT scan data of the same paper type had a $\varepsilon_{\text{bulk, avg}}$ of 84.1%. The $\varepsilon_{\text{bulk, avg}}$ determined by nanoCT is close to but slightly higher than the µCT porosity range. The porosity gathered from the higher resolution scan falls approximately one standard deviation away from the lower resolution scan results. From this analysis, we believe the lower resolution (2.44µm sized voxels) scan to be sufficient to capture the carbon fibre structure. The nanoCT reconstruction (Fig. 3.6) is also
useful to provide a visualization of the morphology. It can be observed that individual carbon fibres are less distinct due to clusters of structure in the regions near the surface layers. Since this GDL sample is not treated with PTFE, these clusters are attributed to the binder material, which also correspond to the local minima between the transitional surface and the core regions.

3.3.2 Felt GDL

Representative binary GDL µCT images of the IP and TP cross-sections of an SGL Sigracet 10AA felt GDL are shown in Fig. 3.7. Compared to the IP slice of paper GDL with straight carbon fibres (Fig. 3.3), the µCT image reveals the more entangled carbon fibres of the felt microstructure. As well, there are no apparent cluster structures due to the lack of binder in the entangled material. Both of the TP slices in Fig. 3.7 (top & left) illustrate the rougher and less planar surface region of the felt GDL.

The TP and IP porosity distributions of felt GDL Freudenberg H2315 are illustrated in Fig. 3.8. The TP porosity distribution (Fig. 3.8(a)) varies significantly from the carbon paper GDL materials measured. Specifically, the TP core porosity is much more uniform for the felt GDL materials than the paper GDLs. As well, the distribution does not possess local minima where the surface regions change to the core region. The transitional surface region is thicker with a smaller slope compared to Toray TGP-H (Fig. 3.4). This distribution results in a large difference between $\varepsilon_{\text{bulk, avg}}$ and $\varepsilon_{\text{core, avg}}$ (See Table 3.3). The porosity distribution resembles the modelled porosity distribution of an optimized fibrous insulation [78] but with a less-porous core region. Whereas both of the IP porosity distributions of the paper GDLs fluctuate randomly, only one of the IP porosity distributions of the felt GDLs is random (Fig. 3.8(b)). The other IP porosity distribution of the felt GDL (Fig. 3.8(c)) contains an oscillation. The local peaks of this IP porosity oscillation are approximately 500µm apart.

The IP porosity oscillations observed in Fig. 3.8(c) for Freudenberg H2315, can be further confirmed with Fig. 3.9, which is generated by adding the material content voxels of every IP µCT binary cross-section for the entire GDL thickness. The greyscale bar represents the summation of material voxels through the thickness. This unique image provides a visualization of overall trends in the internal GDL structure, which would not otherwise be captured by an individual IP cross section or a typical 3D reconstruction. In Fig. 3.9, several vertically aligned striations are evident. These striations correspond to the porosity peaks observed in the IP
porosity oscillations, where the porosity maxima are the light regions and the porosity minima are the dark regions.

A comparison of the TP porosity distributions of two felt GDLs: SGL Sigracet 10AA and Freudenberg H2315, is presented in Fig. 3.10. Both felt GDLs H2315 have similar porosity distributions with uniform core regions, despite being produced by separate companies. The SGL Sigracet 10AA is slightly thicker than the Freudenberg H2315 but has a higher $\epsilon_{\text{core, avg}}$. $\Delta\epsilon_{\text{avg}}$ is approximately 6.3% for the felt GDLs, which is a greater porosity change compared to most of the paper GDLs. The transition gradient from surface to core porosity for the felt GDLs is 0.4%/µm, less than the paper GDLs (0.7%/µm). The core region begins at a depth of approximately 60-70µm from the material edge. The surface regions contribute approximately 35% and 41% for SGL Sigracet 10AA and Freudenberg H2315, respectively, as a percentage of the thickness of the felt GDLs.

### 3.3.3 Cloth GDL

The IP and TP µCT cross-sections of AvCarb 1071HCB binary structure (Fig. 3.11) elucidate the woven structure of the cloth GDL. The IP slice pictured (bottom right) shows the middle of the weave where there is a large amount of yarn overlap. This plane is not visible through conventional top-down microscopy techniques. The large macro-pores between the yarns are complete through-holes of the GDL. The top TP slice and the left TP slice of Fig. 3.11 portray the two main types of alternating TP cross-sections. The top TP slice is a cross-section of yarns in which only one direction of yarns is observed. The left TP slice is a cross-section showing yarns, between which one perpendicular yarn is observed. For consistency, a rectangular boundary is utilized to define the bulk volume of the cloth GDL material, which is the same analysis method that was applied to the paper and felt GDL. This rectangular volume requires the inclusion of the macro-pores and the entire woven yarn structure.

The TP porosity distribution of this cloth GDL (Fig. 3.12(a)) exhibits similar transitional surface porosities identified for the paper and felt GDLs discussed earlier. However, the decreasing and increasing TP porosity of the cloth GDL is caused by the overlapping of carbon fibre yarns, rather than the surface roughness. The porosity decreases towards the middle of the cloth, where the two intersecting perpendicular yarns exhibit the most overlap. At this location, the TP porosity minimum of cloth GDL is 73.3% (see Table 3.4). The yarn overlap transition occurs at a
rate of 0.18%/µm. The cloth GDL does not have an identifiable core region, in contrast to the paper and felt GDL materials.

The IP porosity distributions of the cloth GDL have large oscillations in both TP directions (Fig. 3.12(b) and (c)) due to the repeating perpendicular weave construction of the textile. The local porosity peaks represent the TP cross-sections shown in Fig. 3.11, top. The local porosity troughs represent cross-sections shown in Fig. 3.11, left. The average porosity of the peak regions is 91.3% and the average porosity of the trough regions is 80.5%. It is interesting to note that the porosity of an uncompressed yarn cross-section is 73% ± 6%, while the bulk average porosity of the cloth is 85%.

3.4 Discussion

Many PEMFC models [56-58] and experimental analyses [50,53,61,77] have relied on a uniform porosity value when considering water saturation, diffusion, and permeability. The µCT data presented here illustrates that a uniform porosity value (ε_{bulk,avg}) is only appropriate for transport in the IP of some GDL microstructures but not for the TP direction. Specifically, the IP porosity is approximated by ε_{bulk,avg} for paper GDLs in both directions and the IP porosity of felt GDLs in one direction. For paper GDLs, ε_{bulk,avg} from our µCT image analysis is in good agreement with other measurements found in literature, as can be seen when comparing Table 3.1 and Table 3.2. For SGL Sigracet 10AA (felt material), ε_{bulk,avg} is less than previously reported values by 6.3%, as can be seen when comparing Table 3.1 and Table 3.3. We recommend that future studies involving models of the GDL TP take into consideration the surface and core regions investigated in this study.

We attribute the significant variations of core porosity distributions between different GDLs to their manufacturing processes; however, it is important to note that the manufacturing literature is limited due to the proprietary nature of GDL fabrication. The Toray paper GDLs seen in Fig. 3.5 exhibit an increasing degree of heterogeneity in the core region with increasing thickness. According to Mathias et al. [2], the manufacturing of thicker paper GDLs involves the compression of multiple plies, known as the “molding” step. Gao et al. [60] noted the same ply layering for manufacturing Toray GDL and that the thicker GDLs could be multiples of the TGP-H-030 ply. Furthermore, Maheshwari et al. [79] observed comparable PEMFC performance for both Toray paper GDL and their custom 3-ply paper GDL, indicating that the Toray material
may have been manufactured with a similar procedure. From the results of this work combined with the background literature, we attribute the varying TP porosity of the paper GDL core region to this ply molding process. The local porosity maxima in the core region of the thicker paper GDLs (Fig. 3.5) are attributed to the high porosity surface regions of individual plies prior to molding compression. The result of compressing two high porosity surface regions would be a new region with a lower porosity. The amplitude and frequency of the porosity distribution variation may be dependent on the number of plies and degree of compression for molding thicker GDLs.

For felt GDLs, the TP core porosity, without peaks and valleys, is likely generated from the hydro-entanglement process employed in fabrication [2]. The similarity between the SGL and Freudenberg GDLs is indicative of the underlying common manufacturing technique employed for fabrication. The entanglement could also explain the change in $\varepsilon_{\text{slope}}$ between the felt GDL and the paper GDL. Since the felt GDL carbon fibres are bent out of plane, more fibres will protrude from the core region. This will generate a thicker surface region than the paper GDL, which is pressed flat.

The hydro-entanglement manufacturing process utilizes fine water jets with a diameter reported to range from 80-150$\mu$m with a spacing of 15-50 jets/cm [2]. The IP porosity oscillation peaks observed in Fig. 3.8 and the corresponding vertically aligned material summation striations in Fig. 3.9 are approximately 500$\mu$m apart. Although this distance does not coincide with the reported water jet spacing, we attribute the IP porosity oscillation to the hydro-entanglement water jets as the repeating and highly aligned striations suggest a manufacturing process. The water jet spacing utilized may have changed for the fabrication of this particular material. If this process is indeed responsible for the local porosity oscillations, then the local porosity peaks and the light region striations would correspond to water jet paths where carbon fibres are displaced.

The cloth GDL IP and TP porosity distributions elucidate a strong the dependence on the weave construction. The cloth IP porosity distributions, which vary by as much as 10%, are produced by the perpendicular woven yarn construction. The 0.18%/µm transition gradient through the thickness could be a function of the tightness of the weave. Altering the weaving process to achieve a different porosity distributions is worthy of further investigation in future cloth manufacturing studies.
3.5 Conclusion

In this work, we employ high-resolution µCT to obtain three-dimensional reconstructions of commercially available felt and paper GDL materials. This is the first comparison of measured TP porosity distributions for multiple commercially available GDL materials. Cross-sectional slices are utilized to calculate the TP and IP porosity distributions. We determine that the TP porosity is not a uniform property due to the GDL manufacturing techniques. A catalogue has been developed of the TP porosity distributions for paper, felt and cloth GDLs.

GDLs with a paper microstructure with varying thicknesses are studied, and the erratic core region of the pore structure is attributed to the ply molding manufacturing process. GDLs with a felt microstructure possess a core region that is more uniform than paper GDLs and exhibits a greater difference between the average core porosity and effective bulk porosity. A GDL with a cloth microstructure is also investigated, and the extent of IP variation from the weave structure is quantified. All GDL materials possess a linear transitional region that contributes high porosity regions to the GDL. A discussion of how the porosity distributions for paper, felt, and cloth are related to their manufacturing process is also provided. Based on previous models relating porosity to water saturation, we recommend that the paper GDL manufacturing process is modified to reduce the peaks and valleys in the GDL core. Our investigation provides valuable insight into the heterogeneous porosity distributions of paper, felt, and cloth GDL materials. These heterogeneous porosity distributions can be used to inform numerical models for advanced PEMFC design and performance.
3.6 Figures

Fig. 3.1. In-plane sub-section (200pixel x 200pixel = 488µm x 488 µm) of paper GDL Toray TGP-H-060 at different stages of our analysis method: (a) raw greyscale, (b) greyscale with median filter, (c) binary image with Otsu’s method and (d) final binary image after unconnected noise filter.
Fig. 3.2. Thresholding value with respect to greyscale distribution: (a) a greyscale value histogram of the median filtered raw image data (Fig. 3.1(b)) with a dashed line indicating the threshold level determined by Otsu’s method. (b) A profile of the greyscale values across the distance of the same image.
Fig. 3.3. Binary orthogonal views of the GDL microstructure reconstructed from μCT imaging: TP slices (top & left) and an in-plane slice (bottom right) of a Toray TGP-H-060 paper GDL. Black voxels represent void space, and white voxels represent material space. The length bar represents 1mm.
Fig. 3.4. Porosity distributions for Toray TGP-H-060: (a) through-plane, (b) & (c) in-plane. Average porosity values are shown in red. The TP porosity distribution is divided into three segments: two transitional surface regions and a core region. The transitional surface regions are overlaid with best fit lines (green). The average porosity of the core region is shown as a dashed magenta line.
Fig. 3.5. The TP porosity distributions for Toray TGP-H- (a) 030, (b) 060, (c) 090, and (d) 120. The porosity distributions are centred at the mid-point of each material.
Fig. 3. A subsection of a 3D reconstruction of Toray TGP-H-090 from nanoCT imaging. The subsection pictured measures 117μm across and 117μm deep. The length bar represents 50μm.
Fig. 3.7. Binary orthogonal views of the GDL microstructure reconstructed from μCT imaging: TP slices (top & left) and an in-plane slice (bottom right) of an SGL Sigracet 10AA felt GDL. Black voxels represent void space, and white voxels represent material space. The length bar represents 1mm.
Fig. 3.8. Porosity distributions for Freudenberg H2315: (a) through-plane, (b) & (c) in-plane. Average porosity values are shown in red. The TP porosity distribution is divided into three segments: two transitional surface regions and a core region. The transitional surface regions are overlaid with best fit lines (green). The average porosity of the core region is shown as a dashed magenta line.
Fig. 3.9. An image produced by the sum of binary in-plane μCT cross sections of Freudenberg H2315. The μCT sum image provides an overall snapshot of the entire internal GDL structure. The color bar represents the sum of the material voxels through the GDL thickness.
Fig. 3.10. Comparing the TP porosity distributions for felt GDLs: SGL Sigracet 10AA (●) and Freudenberg H2315 (■).
Fig. 3.11. Binary orthogonal views of the GDL microstructure reconstructed from μCT imaging: TP slices (top & left) and an in-plane slice (bottom right) of an AvCarb 1071HCB cloth GDL. Black voxels represent void space and white voxels represent material space. The length bar represents 1 mm.
Fig. 3.12. Porosity distributions for AvCarb 1071HCB: (a) through-plane, (b) and (c) in-plane. Average porosity values are shown in red. The transitional regions of the TP porosity distribution are overlaid with best fit lines (green).
### 3.7 Tables

<table>
<thead>
<tr>
<th>GDL Type</th>
<th>ε (%)</th>
<th>t (µm)</th>
<th>Reference</th>
</tr>
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<td>[54]</td>
</tr>
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</tr>
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<td>350</td>
<td>[52]</td>
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</tbody>
</table>

Table 3.1. Comparing the uniform porosity values (ε) and thicknesses (t) of various commercially available GDLs.

| GDL Type               | t₀ (µm) | |εslope 1| |εslope 2| |ε bulk, avg| |ε core, avg| |Δε avg|
|------------------------|--------|---|--------|---|--------|---|---------|---|---------|
| Toray TGP-H-030        | 117    | 0.706 | 0.953 | 82.9 | 74.2   | 8.7|
| Toray TGP-H-060        | 220    | 0.625 | 0.664 | 82.1 | 79.4   | 2.7|
| Toray TGP-H-090        | 298    | 0.553 | 0.578 | 82.6 | 80.1   | 2.5|
| Toray TGP-H-120        | 359    | 0.594 | 0.809 | 78.7 | 76.0   | 2.7|
| Average ± St. Dev.     | -      | 0.620 ± 0.065 | 0.751 ± 0.165 | 81.6 ± 1.95 | 77.4 ± 2.79 | 4.1 ± 3.0|

Table 3.2. Comparing the TP porosity distributions of Toray paper GDLs.
| GDL Type              | $t_0$ (µm) | $|\varepsilon_{\text{slope 1}}|$ (%/µm) | $\varepsilon_{\text{slope 2}}$ (%/µm) | $\varepsilon_{\text{bulk, avg}}$ (%) | $\varepsilon_{\text{core, avg}}$ (%) | $\Delta\varepsilon_{\text{avg}}$ (%) |
|----------------------|-----------|------------------------------------------|----------------------------------------|---------------------------------------|----------------------------------------|---------------------------------------|
| SGL Sigracet 10AA    | 344       | 0.270                                    | 0.312                                  | 84.7                                  | 79.3                                   | 5.4                                   |
| Freudenberg H2315    | 290       | 0.519                                    | 0.488                                  | 80.2                                  | 73.0                                   | 7.2                                   |
| Average ± St. Dev.   | -         | 0.395 ± 0.176                            | 0.400 ± 0.125                          | 82.4 ± 3.18                           | 76.1 ± 4.45                            | 6.3 ± 1.3                             |

Table 3.3. Comparing the TP porosity distributions of SGL and Freudenberg felt GDLs.

| GDL Type              | $t_0$ (µm) | $|\varepsilon_{\text{slope 1}}|$ (%/µm) | $\varepsilon_{\text{slope 2}}$ (%/µm) | $\varepsilon_{\text{bulk, avg}}$ (%) | $\varepsilon_{\text{IP peaks, avg}}$ (%) | $\varepsilon_{\text{IP trough, avg}}$ (%) |
|----------------------|-----------|------------------------------------------|----------------------------------------|---------------------------------------|------------------------------------------|------------------------------------------|
| AvCarb1071HCB        | 400       | 0.182                                    | 0.178                                  | 85.1                                  | 91.3                                    | 80.5                                    |

Table 3.4. The TP porosity distribution of AvCarb1071HCB cloth GDL.
4.0 Heterogeneous through-plane distributions of tortuosity, effective diffusivity, and permeability

4.1 Introduction
The PEMFC community’s understanding of the dominating mechanisms that govern multiphase flow within the GDL stand to benefit from detailed knowledge of the material’s microstructure. Unfortunately, the complex internal structure of the GDL has been difficult to visualize in the past with conventional microscopy. Recent visualizations from Chapter 3.0 have provided evidence that GDLs exhibit heterogeneous porosity distributions [5,70], but their impacts on the tortuosity, relative diffusivity, and single phase permeability have not yet been investigated. These important properties of the material govern the transport of reactants and products in the PEMFC. Specifically, diffusivity and permeability affect the concentration and pressure of reactant air and product water in the GDL, according to Fick’s first law [81,82] and Darcy's law [83], respectively. Increasing the GDL porosity, and therefore decreasing the tortuosity, have been shown to enhance PEMFC performance at high current densities by facilitating higher rates of oxygen mass transfer to the catalyst layer [48].

4.1.1 Effective Diffusivity
The effective diffusivity of an unsaturated porous medium is defined as [53,71]:

\[ D_{\text{eff}} = f(\varepsilon)D_{AB} = \frac{\varepsilon}{\tau}D_{AB} , \]  

(4.1)

where \( D_{AB} \) is the binary diffusivity of two species in open space, \( \varepsilon \) is the material porosity, and \( \tau \) is the material tortuosity. \( f(\varepsilon) \) [57,58,84] is referred to as a normalized relative diffusivity [50,71,76], otherwise known as the obstruction factor [85].

In literature, a large variability of \( \tau \) and \( f(\varepsilon) \) values have been reported for determining GDL diffusivity [50,57,71,76,86-89]. Fractal models have been used to calculate \( \tau \), resulting in values of 1.25 [86] and 1.14 [87]. An average \( \tau = 1.2 \) was calculated from flow simulations with a three-dimensional (3D) stochastic GDL model [88]. Thiedmann et al. [89] employed a 3D stochastic model of the GDL and calculated \( \tau \) values ranging from 1.51 to 1.73, which varied depending on
the amount of binder content. Fluckiger et al. [50] reported $\tau \approx 2.2$ for the through-plane (TP) direction of an untreated and uncompressed GDL, based on a unit-cell model analysis of the GDL. There has also been a wide range of calculated TP $f(\varepsilon)$ values calculated from a 3D $\mu$CT reconstruction (0.304 [71]), 3D fibre lattice model (0.65 [57]), GEODICT computational solver (0.518 [76]), and 2D GDL pore unit cell model (0.35 [50]). In light of this variability, further work is necessary for determining $\tau$ values and their dependence on the heterogeneity of GDL materials.

The Bruggeman model has been commonly employed [48,49,90-92] to determine $D_{\text{eff}}$ using:

$$f(\varepsilon) = \varepsilon^{1.5} \text{ or } \tau = \varepsilon^{-0.5}. \quad (4.2)$$

However, the Bruggeman model is based on the porosity of packed spherical particles [57], rather than cylindrical fibres that make up the GDL. In contrast to the Bruggeman model, Tomadakis & Sotirchos proposed the following $f(\varepsilon)$ model for randomly oriented fibrous porous media to investigate chemical vapour infiltration through fibrous composite materials with porosity gradients, termed the TS model [93,94]:

$$f(\varepsilon) = \varepsilon \left( \frac{\varepsilon - \varepsilon_p}{1 - \varepsilon_p} \right)^{\alpha}, \quad (4.3)$$

where $\varepsilon_p$ is the percolation threshold porosity, and $\alpha$ is a model-fitted value obtained from the TS model [93,94]. The percolation threshold porosity is the minimum porosity required for diffusion or permeation through the material. Tomadakis & Sotirchos found that $\varepsilon_p = 0.11$ was the percolation threshold porosity for a random, 2D fibrous structure [93,94]. They also found that for through-plane diffusion, $\alpha = 0.785$, and for in-plane diffusion, $\alpha = 0.521$. As described by Tomadakis & Robertson [95] and by Gostick et al. [53], the TS model can also be employed to calculate the tortuosity of the porous GDL as follows:

$$\tau = \left( \frac{1 - \varepsilon_p}{\varepsilon - \varepsilon_p} \right)^{\alpha}. \quad (4.4)$$
Careful consideration must be made in selecting the relationship between tortuosity and porosity. In previous investigations of GDL transport [64,92,96-99], \( \tau = 1.5 \) was selected, however, with the Bruggeman model (Eqn. 4.2) this results in \( \varepsilon = 0.444 \) or with the TS model (Eqn. 4.4) this results in \( \varepsilon = 0.641 \). Nam et al. [100] recommended the Bruggeman model for the catalyst layer and the TS model for the GDL when modelling the PEMFC cathode.

The applicability of the TS model to various paper and felt GDL materials has been verified with numerical [57] and experimental [53] investigations. Furthermore, the TS model for \( f(\varepsilon) \) (Eqn. 4.3) has since been utilized to evaluate the effective diffusivity of the GDL in numerous studies [53,56-58,67,101,100]. However, Zamel et al. [84,102] found that the TS model over-predicted the effective diffusivity of GDL materials compared to their experimental measurements. In previous investigations, the TS model has been employed to investigate either average bulk porosities [56,67] or uniform porosities that vary due to GDL compression [53], but the TS model has not yet been employed to investigate the effect of heterogeneous porosity distributions on \( \tau \) and \( f(\varepsilon) \). Previously reported [48,65,66] porosity gradients and non-uniform effective diffusivity have been utilized to account for the liquid water distributions in the GDL; however, these studies did not account for the heterogeneity of the GDL structure itself.

4.1.2 Permeability

In investigations of permeability utilizing experimental techniques [53,103-105], lattice Boltzmann (LB) simulations [55,63,106], and computational fluid dynamics (CFD) [71,76], a homogeneous porosity has been assumed for the GDL. However, experimental measurements of GDL single phase permeability have indicated that the GDL is highly anisotropic [53]. The LB technique has been employed to determine \( K [55,63,106] \) based on 3D GDL reconstructions from \( \mu \)CT analysis [55,71,106] and random cylinder models [63,71,76]. Although good agreement has been shown between the experimentally measured and LB-determined \( K \) values by Rama et al. [106], LB simulations are time intensive (up to 4 hours per simulation) [106], and there is a wide range of values within the literature, as shown in Table 4.1. These works do not specifically refer to porosity values as “homogeneous” since a heterogeneous local porosity was not yet known for comparison.

The TS model for effective diffusivity can be extended to calculate single phase permeability in random fibrous and porous media [95]:

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where \( r_f \) is the carbon fibre radius, taken to be 4.6\( \mu \)m in this work to be consistent with the 9.2\( \mu \)m diameter reported [53]. Gostick et al. [53] employed this model and reported reasonable agreement with experimentally measured values. Eqn. 4.5 is also convenient for GDL modeling since material specific fitting parameters are not required, as noted by [53] compared to the Carman–Kozeny model. In this work, we employ heterogeneous TP porosity distributions measured in [5] to calculate the following local spatial distributions: \( \tau(\varepsilon) \), \( f(\varepsilon) \), and \( K(\varepsilon) \), based on the TS model defined in Eqns. 4.3-4.5.

### 4.2 Application of TS model for heterogeneous material properties

In the previous Chapter [5], the heterogeneous porosity distributions of the GDL were measured using microscale computed tomography (\( \mu \)CT) imaging, and their impact on liquid water transport behaviour was discussed in Hinebaugh et al. [107]. Uncompressed paper, felt, and cloth GDLs were studied, and the TP and in-plane porosity distributions were obtained. Here, our investigation is focused on the TP direction, since the effective transport of reactants and products between the catalyst layer and flow fields are key to the performance of the PEMFC.

To apply the TS model to our previously determined porosity distributions, we consider the binder cluster material to be fibrous material. Although the TS model is based on a structure of straight fibres, Nabovati et al. [108] found with a LB model that porous media with curved fibres can be modelled as straight fibres to determine the permeability. Therefore, we have applied the TS model to felt, as well as paper. The TS model cannot be applied to cloth GDL porosity distributions because the woven cloth does not conform to the randomly stacked fibre geometry assumed in the model.

Equation 4.4 was employed to calculate the TP \( \tau \) distributions of Toray paper GDLs (TGP-H-060, TGP-H-090, and TGP-H-120) and an SGL felt GDL (SGL 10AA), which are presented in Fig. 4.1. Similar to the heterogeneous TP porosity distributions [5], the \( \tau \) distributions exhibit distinct core regions and transitional surface regions, as illustrated for Toray TGP-H-060 in Fig. 4.1(a). The average bulk tortuosity (\( \tau_{\text{bulk, avg, red}} \)), average core tortuosity (\( \tau_{\text{core, avg, magenta}} \), and
linearly fit slope of the transitional surface region tortuosity ($\tau_{\text{slope}}$, green) were calculated and tabulated in Table 4.2. The difference between the average bulk and core tortuosity is defined as:

$$\Delta \tau_{\text{avg}} = \tau_{\text{bulk,avg}} - \tau_{\text{core,avg}}.$$  \hspace{1cm} (4.6)

The TP heterogeneous tortuosity distributions of the paper and felt GDLs are inversely proportional to the porosity distributions. For the paper GDLs, local tortuosity maxima correspond to the local porosity minima. The tortuosity in the core region of paper GDL becomes increasing more heterogeneous as the thickness of the Toray GDL material increases. For the Toray paper materials studied, on average, $\tau_{\text{bulk,avg}} = 1.213$ and $\tau_{\text{core,avg}} = 1.244$, which closely agree with tortuosity values predicted from fractal models (1.25 [86], 1.14 [87]) and a stochastic model (1.2 [88]). It is important to note that all values in our $\tau$ distributions fall below the 1.5 value commonly utilized in literature [64,92,96-99]. Felt exhibited a much more uniform core region compared to that of paper, as can be seen in Fig. 4.1(d). However, the $\tau_{\text{core,avg}}$ for both felt and paper are similar, despite the differing degree of heterogeneity in the material porosities.

Equation 4.3 was employed to calculate the TP distributions of $f(\varepsilon)$, which are presented in Fig. 4.2. The surface transition slopes, average bulk, and average core values for $f(\varepsilon)$ are reported in Table 4.3. The $f(\varepsilon)_{\text{core,avg}}$ for paper and felt are in reasonable agreement with the values reported in literature (0.518 [76], 0.65 [57]), providing verification for the heterogeneous distributions that were measured. According to Eqn. 4.1, the TP distribution for $D_{\text{eff}}$ is proportional to the $f(\varepsilon)$ distribution. However, the exact value of $D_{\text{eff}}$ depends on the specific binary diffusivity, $D_{AB}$, under consideration. For example, if $D_{AB} = 2.5 \times 10^{-5}$ m$^2$s$^{-1}$ (for oxygen diffusion into water vapour) [109] and $f(\varepsilon)_{\text{core,avg}}$ of Toray TGP-H-060 is considered, the result is $D_{\text{eff}} = 1.6 \times 10^{-5}$ m$^2$s$^{-1}$.

Using Eqn. 4.5, the TP permeability distributions of the GDLs were calculated and plotted with a logarithmic y-axis, as shown in Fig. 4.3. The $\log(K_{\text{slope}})$, $K_{\text{bulk,avg}}$, and $K_{\text{core,avg}}$ values are reported in Table 4.4. The $K_{\text{core,avg}}$ agrees well with the TP permeability results of paper GDL from the literature summarized in Table 4.1, with values ranging from $7.40 \times 10^{-12}$ m$^2$ to $9.24 \times 10^{-12}$ m$^2$ [53,63,71,76]. We correlated values from the literature with our $K_{\text{core,avg}}$ values, rather than with the $K_{\text{bulk,avg}}$ values since previous GDL models lacked the identification of surface regions. The
$K_{\text{core, avg}}$ of felt evaluated with the TS model (8.64x10^{-12} \text{ m}^2) is smaller than the TP permeability results from literature (21.1x10^{-12} \text{ m}^2 to 37.4x10^{-12} \text{ m}^2 [53,63,103]). This range of literature values actually falls in between the $K_{\text{core, avg}}$ and $K_{\text{bulk, avg}}$ for felt GDLs.

The absence of surface regions in experimental investigations can be explained by contact of the GDL surface with an experimental apparatus. Compared to GDLs in open space in this work (completely uncompressed), a GDL with surface contact would be lightly compressed enough to truncate the high porosity distributions of the surface regions. Therefore, the bulk region volume would be reduced to approximately the core region and the surfaces may not be captured in experiments. In numerical models of the GDL, a pore can be defined as the largest sphere inscribed between carbon fibres [89]. In these models, the porosity of the surface region is difficult to include because the surface pores do not have an outer bound for pore definition.

4.3 Conclusion

This is the first calculation of heterogeneous TP $\tau, f(\epsilon)$ for $D_{\text{eff}}$, and $K$ distributions of paper and felt GDLs based on the TS model and previously measured heterogeneous TP porosity distributions. For each property, the average was determined for the bulk material region and for the core region. As well, the slopes of the surface transitional regions were determined for each transport property. Between the bulk material region and the core region, better agreement was found with the average core region and values reported in literature, since high porosity surface regions were not considered in the literature. For these properties, the felt GDL core region was more uniform than paper GDLs. While average core values generally agreed well with the literature, in an operating PEMFC, pressure and concentration gradients may be expected within the GDL TP because the effective diffusivity and permeability are the proportionality constants of Fick’s law and Darcy's law, respectively. This work establishes heterogeneous distributions of $\tau, f(\epsilon)$, and $K$ of uncompressed GDL materials, which provides local properties that will inform future multiphase transport models for the PEMFC GDL.
4.4 Figures

Fig. 4.1. The TP $\tau$ distributions for (a) Toray TGP-H-060, (b) Toray TGP-H-090, (c) Toray TGP-H-120, and (d) SGL Sigracet 10AA. The solid red line represents $\tau_{\text{bulk, avg}}$, the magenta dashed line represents $\tau_{\text{core, avg}}$, and the dashed green line represents $\tau_{\text{slope}}$. For clarity, distributions are centred at the mid-point of each material.
Fig. 4.2. The through-plane $f(\varepsilon)$ distributions for (a) Toray TGP-H-060, (b) Toray TGP-H-090, (c) Toray TGP-H-120, and (d) SGL Sigracet 10AA. For clarity, the distributions are centred at the mid-point of each material.
Fig. 4.3. The through-plane single phase $K$ distributions for (a) Toray TGP-H-060, (b) Toray TGP-H-090, (c) Toray TGP-H-120, and (d) SGL Sigracet 10AA. For clarity, the distributions are centred at the mid-point of each material.
4.5 Tables

### Table 4.1. Comparison of the TP permeability values ($K$) of GDLs reported in the literature.

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Method</th>
<th>$K$ [e-12 m$^2$]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper GDL</td>
<td>Experimental</td>
<td>8.99</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>GEODICT – GDL Model</td>
<td>9.24</td>
<td>[76]</td>
</tr>
<tr>
<td></td>
<td>CFD solver – GDL Model</td>
<td>8.93</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td>CFD solver – µCT GDL</td>
<td>2.91</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td>LB – µCT GDL</td>
<td>2.10</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td>LB – µCT GDL</td>
<td>0.402</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>LB – GDL Model</td>
<td>7.40</td>
<td>[63]</td>
</tr>
<tr>
<td>Felt GDL</td>
<td>Experimental</td>
<td>37.4</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cloth GDL</td>
<td>Experimental</td>
<td>12.36</td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2. Heterogeneous TP $\tau$ characterization of paper and felt GDLs.

<table>
<thead>
<tr>
<th>GDL Type</th>
<th>$\tau_{slope 1}$ ($\mu m^{-1}$)</th>
<th>$\tau_{slope 2}$ ($\mu m^{-1}$)</th>
<th>$\tau_{bulk, avg}$</th>
<th>$\tau_{core, avg}$</th>
<th>$\Delta \tau_{avg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toray TGP-H-060</td>
<td>0.0080</td>
<td>0.0088</td>
<td>1.199</td>
<td>1.230</td>
<td>-0.031</td>
</tr>
<tr>
<td>Toray TGP-H-090</td>
<td>0.0066</td>
<td>0.0067</td>
<td>1.191</td>
<td>1.220</td>
<td>-0.029</td>
</tr>
<tr>
<td>Toray TGP-H-120</td>
<td>0.0075</td>
<td>0.0100</td>
<td>1.248</td>
<td>1.282</td>
<td>-0.034</td>
</tr>
<tr>
<td>SGL Sigracet 10AA</td>
<td>0.0029</td>
<td>0.0034</td>
<td>1.165</td>
<td>1.232</td>
<td>-0.067</td>
</tr>
<tr>
<td>GDL Type</td>
<td>(</td>
<td>f(\varepsilon)_{\text{slope } 1}</td>
<td>) (( \mu \text{m}^{-1} ))</td>
<td>( f(\varepsilon)_{\text{slope } 2} ) (( \mu \text{m}^{-1} ))</td>
<td>( f(\varepsilon)_{\text{bulk, avg}} )</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------------------</td>
<td>-------------------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Toray TGP-H-060</td>
<td>0.0108</td>
<td>0.0121</td>
<td>0.691</td>
<td>0.646</td>
<td>0.045</td>
</tr>
<tr>
<td>Toray TGP-H-090</td>
<td>0.0093</td>
<td>0.0098</td>
<td>0.699</td>
<td>0.657</td>
<td>0.042</td>
</tr>
<tr>
<td>Toray TGP-H-120</td>
<td>0.0097</td>
<td>0.0133</td>
<td>0.639</td>
<td>0.595</td>
<td>0.044</td>
</tr>
<tr>
<td>SGL Sigracet 10AA</td>
<td>0.0043</td>
<td>0.0050</td>
<td>0.736</td>
<td>0.643</td>
<td>0.093</td>
</tr>
</tbody>
</table>

Table 4.3. Heterogeneous TP \( f(\varepsilon) \) characterization of paper and felt GDLs.

| GDL Type       | \( |\log(K_{\text{slope } 1})| \) (\( \mu \text{m}^2/\mu \text{m} \)) | \( \log(K_{\text{slope } 2}) \) (\( \mu \text{m}^2/\mu \text{m} \)) | \( K_{\text{bulk, avg}} \) (\( \mu \text{m} \)) | \( K_{\text{core, avg}} \) (\( \mu \text{m} \)) | \( \Delta K_{\text{avg}} \) (\( \mu \text{m} \)) |
|---------------|---------------------------------|-------------------------|-----------------|-----------------|-----------------|
| Toray TGP-H-060 | 0.0522                          | 0.0643                  | 1.43e-10       | 9.18e-12        | 1.34e-10        |
| Toray TGP-H-090 | 0.0501                          | 0.0562                  | 1.79e-10       | 9.88e-12        | 1.69e-10        |
| Toray TGP-H-120 | 0.0485                          | 0.0581                  | 1.16e-10       | 6.34e-12        | 1.09e-10        |
| SGL Sigracet 10AA | 0.0263                         | 0.0309                  | 3.52e-10       | 8.64e-12        | 3.43e-10        |

Table 4.4. Heterogeneous TP \( K \) characterization of paper and felt GDLs.
5.0 Heterogeneous through-plane porosity distributions of PTFE-treated GDLs

5.1 Introduction
The GDL is typically treated with polytetrafluoroethylene (PTFE) to enhance its hydrophobicity for improved liquid water management [1,2]. Previous investigations have illustrated the benefits of PTFE treatments through the experimental performance of PEMFCs [77,80,110]; however, there is an important trade-off between the enhanced hydrophobicity and reduced conductivity [111,112] and permeability [112] that must be considered. Discrepancies for optimizing PTFE application exist in the literature (10 wt. % [112] or 30 wt. % [51]), and numerical evidence has indicated that porosity distributions impact liquid water distributions in the GDL [107]. Therefore, a greater understanding of the effect of PTFE treatment on the GDL microstructure is vital for informing transport models and improving their accuracy.

The decreasing porosity as a function of increasing PTFE treatment has been reported by several authors using mercury intrusion porosimetry (MIP) [51,77,80,110,112]. Park et al. [77] reported decreasing bulk porosity, pore sizes, and permeability due to PTFE applications on Toray TGP-H-060 and 090 paper GDLs. They [77] observed that PTFE treatments resulted in bulk porosity decreases and that thinner GDLs provided better water management, which led to improved PEMFC performance. However, Lin et al. [80] reported that thinner GDLs, compared to thicker ones, were more sensitive to liquid water flooding. Lobato et al. [112] used MIP to measure the decrease in bulk porosity of Toray TGP-H-120 when adding PTFE treatments and reported corresponding increases in tortuosity. Rather than using MIP, Zamel et al. [84] estimated the porosity of PTFE-treated GDLs based on the densities of carbon and the GDL mass. They reported a lower rate of porosity decrease with PTFE application compared to [112]. Fig. 5.1 illustrates the relationship between decreasing porosity and increasing PTFE treatments for Toray TGP-H-060, 090, and 120 based on measurements from literature [77,80,84,110,112]. On average, for the Toray papers mentioned above, the porosity decreased at a rate of $0.35 \pm 0.09\%$ porosity per wt. % PTFE added. Although this change in bulk porosity as a function of PTFE treatment does not vary significantly between different Toray thicknesses, the techniques utilized by these authors were not equipped for measuring the effect of PTFE treatments on the local through-plane (TP) porosity distributions of GDLs.
It is important to investigate the effect of heterogeneous PTFE distributions on the local GDL porosity since the PTFE drying speed after immersion has been observed to impact the PTFE spatial distribution within the material [2,111]. Fast dried suspension results in two regions of high PTFE concentrations near the surfaces of the GDL, whereas slow dried suspension results in a high PTFE concentration in the GDL central region [2]. TP porosity distributions are also useful for elucidating the location of PTFE within the material by comparing porosities of treated to untreated GDLs.

In the previous chapter [5], the heterogeneous TP porosity distributions of untreated and uncompressed paper, felt, and cloth GDLs were evaluated using microscale computed tomography (µCT) imaging. The TP porosity distributions of the paper and felt GDLs possessed distinct core and surface transition regions. To the authors’ best knowledge, the work presented here is the first parametric investigation of the effect of PTFE treatments on the heterogeneous TP local porosity distributions of PTFE-treated paper GDLs.

5.2 Experimental

µCT visualizations were performed for Toray TGP-H-030, 090, and 120 with 0% (untreated) and 10 wt. % PTFE. A more in-depth parametric study was performed for Toray TGP-H-060 with 0, 5, 10 and 20 wt. % PTFE treatments. Although regions of the GDL will experience compression effects in the PEMFC [26], it is necessary to investigate uncompressed materials in order to isolate the contributions of varying PTFE treatments to the local GDL porosity distributions. It is important to note that all GDLs (including PTFE-treated) were purchased from commercial vendors, and some batch-specific variation is expected due to the differences between manufacturing lots. However, the emphasis of the work presented here will be to provide insight into the trends in porosity distributions observed when PTFE treatments are applied to the GDL. The X-ray µCT imaging was performed on the treated GDLs with the same settings, resolution and analysis process as the untreated GDLs mentioned in Chapter 3 of this thesis. The resolution of the µCT analysis in this work is insufficient for distinguishing between the carbon fibres, binder, and PTFE material in the GDL because the binder and PTFE coat the carbon fibres.
5.3 Effect of PTFE on TP porosity distributions

The porosity distributions were analyzed in the same fashion as Chapter 3 of this thesis [5], whereby distinct surface transition and core regions of the GDLs were identified, as shown in Fig. 5.2(a) for Toray TGP-H-030 with 10 wt. % PTFE. The TP porosity distributions for GDLs Toray TGP-H-030, Toray TGP-H-090, and Toray TGP-H-120 with 10 wt. % PTFE (grey) and without PTFE treatment (black) are provided in Fig. 5.2. Significant changes in the regions of local porosity minima are observed for all GDLs presented. For these materials, the two local porosity minima become more distinct with the addition of 10 wt. % PTFE, and the slopes of the transitional surfaces generally increased, as shown in Table 1. There is a porosity decrease of approximately 10% for Toray TGP-H-090 and 120 ((Fig. 5.2(b) and (c)) at the local porosity minima. The TP porosity distributions present a slight variation of GDL thickness ($t_0$) with increasing PTFE application. Characterizations of the porosity distribution ($t_0$, $\varepsilon_{\text{slope}}$, $\varepsilon_{\text{bulk, avg}}$, $\varepsilon_{\text{core, avg}}$, and $\Delta\varepsilon_{\text{avg}}$) are presented in Table 1. For Toray TGP-H-030 and 090, the overall $\varepsilon_{\text{bulk, avg}}$ decreases with the addition of PTFE, in agreement with literature [77,80]; however, as seen in Fig. 5.2, the porosity distribution is not affected by the PTFE treatment uniformly in the TP direction.

For the thickest paper GDL investigated, Toray TGP-H-120, the TP porosity distribution with PTFE exhibits the same porosity decreases at the local minima and the transitional slope increases as the thinner paper GDLs. However, the TP porosity distribution of this GDL exhibits a counter-intuitive porosity increase with the addition of PTFE, as shown in Fig. 5.2 (c). The $\varepsilon_{\text{bulk, avg}}$ and $\varepsilon_{\text{core, avg}}$ values for the treated material are slightly greater compared to the untreated material, even though the average porosities of the PTFE-treated materials are expected to be lower. Possible reasons for these counter-intuitive results are explored in the discussion section. Multiple visualizations were performed on separate samples from the same lot to confirm the TP distributions were repeatable. The two untreated Toray TGP-H-120 porosity distributions have an average difference of only 2.5%. The three 10 wt. % treated porosity distributions have an average difference of only 3.0%.

A more in-depth parametric investigation of the effects of PTFE application on TP porosity distributions was performed for Toray TGP-H-060 with the following PTFE treatments: 0, 5, 10, and 20 wt. % (Fig. 5.3). Significant porosity decreases are observed at the local minima near the surface region, and similarly to the other Toray materials, the porosity distributions are not
affected by PTFE treatments uniformly in the TP direction. A trend is observed whereby the local porosity in the regions of local minima decreases with increasing PTFE treatment. The GDLs with 10 and 20 wt. % PTFE also show a significant decrease in the core regions of the porosity distributions. As shown in Table 2, Toray TGP-H-060 exhibits $\varepsilon_{\text{slope}}$ values that generally increase with PTFE application. There is also a slight decrease in GDL thickness with increasing PTFE application, which is attributed to the batch-specific nature of manufacturing mentioned earlier.

Raw greyscale cross-sections of Toray TGP-H-060 with 0 and 10 wt. % PTFE treatment are illustrated in Fig. 5.4. The $\mu$CT slices correspond to the local porosity minima (Fig. 5.4(a)) and maxima (Fig. 5.4(b)) of the 0 wt. % TP porosity distribution, respectively. Likewise, the $\mu$CT slices correspond to the local porosity minima (Fig. 5.4(c)) and maxima (Fig. 5.4(d)) of the 10 wt. % TP porosity distribution, respectively. Fig. 5.4 illustrates the overall decrease in porosity for the treated GDL. In particular, the core regions for untreated and treated materials (a and c) exhibit higher local porosity than the surface transition regions (local porosity minima, b and d).

The $\varepsilon_{\text{bulk, avg}}$ and the $\varepsilon_{\text{core, avg}}$ values of Toray TGP-H-060 are plotted in Fig. 5.5, along with values from the literature [77]. From our measurements, $\varepsilon_{\text{bulk, avg}}$ decreases steadily with increasing PTFE application, from 0.821 for untreated to 0.783 with 20 wt. % PTFE. Likewise, $\varepsilon_{\text{core, avg}}$ decreases steadily with the increasing PTFE application, from 0.794 for untreated to 0.740 with 20 wt. % PTFE. The $\varepsilon_{\text{bulk, avg}}$ and $\varepsilon_{\text{core, avg}}$ rates of porosity decrease are 0.19 and 0.28 % porosity per wt. % PTFE, respectively, which reasonably agree with the decrease of 0.31 % porosity per wt. % PTFE from [77]. The $\varepsilon_{\text{core, avg}}$ rates of porosity decrease are in better agreement with the values from literature, compared to the $\varepsilon_{\text{bulk, avg}}$ values. This is likely caused by the absence of surface region consideration in the literature.

**5.4 Discussion**

Fig. 5.2 and Fig. 5.3 illustrate that the porosity distributions are not impacted uniformly across the entire thickness of the GDL with the addition of PTFE treatments, but in fact, the porosity distribution is most impacted at the local porosity minima between the core and surface regions. In Chapter 3 and [5], the existence of local porosity minima was attributed to the high concentration of binder material in paper GDLs. Here, we attribute the decrease in local porosity of these regions to the preferential agglomeration of PTFE at the same TP location as the binder.
material. Mathias et al. [2] reported that the TP distribution of fast dried PTFE contained two PTFE peaks near the surfaces of a paper GDL sample, whereas the slow dried sample resulted in a higher concentration of PTFE in the GDL core. The local porosity minima of the GDL substrate prior to PTFE treatment presented in [5] provide key insight into the location of PTFE peaks in the fast dried application process reported by Mathias et al. [2]. Based on these findings, we would recommend a slow-drying process for PTFE-treated paper to avoid the preferential accumulation of PTFE in regions of high binder concentration.

We also observed a trend of increasing transitional porosity surface region slopes with increasing PTFE treatments. The steeper slopes correspond to additional material agglomerating at the surface of the GDL and reducing the surface roughness. These GDL surface changes coincide with the slight variations of GDL thickness observed, as shown in Table 1. However, changes in thickness were at most 30 µm, which is approximately the equivalent distance of only three carbon fibre diameters. Therefore, it cannot be determined whether the thickness change is only due to only PTFE application or due to the random variations associated with the commercial manufacturing process.

For most paper GDLs investigated here, the $\varepsilon_{\text{bulk, avg}}$ and $\varepsilon_{\text{core, avg}}$ values decreased with increasing PTFE treatment, which was expected since the addition of PTFE should reduce the available pore space. However, a counter-intuitive porosity increase after PTFE treatment was observed for Toray TGP-H-120 (Fig. 5.2(c)). We attribute this observation to the batch-specific variations of GDL manufacturing. The porosity increase can be explained if the treated GDL batch was initially more porous than the untreated materials investigated here. This issue arose because the GDLs were ordered with varying PTFE treatment rather than progressively applying increasing amounts of PTFE to the same GDL between µCT scans. The multiple scans of Toray TGP-H-120 still resulted in repeatable results within each lot. Ismail et al. [103] reported non-sequential experimentally-determined permeability trends for felt GDLs with increasing PTFE content. Like the porosity, the permeability is expected to decrease steadily with increasing PTFE. Their non-sequential permeability trend [103] agrees with the batch-specific properties of GDLs observed in this work. Therefore, small changes to bulk and core average porosities are not as significant as the trends in distribution shape changes. For Toray TGP-H-060 (Fig. 5.3), there is only a 2% $\varepsilon_{\text{bulk, avg}}$ decrease between untreated and 10 wt. % PTFE GDLs. Furthermore, Fig. 5.5 illustrates small porosity changes with PTFE applications. In fact, most average porosity variation due to
the addition of PTFE is within the 5.1% standard deviation for porosity measurements described by Gostick et al. [52]; therefore, the average bulk porosity values alone are not sufficient for understanding the impact of PTFE treatments on the GDL microstructure.

5.5 Conclusion
In this Chapter, we investigate the effect of varying PTFE treatments on the heterogeneous TP porosity distributions of uncompressed GDLs. The paper GDLs analyzed utilizing μCT analysis included Toray TGP-H-030, 090, and 120 with 0 and 10 wt. % PTFE, as well as TGP-H-060 with 0, 5, 10, and 20 wt. % PTFE. Based on the porosity distributions of untreated materials, insight is provided on the distribution of PTFE in treated GDLs. PTFE is observed to preferentially accumulate at the local minima near the surfaces of the paper GDLs. Furthermore, we compare the average bulk porosity to the average core porosity, and we find that the average core porosity agreed well with the values from literature. The rates of porosity decrease with increasing PTFE application are compared to and found to be in reasonable agreement with literature values. A counter-intuitive porosity increase observed with PTFE application is attributed to the batch-specific nature of GDL manufacturing; thus, it is recommended that more attention should be paid to the shape of TP porosity distribution, rather than the average bulk porosities. This work provides new insight into the effect of PTFE treatments on GDL TP porosity distributions, which are expected to inform future PEMFC models.
Fig. 5.1. Summary of bulk porosity measurements from literature for Toray TGP-H paper GDLs with varying PTFE treatments.
Fig. 5.2. TP porosity distributions for Toray TGP-H- (a) 030, (b) 090 and (c) 120 without PTFE treatments (0 wt. %) and with PTFE treatments (10 wt. %). For clarity, the porosity distributions are centred at the mid-point of each material.
Fig. 5.3. TP porosity distributions for Toray TGP-H-060 with: 0, 5, 10, and 20 wt. % PTFE treatments. For clarity, porosity distributions are centred at the mid-point of each material.
Fig. 5.4. μCT cross-sections of Toray TGP-H-060 with 0 and 10 wt. % PTFE treatment. Cross-sections are located at the local porosity minima (a) and maxima (b) of the 0 wt. % TP porosity distribution, respectively. Likewise, cross-sections are located at the local porosity minima (c) and maxima (d) of the 10 wt. % TP porosity distribution, respectively. The length bar represents 500µm.
Fig. 5.5. Comparison of measured average bulk and core porosities as a function of PTFE treatments for Toray TGP-H-060 paper GDLs with values from Park et al. [77].
### 5.7 Tables

| GDL Type   | PTFE Treatment | $t_0$ (µm) | $|\varepsilon_{\text{slope}}|$ (µm⁻¹) | $\varepsilon_{\text{slope}}$ (µm⁻¹) | $\varepsilon_{\text{bulk, avg}}$ | $\varepsilon_{\text{core, avg}}$ | $\Delta\varepsilon_{\text{avg}}$ |
|------------|----------------|------------|---------------------------------|----------------------------------|------------------|------------------|------------------|
| Toray TGP-H-030 | 0 wt. %        | 117        | 0.0071                          | 0.0095                           | 0.829            | 0.742            | 0.087            |
| Toray TGP-H-030 | 10 wt. %       | 122        | 0.0092                          | 0.0087                           | 0.819            | 0.752            | 0.067            |
| Toray TGP-H-090 | 0 wt. %        | 298        | 0.0055                          | 0.0058                           | 0.826            | 0.801            | 0.025            |
| Toray TGP-H-090 | 10 wt. %       | 273        | 0.0096                          | 0.0110                           | 0.796            | 0.780            | 0.016            |
| Toray TGP-H-120 | 0 wt. %        | 359        | 0.0059                          | 0.0081                           | 0.787            | 0.760            | 0.027            |
| Toray TGP-H-120 | 0 wt. %        | 356        | 0.0070                          | 0.0084                           | 0.799            | 0.780            | 0.019            |
| Toray TGP-H-120 | 10 wt. %       | 386        | 0.0085                          | 0.0076                           | 0.815            | 0.804            | 0.011            |
| Toray TGP-H-120 | 10 wt. %       | 361        | 0.0122                          | 0.0125                           | 0.784            | 0.776            | 0.008            |
| Toray TGP-H-120 | 10 wt. %       | 361        | 0.0114                          | 0.0096                           | 0.805            | 0.798            | 0.007            |

Table 5.1. Comparison of the TP porosity distributions of untreated and PTFE-treated Toray TGP-H-030, TGP-H-090 and TGP-H-120.

| PTFE Treatment | $t_0$ (µm) | $|\varepsilon_{\text{slope}}|$ (µm⁻¹) | $\varepsilon_{\text{slope}}$ (µm⁻¹) | $\varepsilon_{\text{bulk, avg}}$ | $\varepsilon_{\text{core, avg}}$ | $\Delta\varepsilon_{\text{avg}}$ |
|----------------|------------|---------------------------------|----------------------------------|------------------|------------------|------------------|
| 0 wt. %        | 220        | 0.0063                          | 0.0066                           | 0.821            | 0.794            | 0.027            |
| 5 wt. %        | 217        | 0.0076                          | 0.0090                           | 0.813            | 0.787            | 0.025            |
| 10 wt. %       | 190        | 0.0099                          | 0.0098                           | 0.801            | 0.770            | 0.031            |
| 20 wt. %       | 202        | 0.0080                          | 0.0101                           | 0.783            | 0.740            | 0.043            |

Table 5.2. Comparison of the TP porosity distributions of untreated and PTFE-treated Toray TGP-H-060.
Conclusions

In this thesis, investigations of the surface and internal structure of various PEMFC GDL microstructures were presented. A background was provided in Chapter 1, which described the general topography of paper, felt, and cloth GDLs, accompanied by SEM images. In Chapter 2, the surface roughness of each GDL was characterized with non-contact profilometry, and these surface roughnesses were correlated to water droplet pinning behaviour. The paper GDL possessed the surface with the lowest roughness compared to felt and cloth GDLs, and it was observed that lower roughness GDLs exhibited the strongest degree of droplet pinning at the three phase boundary point.

To investigate the internal structure of the GDL, μCT images of paper, felt, and cloth were investigated in Chapter 3. Through image analysis, we elucidated the IP and TP local porosity distributions of untreated GDLs. We determined that the TP porosity was not uniform due to GDL manufacturing techniques employed by the commercial supplier. Felt GDLs exhibited the most uniform core region compared to paper and cloth GDLs. All GDL materials possessed a linear transitional region that contributed high porosity regions to the GDL.

In Chapter 4, heterogeneous TP porosity distributions were applied to the TS model to determine the corresponding heterogeneous $\tau, f(\varepsilon)$, and $K$ distributions of paper and felt. For each property, the average was determined for the bulk material region and for the core region. Between the bulk material region and the core region, better agreement was found with the average core region and values reported in literature, since high porosity surface regions were not considered in the literature.

In Chapter 5, by comparing local porosity distributions of paper GDLs with hydrophobic treatments, we observed the preferential accumulation of PTFE at the local minima near the surfaces. Due to the non-homogeneous porosity changes from PTFE, it was recommended that more attention should be paid to the shape of TP porosity distribution, rather than the average bulk porosities.

Recommendations for future work were also presented. In summary, this thesis provides important insight into the impact that the material-specific topology has on water droplet
behaviour as well as insight into the heterogeneous microstructure of paper, felt, and cloth GDLs. These insights are expected to inform the development of predictive numerical models and new materials for improved PEMFC designs.
Future Work

Chapter 1 describes a necessary first step to investigating droplet pinning on untreated GDL surfaces and without the presence of air flow by isolating the topographical effects. Future work is required to investigate the effect of hydrophobic PTFE treatments on droplet pinning for the three different GDL microstructures. The distinction between treated and untreated GDLs is especially important in light of potential hydrophobic treatment durability issues in the GDL [113]. This future work can determine whether the PTFE treatment or the topographical features dominate the droplet pinning behaviour. As well, the pinning of droplets moving in an air flow on various GDLs would be applicable to flow field flooding issues.

As described in Chapters 1, 2, and 3 of this thesis, the woven cloth GDL presents a fundamentally different microstructure than paper or felt GDL. Since the TS model could not be applied to woven cloth microstructure, LB modelling can be performed in the future on cloth GDL µCT 3D reconstruction, as was done by Nabovati et al. [114] for general multi-filament woven materials. Furthermore, future work could be done to investigate different weave configurations and their effect on IP and TP heterogeneous porosity distributions of cloth GDL. In the Chapter 4, it was noted that pressure and concentration gradients may be expected within the GDL TP due to the heterogeneous effective diffusivity and permeability. Future modelling work would be beneficial to investigate pressure and concentration gradients and their impact on multiphase flow within the GDL.

In Chapter 5 of this thesis, the TP porosity distributions of GDLs with hydrophobic PTFE treatment were investigated. Future work should be done to investigate the TP porosity distributions of GDLs with a microporous layer (MPL) coating that is also typically applied to the GDL on the side facing the catalyst layer. These µCT generated TP porosity distributions could enable analysis that isolates the MPL porosity from the GDL. This could contribute to the understanding of the PEMFC cathode since the porosity of the combined GDL and MPL are often reported with a single bulk average value [62,115].

In an operating PEMFC, the GDL is under compression in between two bipolar plate flow fields [26]. In this thesis, uncompressed GDLs are investigated to isolate the impact of the GDL heterogeneity and PTFE treatments on the local porosity distributions. Future work is needed to
investigate the TP porosity distributions of GDLs under the compression of the flow fields. Compressed GDL distributions are expected to minimize the transitional surface region and to decrease the average bulk porosity.
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