Characterization of Porous Transport Layers of Polymer Electrolyte Membrane Fuel Cells using X-ray Micro-computed Tomography

by

Sadegh Hasanpour

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The undersigned certify that they have read, and recommend to the College of Graduate Studies for acceptance, a thesis entitled: CHARACTERIZATION OF POROUS TRANSPORT LAYERS OF POLYMER ELECTROLYTE MEMBRANE FUEL CELLS USING X-RAY MICRO-COMPUTED TOMOGRAPHY submitted by SADEGH HASANPOUR in partial fulfilment of the requirements of the degree of Master of Applied Science

Dr. Mina Hoorfar, School of Engineering, UBCO

Supervisor, Professor (please print name and faculty/school above the line)

Dr. André Phillion, School of Engineering, UBCO

Co-supervisor, Professor (please print name and faculty/school above the line)

Dr. Joshua Brinkerhoff, School of Engineering, UBCO

Supervisory Committee Member, Professor (please print name and faculty/school above the line)

Dr. Keekyoung Kim, School of Engineering, UBCO

Supervisory Committee Member, Professor (please print name and faculty/school above the line)

Dr. Aimy Bazylak, Mechanical and Industrial Engineering, University of Toronto

External Examiner, Professor (please print name and faculty/school above the line)

July 6 2016

(Date Submitted to Grad Studies)
Abstract

Among different methods available for the estimation of the transport properties of porous transport layers (PTLs) of polymer electrolyte membrane fuel cells, X-ray micro-computed tomography (X-µCT) imaging has been recognized as a viable tool. This method provides the 3D structure of materials with a high resolution. Despite the general success of X-µCT, the following topics have not been explored: first, the porosity obtained for one PTL sample using different methods varies due to arbitrary assumptions made in finding the surface of PTLs. Second, the minimum volume required to obtain permeability and effective diffusivity has not been introduced. Finally, the effect of the cracks of the micro porous layer (MPL) (i.e., the second layer of a dual-layer PTL) on porosity has thoroughly been studied but not for permeability and effective diffusivity.

In this thesis, a robust surface identification method, named as “Rolling Ball”, is introduced to systematically identify the surface and consequently to measure the porosity of PTLs. The main advantage of this method is that it uses the carbon fibre radius (instead of arbitrary assumptions) to identify the surface and also preserves the surface roughness by following the topology of the surface.

Different 3D image sizes of PTLs are also analyzed using Avizo software to identify the representative volume for which the estimated permeability and effective diffusivity are independent of the size. The results of these analyses are compared to the comprehensive model of Tomadakis-Sotirchos (TS), which shows the TS model overestimates through-plane permeability and effective diffusivity.

The effect of the cracks in MPL on permeability and effective diffusivity is studied for PTL samples with MPL and the segmented MPL from the PTL. The permeability and effective diffusivity results show a decreasing trend due to the presence of the MPL, which is similar to the results of numerical models previously developed based on the nanopores of the MPL. The consistency between these results and previous models suggests that the cracks play the major role in the transport properties.
Preface

This thesis is the original work of the author. This research was supervised by Dr. André Phillion and Dr. Mina Hoorfar. The X-ray micro-computed tomography imaging was performed at the UBC Okanagan. The porosity analysis of this thesis was presented in the ASME conference and also the comprehensive analysis was published in the journal of Electrochimica Acta. The permeability analysis was presented in the 3rd Zing Conference 2015.

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Chapter 1

Introduction

Energy is one of the major issues in the modern world. In the last four decades, energy consumption has doubled [1]. The constant growing need for energy leads to a continual increase in its generation using well-known fossil fuel technologies. Many daily tasks such as commuting crucially depend on fossil fuel sources. These growing demands have led to many disastrous consequences, such as global warming and air pollution, that significantly affect human life every day. Replacing fossil fuel technologies with clean alternatives is the goal. Currently, renewable energies, such as wind and solar energy, are rapidly growing. However, because of the intermittent nature of these sources, it is vital to store renewable energy so that it can be used at a later time. Energy storage systems are another difficulty; it is more practical to convert the generated energy into a storable medium than to convert it to electricity. A promising energy storage medium is hydrogen, which can be produced in different ways, such as electrolysis of water, splitting of water using thermochemical processes and natural gas steam reformation [2]. Hydrogen is the energy carrying medium used in fuel cells to generate electricity through electrochemical reactions. Fuel cells are an emerging technology that directly use hydrogen and generate electricity through clean reactions.

1.1 Fuel Cell

The principle of the fuel cell was introduced in 1839 by William Grove and Christian Friedrich Schonbein [2]. However, due to the invention of internal combustion engines, this technology was not used until more than a century later by NASA for space programs [3]. Fuel cells have received widespread attention since the oil crisis in 1973, and the more recent world-wide acknowledgement that greenhouse gases pose a major risk to the planet [4]. Presently, many major automotive companies are investing considerable research and development funding in fuel cell technology [5]. A promising technology is the polymer
1.1. Fuel Cell

electrolyte membrane fuel cell (PEMFC). This design, with high energy density, low working temperature, zero carbon emission and no moving parts, could potentially replace traditional fossil fuels technology. PEMFCs create electrical power through electrochemical reactions during which hydrogen (i.e., fuel) reacts with oxygen (i.e., oxidant), producing heat, water and electrical power. The core of PEMFCs is the membrane electrode assembly (MEA). The MEA generally consists of catalyst layers, a proton conductive membrane, and porous transport layers (PTLs), as shown in Figure 1.1.

The operation of a fuel cell involves splitting hydrogen ($H_2$) into protons and electrons at the anode (see Equation 1.1). The electrons then travel through an external load, while the protons are transferred through the membrane. At the cathode, the transferred electrons and protons react with oxygen to produce the by-products of water and heat, Equation 1.2, 1.3 [6].

![Figure 1.1: Schematic of different components of MEA and occurring reactions in each part.](image)

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

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

\[
2H_2 + 4O_2 \rightarrow 2H_2O + \text{Energy} \quad (1.3)
\]
1.2 Porous Transport Layer

The porous transport layer (PTL) is the component in the fuel cell that facilitates the permeability of the reactants and by-product, electron conductivity from the catalyst layer to the bipolar plates, heat conductivity for removing the generated heat, and mechanical support for the membrane electrode assembly (MEA) [7]. In order to perform these vital functions, PTLs should be highly porous and have good electrical conductivity. The most common PTLs are made of carbon fibre materials, which are used for a multitude of applications, such as phosphoric acid fuel cells, automotive transmissions and aircraft brakes [7]. One of the main roles of PTLs is the control of water migration within the MEA. In essence, if the membrane is not wet enough, protons cannot move through it [8]. However, excess water leads to the problem of flooding, i.e. blockage of passages which inhibits the reactants from reaching the reaction sites. In order to improve water removal from the PTLs, the carbon fibres are treated with polytetrafluoroethylene (PTFE) to increase the hydrophobicity of materials. Although water is only produced at the cathodic side of a PEM fuel cell, PTFE is added to the both sides, anodic and cathodic parts. The reason is that in a cold start up, the humidified reactants in the anodic part condense liquid water, which could freeze if not removed [7]. Further, back diffusion of water from the cathode to anode through the membrane can also lead to flooding at the anode side. The amount or loading of PTFE plays a role in controlling water within the PTL. The effects of PTFE loading on PTLs have been extensively studied in the literature, e.g. Ref [9].

PTLs are generally classified as single layer or double layer. The single-layer PTL is mostly made of carbon-based materials with a thickness between 150 to 500 µm and a pore size distribution of approximately 10 to 30 µm, Figure 1.2(a). The dual-layer PTL has an additional micro porous layer (MPL) coated onto the single-layer PTL, Figure 1.2(b). This layer consists of carbon or graphite particles mixed with PTFE loading [7]. Scanning-electron microscopy combined with energy dispersive spectroscopy (SEM-EDS) performed on a dual-layer PTL (SGL 35BC) has shown that the MPL contains approx. 83% carbon and 17% fluorine, and that the pore size distributions within the MPL is around 100 to 500 nm, Figure 1.3 [10]. This layer wicks the produced water from the catalyst layer into the PTL and also reduces the electrical contact resistance [7]. In some commercial PTLs, MPLs have cracks, Figure 1.2 (b). These cracks are formed during the manufacturing
1.2. Porous Transport Layer

process, specifically at the drying stage.

Within the literature, there is no convention on naming of sub-layers within the PTL. In this thesis, the first layer (carbon-fibre + PTFE) will be called GDL, while the second layer will be called MPL. Thus, a single-layer PTL consists of only GDL, while a dual-layer PTL consists of both GDL and MPL.

![SEM image of single-layer PTL, SGL35BA, in two different directions.](image1)

![SEM image of dual-layer PTL, SGL35BC, in two different directions.](image2)

Figure 1.2: SEM image of two PTLs, single and dual layers.

![MPL carbon and PTFE particles.](image3)

Figure 1.3: MPL carbon and PTFE particles.
1.3 3D Imaging

Porous materials by their intrinsic nature are heterogeneous. Having the 3D structure of a porous material significantly helps to characterize its properties. X-ray micro-computed tomography (X-µCT) is a recently-developed test method that can demonstrate the internal 3D structure of materials at a micro-scale resolution. This novel characterization technique, which is similar to CT scanner in medical imaging [11], is a non-invasive method to capture the 3D structure of materials.

3D images are obtained using X-µCT by first taking many 2D radiographs of a sample as it is rotated through 360° [12]. From these images, the 3D volume is reconstructed. PTLs are highly porous, making them ideal candidates to be scanned using X-µCT as the resolution of scanning is high enough to observe internal pores. Afterwards, the obtained 3D dataset can be used as an actual model/geometry to characterize PTLs and simulate its physical properties.

1.4 Thesis Overview

This thesis consists of seven chapters. Chapter 1 provided an introduction of PEMFCs, and briefly overviewed the fundamental operation of this technology and functionality of the PTL, and the use of X-µCT to characterize PTL’s properties. In Chapter 2, recent literature on PTL transport properties is reviewed, along with literature on the use of X-µCT to analyze porosity, permeability and effective diffusivity. The scope and objectives of this thesis are elaborated in Chapter 3. In Chapter 4, the experimental procedure for scanning PTLs using X-µCT, and subsequent image processing, are described. Chapter 5 describes the new methods for determining porosity, permeability and effective diffusivity of PTLs; furthermore, it introduces methods to investigate the effect of MPL on transport properties. In Chapter 6, the developed analysis methods are applied to different commercially available PTLs to compare their transport properties. Chapter 7 will conclude this study and suggest new insights for further research.
Porous transport layers (PTLs) are highly porous materials providing pathways for the reactants and the by-product. An important element within the PTL is the fibrous layer, which is called gas diffusion layer (GDL). GDLs are made of carbon-fibre-based products. Carbon fibres, with light weight, high strength, high stiffness, and a diameter around $7\text{-}10\ \mu m$, are used for a variety of different applications. Carbon-based products have high porosity and good electrical conductivity, making them an ideal candidate for the GDL in the PEM fuel cells [7].

Based on the manufacturing process, GDLs can be divided into three main categories: non-woven paper, non-woven felt and woven cloth [7, 13]. The non-woven paper GDLs are made of randomly dispersed straight carbon fibres that are mostly aligned perpendicular to the thickness of the GDL sheet. The non-woven felt GDLs, known as fleece mat [7], consist of carbon fibres that are randomly dispersed and are not straight. In comparison to paper GDLs, the non-woven felt GDLs have a more tortuous structure. The woven cloth GDLs are based on a group of carbon fibres, 200-300, that are sewn together to make a yarn. The yarns are weaved, producing strong fabrics. Although all of these GDLs are quite thin and have high porosity to facilitate the transport of species, the woven GDLs are thicker and more flexible in comparison with non-woven GDLs. Further, as mentioned in Chapter 1, PTFE is added to GDLs to increase its hydrophobicity. The amount of PTFE loading can vary between 5 to 30%, and can be applied on the GDL in a number of different ways including: suspension, spraying, and brushing [7]. For more information about the detailed manufacturing processes, the reader is referred to Mathias et al. [7].

Figure 2.1 shows the 3D structure of a non-woven paper-based GDL. This image, acquired using X-µCT, details the highly porous internal structure of this material. GDLs are very similar to a paper sheet in the direction of their thickness; i.e., they are very thin in comparison to the other two directions. As a result, the material properties are anisotropic, having different properties in the “in-plane” directions (across the thickness)
and the “through-plane” direction (along the thickness). In Figure 2.1, X and Z represent the in-plane (IP) directions and Y represents the through-plane (TP) direction. The role of the PTL within the PEM fuel cell is to facilitate the movement of gaseous compounds along the through-plane direction. Thus, their main properties of interest relate to transport properties [14], i.e. porosity, permeability and effective diffusivity [15]. *Porosity* is the term used to define the relative void volume of a porous medium. The term *Permeability* represents the structural resistance in front of a pressure driven flow, while the term *Effective Diffusivity* represents the structural resistance against the movement of species from a region of high concentration to a region of low concentration. In the following sections, relevant literature on different characterization methods developed to obtain these transport properties for PTLs is reviewed, and the limitations of current methods are discussed.

Figure 2.1: 3D structure of PTL, SGL35BA, three different directions in this sample.
2.1 Porosity

The definition of bulk porosity is the total pore volume divided by the summation of solid volume and pore volume [16]. Bulk porosity is thus the main parameter within porous media. Different properties such as tortuosity, permeability, effective diffusivity [17], and capillary pressure [18] are all connected to porosity. In addition, correlations between porosity and these other transport properties exist within the literature (see for example [17]).

A number of different experimental methods have been developed to measure the bulk porosity of PTLs, including capillary flow porometry (CFP), gas adsorption porosimetry, decane wetting porosimetry and mercury intrusion porosimetry (MIP)[19]. Among these methods, MIP is the most widely used method [20, 21]. Mercury is a non-wetting liquid with high contact angles, more than 90°, requiring pressure to penetrate into the pores. By measuring pressure, the size of pores can be calculated based on the Young-Laplace equation [22]. By measuring the volume of mercury passing through the material, the bulk porosity can be obtained. Therefore, MIP provides both the bulk porosity and the pore size distribution of samples. A detailed explanation of this technique can be found in [19]. Although this method measures the pore size distribution to a good level of accuracy, it is a destructive method in which the internal pores of samples are collapsed and destroyed after the test, and it uses a hazardous material.

An alternative to MIP is X-ray micro-computed tomography (X-µCT). This non-destructive imaging technique obtains the internal 3D structure of porous media at a fine level of detail. This method has been used lately [23] to characterize PEMFCs components and more specifically PTLs. To the authors knowledge, Sinha et al. [23] were the first group used X-µCT (with a 10 µm resolution) for imaging PEMFCs. Their interest was to visualize water distribution inside a PTL, to estimate an optimum water purging time. The use of X-µCT to determine porosity in PTLs was first proposed by Buchi et al. [24]. They employed synchrotron-based X-µCT with a resolution of 1 µm to capture water distribution in PTLs. A series of experiments were performed in which water, at different defined pressures, was applied on one side of the PTL, and a 3D image showing the distribution of water within the PTL was captured. The breakthrough pressure, i.e. the pressure that water passes through the PTLs, was also obtained. This experiment showed that water covers PTLs in
2.1. Porosity

a non-homogenous fashion, and the effective porosity varies at different water pressures.

Buchi’s [24] study was the starting point for a series of structural analyses of PTLs using X-\(\mu\)CT. Bazylak and coworkers, in a series of comprehensive studies [9, 15, 25, 26, 27], employed this method to investigate the microstructure of PTLs. First, they characterized the porosity distribution along different axes, through-plane and in-plane, for three different categories of PTLs: carbon fibre paper, felt and cloth. The results indicated that the porosity distribution is not homogeneous. Among these three different categories, felt-based PTLs showed more homogenous through-plane porosity distribution as compared to carbon fibre and cloth samples [15]. In their next study [9], they investigated the effect of PTFE loading on the porosity distribution through the thickness of PTLs. In this study, different PTLs with different thicknesses (between 110 \(\mu\)m to 400 \(\mu\)m) and with different containing PTFE loading (between 0% to 20%) were scanned and analyzed. The results indicate that PTFE is also distributed non-homogenously across the thickness of PTLs, and it depends on PTL thickness. Specifically, PTFE was found to mostly agglomerate at the surface of PTLs. Furthermore, as it is expected from experimental analysis [28], the porosity of the samples decreased with increasing PTFE loading. The PTFE agglomeration, observed via X-\(\mu\)CT, was then verified using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy imaging (EDS) in the through-plane direction [25]. They also investigated the effect of cracks within MPLs on the porosity of the PTL. Since cracks within MPL are quite large, while the pores are quite small, the MPLs crack size plays a significant role in the transport properties. In this work, first the size of cracks was quantified, along with the porosity. Then, it was shown that the overall porosity distribution from the GDL part toward the MPL, decreases towards the catalyst layer. This was an interesting finding, however, the voxel size of their tomography scan, i.e., 2.44 \(\mu\)m, was rather large compared to the size of the pores.

Another important factor with respect to porosity in PTLs is the effect of compression [29, 30] since this component is in contact with the bipolar plate and is compressed during assembly. As a result, the internal structure of the PTL is deformed, and there is an optimal amount of compression that leads to better PEMFCs performance [29]. Bazylak and colleagues [27] imaged in 3D both paper- and felt-based PTLs compressed to 1.2 MPa, and compared the measured porosity distributions to uncompressed PTLs. Their results showed that the effect of compression is not uniform through the thickness of the samples,
2.1. Porosity

and the felt-based PTL is more sensitive to compression in comparison to the paper-based PTL. James et al. [12] also examined the effects of compression on the transport properties of PTLs by creating a sample holder mimicking the channels and ribs of the bipolar plate. Using X-µCT, they showed that the area under compression is less porous.

The analysis of X-µCT datasets to observe porosity within PTLs involves several steps, including filtering, binarization and volume rendering. Among them, the most challenging step is binarization, which is used to separate the material from background. This step requires a method to obtain threshold value. The most common method for thresholding is Otsu’s method [31], which has been used to analyze different PTLs [10, 12, 15]. In one study, Ostadi et al. [32] investigated the effect of different threshold values on the properties of the PTLs. This was accomplished by first visually selecting a global threshold value, and then varying the threshold value in increments of 1 grayscale unit, calculating porosity at each increment. The results indicated that porosity changes 2% when the threshold value is changed 3%. Following this, Ostadi et al. [33] compared the 3D images of PTLs obtained using X-µCT with the 2D images obtained via SEM. The fibre diameter obtained from the SEM images was used as a reference in order to identify the right threshold value for processing the X-µCT images. Odaya et al. [34] used a global thresholding method (instead of the Otsu method [31]) to extract the PTL from the background in both single and dual-layer PTLs. Although global thresholding is considered unsophisticated, the results showed that for some cases the use of a global threshold is equivalent to and sometimes even better than those obtained from the Otsu method.

Regardless of the image processing steps employed for determining porosity of the sample, a method must also be used to identify the surface of the sample. Assuming that porosity is calculated by:

\[ \epsilon = 1 - \left( \frac{V_{PTL}}{V_{total}} \right) \]  

(2.1)

where \( V_{PTL} \) is the volume of the PTL material and \( V_{total} \) is the total volume, surface identification is a key step since it affects \( V_{total} \). The difficulty in highly porous materials, like PTLs, is that the surface is not clear and/or quite rough. An example of a single layer PTL is shown in Figure 2.2. In most studies mentioned above, subjective assumptions were made to identify the surface of the PTL. Fishman et al. [15] assumed the surface of
2.2 Permeability

In porous media, permeability describes the resistance of the material to fluid flow resulting from a pressure gradient. Permeability is an intrinsic material property and has been widely investigated [35, 36]. This property is independent of pressure, pressure gradient, and fluid passing through the medium. For PTLs, knowledge of permeability is highly important, since flow of the reactants and products is one of its main functionalities.

For creeping flow [7, 37], i.e., the flow with low Reynolds numbers (Re < 1), flow in porous media is mainly described by Darcy’s law, Equation 2.2. In this flow regime, viscous interactions between the fluid and porous solid are the main source of the pressure drop in a medium.

\[-\nabla P = \frac{\mu}{k} \vec{v}\]  \quad (2.2)

In the above equation, \(k\) is the absolute permeability of the porous medium, \(\mu\) is the viscosity of the flow, \(\vec{v}\) is the velocity of fluid and \(P\) is the pressure. Flow in porous media can also be described by the Forchheimer equation [37], but this is used for fluids at high Reynolds numbers. The Forchheimer effect in PTLs was investigated by Gostick et al. [37]. This research showed that the experimental permeability values and Darcy’s law formula were different by maximum value of 5%, and that such deviations only occurred for low
2.2. Permeability

thickness PTLs, 100 µm or less. Consequently, the Forchheimer effect can be assumed to be negligible.

Various equations have been developed to relate permeability to other, more easily measured properties. One of the well-known formulas is the Kozeny-Carman equation [38, 39]:

$$k = \frac{d_f \epsilon^3}{16K_c(1-\epsilon)^2} \quad (2.3)$$

where $\epsilon$ is the porosity of the sample, $d_f$ is the fibre diameter and $K_c$ is the Kozeny constant, which must be defined separately for each sample. Permeability predictions using the Kozeny-Carmen equation are isotropic, so this equation is mostly used for homogenous samples. To obtain the Kozeny constant in different directions, experimental results are needed [29]. As shown by Gostick et al. [37], the average error in the permeability calculated using Equation 2.3 is on the order of 25%. Consequently, using this formula for PTLs may lead to over prediction of permeability. The other equation, which is developed by performing Monte Carlo simulation on the fibrous porous media to obtain permeability as a function of porosity [17, 40, 41, 42] is Tomadakis-Sotirchos (TS) model.

$$k = \frac{\epsilon}{8\ln(\epsilon)^2 \times (1-\epsilon_p)^{\alpha+2}r_f^2} \quad (2.4)$$

In the above equation, $r_f$ is the fibre radius, and $\alpha$ and $\epsilon_p$ are constant values that are dependent on the direction of flow, fibre orientation and also the distribution of fibre in one direction, two directions and three directions. The nature of this model is based on random fibres distribution, so it is usable for non-woven carbon fibres, paper- and felt-based PTLs. In comparison to the Kozeny-Carman equation, the TS model shows better agreement with experimental results [37]. Fishman et al. [43] used the porosity distribution data from X-µCT in combination with the TS model [42] to determine the distribution of transport properties along different axes within PTLs, showing that permeability is a function of position.

Different experimental methods have been used to measure the permeability of PTLs along different directions, through-plane and in-plane. Many experimental studies focused on the through-plane permeability of the material [7, 14, 37, 44], because the thickness of PTLs is small, 100 to 500 µm, and measuring the in-plane permeability is quite difficult.
2.2. Permeability

However, there are a few studies which were able to measure in-plane permeability [37, 45]. Gostick et al. [37] designed an experimental setup to measure the through-plane and in-plane permeability for different single-layer PTLs. In one phase of the study, they showed that the in-plane permeability is higher than the through-plane value. In another phase, samples were compressed and they showed that permeability decreases with increasing compression.

In addition to the experimental methods developed for the measurement of PTL permeability, numerical methods also exist [46], such as pore networking modeling in PTLs [47], in which the pore and throat are obtained from porosimetry results and stochastic modeling [48]. For the latter, in which a 3D structure of PTLs is generated based on bulk porosity and porosity distribution. These methods model the complex geometry of PTLs and thus require many input parameters. X-µCT, which provides a realistic image of the internal structure of materials, on the other hand, does not need additional experimental results to produce a model. Becker et al. [49] were the first to use X-µCT data to obtain the transport properties of PTLs (i.e. permeability, effective diffusivity, and electrical conductivity). In this study these properties were first obtained by experimental measurements, and then, numerical methods were applied to the 3D image [50]. Finally, the results of two approaches, experimental and numerical methods, were compared. In general, the simulated values were in agreement with experimental data. The effective diffusivity and permeability results showed very good agreement; however, the electrical conductivity results deviated somewhat from the experimental results, especially in the through-plane direction. This method showed the effectiveness of 3D image of X-µCT to investigate the sample permeability. In another study [51], the effect of heterogeneous porosity distribution on the permeability of PTLs was investigated, and the permeability values were determined in the three main orthogonal directions. This study concluded that higher through-plane heterogeneity leads to higher in-plane permeability. Instead of directly using the X-µCT data for calculation of permeability, this study used the porosity distribution data from X-µCT to make a stochastic model with a simplified 3D structure.

At present, all studies in literature conducted regarding the use of the X-µCT data for permeability in PTLs have focused on single-layer materials. However, the second layer, MPL, has a significant effect on the permeability of PTL. In general, MPL contains lower overall porosity and very small pores, causing the permeability to decrease by multiple orders of magnitude [52] as compared to single-layer PTLs. However, the MPL surface also
2.3 Effective Diffusivity

The dominant transport mode for the gases in PTLs is diffusion. To ensure that the fuel cell is efficient, the diffusion of oxygen to the catalyst layer at the cathode must be as high as possible. The property controlling the diffusion of gases within PTLs is the effective diffusivity. The word effective stands for the structural resistance against diffusion. If the effect of water saturation in PTLs is ignored, the effective diffusion coefficient, $D_{\text{eff}}$, of a chemical species is given as:

$$D_{\text{eff}} = f(\epsilon)D_0$$

(2.5)

where $D_0$ is the bulk diffusion coefficient of a chemical species, $f(\epsilon)$ is the structural resistance of the porous media against diffusion, i.e. the effective diffusivity. Most studies have shown that this structural resistance, effective diffusivity, is strongly linked to the porosity, $\epsilon$, of the porous medium [54]. The parameter $f(\epsilon)$ is found to have a number of different names in the literature: effective diffusivity, effective relative diffusivity, and diffusibility to name a few. In this study, this term is referred to as effective diffusivity.

Similar to permeability, there are also a few analytical formulas to relate the effective diffusivity to the other measurable properties. The most widely used formula is the Bruggeman equation, which correlates the effective diffusivity with porosity.

$$f(\epsilon) = \epsilon^{1.5}$$

(2.6)

In the above equation, $\epsilon$ is the porosity of the sample. This relation has been developed based on spherical particles in porous media, which is clearly isotropic. As PTLs have a heterogeneous structure, this formula thus results in a high number of errors. Tomadakis-
Sotirchos study (TS) [17], have also developed a model for the effective diffusivity

\[ f(\epsilon) = \epsilon \left( \frac{\epsilon - \epsilon_p}{1 - \epsilon_p} \right)^\alpha \]  

(2.7)

where \( \epsilon \) is the porosity of the sample, \( \epsilon_p \) is the percolation threshold porosity and \( \alpha \) is a fitted value, which is found from the TS model. Similar to the analytical formula derived for permeability, Equation 2.4, this model is defined based on different fibre distributions in 1D, 2D and 3D directions and also the flow direction, parallel or perpendicular to the fibres. Therefore, the constant value, \( \alpha \) and \( \epsilon_p \), can be found based on these different conditions.

Many experimental studies have been carried out on PTLs in order to investigate their effective diffusivity [55, 56, 57, 58, 59, 60, 61]. Most of these experimental techniques have focused on measuring the effective diffusivity in the through-plane direction, since the thickness of PTLs is low and measuring diffusivity in-plane is quite difficult (although it has been carried out before, e.g. [57, 58]). These experimental studies have shown that analytical formulas, in general, cannot predict the effective diffusivity of PTLs.

Along with experimental methods, numerical analyses have been performed to thoroughly characterize the effective diffusivity [55, 62, 63, 64, 65, 66, 67, 68, 69]. Different methods have been used to define a 3D model for PTLs. Pore networking modeling [62, 66, 67, 68], stochastic modeling [55, 63, 64, 65] and X-\( \mu \)CT are the main techniques that have been used in literature for predicting effective diffusivity, in a similar fashion to what was used for permeability assessment. The advantage of X-\( \mu \)CT imaging is that it can provide a realistic model of PTLs without any other external input data [43, 12, 10, 69]. Fishman et al. [43] used the porosity distribution data from X-\( \mu \)CT and the TS formula in order to find the effective diffusivity distribution along the thickness of PTLs. This study revealed the variation of effective diffusivity along different directions within PTLs. In another study, James et al. [12] designed a sample holder, mimicking the channel and land, and compressed the sample inhomogenously. Three compression rates were investigated: 0%, 20% and 40%. After the compression tests were completed, X-\( \mu \)CT imaging was performed to obtain the 3D structure, which was then used as the geometry for modelling/predicting diffusivity. The results indicate that the effective diffusivity of a sample decreases with increasing the compression pressure. Furthermore, higher compression leads to a decrease in porosity. As a result, low porosity samples have lower effective diffusivity [12]. However,
in this work, the point that was neglected is the size of the sample: the representative size for PTLs was fixed, and the effect of different sizes has not been investigated. Becker et al. [49] also employed X-μCT to find the effective diffusivity of PTLs. In this study, the 3D image was uniformly compressed in a virtual manner prior to the effective diffusivity simulations [63]. Numerical methods were then used to determine the effective diffusivity for in-plane and through-plane directions. The results showed that the compressed sample has lower effective diffusivity in all directions, and that the effective through-plane diffusivity is lower than in-plane by factor of 2 for all levels of compression. These numerical results were also validated against experimental measurements, finding good agreements in both through-plane and in-plane directions.

Although the use of X-μCT for the effective diffusivity analysis has shown to be quite effective and informative, two main questions still remain: 1) the effect of the sample size, and 2) the effect of cracks on diffusion. The study conducted by Bernard et al. [70] on Al-Cu alloys showed that sample size plays a large role when simulating transport phenomena in porous media using X-μCT datasets. Thus, it is necessary to find an optimum sample size in order to accurately predict the permeability and effective diffusivity. In PTL studies, this behaviour has not yet been investigated.

2.4 Summary

This chapter reviewed briefly the available manufacturing processes as PTLs and different categories of PTLs, which have been used lately in different analyses. Then, it reviewed studies that have been carried out to characterize porosity, both experimentally and using X-μCT. In the next sections, the prior research on characterizing permeability and effective diffusivity within PTLs was reviewed, including the various different approaches, analytical formulas, experimental methods, numerical methods and specifically X-μCT.
Chapter 3

Scope and Objective

The membrane electrode assembly (MEA) is the core component of PEMFCs, consisting of a membrane, catalyst layers, and the porous transport layers (PTLs); a dual-layer PTL consists of two parts, the gas diffusion layer (GDL) and the micro porous layer (MPL). As discussed in Chapter 2, the porous transport layers play a vital role in PEMFCs and have been characterized using many different techniques.

X-ray microtomography, a non-destructive method developed for capturing the internal 3D structure of materials, is a very powerful technique for characterizing porous transport layers in PEMFCs. The goal of this thesis is to characterize the key material properties (porosity, permeability, and effective diffusivity) of single-layer and dual-layer PTLs in order to compare and contrast commercially available products. While previous studies have already revealed some of this information, there has never before been a systematic study of this nature. Furthermore, different studies have made different assumptions regarding the methodology used for the determination of transport properties. Lastly, the effect of cracks within MPL on the permeability and effective diffusivity of PTLs is still not well understood. With these issues in mind, the objectives of this thesis are as follows:

1. To develop a robust method for quantifying the porosity of highly porous material based on physical properties of the sample;

2. To quantify permeability and effective diffusivity of PTLs using image-based modelling, and determine the minimum size requirement of a representative volume;

3. To characterize the effect of cracks within the MPL on the permeability and effective diffusivity of dual layer PTLs;

4. To analyse different commercially available porous transport layer with these new methods.
Chapter 4

Experimental Methods

This chapter describes the methodology used to obtain a 3D structure of PTLs. This methodology consists of three main sections. First, the materials will be introduced. Then, the scanning procedure used to obtain the 3D structure of the PTLs will be reviewed. Lastly, image processing methods that are applied to extract the geometry of the PTLs will be explained in detail.

4.1 Materials

For this project, five commercially available PTLs were investigated, three from the SGL Carbon Group (SGL 25BA, SGL 35BA, and SGL 35BC, provided by SGL Carbon group, Wiesbaden, Germany), as well as, Toray 090, and Freudenberg H2315 I6 (both purchased from College Station, TX, United States). The materials from the SGL Carbon Group were used to develop the numerical methods. SGL 25BA and SGL 35BA are single-layer PTLs with 5 wt% PTFE loading and a specified thickness of 190 µm and 300 µm, respectively. SGL 35BC is a dual-layer PTL with 5 wt% PTFE loading and a specified thickness of 325 µm [71, 72]. In Chapter 6 (Results and Discussion), additional analysis is presented for the samples from Toray 090 and Freudenberg H2315 I6. These two samples were chosen for their thickness and PTFE loading which are similar to SGL 35BA, allowing for conducting comparison between different manufacturing processes. Table 4.1 summarizes these samples based on the specification sheets provided by manufacturer.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Material</th>
<th>MPL</th>
<th>Thickness [µm]</th>
<th>PTFE loading (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL</td>
<td>25BA</td>
<td>No</td>
<td>190</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>35BA</td>
<td>No</td>
<td>300</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>35BC</td>
<td>Yes</td>
<td>325</td>
<td>5%</td>
</tr>
<tr>
<td>Toray</td>
<td>090</td>
<td>No</td>
<td>280</td>
<td>5%</td>
</tr>
<tr>
<td>Freudenberg</td>
<td>H2315 I6</td>
<td>No</td>
<td>210</td>
<td>7%</td>
</tr>
</tbody>
</table>
4.2 Scanning Procedure

The methodology for scanning the PTL samples is explained in this section. First, a description of the sample holder is given, and then the image acquisition process with X-μCT is introduced.

4.2.1 Sample Holder

As PTLs are quite light, a sample holder is required to fix and support the sample so it remains stable during acquisition of the radiographs for X-μCT. For this work, the sample holder consists of an aluminum tube that is mounted within a sample holder on the rotation stage of the X-μCT apparatus. PTL samples were then cut into small sections, 4 mm², and firmly secured on the sample holder. To minimize fluttering during image acquisition, only a small portion of the sample is exposed above the tape affixing the PTL to the sample holder. Figure 4.1 shows an example of a mounted sample.

![PTL Sample, SGL 35BA.](image1)

![Mounting the sample on the sample holder.](image2)

Figure 4.1: Sample preparation for scanning.
4.2.2 Image Acquisition

The tomographic imaging was performed using a Zeiss MicroXCT-400 computed tomography microscope. The imaging components, source, detectors and the sample are shown in Figure 4.2. The sample is positioned in the middle to obtain the 3D structure of PTLs. The tomography images were acquired using a voltage of 40 kV, and an exposure time between 8 and 10 s depending on the thickness of the PTL. For image acquisition, the binning for the system was set to 2. In total, 2500 radiographs were acquired spanning 360° using the 20X objective with the image captured via a CCD camera. Additional machine settings included a source-to-sample and detector-to-sample distance of 56 mm and 8 mm, respectively, resulting in a field-of-view of approx. 1 mm × 1 mm. These radiographs were then used to reconstruct a 3D volume containing \(900 \times 900 \times 300\) voxels each with an edge length of 1.167 µm. Generally, the smallest particle that can be observed via tomography requires three to five voxels along any side [73]. As a result, the use of a 1.167 µm voxel size is sufficient to resolve the majority of the internal pores in GDLs and cracks in MPLs. Furthermore, the overall size of the sample is large enough to identify the structural properties of PTLs [15]. The effect of scattered X-rays on the 3D image is neglected.

![Figure 4.2: Inside of The Zeiss MicroXCT-400 computed tomography microscope.](image)

4.3 Image Processing

After image acquisition, each 3D dataset was post processed to reduce noise and converted to a binary form (black and white). The process of binarization is explained below.
As it is pointed out in Chapter 3, one objective is to characterize the effect of MPL on the transport properties. Therefore, it is necessary to also segment the GDL and MPL from each other. This segmentation process is also explained. The ImageJ and Avizo software packages were used for image processing.

### 4.3.1 PTL Binarization

For binarization, first, the bottom 5% of the volume (near the sample holder), was removed. This section was quite blurry because of the interference from the aluminum tube. Then, a median filter with kernel size of 2 was applied to the remaining data to remove noise and smooth the image. This filter basically removes small artifacts [74], and variations in radiograph quality. Second, the data was binarized to separate the PTL from the background. Although several thresholding techniques could be used, in this study global thresholding [34, 75] was applied since it was found to produce the best results (see Chapter 2). Figure 4.3 demonstrates the process of denoising and thresholding from the raw data, Figure 4.3(a), filtered image, Figure 4.3(b), and the binary image, Figure 4.3(c).

### 4.3.2 Separating MPL from GDL

For dual-layer PTLs, there is the additional requirement to segment the MPL. MPLs contain cracks on the surface as well as very small pores around 100 to 500 nm [7]. Although imaging the nanopores is beyond the resolution of the X-µCT, the technique can easily capture the cracks within the MPL. Figure 4.4 shows two images of an MPL with cracks. The image on the left was taken via scanning electron microscopy, while the one on the right is from X-µCT. As it can be seen, the images are nearly identical.

A cross-sectional image of a dual-layer PTL is shown in Figure 4.5(a). Although the GDL and MPL can be easily distinguished by eye, their greyscale values are relatively similar. Segmentation is achieved as follows. First, PTL materials are segmented from the background using global thresholding, Figure 4.5(b). Then, using hysteresis thresholding, GDL materials are separated from the background, Figure 4.5(c). Finally by subtracting the PTL from the GDL, the MPL materials can be segmented, Figure 4.5(d). This process is shown step by step in Figure 4.5.
4.3. Image Processing

(a) Original image.

(b) Filtered image.

(c) Binary image.

Figure 4.3: A cross-sectional view of PTL, SGL 25BA.
4.4 Summary

(a) SEM image.  
(b) X-µCT image.

Figure 4.4: Micro porous layer of PTL.

4.3.3 3D Structure

The denoised, binarized, and segmented 3D structure of PTLs are shown in Figures 4.6 and Figure 4.7. Figure 4.6 shows the single-layer PTL. In this 3D structure, the anisotropic distribution of carbon fibres is clear, as is the non-uniform binder and PTFE. By segmenting the dual-layer PTLs, Figure 4.7, the 3D structure of each layer is obtained. As it can be seen in Figure 4.7(b), the cracks in the MPL are distributed heterogeneously throughout the surface of the PTL. Furthermore, some parts of carbon fibres are protruding through the MPL. The reason is that the GDL surface is quite uneven, and some of the carbon strands can be seen on the surface of the MPL.

4.4 Summary

This chapter described the methodology that was used to obtain the 3D geometry of PTLs using the X-µCT technique. The first section introduced the materials studied in this thesis. The second section summarized the scanning procedure for imaging PTLs via X-µCT, and the design of the sample holder. Finally, a description of the image processing methodology used to binarize the datasets as well as to separate the MPL from the GDL in a dual-layer PTL was provided.
4.4. Summary

(a) Cross-sectional view of PTL.

(b) Dual-layer PTL.

(c) GDL part of PTL.

(d) MPL part of PTL.

Figure 4.5: The segmentation process of MPL from GDL in a dual-layer PTL, SGL 35BC.
Figure 4.6: The 3D structure of a single layer PTL, SGL 35BA.
4.4. Summary

(a) 3D structure of GDL part.

(b) 3D structure of MPL part.

(c) 3D structure of dual layer PTL.

Figure 4.7: 3D structure of SGL 35BC showing segmented GDL and MPL.
Chapter 5

Numerical Methods

In this chapter, the numerical methods that were utilized to investigate PTLs are presented. This chapter is divided in six sections. The first section explains the method developed to measure the bulk porosity of PTLs, along with two other commonly-used methods available in the literature. The second and third sections explain the methods used to calculate the permeability and effective diffusivity of PTLs. Section four elaborates the effect of different volume sizes investigated for finding the representative volume size for each properties, porosity, permeability and effective diffusivity. In the fifth section, the methodology used to determine the effect of cracks within MPL on transport properties is introduced. The final section reviews and summarizes the numerical methods in this chapter.

5.1 Porosity Determination

5.1.1 Bulk Porosity Measurement

X-μCT provides a 3D image of PTLs, with detailed internal structure. An example of the 3D structure is shown in Figure 5.1. The cross-sectional view on the left-hand side of Figure 5.1 shows the high degree of surface roughness that exists in this material. As discussed in Chapter 2, porosity is defined as the pore volume divided by the total volume of the sample. For PTLs, the evaluation of the sample volume is strongly linked to the identification of the surface, since the sample is so thin. Different assumptions of the surface’s locations result in different values for bulk porosity of the same sample. In this thesis, a robust surface identification method, referred to as the Rolling Ball method, is developed to define the volume of PTLs. In the first part of this section, this methodology is outlined, followed by a description of the alternative methods. In the second section, the porosity distribution along different axes of PTLs are explained based on different surface identification methods.
5.1. Porosity Determination

Figure 5.1: 3D structure of PTL, SGL 25BA with a highlighted cross-sectional view.

**Rolling Ball**

The Rolling Ball method uses a well-known image processing technique [76, 77, 78] for surface identification that is based on a distance transform (DT) function [79]. The Rolling Ball technique is so-named because it can be thought of as the path taken by a ball as it moves over a surface in 3D. The radius of the ball relative to the true surface roughness defines the surface. The developed method is outlined in Figure 5.2 on a 2D set of images as an example, although the method was applied directly to the 3D dataset. First, the image is binarized, Figure 5.2(a). Second, a Euclidean distance transform function is applied, Figure 5.2(b). This function measures the distance between each voxel from the closest white voxel, and then the value for this distance is stored in that same voxel. Third, a value for \( R \), representing the Rolling Ball radius, is chosen to identify the surface. Each voxel that has a value higher than \( R \) is labeled black, while voxels less than or equal to \( R \) are labeled as white. Figure 5.2(c) shows the output for \( R=15 \) voxels. Finally, through binary multiplication of Figures 5.2(a) and 5.2(c), the PTL surface and the internal pores are fully revealed.
5.1. Porosity Determination

(a) Cross-sectional view of binarized PTL.

(b) Euclidian DT applied on 5.2(a).

(c) The area defined as a material by the Rolling Ball method.

Figure 5.2: The process of the Rolling Ball method applied on a 2D cross-sectional view.

With a well-defined surface, porosity can be estimated on a line-by-line basis going through the plane of the PTL. Figure 5.3 shows the original binarized image on the left, and the area defined by the Rolling Ball method combined with the PTL material on the right. A grey line has been added from the top to the bottom surface to demonstrate the calculation of line-by-line porosity. The porosity along each line is calculated by dividing the white voxels by the total number of voxels along the line. By repeating this measurement throughout the 3D dataset, the 3D porosity for entire volume can be calculated.
5.1. Porosity Determination

Figure 5.3: The algorithm for finding porosity. The left side represents the binary image, while the right side shows the area identified by the Rolling Ball method. The linear porosity is given by dividing all the pixels along the dotted line by the internal grey pixels. The calculation can be summed in 3D to calculate percentage porosity.

The most important parameter in the above algorithm is the choice of the Rolling Ball radius, $R$. Figure 5.4 shows the effect of the $R$ value on the identified surface. As it can be seen, by increasing $R$, the surface moves outward, increasing the area identified as “inside” the PTL. Thus, increasing $R$ leads to an increase in apparent porosity. Figure 5.5 shows the variation in bulk porosity as a function of $R$. The difference in porosity with the Rolling Ball radius is considerable, ranging from 0.65 to 0.90 for the same sample.

In order to define porosity in a systematic fashion, the Rolling Ball radius should be defined as a function of another intrinsic property. One intrinsic property of paper-based PTLs that is readily available is the radius of the carbon fibres. All paper-based PTLs are fabricated with fibres of a known and specified radius. Using the fibre radius, the selection of the Rolling Ball radius can directly be linked to the characteristics of the PTL, enabling the robust porosity estimation between different PTLs.

Figure 5.6 shows two scanning electron microscopy images, each taken at a different magnification, which were used to estimate the radius of the carbon fibre. A series of fibre
5.1. Porosity Determination

cross-sections were measured at both resolutions and then averaged. The use of images at two different resolutions resolves the variation in the fibre radius while allowing for a sufficient number of fibres to be measured. Using this technique, a fibre radius of 6.5 µm has been determined for SGL 25BA. This will be used as the radius for the Rolling Ball method.

Figure 5.4: Effect of the Rolling Ball on the segmented area.
5.1. Porosity Determination

Alternative Methods

Two different alternative methods, termed “99% porosity” and “mean surface height” in this thesis, can also be used to identify the volume of the PTL, and hence the bulk porosity. These methods define the volume based on different assumptions, which leads to different porosity results.

99% Porosity

In addition to determining the bulk porosity, the X-µCT datasets of PTLs can be used to calculate the porosity variations along each direction of the sheet, as will be explained in detail in Section 5.1.3. Fishman et al. [15] employed this knowledge to plot porosity distributions along different axes. Along the thickness of the PTL, the “through-plane” porosity approaches 100% as the surface of the PTL is reached. Fishman et al. [15] assumed that the bulk porosity was defined using a bounding box that was large enough to encompass all PTL materials until the through-plane porosity reached a value of 99%.
5.1. Porosity Determination

![SEM images with two different magnifications of SGL 25BA.](image)

Figure 5.6: SEM images with two different magnifications of SGL 25BA.

**Mean Surface Height**

Although the surface itself is difficult to identify, the mean surface position, $Y$, for the top of the sheet can easily be calculated (using an arbitrary coordinate system) by $Y = \frac{\sum Y}{n}$, where $Y$ is the position of the first white particle in the 2D image and $n$ is the number of the columns in the 2D image. A similar procedure can be used to calculate the bottom surface.

**Assumptions within Alternate Methods**

Figure 5.7 shows two lines, solid and dashed that represent the top and bottom surfaces identified by the 99% porosity and mean surface height methods, respectively. There is a considerable difference in the position. The 99% porosity method creates a very large total volume for the porosity estimation, while the mean surface height method only covers a very small portion of the volume. The resulting bulk porosity estimates will vary considerably.

**5.1.2 Spatial Variations in Porosity**

The section above described methods used to characterize the bulk porosity. However, the porosity distribution along the main axes of materials is also a key parameter for porous media, and is often reported for PTL materials.
5.1. Porosity Determination

Figure 5.7: The solid line represents the 99% porosity method, while the dashed line represents the mean surface height.

In-plane Porosity Distribution

The term “in-plane” refers to the direction across the thickness of a sample, as shown in Figure 5.8, along with 6 slices of PTL. Each slice has a different porosity, and further each slice has two different in-plane directions, shown by the red and blue arrows. No matter what direction of the sample is chosen, again identifying the border of the sample is the challenge. The surface identification methods, Rolling Ball, 99% porosity and mean surface height, can be used to investigate the porosity in each slice. These different methods result in variations in the in-plane porosity for each sample.
Figure 5.8: Different cross-sectional views across the thickness of PTL, SGL 25BA.
Through-plane Porosity Distributions

The term “through-plane” refers to the direction along the thickness of a sample, as shown in Figure 5.9, along with 3 slices of PTL. Unlike the in-plane porosity, which requires surface identification, through-plane slices are square in the shape, and thus the identification surface is not relevant. Consequently, the different surface identification methods are not applicable for the through-plane porosity distribution.

Figure 5.9: Different cross-sectional views along the thickness of PTL, SGL 25BA.
5.2 Permeability Determination

5.2.1 Permeability Definition

Another structural property in porous media is permeability, which is defined as the resistance in front of a pressure driven flow for slow steady Newtonian fluid. The well-established formula to define this characteristic is Darcy’s law, Equation 5.1.

$$k = -\frac{\mu}{\nabla P} \vec{V}$$  \hspace{1cm} (5.1)

To perform the numerical analysis, it is necessary to define governing equations of fluid in porous media. Since the Darcy flow is defined as Newtoninan and with low Reynolds number, the governing equations are the Stokes equations. The Stokes equations are defined as

$$\nabla . \vec{V} = 0$$  \hspace{1cm} (5.2)

$$\mu \nabla ^2 \vec{V} - \nabla P = 0$$  \hspace{1cm} (5.3)

where $\nabla .$ is the divergence operator, $\vec{V}$ is the velocity vector of the fluid,$\nabla$ is the gradient operator $\mu$ is the dynamic viscosity, $P$ is the pressure of fluid and $\nabla ^2$ is the Laplacian operator. As permeability is the structural property of porous media, the fluid properties (viscosity) initial conditions (pressure and velocity) do not have any effects on its value.

5.2.2 Numerical Simulation

Permeability of a porous medium can be determined by simulating fluid flow, solving the Stokes equations (Equations 5.3 and 5.4), and then inputting the relevant values into Darcy’s law (Equation 5.2). In order to find the permeability of PTLs, the Absolute Permeability Experiment Simulation tool within the Avizo Xlab module of the Avizo commercial software has been employed. The advantage of this software is that it calculates permeability directly from a binarized 3D dataset, without the need to generate an additional mesh for numerical simulation. As permeability is a structural property, and PTLs are anisotropic, with different fractions of porosity in each direction, it must be determined in each of the three main axes: in-plane (X), in-plane (Z), and through-plane (Y) (see the axes in Figure 5.8).
5.2. Permeability Determination

The main assumptions, initial conditions, and boundary conditions within this software are as follows: (1) four planes are parallel to the main flow direction are added to the simulation domain and act as a wall in order to prevent fluid loss; (2) two regions perpendicular to the main flow direction faces are added to the simulation domain. These regions act as stabilization zones, where the pressure is quasi-static; (3) the initial conditions of the simulation, the inlet and outlet pressure, are set to 130 and 100 kPa, and the dynamic viscosity of the fluid is assigned a value of 0.001 Pa.s; (4) and the solid phase is impermeable.

A schematic of the permeability simulation is shown in Figure 5.10. The two stabilization zones are placed on the left and right hand sides of the image, and two of the four walls located on the top and bottom are visible.

Figure 5.10: Schematic of permeability simulation in PTL, SGL 35BA.
Since permeability is independent of pressure gradient and fluid properties, the most important factor in accurately determining its value is the convergence criterion of the simulation. In Avizo Xlab, the convergence criterion is computed based on:

\[
\max\left(\frac{|V_x(n) - V_x(n-1)|_{\infty}}{c^2 \Delta t}, \frac{|V_y(n) - V_y(n-1)|_{\infty}}{c^2 \Delta t}, \frac{|V_z(n) - V_z(n-1)|_{\infty}}{c^2 \Delta t}, \frac{|P(n) - P(n-1)|_{\infty}}{c^2 \Delta t}\right)
\]

(5.4)

where \(n\) is the current iteration, \(V = (V_x, V_y, V_z)\) is the velocity vector, \(P\) is the pressure field, \(\partial t\) is the time step and \(c^2\) is the artificial compressibility coefficient. In this analysis, the convergence criterion has been set, through trial and error, to a value of \(10^{-6}\).

With the above theory established, a permeability analysis on 3D models of PTLs can be performed. An example geometry and streamlines from the fluid flow is shown in Figure 5.11.

Figure 5.11: Streamlines of flow through the PTL, SGL 35BA.
5.3 Effective Diffusivity Determination

5.3.1 Diffusivity Definition

The effective diffusivity is another important structural property of porous media. Similar to permeability, this property is independent of the concentration and the material that diffuses through a medium. The effective diffusivity is linked to the species diffusion as

\[ f(\epsilon) = \frac{D_{\text{eff}}}{D_0} \]  

(5.5)

where \( D_0 \) is the bulk diffusion coefficient, \( D_{\text{eff}} \) is the effective diffusion coefficient and \( f(\epsilon) \) is the effective diffusivity. The governing equations that define the diffusion in the steady and transient states can be described using Fick’s laws given as

\[ \vec{J} = -D_{\text{eff}} \vec{\nabla}c \]  

(5.6)

\[ \frac{\partial c}{\partial t} - D_{\text{eff}} \nabla^2 c = 0 \]  

(5.7)

where \( vecJ \) is the solute mass flux, \( c \) is the concentration of solute, \( \partial t \) is the time step, \( \vec{\nabla} \) is the divergence operator and \( \nabla^2 \) is the Laplacian operator.

5.3.2 Numerical Simulation

Effective diffusivity is modeled using the Molecular Diffusivity Experiment Simulation tool within the Avizo Xlab module of the Avizo commercial software. To model diffusivity, two reservoirs having the same volume but different concentrations are located on each side of the binarized dataset. The volume of these reservoirs is defined as 10 times the void space volume within the porous media. The remaining four sides are sealed, allowing for no diffusion to occur. A schematic of the model is shown in Figure 5.12. The initial concentrations of each reservoir are given by \( C_{\text{in}}(t = 0) \) and \( C_{\text{out}}(t = 0) \). Also, the void space within the PTL is filled with \( C_{\text{in}}(t = 0) \). Note that the influence of gravity is neglected. The output from the simulation is the effective diffusion coefficient. The effective diffusivity is then calculated using Equation 5.5 assuming \( D_0 = 1\text{m}^2\text{s}^{-1} \).

The simulation of diffusion within PTLs is initialized at \( t = t_0 \), and is terminated when equilibrium is reached, i.e., when \( \frac{\partial C_{\text{in}}(t)}{\partial t} = -\frac{\partial C_{\text{out}}(t)}{\partial t} \). For these simulations, the initial
concentrations were set to 1711 \( \text{mol m}^{-3} \) and 0; however, these initial values do not change the effective diffusivity results. The convergence criterion was given a value of \( 10^{-6} \), matching the permeability simulation.

Figure 5.12: Schematic of diffusivity model for PTL, SGL 35BA.
5.4 Representative Volume Size

Numerical simulations of material properties of porous media on micro-scale models require the selection of an appropriate representative volume size [70]. The X-\(\mu\)CT data of PTLs consists of the sample area of \(1 \text{ mm} \times 1 \text{ mm}\), and thin thickness, \(0.3 \text{ mm}\). With \(1 \mu\text{m}\) resolution, the 3D dataset is approximately \(1000 \times 1000 \times 300\). However, simulation on this large domain incurs a considerable computational cost. To determine the optimum domain size, the estimation of permeability, effective diffusivity, and porosity must be carried out based on sample volumes of different sizes. As it is mentioned, PTL materials have small thickness; therefore, the thickness size remains constant. For the other two in-plane directions, different sizes are chosen. The volume size was chosen as \(N \mu\text{m} \times N \mu\text{m} \times \) thickness started at \(50 \mu\text{m}\) and increased by increments of \(50 \mu\text{m}\). For each domain size, the bulk porosity, in-plane and through-plane permeability and effective diffusivity are calculated. The results are drawn in a way to find steady state values for the mentioned property. The minimum volume that can be a representative volume size for the properties (bulk porosity, in-plane and through-plane permeability and effective diffusivity, will be determined from Figures 5.14-5.16).

Figure 5.13: Different volume sizes for PTL, SGL 35BA.
5.4. Representative Volume Size

The bulk porosity is obtained based on the Rolling Ball method and the results for each domain size is drawn in Figure 5.14. Bulk porosity reaches to the steady results for the volume size of 500 µm × 500 µm × thickness. The effect of the volume size is minimal after this size, which indicates that the bulk porosity results are stable. Hence, to obtain a reliable estimation for the bulk porosity, it is necessary to perform the analysis on a domain of a size of at least 500 µm × 500 µm × thickness.

Figure 5.14: The change in bulk porosity results as a function of the size of the cubical calculation volume.
The same analysis is carried out for the in-plane and through-plane permeability. Different region of interest (ROI) boxes are chosen and the permeability is estimated for each of them. The permeability results for small samples change due to a subtle change in the ROI box sizes, which is shown in Figure 5.15. However, after 350 µm × 350 µm, the through-plane permeability reaches to the stable results. For the in-plane permeability, the required volume size to reach stable results is larger, i.e. 450 µm × 450 µm. Therefore, at least 450 µm × 450 µm is necessary to find the in-plane permeability.

Figure 5.15: The change in permeability results as a function of the size of the cubical calculation volume.
5.4. Representative Volume Size

Figure 5.16 indicates the different sizes ranging from 50 µm to 550 µm do not significantly affect the effective diffusivity results. However, the sample size more than 400 µm × 400 µm provides more reliable results for the through-plane effective diffusivity.

Figure 5.16: The change in effective diffusivity results as a function of the size of the cubical calculation volume.
5.5 Effect of MPL on Transport Properties

The MPL coating plays an important role in the transport properties of PTLs [7]. This layer has numerous cracks, formed through the manufacturing process and dispersed throughout the surface, as shown in Figure 5.17. As explained in Chapter 4, the cracks within the MPL can be captured by X-\(\mu\)CT imaging. The effect of these cracks on permeability and effective diffusivity can be determined by performing multiple Avizo Xlab simulations. For this analysis, first, the 3D model of a dual-layer PTL is used to find the through-plane permeability, effective diffusivity as well as the through-plane porosity distribution. Second, two layers are segmented, and the same analyses are carried out on the segmented layers.

![Figure 5.17: The crack within MPL, SGL 35BC.](image)

5.6 Summary

This chapter focused on the numerical analyses of the X-\(\mu\)CT datasets of PTLs. A new method for determining the surface of PTLs was described allowing for the robust characterization of the porosity and comparison between different PTLs. Further, the numerical methods for determining permeability and effective diffusivity of the PTLs using the Avizo Xlab software was presented. Also, the representative volume size to obtain the transport properties of PTLs were found. The results showed that it is necessary to perform analyses on a minimum required volume to obtain reliable results. In the last section, the method-
ology to investigate the effect of cracks within MPL was introduced. In the next chapter, these methods will be used to compare and contrast the structural properties of different PTLs studied within this thesis.
Chapter 6

Results and Discussion

The developed methods to characterize the structural properties of PTLs were explained in detail in Chapter 5. In this chapter, these methods are applied to five different, commercially-available PTLs. Further, multiple locations from each PTL sheet were scanned in order to determine material variability within a PTL. For each analysis a particular size is chosen. The volume size for porosity is \(900 \mu m \times 900 \mu m \times \text{thickness}\) and for permeability and effective diffusivity is \(500 \mu m \times 500 \mu m \times \text{thickness}\). Chapter 4 presented the method to segment GDL and MPL parts of a dual-layer PTL. The developed method to find the structural properties of porous media are applied to these layers and effect of MPL cracks on the through-plane porosity, permeability and effective diffusivity will be assessed.

6.1 Porosity

In this section, the porosity of the commercial samples specified in Chapter 4 will be investigated. First, the bulk porosity of each sample will be reported, and then the in-plane and through-plane porosity distribution of the samples are discussed.

6.1.1 Bulk Porosity Results

The methods to measure the bulk porosity of the samples were explained in Chapter 5: Rolling Ball method, 99% porosity, and the mean surface height. These methods are applied to the single-layer PTLs as well as the GDL part of dual-layer PTLs (due to the limitation in the resolution of X-\(\mu\)CT, the porosity of the MPL part cannot be determined).

**Single Layer**

Three different PTLs from different manufacturers were chosen; SGL 35BA, Toray 090 and Freudenberg H2315 I6. The SEM images of these samples are shown in Figure 6.1. As it can be seen, the fibres are positioned differently; the SGL 35BA and Toray 090 samples
6.1. Porosity

(a) SGL 35BA. 
(b) Toray 090. 
(c) Freudenburg H2315 I6.

Figure 6.1: The SEM images for the samples.

have straight fibres while the Freudenburg H2315 I6 sample has bent fibres. Also, the Toray 090 sample appears to have more fibres in comparison to the SGL 35BA sample for a given size. The fibre radius is required for application of the Rolling Ball method (see Chapter 5). From these SEM images, it was determined that the average fibre radius for SGL 35BA is 5.36 µm, for Toray 090 is 3.88 µm, and for Freudenburg H2315 I6 is 5.15 µm.

The 2D binarized cross-sectional view of these samples from the 3D tomographic datasets are shown in Figure 6.2. These figures demonstrate that each PTL has a different distribution of fibres. The fibres in SGL 35BA are the most scattered (the white portion of the figure) among the three PTL samples studied here. The corresponding 3D images are
shown in Figure 6.3. It can be observed that the SGL 35BA sample has the largest surface roughness, while the Freudenberg H2315 I6 sample has the lowest surface roughness with a relatively smooth surface. Thus, it is clear that these three samples cover a wide range of PTLs with different structural characteristics.

(a) SGL 35BA.

(b) Toray 090.

(c) Freudenberg H2315 I6.

Figure 6.2: The 2D cross-sectional view of the samples.
6.1. Porosity

(a) SGL 35BA.

(b) Toray 090.

(c) Freudenberg H2315 I6.

Figure 6.3: The 3D structure of the samples.
The different surface identification methods presented in Chapter 5 define the PTL surface based on different surface assumptions. The 99% porosity method ensures that every fibre is included within the surface definition, Figure 6.4(b). The mean surface height method, on the other hand, removes part of PTL fibres that are located far from the core bulk of the PTLs, Figure 6.4(c). The Rolling Ball method, by considering the radius of fibres, covers all the PTL’s fibres, Figure 6.4(d).

Figure 6.4: Different surface identification methods that are applied on the samples.

The 99% porosity and mean surface height methods define the surface of the PTLs by ignoring the surface roughness. In addition, the 99% porosity method overestimates the bulk porosity of the PTLs by adding the empty volume, which is not inside the material, as a pore. However, the mean surface height method considers many PTL fibres outside of the PTL’s boundary, and the porosity value is the porosity of the core of a PTL. This assumption is questionable where the core of a PTL has a different material density as
6.1. Porosity

compared to the surface, such as SGL 35BA, and the estimation of porosity becomes not reliable. The Rolling Ball method does not remove any PTL’s fibres from the estimation, and also considers the surface roughness of materials. Therefore, this method can estimate the porosity in a systematic manner, without being trapped in a local high or low porous region. For instance, the Rolling Ball method provides a robust surface identification method for thin samples with high surface roughness, similar to SGL 35BA. For samples with a relatively smooth surface, such as Freudenberg H2315 I6, the advantage of the Rolling Ball method is less clear since all three methods provide similar estimates of porosity.

The porosity estimation methods have been applied to four different locations on each sample. The results of these bulk porosity estimates are summarized in Table 6.1. As it can be seen, the variation in porosity exists no matter which method has been used to obtain the bulk porosity. In more heterogeneous PTLs, like SGL 35BA, the variation is larger, whereas it is smaller in more homogenous PTLs, like Freudenberg H2315 I6. The porosity estimation based on the 99% porosity method leads to the largest bulk porosity values in eight of the twelve samples. It was expected that this method would always show the largest bulk porosity, since the mean surface height removes PTL fibres near the surface. However, if the sample is heterogeneous with a low core density, then the porosity predicted by this method can be higher than the 99% porosity method. This occurred in four samples out of twelve samples studied here. These variations show that the use of these methods is questionable, giving results that are difficult to interpret. For smooth surfaces such as the Freudenberg H2315 I6 samples, the results for different methods are very similar. However, for samples with a rough surface, the difference in porosity between the methods can reach to 7%, which shows the importance of not only having a robust tool for estimating porosity but also to indicate the method used to estimate its value.
### 6.1. Porosity

Table 6.1: The bulk porosity results based on different methods.

<table>
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<th>Brand</th>
<th>Sample</th>
<th>99% Porosity</th>
<th>Mean Surface Height</th>
<th>Rolling Ball</th>
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<sup>*</sup>Standard Deviation
6.1. Porosity

**Dual Layer**

An example of the GDL and MPL layer in a dual-layer PTL is shown in Figure 6.5. The pore size in the GDL part is sufficiently large to be imaged using X-µCT imaging; however, the MPL pore size is smaller than the resolution of X-µCT. Consequently, the results of the bulk porosity of only the GDL part will be presented here.

![3D reconstruction of the GDL of a dual-layer PTL segmented from the MPL.](image)

Figure 6.5: 3D reconstruction of the GDL of a dual-layer PTL segmented from the MPL.

Two dual-layer samples from the same sheet of SGL 35BC were scanned. SGL 35BC is a dual-layer version of SGL 35BA, meaning that the GDL part between the two PTLs should be fairly similar with the only difference being the addition of the MPL coating. As a result, the fibre radius used with the Rolling Ball method is the same for both SGL 35BC and SGL 35BA. The calculated bulk porosity (the Rolling Ball method) for both the GDL part of SGL 35BC and SGL 35BA are shown in Table 6.2. The porosity values for
6.1. Porosity

SGL 35BC are similar (the difference between the average values of porosity of different samples of SGL 35BA and that obtained for SGL 35 BC is 1.54 which is within in the STD value obtained for these samples) to SGL 35BA, indicating the validity of the segmentation method used to separate the two layers, Chapter 4.

Table 6.2: Porosity comparison between the GDL part of a dual-layer PTL and single-layer PTL.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Sample</th>
<th>Rolling Ball</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 35BA</td>
<td>1st</td>
<td>85.08</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>80.06</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>85.00</td>
</tr>
<tr>
<td></td>
<td>4th</td>
<td>86.59</td>
</tr>
<tr>
<td>SGL 35BC</td>
<td>1st</td>
<td>81.76</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>83.52</td>
</tr>
</tbody>
</table>

6.1.2 In-plane Porosity Distribution Results

The in-plane porosity distribution represents the porosity of each slice across the thickness of a PTL. In this section, the porosity distribution of the mentioned single-layer PTLs is investigated. Each sample has one through-plane and two in-plane directions. Figures 6.6, 6.7 and 6.8 compare the in-plane porosity along one direction for SGL 35BA, Toray 090, and Freudenberg H2315 I6, respectively. Only one of the in-plane directions is plotted since the both provide similar results [34]. These figures indicate that the porosity is distributed heterogeneously for all samples. Among them, SGL 35BA is most heterogeneous and Toray 090 is most homogenous. The largest porosity value can be seen for the SGL 35BA sample, Figure 6.6, and the lowest is for the Freudenberg H2315 I6 sample, Figure 6.8, as was expected from the bulk porosity results. In addition, these figures show the porosity distribution based on different methods. For the Toray 090 and Freudenberg H22315 I6 samples, the results indicate that the lowest porosity can be seen for the Rolling Ball and mean surface height methods, and the highest porosity estimation belongs to the 99% porosity method, Figures 6.7 and 6.8. However, for the more porous and heterogeneous sample, SGL 35BA, the mean surface height has larger estimation in some regions than the 99% porosity method. Furthermore, the range of porosity deviations changes more for the 99% porosity and mean surface height in comparison to the Rolling Ball method, Figure 6.6.
6.1. Porosity

Figure 6.6: The effect of the porosity estimation method on the in-plane porosity distribution for SGL 35BA.

Figure 6.7: The effect of the porosity estimation method on the in-plane porosity distribution for Toray 090.
6.1. Through-plane Porosity Distribution Results

The through-plane porosity represents the porosity of each sample along the thickness of a PTL. Because the geometry is square with an arbitrary surface, the different surface identification methods do not result in different through-plane porosity distributions. In this section, this property for single-layer and dual-layer PTLs will be discussed.

**Single Layer**

Figures 6.9, 6.10 and 6.11 show the through-plane porosity distributions for each sample from each PTL. Four different locations of each PTL sheet are chosen; therefore, four lines are drawn in each figure. As it can be seen, samples that are manufactured by the same company show a similar through-plane porosity distribution. In comparison with the in-plane porosity, the through-plane porosity shows significantly more variation in value; at the surface the porosity is 100%, moving to a lower value in the core of the sample. The Toray 090 and Freudenberg H2315 I6 samples contain a core that is relatively homogeneous in porosity, Figures 6.10 and 6.11, respectively, while the SGL 35BA samples show more variations in porosity, even at the core part of the sample, Figure 6.9. As it is expected from the bulk porosity analysis, the SGL 35BA samples have the largest porosity value,
6.1. Porosity

while the Freudenberg H2315 I6 samples are the lowest.

Figure 6.9: Variation in area porosity through the thickness of the sample; the results for all 4 specimens are provided for SGL 35BA.
6.1. Porosity

Figure 6.10: Variation in area porosity through the thickness of the sample; the results for all 4 specimens are provided for Toray 090.
Figure 6.11: Variation in area porosity through the thickness of the sample; the results for all 4 specimens are provided for Freudenberg H2315 I6.
6.1. Porosity

**Dual Layer**

Two samples of a dual-layer PTL were chosen to investigate the through-plane porosity distribution. As mentioned before, the MPL images using X-µCT represents the cracks within the MPL and not the nanopores due to the limited resolution. Figure 6.12 shows the porosity distribution of two samples. Just like the single-layer PTLs, the through-plane porosity starts from a 100% porosity value and decreases towards the region where the MPL exists. As can be seen, both samples have the same porosity distribution, demonstrating that the level of porosity in both GDL and MPL parts (including the percentage of cracks) are similar between different specimens.

![Figure 6.12: Variation the in area porosity through the thickness of the sample for dual-layer SGL 35BC.](image)
6.1. Porosity

The segmentation of two layers, MPL and GDL, makes it possible to investigate the effect of each layer. One of the samples is chosen to find the through-plane porosity distribution, Figure 6.13. The left side of the figure is the GDL part and the right part is the MPL part. As it can be seen, the porosity starts from 100% and dropped to 30% in the MPL regions. This figure shows that the MPL particles are distributed in the middle of the GDL. There are regions that MPL and GDL parts overlap, as also indicated in the literature [34, 26]. Based on the porosity value of 40% of an MPL layer reported in the past [10], it can be concluded from the results shown in Figure 6.13 that the porosity value due to the presence of the cracks is considerable. Of course, this porosity depends on the number and size of the cracks in the MPL layer. Nevertheless, the most important point is that the cracks can influence the transport properties of the MPL and hence need to be considered.

Figure 6.13: Variation in area porosity through the thickness of the sample; Effect of GDL part and MPL part of a PTL, SGL 35BC.
6.2 Permeability

The methodology to obtain the permeability based on X-µCT images was described in Chapter 5. This methodology is used to perform the numerical simulation to acquire the permeability of different PTLs. The results of single- and dual-layer PTLs will be presented in the following sections.

6.2.1 Single Layer

The 3D image of single-layer PTLs, which were introduced in Chapter 4, are used as a model to investigate the through-plane and in-plane permeability of the samples. Similar to the porosity assessment, the permeability analysis has been carried out for four different samples of each PTL sheet. The results for the 12 samples are presented in Table 6.3. The heterogeneous nature of the PTL samples leads to different permeability values among different samples of the same PTL sheet. Moreover, the through-plane permeability is approximately 2 to 10 times lower than the in-plane permeability, similar to the result reported in literature [7]. Compared to SGL 35BA, Freudenberg H2315 I6 and Toray 090 samples show more consistent results in term of both in-plane and through-plane permeability (standard deviation of the three different PTLs). It was also noted that the in-plane permeability results among different samples of SGL 35BA varies significantly (from 16.68 to 109.05 µm²) as compared to the through-plane results.

One of the comprehensive relations that has been used to find the permeability of fibrous materials in the literature is the Tomadakis-Sotirchos (TS) model [37], given as

\[
K = \frac{\epsilon}{8(ln\epsilon)^2 \left(1 - \epsilon_p\right)^\alpha [(\alpha + 1)\epsilon - \epsilon_p]^2} \tag{6.1}
\]

where \(\epsilon\) is the porosity of the sample, and \(r_f\) is the fibre radius, and \(\alpha\) and \(\epsilon_p\) are constant values that depend on the orientation of fibres, the way the fibres are distributed and the direction of the flow. For PTL, the fibres are distributed in 2D and along the in-plane direction. For the in-plane and through-plane permeability estimation, the flow direction is assumed parallel and perpendicular to the fibers, respectively. For such conditions, the values of \(\alpha = 0.521\) and \(\epsilon_p = 0.11\) are considered for the in-plane direction and \(\alpha = 0.785\) and \(\epsilon_p = 0.11\) for the through-plane direction.

To determine permeability value from Equation 6.1, porosity is required. Based on the
Table 6.3: Through-plane and in-plane permeability results of different samples.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Sample</th>
<th>TP (Y) [µm²]</th>
<th>IP (X) [µm²]</th>
<th>IP (Z) [µm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 35BA</td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>6.80</td>
<td>59.74</td>
<td>53.36</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>7.00</td>
<td>28.84</td>
<td>16.68</td>
</tr>
<tr>
<td></td>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>9.64</td>
<td>109.05</td>
<td>77.19</td>
</tr>
<tr>
<td></td>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>8.27</td>
<td>41.49</td>
<td>39.71</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>7.93</td>
<td>59.78</td>
<td>46.74</td>
</tr>
<tr>
<td></td>
<td>SD *</td>
<td>1.14</td>
<td>30.49</td>
<td>21.93</td>
</tr>
<tr>
<td>TGP 090</td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>3.59</td>
<td>10.14</td>
<td>12.77</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>2.81</td>
<td>10.60</td>
<td>7.41</td>
</tr>
<tr>
<td></td>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>4.04</td>
<td>11.18</td>
<td>12.61</td>
</tr>
<tr>
<td></td>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>3.59</td>
<td>10.14</td>
<td>9.03</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>3.51</td>
<td>10.51</td>
<td>10.46</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.44</td>
<td>0.43</td>
<td>2.31</td>
</tr>
<tr>
<td>Freudenberg H2315 I6</td>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>1.94</td>
<td>6.31</td>
<td>5.38</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>2.40</td>
<td>7.18</td>
<td>6.42</td>
</tr>
<tr>
<td></td>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>2.02</td>
<td>4.7</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>1.34</td>
<td>4.75</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>1.92</td>
<td>5.73</td>
<td>5.19</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.38</td>
<td>1.06</td>
<td>0.78</td>
</tr>
</tbody>
</table>

*Standard Deviation

Porousity values calculated in the region of interest, the results of through-plane and in-plane permeability were calculated and shown in Figures 6.14 and 6.15. Figure 6.14 shows the results of simulation and the TS model for the three PTL samples studied here. This figure indicates that highly porous samples (SGL 35BA) have higher in-plane permeability, as expected. Three different lines show the TS permeability prediction for the range of porosity. The reason of different lines is that the samples have different fibre radius. In the figure, the dotted line represents the Freudenberg H2315 I6, the solid line represents Toray 090 and the dashed-dotted line represents SGL 35BA. The simulation results are shown by different symbols in this figure. For samples with lower porosity, which are Toray 090 and Freudenberg H2315 I6, the simulation and the TS model report similar results. However, the simulation results deviate from the TS formula for the sample with higher porosity, SGL 35BA. In general, the TS model overestimates the in-plane permeability for high porosity samples. The same study was conducted for the through plane permeability (see Figure 6.15). Similar to the in-plane permeability, higher porosity results in higher permeability values. The predictions of the TS model are also shown in the figure. It shows that the permeability estimation of the sample with lower porosity is in good agreement with the simulation results. But, the permeability estimation of the sample with higher porosity is
6.2. Permeability

significantly larger than the simulation results. This discrepancy is more noticeable in the through-plane permeability results.

Figure 6.14: Comparison between in-plane permeability of the simulation and estimation of the TS formula.
6.2. Permeability

Figure 6.15: Comparison between through-plane permeability of the simulation and estimation of the TS formula.
6.2.2 Dual Layer

The 3D image of the dual-layer PTL is used to find the through-plane permeability. In contrast to the single-layer analysis, only the through-plane permeability analysis is performed on the dual-layer sample. The reason is that the imaging resolution is not sufficient to observe the internal structure of MPL; therefore, the in-plane permeability cannot be measured. However, the effect of the cracks within MPL on the through-plane permeability can be investigated, since MPL cracks influence the porosity and the through-plane porosity of PTLs. Thus, the through-plane permeability is the representative of the permeability of the cracks within MPLs. The representative volume size for the dual-layer PTL is the same size as that of single-layer PTLs, 500 µm × 500 µm × thickness. The reason is that the GDL part in the dual-layer PTL is similar to that in the single-layer PTL. Thus, it is necessary to have a minimum volume that can represent the GDL part.

The simulations of flow through the dual-layer PTL are shown in Figures 6.17, 6.18 and 6.16 for the entire PTL, the GDL and the MPL segments, respectively. The permeability results of the GDL, MPL and PTL geometries are summarized in Table 6.4. The through-plane permeability of the GDL part is 16.4 µm² and for the cracks within MPL is 2.7 µm². The permeability of the dual-layer PTL is 0.93 µm², which is an order of magnitude lower than the permeability of the GDL part. These results are in general agreement with those reported in [52]. From these results it can be concluded that cracks have a major contribution on the permeability results. Furthermore, The comparison between the permeability results of the dual-layer PTL and MPL shows that the GDL fibres structure and MPL cracks act as series resistances, which decreases the permeability of the dual layer PTL. The assumption of series of resistance is applied to the permeability results, which is the summation of GDL’s thickness (300 µm) divided by the GDL’s permeability and the MPL’s thickness (25 µm) divided by MPL’s permeability represent the PTL’s thickness (325 µm) divided by PTL’s permeability. The result based on this assumption is 11.83 µm² and Avizo software result is 0.93 µm² that shows the prediction overestimates the result. However, this point needs further investigation.
6.2. Permeability

Figure 6.16: The streamlines in SGL 35BC.

Table 6.4: The permeability results of the dual-layer SGL 35BC, and segmented GDL and MPL.

<table>
<thead>
<tr>
<th>Permeability</th>
<th>Through-plane $[\mu m^2]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDL</td>
<td>16.44</td>
</tr>
<tr>
<td>MPL</td>
<td>2.71</td>
</tr>
<tr>
<td>PTL</td>
<td>0.93</td>
</tr>
</tbody>
</table>
6.2. Permeability

Figure 6.17: The streamlines in the GDL part of SGL 35BC.

Figure 6.18: The streamlines in the MPL part of SGL 35BC.
6.3 Effective diffusivity

Chapter 5 explained the methodology used to obtain the effective diffusivity based on X-µCT images. This methodology was applied to single- and dual-layer PTLs, results of which presented in the following section.

6.3.1 Single Layer

The 3D images of different PTLs, SGL 35BA, Freudenberg H2315 I6 and Toray 090, are used to perform the effective diffusivity analysis for the in-plane and through-plane directions. Similar to Section 6.1 and 6.2, four different locations of each of PTL sheet were selected. The sample size is the same as chosen for the permeability analysis. The summary of the results is shown in Table 6.5. The analysis shows less variations in the diffusivity results as compared to permeability (see Table 6.3). Also, the in-plane effective diffusivity was found to be at most two times higher than the through-plane results.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Sample</th>
<th>Through-plane (Y)</th>
<th>In-plane (X)</th>
<th>In-plane (Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 35BA</td>
<td>1st</td>
<td>0.71</td>
<td>0.84</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>0.63</td>
<td>0.78</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>0.67</td>
<td>0.85</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>4th</td>
<td>0.71</td>
<td>0.83</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.68</td>
<td>0.82</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>TGP 090</td>
<td>1st</td>
<td>0.34</td>
<td>0.61</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>0.36</td>
<td>0.64</td>
<td>0.56</td>
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<tr>
<td></td>
<td>3rd</td>
<td>0.36</td>
<td>0.62</td>
<td>0.69</td>
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<td>4th</td>
<td>0.37</td>
<td>0.67</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.36</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Freudenberg H2315 I6</td>
<td>1st</td>
<td>0.5</td>
<td>0.59</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>0.51</td>
<td>0.66</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>0.48</td>
<td>0.60</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>4th</td>
<td>0.47</td>
<td>0.62</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.49</td>
<td>0.62</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*Standard Deviation
6.3. Effective diffusivity

The relation between the effective diffusion coefficient, \(D_{\text{eff}}\), and the bulk diffusion coefficient, \(D_0\), can be defined as \([26]\)

\[
D_{\text{eff}} = \frac{\epsilon}{\tau} D_0
\]  

(6.2)

where \(\tau\) represents tortuosity, which is defined as the ratio of the mean effective path length to the thickness of the sample \([80]\). Using the results presented in Table 6.5, one can find the tortuosity values in the through-plane directions for the samples studied here (see Table 6.6). The tortuosity results obtained here found be in agreement with \([58]\).

Table 6.6: Through-plane tortuosity results of different samples.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Sample</th>
<th>Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 35BA</td>
<td>1st</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>4th</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>SD*</td>
<td>0.05</td>
</tr>
<tr>
<td>Toray 090</td>
<td>1st</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>4th</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.07</td>
</tr>
<tr>
<td>Freudenberg H2315 I6</td>
<td>1st</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>3rd</td>
<td>1.47</td>
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<td></td>
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<td></td>
<td>Average</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*Standard Deviation

The simulation results presented here were also compared against the TS model. The model introduces the effect diffusivity \((D_{\text{eff}}/D_0) \text{ or } \frac{\epsilon}{\tau}\) as

\[
f(\epsilon) = \epsilon \left(\frac{\epsilon - \epsilon_p}{1 - \epsilon_p}\right)^\alpha
\]  

(6.3)

where \(\epsilon_p\) and \(\alpha\) are constants with the values similar to those presented for permeability. Figures 6.19 and 6.20 show that results of the TS model and simulation for the in-plane and through-plane directions, respectively. The simulation results of in-plane effective diffusivity follows the TS model for the porosity range studied here. However, for the through-plane
direction, the TS model overestimates the effective diffusivity for samples with different porosity. This discrepancy has also been reported before [12]. This indicates that the porosity is not the only parameter that has to be considered in the through-plane estimation.

Figure 6.19: Comparison between the in-plane effective diffusivity of the simulation and the estimation of TS formula.
Figure 6.20: Comparison between the through-plane effective diffusivity of the simulation and the estimation of the TS formula.
6.3.2 Dual Layer

Three different geometries are chosen to perform the analysis including GDL, MPL and PTL. The 3D models are the same as those selected for the permeability analysis of the dual-layer PTL. The representative volume size to find the reliable results for diffusivity is defined as $500 \mu m \times 500 \mu m \times$ thickness.

Table 6.7 shows the results of GDL, MPL and PTL. The result of GDL part is similar to that of the single-layer PTL. But, the effective diffusivity of the MPL was found to be three times less than that of the GDL part. The result shows that GDL and MPL hinder the diffusion of species in the PTL, similar the permeability results presented in Section 6.2.3. The assumption of series of resistance is applied to the effective diffusivity of a PTL, which is the summation of inversion of effective diffusivity of GDL and MPL represent the inversion of the effective diffusivity of PTL. The result based on this assumption is 0.13 and Avizo software result is 0.101 that shows a great agreement. However, this point needs further investigation.

Table 6.7: The effective diffusivity results of the dual-layer SGL 35BC, and segmented GDL and MPL.

<table>
<thead>
<tr>
<th>Effective diffusivity</th>
<th>Through-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDL</td>
<td>0.555</td>
</tr>
<tr>
<td>MPL</td>
<td>0.168</td>
</tr>
<tr>
<td>PTL</td>
<td>0.101</td>
</tr>
</tbody>
</table>
Chapter 7

Conclusions

This thesis involves the characterization of the porous transport layer (PTL) properties using high resolution X-ray micro-computed tomography (X-µCT) providing 3D images of a sample with a detailed internal structure. In the first step, a new surface identification method, which is known as the “Rolling Ball” method, was introduced to estimate the porosity of PTLs in a systematic manner. This method was compared to conventional methods used in literature. It was shown that it is necessary to use a robust method (which does not depend on arbitrary assumptions) as well as to indicate the method used to estimate the porosity values. In the second step, the Avizo software was used to estimate the permeability and effective diffusivity of samples from the 3D images. Along with the process of finding the properties of the PTLs, the representative sample volumes for which the underlying properties are independent of the size were identified. The simulation results obtained in this work were compared against the results of the well-known Tomadakis-Sotirchos (TS) model. It was shown that for samples with high porosity the TS model tends to overestimate the through-plane properties, especially for permeability. Finally, the effect of cracks within the micro porous layer (MPL) of the dual-layer PTL on the transport properties of the porous material was investigated. The results were compared against those obtained using a nanopore based model. The agreement between the results of these two approaches indicated that cracks play a major role in the transport properties of PTLs.

below the summary of findings, contributions and recommendations for future work are presented:

7.1 Summary of Findings

- The 3D structure for three different commonly available PTLs was obtained. The 3D images illustrate that different manufacturing process leads to different 3D structures for PTLs.
The distribution of the in-plane and through-plane porosity showed that higher porous samples have more heterogeneous results.

There is a significant variation (up to 5%) in the bulk porosity results obtained for each PTL sample at different locations. Higher porous samples show more variations.

Despite the variations in the bulk porosity values, there is a similar trend in the through-plane porosity distribution for samples from the same manufacturer.

The results obtained for the through-plane porosity distribution of the dual-layer PTL and the segmented MPL part show that the drop in the porosity value of the dual-layer PTL is due to the presence of the cracks in the MPL.

The higher the porosity of the sample the higher the in-plane and through-plane permeability and effective diffusivity.

The through-plane permeability is smaller than the in-plane by a minimum factor of 2.

The variations in the permeability results, especially for the in-plane directions, obtained for different parts of a PTL sample are larger for higher porosity samples.

The permeability and effective diffusivity of a dual-layer PTL is an order of magnitude less than those of a single layer.

The comparison between the results of the permeability and effective diffusivity obtained from Avizo and TS analytical formulas showed that the latter overestimates the through-plane effective diffusivity for all ranges of porosity and the through-plane permeability for samples with high porosity.

7.2 Contributions

A robust method, referred to as the Rolling Ball method, is introduced for the first time for PTL samples of fuel cells. This method can be applied to sample with a wide range of porosity, especially thin porous samples with high surface roughness for which tracking the surface morphology is of importance. For this purpose, a physical property of the sample (i.e., the fibre radius) was used. It has been shown that
the Rolling Ball method estimates porosity without overestimating or reporting local minimum or maximum dense regions.

- Since variations in the values of the transport properties (especially permeability) increases as the size of the scanned sample is reduced, a representative sample size was identified for the first time. This size was defined as the minimum required size for which the transport properties are independent of the sample volume.

- The results obtained from Avizo simulation were in a general agreement with experimental and analytical models in the literature. The reliability of these results prove the capability of X-ray imaging in determining the transport properties of the PTLs.

- Upon the success of the simulation performed for the permeability and effective diffusivity, the segmented MPLs from the 3D images of PTLs were analyzed for the first time considering the role of the cracks on the transport properties of PTLs.

### 7.3 Recommendations for Future Work

- The binarization method (e.g., the Otsu method and global thresholding) used to find the right greyscale value for segmenting PTL particles (which includes fibres, binders, and PTFE) from the background is still questionable. One way to identify the most accurate binarization method would be to use the weight of the sample and compare it to that obtained from the volume of the 3D structure. For this purpose, the density of the sample must be known. The density can be obtained by crushing the sample into powders which can be compressed into a disc with a measurable volume.

- In this thesis, the Rolling Ball method was used to find the surface and hence the volume in the 3D image for the estimation of porosity. This method can be used further in the estimation process of the in-plane permeability and effective diffusivity for which significant variations were observed between different samples. These variations could be the result of the fact that surface topology was not considered for the estimation for these two properties.

- The results from the TS model were significantly larger than those obtained here and previous measurements in the literature. The TS model should be modified by
including the fibre radius and porosity distribution in the estimation of the through-plane effective diffusivity and permeability, respectively. More experimental analyses should be collected for highly porous samples, and the effect of other properties on the permeability and effective diffusivity can be investigated using design of experiments analysis.

- It is recommended to extend the study performed here to the woven PTLs materials.
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Appendix
Appendix A

Image Analysis

The output data of X-µCT is many 2D cross-sectional views of the sample. These 2D cross-sectional views were reconstructed in 8-bit greyscale Tiff format. As a result, each sample consists of around 1000 cross-sectional images. An example of one output image is shown in Figure A.1. Each pixel of this image has a greyscale value between 0 and 255. 0 represents the black pixels and 255 represents the white pixels. This original image is used to perform filtering and binarization method, which will be explained in the following sections.

Figure A.1: Original image.

A.1 Median Filter

In general, filters used to extract the useful information from the original image. One of the commonly used filters is Median filter. This filter is used to smooth and reduce noises; however, this filter reduces the contrast and softens the edge of the image. This filter assigns the median value for the defined geometry. In the defined geometry all the greyscale values are sorted from the smallest to the largest one. The median number is chosen for the pixel.
An example is shown in the array below.

\[
\begin{bmatrix}
11 & 17 & 15 \\
19 & 14 & 16 \\
18 & 19 & 13 \\
\end{bmatrix}
\]

The greyscale values are sorted and 16 is the median number that will be assigned for the output pixels. The example of the filtered image is shown in Figure A.2.

![Filtered image](image)

Figure A.2: Filtered image.

### A.2 Binary Image

To segment two parts in a greyscale image (PTL materials from the background), it is necessary to change greyscale image to a black and white image (binary image). To transform a image from greyscale to binary one, a thresholding method should be used. Thresholding means choosing the greyscale value that any voxel has higher value than this pixel will be assigned to 255 (white), and each voxel has lower greyscale value assigns to 0. In this thesis, the global thresholding is used. In this method, the greyscale value is chosen visually to segment PTL materials from the background. The result is shown in Figure A.3.

### A.3 Distance Transform

Different distance transform functions exist such as chessboard, cityblock and Euclidian. These functions can be applied to a binary image. In this thesis, Euclidian distance trans-
A.3. Distance Transform

Figure A.3: Binary image.

form function is used. This function changes the value of each pixel to the distance between that pixel and the nearest non zero pixel of a binary image. In the following matrices the effect of applying distance transform are shown. Matrix A, is the binary array with zero and non zero elements that is changed to the Euclidian distance transform format, matrix B.

\[
A = \begin{bmatrix}
255 & 255 & 255 \\
255 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix} \Rightarrow B = \begin{bmatrix}
0 & 0 & 0 \\
0 & 1 & 1 \\
1 & 1.41 & 2
\end{bmatrix}
\]
Appendix B

Avizo Analysis for Permeability and Effective Diffusivity

B.1 Permeability

The Avizo Absolute Permeability Experiment Simulation is used to obtain the in-plane and through-plane permeability of PTLs. In this simulation, single-phase fluids are considered. Figure B.1 shows different parameters that should be chosen to start the simulation. The convergence criterion is $10^{-6}$, and three different directions are marked to be calculated. The minimum and maximum number of iterations are 500 and $10^{-6}$. The error graph with number of iterations is shown in Figure B.2.

The Stokes equations are valid for the low Reynolds number. A simple estimation based on the experimental results were carried out to find a Reynolds number. The characteristic length in porous media [81] is the particle diameter. For the PTL analysis is assumed fibre diameter. To perform this analysis, results of Gostick et al. [37] study are used. The Toray 090 sample has a thickness of 290 $\mu$m, fibre diameter 7.7 $\mu$m, porosity 80%, density of air is $1.225 \frac{kg}{m^3}$ and viscosity is $1.85 \times 10^{-5} Pa.s$ and the through-plane permeability is $8.99 \times 10^{-12} m^2$. The differential pressure is assumed 15 kPa. The Reynolds number out of this data is 13.3. This Reynolds is in the range of Darcy’s flow [81].

To solve the Stokes equation, the boundary conditions are defined as: (1) a no-slip condition at fluid-solid interfaces; (2) four surfaces which are not in the flow direction defined as walls with a no-slip condition; (3) two regions are added on both sides of the flow direction, in order to stabilize the flow; (4) inlet and outlet pressure is chosen and the flow rate is estimated based on those chosen pressures.

The Stokes equations cannot be solved in fully implicit methods, because the matrices are singular. This is the reason of adding an artificial compressibility coefficient and time derivative terms in the system. Having term dependent in the system allows us to use
B.1. Permeability

Figure B.1: Permeability panel.

Figure B.2: Error of permeability simulation.
B.2 Effective Diffusivity Analysis

An iterative resolution to solve the problem. This method is used to find a solution for equations without time derivatives. However, the time in these equations has no physical sense. The detailed simulation information refereed to Avizo Help document.

The simulation performed on the PC having 36 Gb of RAM and Intel(R) Xenon(R) E5620 CPU(2 processors) on the volume of image consists of approximately (as an example for one sample is 428 428 214) 40 000 000 voxels. The simulation of permeability in each direction took around 10 hours.

B.2 Effective Diffusivity Analysis

The Avizo Molecular Diffusivity Experiment Simulation is used to obtain the in-plane and through-plane effective diffusivity of PTLs. In this simulation, only one fluid and one solid phase are considered. In the solid phase the diffusion coefficient is assumed to be zero. There is no reaction in the fluid-solid interface and also the solvent filled all the fluid phase and there is no flow in the fluid phase and just diffusion of one species is studied. Figure B.3 shows different parameters that should be assigned before starting the simulation. First, the region of interest (ROI) box for the analysis should be chosen, which is the representative volume size for PTLs. The label of pores should be assigned (pore’s label is 1 in this example). All three transport directions are chosen to be calculated. The input and output concentrations and bulk diffusivity is assigned. The convergence criterion is $10^{-6}$ and number of iterations has min and max, which minimum number of iteration assign to 500 to avoid ending computation very soon, and maximum number of iteration assigns to 100000 to finish the simulation even the convergence criterion cannot be reached.

The error graph with number of iteration is shown in Figure B.4.

A finite volume method is used to solve equation systems in Avizo Xlab Molecular, and the discretization scheme assumes that the voxel is isotropic (cubic). Avizo help documents can be used for more detailed information.

The simulation performed on the PC having 36 Gb of RAM and Intel(R) Xenon(R) E5620 CPU(2 processors) on the volume of image consists of approximately (as an example for one sample is 428 428 214) 40 000 000 voxels. The simulation of effective diffusivity in each direction took around 10 hours.
B.2. Effective Diffusivity Analysis

Figure B.3: Effective diffusivity panel.

Figure B.4: Error of effective diffusivity simulation.