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MODELING MASS AND THERMAL TRANSPORT IN THIN POROUS MEDIA
OF PEM FUEL CELLS

By

Vinaykumar Konduru

A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

In Mechanical Engineering - Engineering Mechanics

MICHIGAN TECHNOLOGICAL UNIVERSITY

2017

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This dissertation has been approved in partial fulfillment of the requirements for the Degree of DOCTOR OF PHILOSOPHY in Mechanical Engineering - Engineering Mechanics.

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Dedication

To my parents, K. Lalitha Raju and K. Shankar Raju, and my sister, K. Pratima Raju, who encouraged and guided me throughout my life, and my wife, Shweta Gujrathi, who was always supportive at every stage.

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List of Abbreviations

C	Vapor concentration
D	Binary diffusivity
l	Pore tube length
ΔP	Pressure drop across pore
P_c	Capillary Pressure
PDF	Probability Distribution Function
PEM	Polymer Electrolyte Membrane
PTL	Porous Transport Layer
R	Thermal resistance
T	Temperature
x	Meniscus position in por
γ	surface tension
μ	viscosity
θ	contact angle
κ	shape parameter
λ	scale parameter

Abstract

Water transport in the Porous Transport Layer (PTL) plays an important role in the efficient operation of polymer electrolyte membrane fuel cells (PEMFC). Excessive water content as well as dry operating conditions are unfavorable for efficient and reliable operation of the fuel cell. The effect of thermal conductivity and porosity on water management are investigated by simulating two-phase flow in the PTL of the fuel cell using a network model. In the model, the PTL consists of a pore-phase and a solid-phase. Different models of the PTLs are generated using independent Weibull distributions for the pore-phase and the solid-phase. The specific arrangement of the pores and solid elements is varied to obtain different PTL realizations for the same Weibull parameters. The properties of PTL are varied by changing the porosity and thermal conductivity. The parameters affecting operating conditions include the temperature, relative humidity in the flow channel and voltage and current density.

In addition, a novel high-speed capable Surface Plasmon Resonance (SPR) microscope was built based on Kretschmann's configuration utilizing a collimated Kohler illumination. The SPR allows thin film characterization in a thickness of approximately 0-200nm by measuring the changes in the refractive index. Various independent experiments were run to investigate frost propagation velocities in subcooled water, and film thickness during droplet coalescence during condensation.

Chapter 1

Introduction

A Polymer Electrolyte Membrane (PEM) Fuel Cell is an electrochemical device in which hydrogen and oxygen react to produce electricity. Heat and water are also produced during the operation of the fuel cell. As the name suggests, a PEM fuel cell consists of a solid polymer electrolyte membrane typically comprised of sulphonated fluoropolymer. Nafion is one of the most widely used material as the membrane. Nafion is an ionomer which consists of polytetrafluoroethylene (PTFE) with perfluorinated side chains ending with the sulfonic acid group (SO_3^-). The backbone PTFE is hydrophobic while the side chains are hydrophilic. The perfluorosulphonic side chains are responsible for the proton conductivity when hydrated. Typical thickness of the membrane varies from 25-250 μm . A catalyst layer is present on both

sides of the membrane. A typical catalyst layer of the PEM fuel cell consists of platinum on carbon black support particles and the nafion ionomer. The cathode and the anode electrodes consists of porous carbon paper/cloth which is called as Porous Transport Layer (PTL) or Gas Diffusion Layer (GDL). A Micro-Porous Layer (MPL) is usually attached to the PTL and is located between the PTL and the catalyst layer. The PTL is characterized by pores with diameter varying from 5-40 μm and porosity ranges from 70-90% [2]. MPL has much smaller pores ranging from 30 nm - 1 μm [2, 3].

Water management in PEM fuel cell is a balance between the water produced during the fuel cell operation and water removal. Excessive water removal during fuel cell operation results in the drying of the membrane, decreasing the proton conductivity and increasing the ohmic losses. Water flooding in catalyst layer results in blocking of the reaction and flooding in the PTLs blocks the paths of reactant gases. The water generated in the catalyst layer can be removed in two modes from the PTL - gaseous phase and liquid phase. During the operation of the fuel cell, the reactant gases and the generated water, in both vapor and liquid form, are present in the PTL. The mechanics of complex processes such as evaporation and condensation occurring in the PTL are not clearly understood. Moreover, the fuel cell operating conditions vary significantly further introducing a large range of variables in these processes. For optimal operation, an ideal water removal rate is necessary to prevent flooding of the PTL and at the same time prevent drying of the membrane. During startup, the low

temperatures of 20°C - 30°C result in water withdrawal primarily in liquid phase. At steady operating conditions of 80°C, a significant amount of water can be expected to be withdrawn in vapor phase. Understanding and predicting the water transport through the PTL is of the highest importance in the development of PEM fuel cells.

The thermal conductivity of the PTLs also play a vital role in the operation of the fuel cell. The temperature differential inside a single cell is typically only a few degrees. However, the small thickness of the PTLs mean that large thermal gradients are present in the different components of the fuel cell. In addition, a uniform distribution of the temperature might be absent due to the geometry of the fuel cell. A non-uniformity in the thermal distribution significantly affects the location of water condensation [4].

1.1 Outline

The overall scope of the dissertation is divided into 3 parts: determining the material specific constants of the PTLs, coupling of the solid-phase and the pore-phase, development of the SPR for nano-scale transport identification, and and development of the SPR for nano-scale transport identification, followed by summary and final recommendations.

The core focus of this research was to model the multi-phase transport in the PTL of the PEM fuel cells. Thermal transport occurs primarily through the solid-phase (carbon) of the PTL and the liquid and vapor transport along with thermal transport occurs through the pore-phase of the PTL. Compression of the PTLs, which occurs during the assembly of the fuel cell stack, results in a non-uniform distribution of thermal profile in the PTL. In the current work, a computational model is developed to incorporate the properties of the PTL into morphology and material specific properties, which can be incorporated into the pore network model. Two separate networks representing the solid-phase and pore-phase are generated from the experimentally measured PTL properties. The networks are coupled which allows simultaneous study of transport in separate yet coupled networks. Using the coupled PNM, the performance of different PTLs was evaluated at different operating conditions by studying the transient gas permeability characteristics of the PTLs.

In addition, a Surface Plasmon Resonance (SPR) imaging microscope was developed to study the transport in thin films. Several mechanisms of water transport exists in the catalysts layer such diffusion, evaporation and condensation [5, 6]. Understanding of behavior of ionomer is important in designing better catalyst layer for fuel cells. The proton conductivity in Nafion is directly related to the water uptake properties of Nafion. Water transport through the catalyst layer is therefore an important aspect that needs to be studied. Siroma et al. [7] found that conductivity of cast thin film Nafion is smaller than bulk Nafion and was lower by an order of magnitude [8]

in lateral direction. There has been a recent effort to characterize thin Nafion films [8, 9, 10]. However, more efforts are needed to better understand the properties of thin film Nafion in order to develop better catalyst layer. The SPR system can characterize ultra-thin nano-films (0 - 200 nm) by detecting small changes in the refractive Index (RI) of the thin film. Additionally, it can be used to study various physical phenomena that result in changes in small changes in RI or nano-scale thickness.

These multiple parts of the research are detailed in the six chapters as follows:

- † **Chapter 1:** The motivation and the goals behind the project are listed.
- † **Chapter 2:** The method to generate the solid-phase and couple the solid and pore-phase is described.
- † **Chapter 3:** The Solid-cylinder Material Model and the procedure to obtain the material constants of the solid phase are detailed.
- † **Chapter 4:** This chapter details the numerical model and the results of parametric study used to identify the characteristics of the PTL based on the gas permeability.
- † **Chapter 5:** This chapter describes the development of the Surface Plasmon Resonance (SPR) microscopy
- † **Chapter 6:** This chapter includes the recommendations and the future work.

Chapter 2

Coupling of Pore-Phase and Solid-Phase Networks for Simulating Heat and Mass Transport in Porous Transport Layers

The stochastic morphology of a PTL can be characterized using a probability distribution of void volume size, known as a pore size distribution. Pore size distribution data can be obtained using porosimetry or tomography and is almost universally based on

spherical pore volumes. This presentation discusses a methodology for transforming a spherical pore size distribution data, which is invariant with respect to sample size, into a pore-network model (PNM) that is size dependent. This methodology maintains the appropriate stochastic distribution, physical size and bulk porosity of the original PTL. The resulting PNM domain is unique to the original PTL sample; meaning that the pore-network is material or manufacturer specific. Thus, simulation of reactant and water transport is also material or manufacturer specific.

2.1 Introduction

Reactant, water, and heat transport through Porous Transport Layers (PTL), also known as Gas Diffusion Layers (GDL), can be simulated using a variety of computational architectures and transport models. A common approach is to create detailed reconstruction of geometry from tomographic data and use a Lattice-Boltzmann model for computing transport within the material. Another common approach is to simulate the material using a network of transport resistance elements and then use continuum, phenomenological, or Lattice Boltzmann models for computing transport through the network.

For either approach the computational domain should be representative of the morphology and structure of the PTL being simulated. Geometric reconstructions of

tomographic data naturally capture the morphology and structure, but at great computational expense when simulating heat and mass transport. A computationally efficient method is to create an abstraction of the PTL in a simple, regularized domain known as a pore-network model (PNM). This latter approach resolves the issue of computational expense, but lacks a clear relationship to the original structure and morphology of the PTL that is generally stochastic.

The stochastic morphology of a PTL can be characterized using a probability distribution of void volume size, known as a pore size distribution, which is invariant with respect to sample size. Pore size distribution data can be obtained using porosimetry or tomography and is almost universally based on spherical pore volumes.

This presentation expands upon a methodology [11, 12] for transforming a spherical pore size distribution data into a pore-network model domain. This methodology maintains the appropriate stochastic distribution, physical size and bulk porosity of the original PTL. The resulting PNM domain is unique to the original PTL sample; meaning that the pore-network is material or manufacturer specific. Thus, simulation of reactant and water transport is also material or manufacturer specific.

The methodology developed transforms a spherical-pore size distribution into a regularly-spaced network of pore cylinders; referred to as the pore-phase network. In order to simulate thermal transport in a PTL using the PNM architecture, the

solid portion of the original material must also be transformed into a complimentary solid-phase network. The solid-phase network should also preserve the original stochastic morphology and bulk porosity of the PTL. In this methodology, the two networks (pore-phase and solid-phase) are generated independent of one another, connected only through the distribution of unit cell porosities. In this manner thermal transport through the solid-phase network can be validated independently of liquid water transport through the pore-phase network and vice-versa. When combined, the dual PNM networks capture the coupled thermal and mass transport through the PTL.

Transport in thin porous materials can be modeled using a variety of model architectures and transport models. A common approach is to create detailed reconstruction of geometry from tomographic data and use a Lattice-Boltzmann model for computing transport within the material. Another common approach is to simulate the material using a network of elements and then use continuum, phenomenological, or Lattice Boltzmann models for computing transport. In both examples the division of the computational domain representing the porous material may be regularly or irregularly spaced.

The approach used herein is to create an abstraction of the porous material using a regularly spaced pore network. The solid and pore phases of the material are simulated using independent networks; each with the same element spacing and connected

to one another at common nodes. The elements can be considered as transport paths with a resistance. This resistance varies from element to element and the distribution of resistance throughout the network is related to the particular transport property of interest. There are different methods for modeling these distributions. The methodology presented modifies the pore-network model developed by Medici [13]. In that model, the solid phase was part of the same network as the pore phase, with the solid volume directly coupled to the pore volume at each point in the network. This coupling effectively imposed uniform porosity throughout the entire domain. However, in the PTL the relation between local pore to the solid volume is not fixed. The solid (carbon, PTFE, binding material) and the pores are distributed randomly and local porosity can be significantly different than the bulk porosity. In addition, the thermal contact resistance plays a dominant role in effective thermal conductivity which should be incorporated in the thermal transport through the solid phase [11, 12, 14]. Thus it becomes necessary to incorporate a separate network which is representative of the solid-phase and is coupled to the pore-phase network. By relaxing the coupling between pore and solid, separate networks for each phase can be constructed.

In this paper, a mathematically rigorous methodology for transforming an empirically-derived pore size distribution into independent pore-phase and solid-phase networks is developed. The methodology begins with a transformation of a pore size distribution into cylindrical pore elements. A unit cell porosity distribution derived from the pore-phase network is used to generate an independent solid-phase network. The

resulting networks, coupled together at the nodes, maintain bulk porosity and physical dimensions.

2.2 Network Generation

Pore size distributions obtained via porosimetry or tomographic imaging are often expressed in terms of equivalent spherical diameters or radii. For the pore-network architecture developed in [13], these spherical representations of the material void space must be transformed into a cylindrical representations. Inherently, this requires transforming a probability distribution that is independent of sample size (PDF) to a domain-size-specific distribution.

2.2.1 Network Configuration

Consider a PTL of width W , depth D , and height H with L as the length of each element in the network. Two configurations of this network are illustrated in Figure 2.1. In the two-dimensional configuration (Fig. 2.1a) there is a single plane of elements in one dimension. The thickness or height above and below this plane of elements is equal to L . In the three-dimensional configuration (Fig. 2.1b) there are at a minimum two parallel layers of elements in any dimension.

A unit cell within the domain has a volume L^3 defined by 4 or 12 elements, connected at 4 or 8 nodes, for the 2D and 3D configurations, respectively. Each element represents a resistance and capacitance for transport of a species; reactant, water vapor, liquid water, heat, etc. The stochastic nature of transport in PTL is modeled using a distribution of these resistances across the domain of the network.

The total number of elements (pore cylinders or solid cylinders) in a 3D domain configuration (Fig. 2.1b) is given by

$$n_{3D} = \frac{WDH}{L^3} \underbrace{\left\{ 3 + 2 \left(\frac{L}{W} + \frac{L}{D} + \frac{L}{H} \right) + \left(\frac{L^2}{DH} + \frac{L^2}{WH} + \frac{L^2}{WD} \right) \right\}}_{\text{configuration factor, } f_c} \quad (2.1)$$

The ratio of domain volume (WDH) to unit cell volume (L^3) is modified by a dimensionless configuration factor f_c , which is constant for any given domain. The configuration factor can be thought of as the equivalent number of cylinders in a unit cell as compared to adjacent unit cells. The value of f_c is bounded; $3 \leq f_c \leq 12$. In the limit of a single unit cell ($W = D = H = L$), all twelve elements are contained. As the number of unit cells increase f_c decreases to a limit of 3. Similarly, for the 2D configuration the total number of elements is

$$n_{2D} = \frac{WD}{L^2} \underbrace{\left\{ 2 + \left(\frac{L}{W} + \frac{L}{D} \right) \right\}}_{\text{configuration factor, } f_c} \quad (2.2)$$

with a modification to the configuration factor. In this configuration the bounds are

Figure 2.1: Network configurations considered.

$2 \leq f_c \leq 4$ where the maximum of 4 is for a single, planar unit cell and 2 is the limit of infinite length in W and D . In this paper the networks generated are the 2D configuration.

The domain size, W, D, H , is determined by the physical size of the PTL being studied. The choice of element length L within the domain must be defined in a manner that conserves the bulk porosity of the PTL while simultaneously matching the empirically-derived distribution. Empirical distributions of pore radii are nearly universally based on spherical volumes (pores). The following presents a methodology to convert a pore size distribution that is independent of sample size into a distribution of cylindrical elements (pore and solid) in a domain with specific physical dimensions.

2.2.2 Pore-Phase Distribution

First, we will consider the generation of the pore-phase network. For the pore phase the primary transport of interest is liquid water. The resistance to movement of

liquid water is partially due to viscous losses, but primarily due to capillary pressure. The capillary pressure of a cylindrical meniscus is $2\sigma\kappa_{\text{meniscus}}$, where κ_{meniscus} is the geometric curvature of the liquid surface and σ is surface tension. Geometric curvature for a circular cross section meniscus is related to the geometry of the pore and wettability, $\kappa_{\text{meniscus}} = \cos\theta/r_{\text{pore}}$, where θ is the static contact angle and r_{pore} is the physical radius of a pore. The stochastic nature of capillary pressure resistance can be captured by distributions in pore size r_{pore} , local wettability θ , or a combination of the two. In this work all of the stochastic resistance is assigned to the menisci size (pore radii r) with a constant contact angle.

Empirical data from porosimetry and tomographic imaging are commonly used to generate a normalized probability distribution of pore radii within a PTL sample. Though these distributions are generally based on spherical pores the relationship between radii distribution of spheres (PSD) and cylinders (network) can be directly equated in order to match the distribution of possible meniscus curvatures. Pore size distributions can be represented as a 2- or 3-parameter Weibull distribution or superposition of multiple Weibull distributions. Details on the determining Weibull distribution(s) for generation of cylindrical pore-phase networks are described in previous publications [11, 12, 13, 14, 15, 16]. The mean value of a pore size distribution described using a two-parameter Weibull distribution [17] is:

$$\bar{r}_p = \psi_p \Gamma(1 + 1/\gamma_p) , \quad (2.3)$$

where $\bar{r}$ is the mean, ψ is the scale factor, γ is the shape factor, and Γ is the gamma function. The subscript p indicates distribution parameters based on a pore size PDF. Subscripts pe and se will indicate distribution parameters based on pore elements and solid elements, respectively.

For the pore phase network, the PSD Weibull distribution parameters are set equal to cylindrical pore element distribution parameters in order to accurately capture the stochastic capillary pressure. Thus defining the distribution in r_{pe} is straightforward. However, populating a network realization with pore cylinders also requires defining the element lengths L .

2.2.3 Determining Element Length

The proper value of element length L is determined by conserving pore volume and bulk porosity of a PTL computational domain. The total pore volume in the domain is set equal to the average cylindrical pore volume multiplied by the number of elements present in the domain.

$$\forall_{\text{pore phase}} = \epsilon_B W D H = n_{pe} \pi \bar{r}_{pe}^2 L \quad (2.4)$$

Here, ϵ_B is the bulk porosity of the PTL, n_{pe} is the number of pore elements in the domain, and $\bar{r}_{pe}$ is the average radius of the pore elements which is equal to $\bar{r}_p$ in

equation 2.3. The latter value is the same as the mean of the pore element distribution, which is also the mean of the original empirical PDF. Using the configuration factor defined earlier, this can be simplified to:

$$L = \bar{r}_{pe} \sqrt{\frac{\pi f_c}{\epsilon_B}} \quad (2.5)$$

Summarizing, the element length that conserves pore volume and bulk porosity is found by (i) determining the Weibull distribution parameters that best match the empirical pore size distribution, (ii) using these parameters to find the mean of that distribution which is equal to $\bar{r}_{pe}$, (iii) defining a domain size (W, H, D) , and (iv) iterating on equation 2.5 to solve for the element length L . Iteration is necessary since the configuration factor f_c is weakly dependent upon L . For this work the two-dimensional network configuration, shown in Figure 2.1a, is used.

Using this approach multiple pore-network realizations have been generated for three commercially available PTLs; Fruedenberg H2315, Toray TGP-H060, and MRC 105. Table 2.1 lists for the three PTLs the physical dimensions, mean pore sizes, domain sizes selected, along with other network parameters. Each realization is generated by randomly placing in the domain cylindrical pore elements with varying radii. The pore element radii are constrained by the original pore size distributions shown in Figure 4.3. Three realizations are generated for each network distribution. Use of

Table 2.1

Material and network properties for three PTLs and resulting pore-phase and solid-phase networks. *As reported by manufacturer, **Measured in-house.

	Fruedenberg H2315	Toray TGP-H060	MRC 105
ϵ_B	77 [18]	78*	78 [19]
thickness $[\mu\text{m}]$	210*	190*	210**
$\bar{r}_p$ $[\mu\text{m}]$	10.5	9.7 [1]	5.4
domain size $[\text{mm}]$	$2.992 \times 0.238 \times L$	$2.996 \times 0.224 \times L$	$3.000 \times 0.240 \times L$
L $[\mu\text{m}]$	34	28	24
f_c	2.31	2.27	2.21
n_{elements}	1327	1827	2635
$\psi_{(1-\epsilon)}$	0.265	0.282	0.230
$\gamma_{(1-\epsilon)}$	1.18	2	0.85
$\sigma_{(1-\epsilon)}^2$	0.048	0.015	0.088
$\psi_{se}(r_{se}^2)$ $[\mu\text{m}^2]$	48.03	34.81	20.86
$\gamma_{se}(r_{se}^2)$	1.18	2	0.85
r_{se}^- $[\mu\text{m}^2]$	45.45	30.84	22.77

multiple realizations, subject to the same distribution, is equivalent to studying different sections of the same PTL.

2.2.4 Generating Solid-Phase Network

Coupling of the two independent networks will be through the use of another probability distribution; this time using the distribution of local, or unit cell, porosities. The principle assumption is that the variance in the distribution of unit cell porosities is equivalent to the variance in the size of the cylindrical solid-phase elements (with an appropriate scaling factor). This assumption is valid for sufficiently large domains.

Figure 2.2: Probability distributions for pore size distributions (spherical) in three commercial PTLs.

Unit cell porosity is computed from the pore-phase realization by dividing the unit cell volume L^3 into the equivalent volume of cylindrical pore elements comprising each unit cell. The equivalent volume includes the value of f_c specific to the domain size. The distribution of unit cell solid fraction ($1 - \epsilon$) derived from pore-phase network realizations are shown in Figure 2.3. The unit cell solid fraction is more convenient than the unit cell porosity when determining the variance of the distribution and the variance in the solid fraction, $\sigma_{(1-\epsilon)}^2$, is equal the the variance in the porosity, σ_ϵ^2 .

Figure 2.3: Distribution of the unit cell solid fraction $(1 - \epsilon)$. These distributions are derived from three pore-phase network realizations for each commercial PTL.

The resulting best fit Weibull distribution parameters $\gamma_{(1-\epsilon)}$ and $\psi_{(1-\epsilon)}$ are listed in Table 2.1.

The variance (square of the standard deviation) of the unit cell porosity, described using a Weibull distribution, is:

$$\sigma_{\epsilon}^2 = \bar{\epsilon}_{\epsilon}^2 \left\{ \frac{\Gamma(1 + 2/\gamma_{\epsilon})}{[\Gamma(1 + 1/\gamma_{\epsilon})]^2} - 1 \right\} \quad (2.6)$$

where $\bar{\epsilon}_\epsilon$ is the mean unit cell porosity and is equal to the bulk porosity ϵ_B .

The variance in unit cell porosity is now set equal to the non-dimensional variance of the solid phase elements. The distribution of interest for the solid phase is in the cross sectional area of the elements r_{se}^2 . Thermal transport is of primary interest within the solid-phase network and the distributed resistance will be related to a distribution of solid element areas. Thus,

$$\sigma_\epsilon^2 = \frac{\sigma_{se}^2}{L^2} = \mu_{se}^2 \left\{ \frac{\Gamma(1 + 2/\gamma_{se})}{[\Gamma(1 + 1/\gamma_{se})]^2} - 1 \right\} \quad (2.7)$$

where μ_{se} is the non-dimensional mean of the solid phase distribution that has been normalized using the element length L .

The mean area of the solid phase elements is found in a similar manner to the element length. The total solid volume in the domain can be related to the average solid element volume multiplied by the number of solid elements.

$$V_{\text{solid phase}} = (1 - \epsilon_B) WDH = n_{se} \pi \bar{r}_{se}^2 L \quad (2.8)$$

For the configurations used here, the number of solid phase elements is the same as the number of pore phase elements. The value of the configuration factor is, therefore, also the same. The mean of the solid phase depends on both the shape and scale

factors.

$$\mu_{se} = \psi_{se} \Gamma (1 + 1/\gamma_{se}) \quad (2.9)$$

Conserving solid volume for the domain:

$$\mu_{se} = \left(\frac{\bar{r}_{se}^2}{L^2} \right) = \frac{1 - \epsilon_B}{\pi f_c} \quad (2.10)$$

(a) Freudenberg H2315

(b) Toray TGP-H060

(c) MRC 105

Figure 2.4: Distributions of solid-phase element areas (r_{se}^2) for three commercial PTLs.

Shape and scale factors for the solid phase distribution can be determined from equations 2.7, 2.9, and 2.10. The resulting solid-phase distribution functions for each of the PTLs are shown in Figure 2.4. Using these distributions, realizations of the solid-phase network can be generated independent of the pore-phase networks. If three realizations are generated for the pore-phase and the solid-phase, then nine permutations of coupled networks are possible for a given material.

2.3 Conclusion

In this paper we have demonstrated a technique to define two independent network models, one for the pore phase and second for the solid phase, using the empirically derived pore size distributions of PTLs. These two networks are coupled together and can be used to simulate heat and mass transport in porous media that is representative of actual fuel cell material sets.

Chapter 3

Material and Morphological Heat Transfer Properties of Fuel Cell Porous Transport Layers

The complex structure of the porous transport layer (PTLs), commonly referred to as gas diffusion layers (GDL), makes direct measurement of thermal transport properties difficult. Typically, effective thermal conductivity values are obtained experimentally and computational models are developed to replicate the measurements. This approach is sufficient for generalized one-dimensional models of fuel cell performance, but is not sufficient to predict reactant maldistribution due to the presence of liquid water in the PTL. Further, the anisotropy in the PTL structure results in dissimilar

properties for through-plane and in-plane transport. In this work an analytical model is developed to extract material properties from effective thermal conductivity measurements. The model accounts for the change in the effective thermal conductivity as a function of compression. Geometric changes due to compression are separated from morphological changes using a compression modulation function; the shape of which is indicative of how fiber-to-fiber contact morphology changes with respect to strain. Material and morphological properties are determined using effective thermal conductivity data for three commercial PTLs. The properties also enable prediction of in-plane heat transfer using through-plane empirical data and also provide insight into morphological changes due to compression.

3.1 Introduction

A porous transport layer (PTL), more commonly referred to as a gas diffusion layer (GDL), has multiple purposes in a fuel cell including distribution of reactant gases to the catalyst layer, facilitation of product water removal from the catalyst layer, electronic and thermal conduction to/from the catalyst layer, and redistribution of compressive stresses across the membrane electrode assembly (MEA). A typical PTL consists of carbon fibers, either in fibrous or a non-woven morphology, along with binding agents and non-wetting agents such as polytetrafluoroethylene (PTFE). Examples of a non-woven and a fibrous PTL are shown in Figure 3.1. PTL designation is

Figure 3.1: Optical micrographs of fibrous and non-woven PTLs; scale bar is $100\ \mu\text{m}$.

used herein because the transport phenomena of interest is not restricted to diffusion of reactant gases, but is focused heat transfer.

Heat transfer across a dry PTL is primarily due to conduction. When liquid water is present, then additional heat may be transferred from the catalyst layer via evaporation and conduction via the liquid water occupying the void space. Either mode of heat transfer, conduction or evaporation, may be the dominant effect depending upon the operating conditions [13]. The location of an evaporation front within a PTL depends upon the temperature and temperature gradient within the PTL. The same can be said for water condensation within the PTL as demonstrated by [20]. A highly conductive PTL may increase the conduction of heat, but result in widely distributed condensation that can block reactant transport. A less conductive PTL may decrease the conduction of heat, but result in a sharp temperature gradient that generates a thin, uniform layer of water which also serves as a reactant transport barrier [21]. An accurate prediction of the temperature field within a PTL with and

without the presence of liquid water could enable PTL material and morphology to be optimized for specific operating conditions.

Compression of a PTL may significantly change thermal transport and subsequently the temperature field within the PTL. In a proton exchange membrane fuel cell (PEMFC), this compression is non-uniform with high compression between the ‘lands’ of the reactant flow field and the catalyst layer and no compression between the reactant ‘channels’ and the catalyst layer. As a result temperatures and temperature gradients through the PTL thickness (through-plane) will vary from land to channel locations. This non-uniform compression complicates the prediction of internal PTL temperatures and the subsequent prediction of liquid water location. An additional complication arises in that the PTL exhibits severe anisotropy so that heat conduction through the thickness (through-plane) is much less than heat conduction along the span-wise direction (in-plane). Experimental studies have been conducted to determine effective through-plane thermal conductivities of PTLs [18, 22, 23, 24, 25, 26, 27]. The term effective thermal conductivity is used because these values are not strictly material constants. PTLs are porous and chemically inhomogeneous and thermal conductivity is based on temperatures measured at opposite surfaces of the PTL. There is no realistic method for in-situ or ex-situ measurement of temperatures internal to a PTL. Effective thermal conductivity is nearly always based on a linear temperature profile through the PTL.

Attempts to relax this assumption and determine a more realistic temperature distribution have relied upon idealized heat transfer structures with the intent of determining material properties, as opposed effective properties. [27] performed an analysis of these models and proposed a fractal model to predict through-plane heat transfer to extract an effective thermal conductivity. Similarly, [28] proposed a statistical unit cell model for estimating through-plane thermal conductivity. The challenge inherent in these efforts is that the idealized heat transfer structures and the subsequent temperature and property data are only valid for thermal conduction of dry PTLs in the through-plane direction.

Alternatively, heat and mass transport within a PTL has been modeled using geometrically reconstructed PTL computational domains [2, 29, 30, 31] and with geometric abstractions such as pore-network models [1, 14, 32, 33, 34]. The complex stochastic structure of the PTL makes it difficult and computationally expensive to directly model the thermal and mass transport using techniques such as computational fluid dynamics applied to a geometrically reconstructed domain. Pore-network models are a relatively simple computational approach, but require accurate pore-level material constants. In principle, thermal transport and the resulting internal temperature field can be accurately predicted in dry or wet using different approaches provided accurate material constants are available.

The objective of this work is to develop a methodology for extracting accurate material and morphological properties using effective thermal conductivity data. These properties should remain invariant with compression or in the presence of liquid water.

3.2 Solid-Cylinder Material Model

The methodology for transforming effective thermal conductivity into material and morphological properties involves building an equivalent thermal resistance to the PTL. To determine these material properties (as opposed to effective properties), the solid portion of the PTL is analyzed in isolation from the overall volume of the PTL sample. . This equivalence is referred to as a solid-cylinder material model (SCMM). The solid phase of the PTL is treated as an elastic cylinder with frictionless surfaces so that the effect of geometric changes due to strain (compression) can be separated from material constants and morphological changes (contact resistances).

Nearly all through-plane thermal conductivity measurements on PTLs are based on compression of a stack of 3 to 10 PTLs with insulated peripheral boundaries. Thermal transport property data is extracted using one-dimensional, steady-state conduction through a planar solid with constant thermal conductivity and an assumed linear temperature profile.

$$\dot{Q}_{\text{sample}} = -\frac{k_{\text{eff}}A_{\text{PTL}}}{H_{\text{sample}}} \left(T_{s,1} - T_{s,2}\right) \quad (3.1)$$

In this simplified Fourier's Law, A_{PTL} is the projected area of the PTL stack in the direction of heat conduction, H_{sample} is the thickness of the stack, and T_s is the measured surface temperature on either side of the PTL stack. This is often rearranged into an expression of thermal resistance because $\dot{Q}$ and ΔT are the measured quantities.

$$R_{\text{eff}} \equiv \frac{T_{s,2} - T_{s,1}}{\dot{Q}_{\text{sample}}} = \frac{NH_{\text{PTL}}}{A_{\text{PTL}}k_{\text{eff}}} \quad (3.2)$$

where N is the number of PTLs used and H_{PTL} is the thickness of a single PTL.

When considering the thermal resistance of a single PTL under compression, illustrated in Figure 3.2a, the heat transfer path length is reduced by the change in thickness.

$$H_{\text{compressed}} = H_{\text{PTL}} - \Delta H = (1 - \chi)H_{\text{PTL}} \quad (3.3)$$

where $\chi = \Delta H/H_{\text{PTL}}$ is strain and H_{PTL} is the uncompressed thickness of a single PTL. The projected area of the PTL normal to the direction of heat transfer, A_{PTL} , is considered to remain constant during compression for all data reviewed. Thus, the thermal resistance of a single PTL subject to strain is

$$R_{\text{PTL}} = \frac{H_{\text{PTL}}(1 - \chi)^{0,1}}{A_{\text{PTL}}k_{\text{eff}}} \quad (3.4)$$

The exponent is 1 when k_{eff} is strain corrected and 0 when either the strain is not

Figure 3.2: Equivalent thermal resistances for PTL and solid-cylinder material model.

reported or the uncompressed PTL thickness is used in determining k_{eff} . This distinction is necessary because reported values of effective thermal conductivity may be based on the actual thickness of the compressed sample: $(1 - \chi)H_{\text{PTL}}$ [18, 27], but not always. Effective thermal conductivity may also be reported in relation to the applied stress with an accompanying stress-strain correlation [25, 35]. Other data is correlated to applied stress, but the original uncompressed sample thickness is used in equation 3.2 or the compressed thickness is not reported [22, 23, 36]. In these instances the primary purpose of the measurements may be to model the overall heat transfer in an operating stack and not examine localized effects in the PTL. Thus, the thickness of the sample used in determining the k_{eff} in equation 3.2 may or may not be corrected for strain. In order to separate material and morphological thermal transport properties from PTL geometry and effective thermal conductivity, the PTL thermal resistance R_{PTL} is set equal R_{cyl} which is comprised of two resistances in series. One of the resistances is due to the solid material of the PTL and the second is

a contact resistance between fibers. This analog, illustrated in Figure 3.2b, is referred to as a solid-cylinder material model (SCMM) because only the solid phase of the PTL is considered. The thermal resistance of the SCMM is:

$$R_{\text{cyl}} = R_s + R_c = \frac{H_s}{A_s k_s} + C(\chi) \frac{H_c}{A_c k_c} \quad (3.5)$$

where the subscripts s and c indicate solid and contact, respectively. The contact resistance includes a compression modulation function $C(\chi)$ that accounts for non-geometric effects of compression on the PTL morphology. In principle, the contact area and length of the two cylinders can be arbitrarily set and the value of the thermal conductivities, k_s and k_c , adjusted to match effective thermal conductivities. We have adopted the following convention for establishing contact areas and thicknesses.

The areas of the solid and contact resistances are set equal to one another and the initial length of the resistances are set to the uncompressed thickness of the original PTL sample. The cylinder representing the solid resistance R_s has physical dimensions. The cylinder representing the contact resistance R_c has no physical dimension, but is modeled as though it does. With this convention the contact resistance is a virtual cylinder that does not occupy any physical space even though it is modeled as having a length H_{cyl} . Compression of the solid-cylinder material model is treated as elastic with frictionless interfaces. When compressed the contact area for heat transfer increases while the path length decreases. Conservation of volume for the

elastically strained solid cylinder requires:

$$\text{cylinder volume} = H_{\text{cyl}} (1 - \chi) \frac{A_{\text{cyl}}}{(1 - \chi)} \quad (3.6)$$

As a result the resistance of the solid-cylinder material model when accounting for strain becomes

$$R_{\text{cyl}} = \frac{H_{\text{cyl}}}{A_{\text{cyl}}} (1 - \chi)^2 \left[\frac{1}{k_s} + \frac{C(\chi)}{k_c} \right] \quad (3.7)$$

where H_{cyl} and A_{cyl} are the uncompressed length and area, respectively. Geometric changes in thermal resistance due to compression are accounted for in $(1 - \chi)^2$. The intrinsic thermal conductivity of the solid phase of the PTL is accounted for in k_s , which is determined using mass fractions of carbon and PTFE. The intrinsic resistance to heat conduction due to fiber-to-fiber contact is accounted for in $1/k_c$. And variation in thermal conductivity due to compression-induced morphological changes, as opposed to geometric changes, is accounted for in the compression modulation function $C(\chi)$. The contact resistance components k_c and $C(\chi)$ are determined by equating the experimentally measured resistance R_{PTL} (equation 3.4) to the solid cylinder material model resistance R_{cyl} (equation 4.6).

The geometry of the PTL sample that is experimentally tested is as arbitrary as is the choice of dimensions for the solid cylinder material model. In order to couple the resistances the thicknesses of the PTL and SCMM are set equal, $H_{\text{PTL}} = H_{\text{cyl}}$, with the caveat that the contact resistance thickness is not physical. The areas of the PTL

and the SCMM, however, are not equal. The relationship between the projected area relative to the direction of heat transfer for the PTL and cylinder is determined by considering only the solid phase of the PTL. The solid volume of the uncompressed PTL and SCCM is

$$(1 - \epsilon_B) A_{\text{PTL}} H_{\text{PTL}} = A_{\text{cyl}} H_{\text{cyl}} \quad (3.8)$$

where ϵ_B is the bulk porosity of the PTL. Thus, the relationship between effective heat conduction area of the test sample and SCCM is $A_{\text{cyl}} = (1 - \epsilon_B) A_{\text{PTL}}$.

Equating the PTL and SCCM resistances using this geometric convention provides a relationship between the reported value of effective thermal conductivity and the material and morphological properties, k_c and $C(\chi)$, respectively.

$$\frac{1}{k_{\text{eff}}} = \frac{(1 - \chi)^{1,2}}{(1 - \epsilon_B)} \left[\frac{1}{k_s} + \frac{C(\chi)}{k_c} \right] \quad (3.9)$$

Changes in the rate of heat transfer due to strain-induced geometric changes are accounted for in the $(1 - \chi)^{1,2}$ coefficient. The exponent varies depending on whether reported values of k_{eff} are strain corrected (1) or not strain corrected (2). Non-geometric strain-induced heat transfer effects are accounted for in the compression modulation function $C(\chi)$.

For convenience, resistivity (inverse of conductivity) is used when fitting of the solid-cylinder material model resistance R_{cyl} to empirical resistance R_{PTL} .

$$\rho_{\text{eff}} = \frac{(1 - \chi)^{1,2}}{(1 - \epsilon_B)} \left[\rho_s + C(\chi) \rho_c \right] \quad (3.10)$$

3.3 Solid Resistivity

The solid resistivity is determined using thermal conductivity values of the constitutive PTL materials (carbon and PTFE) in proportion to the mass fractions.

$$k_s = (1 - M_{\text{PTFE}}) k_{\text{carbon}} + M_{\text{PTFE}} k_{\text{PTFE}} \quad (3.11)$$

where M_{PTFE} is the weight percent of PTFE. The thermal conductivity of carbon used in PTLs is taken to be that of dense carbon at 120 W/m K [23] while the value for PTFE is $k_{\text{PTFE}} = 0.245$ W/mK [37]. Addition of PTFE reduces the solid phase thermal conductivity k_s , but may increase the effective thermal conductivity k_{eff} of the PTL due to the reduction in porosity per equation 3.9. Thermal resistivity is the inverse of the thermal conductivity; $\rho_s = 1/k_s$.

3.4 Compression Modulation Function

At zero strain the PTL is uncompressed and the compression modulation function is equal to one which provides for a maximum contact resistance in the uncompressed state. At the other extreme the contact resistance component in equation 3.10 should diminish to zero as the PTL is compressed to some maximum strain;

$$\lim_{\chi \rightarrow \chi_{\max}} [C(\chi)\rho_c] \rightarrow 0 \quad (3.12)$$

In practice this maximum strain can never be achieved and so this value represents a limiting condition on the compression modulation function $C(\chi)$. In the limit of maximum compression only the solid phase of the PTL will remain so the maximum strain is equivalent to the bulk porosity of the PTL, $\chi_{\max} = \epsilon_B$.

$$C(\chi) = \begin{cases} 0, \chi = \epsilon_B \\ 1, \chi = 0 \end{cases} \quad (3.13)$$

3.5 Contact Resistivity

The value of ρ_c and the compression modulation function $C(\chi)$ are determined using empirical data and the limiting conditions for $C(\chi)$. Fitting of the contact resistivity to the empirical data begins by rearranging equation 3.10 in order to isolate the contact resistivity components.

$$\frac{(1 - \epsilon_B) \rho_{\text{eff}}^*}{(1 - \chi)^{1,2}} - 1 = \rho_c^* C(\chi) \quad (3.14)$$

where $\rho^* = \rho/\rho_s$. The left side of the equation 3.14 is the empirical data with adjustments for porosity and strain. The right side is the magnitude of contact resistivity scaled by the solid resistivity and the compression modulation function.

The fitting function used to match the dimensionless effective resistivity that is porosity and strain adjusted (left side of equation 3.14) includes a linear component and a non-linear component. The linear component is used to fit to data at small strains ($\leq 20\%$), which has been observed to follow a linear trend for many different types of PTLs [21]. The non-linear component enforces the limiting condition on the contact resistivity $C(\chi) \rho_c^*$, which decays to zero at maximum strain. For convenience, strain is scaled using the bulk porosity to simplify the fitting of the empirical data to the

dimensionless contact resistivity.

$$\xi = \frac{\chi}{\epsilon_B} \quad 0 \leq \xi \leq 1 \quad (3.15)$$

The fitting function used herein is of the form

$$g(\xi) = a_0 + a_1\xi - (a_0 + a_1)\xi^p \quad (3.16)$$

which is fitted to the the scaled test data, left side of equation 3.14. This approach allows for one additional data point not derived from empirical effective thermal conductivities; that is, $g(1) = 0$. The magnitude of the dimensionless contact resistivity at $\xi = 0$ is $\rho_c^* = a_0$ because $C(0) = 1$. Therefore, the contact resistivity is

$$\rho_c = \rho_s a_0 \quad (3.17)$$

and the compression modulation function becomes

$$C(\xi) = 1 + b_1\xi - (1 + b_1)\xi^p \quad (3.18)$$

where $b_1 = a_1/a_0$. Fitting the scaled test data to $g(\xi)$ yields values for a_0 , a_1 , and p .

3.6 Application to Commercial PTLs

The solid-cylinder material model is applied to three commercial PTLs with published effective thermal conductivity data; Toray TGP 060 [18], Freudenberg H2315 [18], and Mitsubishi Rayon Corp. MRC 105 [35]. Data for two different PTFE weight percents are available for the Freudenberg H2315 PTL. For Toray TGP 060 and Freudenberg H2315 the effective thermal conductivity is reported as a function of PTL compression thickness, from which the strain can be computed. The effective thermal conductivity for the Mitsubishi MRC 105 is reported as a function of compressive stress along with a correlation between stress and strain. The original effective thermal conductivity data for each PTL are listed in Table 3.1 and plotted in Figure 3.3 against strain. The effective thermal conductivity for Toray TGP 060 is approximately three to four times greater than that for the Freudenberg H2315 and Mitsubishi MRC 105; and also exhibits a greater rate of change with respect to compressive strain.

In order to transform effective thermal conductivity data into the fitting function $g(\xi)$ per equation 3.14, the porosity, strain, and value of ρ_s are required and are listed in Table 3.2. For these three PTL data sets, the effective thermal conductivity is tabulated against measured or correlated strain. Therefore, in transforming the effective thermal conductivity into $g(\xi)$, the exponent in equation 3.14 is equal to one. The porosity of the Freudenberg H2315 with 10% PTFE (wt) was not reported,

Figure 3.3: Measured effective thermal conductivity for three commercial PTLs

but can be computed using the density ratio of carbon to PTFE, which can vary depending on the source. The change in porosity due to addition of PTFE based on an unchanged total PTL volume is

$$\epsilon_{B,1} = 1 - (1 - \epsilon_{B,0}) \left[1 + \left(\frac{M_{\text{PTFE}}}{1 - M_{\text{PTFE}}} \right) \left(\frac{\rho_{d,\text{carbon}}}{\rho_{d,\text{PTFE}}} \right) \right] \quad (3.19)$$

where M_{PTFE} is weight percent of PTFE, ρ_d is material density, $\epsilon_{B,0}$ is the bulk PTL porosity without PTFE. The densities are similar with specific gravities of 2.135 [37] and 2.26 [?] for PTFE and carbon, respectively. For this work the density ratio of carbon to PTFE used is 0.90 as per [38]. Thus, for the Freudenberg H2315 PTL with 10% PTFE (wt), the porosity is reduced to $\epsilon_B = 0.747$ as compared to the uncoated sample with $\epsilon_B = 0.77$.

The procedure for determining the fitting function constants a_0 , a_1 , and p requires transforming the effective thermal conductivities into the non-dimensional effective resistivity that is strain and porosity adjusted; i.e., the left side of equation 3.14. The transformed data is tabulated in Table 3.1 as discrete values of $g(\xi)$ and the limiting condition $g(1) = 0$ is added to the tabulation. A regression analysis using the form in equation 3.16 is performed on each PTL data set.

The shape of the fitting function, shown in Figure 3.4, is unique to each PTL. The quality of the fit to data for all three PTLs is very good with correlation coefficients greater than 0.999. Care should be exercised in considering the quality of these fits, however. The effective thermal conductivity data set is sparse with relatively large uncertainty (approximately 10% to 15%) and with large separation in strain from the limiting condition at $\xi = 1$. As a result, if the effective thermal conductivity exhibits little change with small strain, then the quality of the fit is insensitive to the non-linear component characterized by the exponent p . This can be observed in the fit to the two Freudenberg PTLs. For the 0% PTFE (wt) data, the value of p was selected to be 3.5. Whereas for the 10% PTFE (wt) data, the value of p was selected to be 10. Both fits match both sets of data, indicating that the choice of p for the Freudenberg PTLs is somewhat arbitrary. The insensitivity in the non-linear component of the Freudenberg PTLs is due to an absence of morphological changes at small strains.

Table 3.1
Effective thermal conductivities and derived data for for three commercial
PTLs. Data in bold indicates published values.

Toray TGP 060 [18]					
thickness (μm)	strain, χ	$\xi = \chi/\epsilon_B$	k_{eff} (W/m K)	ρ_{eff} (m K/W)	$g(\xi)$
172	0.0947	0.1215	0.41	2.4390	66.58
165	0.1316	0.1687	0.53	1.8868	53.50
159	0.1632	0.2092	0.66	1.5152	44.41
	0.78	1			0
Freudenberg H2315 0% PTFE [18]					
thickness (μm)	strain, χ	$\xi = \chi/\epsilon_B$	k_{eff} (W/m K)	ρ_{eff} (m K/W)	$g(\xi)$
190	0.0952	0.1237	0.14	7.1429	217.895
182	0.1333	0.1732	0.15	6.6667	212.308
177	0.1571	0.2041	0.15	6.6667	218.305
	0.77	1			0
Freudenberg H2315 10% PTFE [18]					
thickness (μm)	strain, χ	$\xi = \chi/\epsilon_B$	k_{eff} (W/m K)	ρ_{eff} (m K/W)	$g(\xi)$
184	0.1238	0.1657	0.15	6.6667	207.9472
175	0.1667	0.2231	0.15	6.6667	218.6416
170	0.1905	0.2550	0.16	6.2500	211.0052
	0.747	1			0
Mitsubishi MRC 105 [35]					
stress (MPa)	strain, χ	$\xi = \chi/\epsilon_B$	k_{eff} (W/m K)	ρ_{eff} (m K/W)	$g(\xi)$
0.1	0.0454	0.0547	0.134	7.4383	158.965
0.5	0.0995	0.1199	0.144	6.9524	157.501
1.0	0.1308	0.1576	0.156	6.4276	150.854
1.5	0.1610	0.1939	0.167	5.9764	145.307
2.0	0.1911	0.2302	0.179	5.5844	140.835
	0.83	1			0

The magnitude of the material constants indicate that the through-plane thermal transport in PTLs primarily depends largely on the contact resistivity, ρ_c . The relative effects of solid vs contact on through-plane thermal transport can be more easily seen in the respective thermal conductivities k_s and k_c . The value of k_s is 165 to 217 times

Table 3.2

Material constants for three commercial PTLs. Data in bold indicates published values; Data indicated by * determined via image processing.

	Toray TGP060 [18]	Freudenberg H2315 [18]		Mitsubishi MRC105 [35]
% PTFE	0.05	0	0.10	0
porosity, ϵ_B	0.78	0.77	0.747	0.83
uncompressed thickness (μm)	190	210	210	210
strain corrected effective data	yes	yes	yes	yes
fiber diameter, d_f (μm)	8 [39]	* 9.4 ± 0.4	* 9.4 ± 0.4	* 7.0 ± 1.1
in-plane fiber length, ℓ_f (mm)	* 1.40	* 1.35	* 1.35	* 1.11
k_s (W/m K)	114.01	120.00	108.02	120.00
ρ_s (m K/W)	0.0088	0.0083	0.0093	0.0083
k_c (W/m K)	0.552	0.555	0.497	0.724
ρ_c (m K/W)	1.812	1.803	2.010	1.382
a_0	206.590	216.310	217.156	165.780
a_1	115.390	2.060	-5.905	-85.660
b_1	0.559	0.010	0.497	-0.027
p	0.350	3.500	10.000	2.000

greater than k_c depending on the PTL. Thus, thermal transport is limited by the contact resistance.

The shape of the fitting function and subsequent compression modulation function provides indication of what happens to the contact morphology due to compression. The non-geometric compression effects for all three PTLs are compared using the compression modulation functions, $C(\xi)$, shown in Figure 3.4d. For the Toray TGP

(a) Toray TGP 060

(b) Freudenberg H2315

(c) Mitsubishi MRC 105

(d) Compression modulation function

Figure 3.4: Fitting function $g(\xi)$ compared to scaled empirical data; values of fitting constants are listed in Table 3.1. (3.4d) comparison of compression modulation function $C(\xi)$ for all three PTLs.

060 PTL data there is a significant change in effective thermal conductivity that cannot be accounted for by geometric changes due to strain. The steep decrease in $C(\xi)$ indicates substantial changes in contact morphology has occurred at small strain. Whereas for the Freudenberg H2315 data there is negligible change in $C(\xi)$ small strain; the variation is within the uncertainty of the original test data. This

Figure 3.5: Effective thermal conductivity (through-plane) vs normalized strain.

indicates that the change in effective thermal conductivity due to compression is only due to geometric changes associated with strain. A moderate change in contact morphology occurs for the Mitsubishi MRC 105 and this change appears to occur over a large range of strain.

Using the material and morphological constants listed in Table 3.2 the through-plane effective thermal conductivity can be predicted. Figure 3.5 illustrates the predicted

k_{eff} vs normalized strain for all three PTLs. The inset in each plot is a magnified perspective for strains less than 0.25 for which the trend is approximately linear as observed by [21]. The prediction matches the empirical data as expected. The utility in this methodology, as opposed to linear fits to effective thermal conductivity with strain, is in application to multi-unidimensional heat and mass transfer in a PTL with the presence of liquid water. The role of thermal conduction through the PTL material can be isolated from that through liquid water in the pore phase. In addition, this methodology allows for prediction of in-plane conduction heat with the PTL under compression using only through-plane data.

3.7 In-Plane Effective Thermal Conductivity

Manufacturing of the PTLs results in the orientation of fibers along the span-wise (in-plane) direction, which results in fewer fiber-to-fiber contacts per unit length. Subsequently, effective thermal conductivities in the in-plane direction should be greater than for through-plane. Measurements of in-plane effective thermal conductivity are limited, but values of in-plane k_{eff} range from 3 to 21 W/m K [36, 40, 41, 42], which is 10 to 40 times greater than typical values for through-plane k_{eff} .

The ratio of the fiber diameter and the projected in-plane length of the fiber provides a scaling parameter proportional to the number of fiber-to-fiber contacts in each

direction. Multiplying the contact resistance in the SCMM by this ratio reduces the overall thermal resistance in the in-plane direction.

$$R_{\text{cyl}} = R_s + \left(\frac{d_f}{\ell_f} \right) R_c \quad (3.20)$$

In terms of effective thermal conductivity, the change includes the ratio of fiber diameter to in-plane length as a multiplier on the contact resistivity.

$$\frac{1}{k_{\text{eff}}} = \left(\frac{1 - \epsilon_B \xi}{1 - \epsilon_B} \right) \left[\frac{1}{k_s} + \left(\frac{d_f}{\ell_f} \right) \frac{C}{k_c} \right] \quad (3.21)$$

This expression is the same as equation 3.9, but with the contact resistivity reduced by the ratio of fiber diameter to length. The strain correction term, which has an exponent of 1 or 2 in equation 3.9 depending on how empirical data is reported, is simplified to an exponent of 1 because equation 3.21 is predictive.

The mean fiber diameter, d_f , is determined by analysis of SEM images and optical micrographs. The values of d_f for each of the PTLs is listed in Table 3.2. To identify the mean fiber lengths in the in-plane direction, images of PTL surface were analyzed to identify the fibers and their orientation with respect to one of the orthogonal axis. First, the distribution of fiber lengths and orientation relative to an orthogonal direction was established using the procedure similar to that described in [43]. The projected fiber length in the in-plane direction, ℓ_f , is found by multiplying the

mean fiber length by the cosine of the mean fiber orientation. This projected length characterizes the mean, in-plane length over which heat transfer occurs without a fiber-to-fiber contact. For a non-woven PTL such as the Freudenberg H2315, the in-plane fiber length distribution is determined using the longest straight segments of individual fibers. This results in wider distributions of in-plane fiber lengths and fiber orientation as compared to the fibrous TGP 060 and MRC 105 PTLs; though the mean is still easily identified. The ratio ℓ_f/d_f is 175, 143.6, and 158.6 for TGP 060, H2315, and MRC 105, respectively.

The effective in-plane thermal conductivity for the three PTLs with compression is shown in Figure 3.6. The same PTL-specific values of k_s , k_c , b_1 and p were used to calculate through-plane k_{eff} (equation 3.9) and in-plane k_{eff} (equation 3.21). At strains less than 0.25 the in-plane effective thermal conductivity for these three PTLs is between 10 and 25 W/m K, which is 40 to 100 times greater than the through-plane effective thermal conductivity. At maximum strain, in-plane and through-plane conductivities become equal. Comprehensive experimental studies for in-plane effective thermal conductivity are lacking, especially for the three commercial PTLs considered. Nonetheless, the predicted values of in-plane effective thermal conductivity for these PTLs are comparable to reported values for similar PTLs, which vary from 3 to 21 W/m K for similar PTLs [36, 40, 41, 42].

The effect of PTFE on the in-plane heat transfer remains uncertain. [40] observed

Figure 3.6: In-plane vs through-plane effective thermal conductivities based on solid-cylinder material model parameters. Effective thermal conductivity includes PTL porosity and strain.

a small increase in in-plane thermal conductivity from 17.39 W/m K to 17.81 W/m K with an increase in PTFE content from 5% to 30%, respectively. In contrast, [44] observed a sharp decrease of approximately 11 W/m K at 60 to 70 $^{\circ}\text{C}$ with addition of 5% PTFE to Toray TGP 120. [41] reported a decrease in in-plane thermal conductivity with increasing PTFE content for SpectraCarb, while [42] observed large increase for SGL with increasing PTFE content. These discrepancies may be due to changes in fiber-to-fiber contact morphology in PTLs with, geometric changes with strain,

changes in porosity, or some combination of each. The shape of the compression modulation function for these PTLs with varying PTFE content may help elucidate these relative importance of these various effects.

3.8 Conclusion

A solid-cylinder model has been developed extracting material and morphological thermal transport properties of PTLs based on through-plane effective thermal conductivity data. The effect of porosity and geometric changes due to strain are isolated from the intrinsic thermal conductivity of the solid material and changed in contact morphology due to strain. As a result, the material properties along with the compression modulation function can be used to predict in-plane and through-plane heat transfer and temperature distributions in a PTL that is non-uniformly compressed.

Through-plane heat transfer is primarily limited by the fiber-to-fiber contact resistance. When compressed, both the geometry of the PTL and the morphology of the fiber-to-fiber contact may change. The shape of the compression modulation function $C(\chi)$ can be used to assess the role of geometry and morphology on heat transfer changed due to compression. Data from the two Freudenberg PTLs with differing PTFE content show no measurable changes in contact morphology at strains below 0.25. The measured differences in k_{eff} with strain are most likely due to geometric

changes in the PTL. Changes in contact morphology do not occur until the strain reaches values that cannot be realistically obtained. In contrast, the Toray TGP 060 PTL data indicates that even small application of strain results in rapid changes in contact morphology, with the rate of change decaying at large strains. In between these two extremes, the Mitsubishi MRC 105 exhibits a relatively linear change in contact morphology across the full range of strain.

Chapter 4

Permeability based performance study of Porous Transport Layers of PEM Fuel Cell using Pore Network Model

4.1 Introduction

High porosity of the PTLs allows the passage of the reactant gases from the gas channels to the reaction sites while simultaneously allow the transfer of the product

water, in liquid or vapor form, out of the reaction sites and into the channels of the bipolar plate. If the product water is not removed at an adequate rate, the pores of the PTL are blocked thereby reducing the passage of reactant gases which results in the decrease in the performance of the fuel cells. During startup, the temperatures are low and the water removal occurs primarily in the liquid phase. Under steady state operations and relatively high temperatures (70-80°C), removal of the water occurs in liquid and vapor form, depending upon the operating conditions. The temporary blockage of pores that occurs during operation is removed by the gas flow at higher temperatures by evaporation. At low temperatures, the capability to remove water by evaporation decreases considerably, thereby increasing the probability of flooding of the PTL [45]. Experiments performed by Williams et. al. [46] show an increase in the limiting current density with the increase in the permeability of the PTL. Similarly, experiments have shown that structured PTLs, with perforations in MPL and PTL, suffer less from liquid water accumulation than their respective non-modified PTLs [47, 48]. The pore network model which simulates the transient transport in the PTL provides a unique capability to characterize the PTLs based on the permeability.

4.2 Pore network model

Multi-phase transport in the PTL is simulated using pore the network model. The network model consists of a two uniformly spaced lattice of cylindrical tubes - one

representing the pore phase and second representing the solid phase of the PTL. Water and vapor transport occurs in the pore-phase network and thermal transport in occurs in both the pore and the solid phase. The pore-phase network and solid-phase network are coupled together at the nodes. The distribution in the radii of the pore-phase network are obtained from the porosimetry data using the Weibull probability distribution function. The distribution in the radii of the solid-phase network are obtained by transforming the pore-size distribution of the pore-phase and is described in detail in Konduru [49]. The two networks are modeled such that the bulk porosity of the PTL is conserved. The network model used in this study was developed by Medici et al. [13, 34] and has been adapted here to include separate but coupled networks representing pore and solid phase, which allows accommodating or simulating the changes that occur due to compression of the PTL under the lands of the bipolar plate. The liquid flow in the individual pore between two nodes, is modeled using a Poiseuille flow:

$$q = \frac{\pi r^4}{8l\mu}(\Delta p - p_c) \quad (4.1)$$

where r is the pore radius, Δp is the pressure drop across the pore, μ is the effective viscosity based upon the position of the liquid meniscus inside the pore and p_c is the modified capillary pressure which imitates the throat effect at the ends of the pores [50]. Many models have constrictions between the pores called as pore throats

[1, 51, 52].

The vapor concentration model obtained using the Fick's law of diffusion and is derived from the model described by Yiotis et al. [53]:

$$v \frac{dC_i}{dt} = D_i \pi r_j^2 \frac{C_i - C_j}{l} \quad (4.2)$$

where C is the vapor concentration, v is the volume, subscript i represent a given node and j represents a given pore.

The amount of water evaporated in a pore (m_{ev}) is calculated from the difference in the concentration of the vapor at the meniscus and at the node that is on the side with the vapor. The vapor is considered as saturated at the meniscus. The location of the meniscus is updated from the mass balance of the injected liquid water and the evaporated vapor in the pore. The evaporation rate in the pore is calculated as:

$$\dot{m}_{ev} = \pi D r_j^2 \Delta t \frac{C_{sat} - C_j}{l}, \quad (4.3)$$

where Δt is the time step, C_{sat} is the concentration of saturated vapor and C_j is the concentration of vapor at the vapor side node of the pore.

The heat transport model is similar to one described by Surasani et al. [54]. In this model all the heat transfer is considered to occur through conduction, including the

heat transfer through the liquid and vapor phase. The two networks are coupled such that between two nodes, one cylindrical tube of the pore-phase and one of the solid-phase is present, both being parallel to each other. Heat conduction between these two nodes takes place through the pore and the solid phase in a parallel configuration (Figure 4.1). The total heat conduction between two nodes is thus calculated as,

$$\dot{Q}_j = \frac{\Delta T}{R_{tot,j}} \quad (4.4)$$

where ΔT is the temperature difference and $R_{tot,j}$ is the equivalent thermal resistance between the nodes

In this configuration, the pore can be completely filled with water, or air or a combination of the two with the presence of a meniscus. In the pore, conduction takes place through the liquid and the vapor and the volume fraction of each phase determines the net resistance of the pore [55]. The equivalent thermal resistance is calculated as:

$$R_{tot,j} = \left(\frac{1}{R_s} + \frac{1}{xR_l + (1-x)R_v} \right)^{-1} \quad (4.5)$$

where x is the fraction of the pore occupied by the liquid in the pore and R_s, R_l and R_v are the thermal resistances of the solid, liquid and the vapor phase. Further, the compression model described in the subsequent section elaborates on the changes in the resistance solid phase to account for the compression that takes place under the lands of the bipolar plate during the fuel cell assembly.

Figure 4.1: Equivalent Thermal Resistance Circuit Between Two Nodes

4.3 Compression Model

During the assembly of the fuel cell stack, the compression applied to fuel cell results in the compression of the PTLs under the lands of the bipolar plates. Experimental studies performed show a increase in the thermal conductivity of the PTL, primarily due to decrease in the fiber-fiber contact resistance. To capture this effect, individual cylinders of the solid-phase (R_s) are modeled as a combination of a solid cylinder and pseudo-contact resistance cylinder in series. The pseudo-contact resistance cylinder had dimensions similar to the the dimensions of the solid-cylinder but does not add volume to the simulation domain and has no thermal capacitance. The solid cylinder resistance is calculated as:

$$R_s = \frac{H_{cyl}}{A_{cyl}} (1 - \chi)^2 \left[\frac{1}{k_s} + \frac{C(\chi)}{k_c} \right] \quad (4.6)$$

where H_{cyl} and A_{cyl} are the uncompressed length and area, respectively. Geometric changes in thermal resistance due to compression are accounted for in $(1 - \chi)^2$. k_s , k_c and $C(\chi)$ represent the thermal conductivity of the solid material, equivalent thermal conductivity of the contact resistance cylinder and the compression coefficient respectively. The compression coefficient provides a scaling parameter which modifies the contact resistance between solid-cylinders as a function of strain (χ). Detailed discussion on the procedure to generate material constants for different PTLs are present in Konduru [56].

4.4 Pore Size Distributions of the PTLs

Figure 4.2 shows the backlit optical micrographs of the PTLs used in the current study. Some morphological differences between the PTLs are visible in the images. A small number of through holes are present in PTLs A and B, while much larger open through pores are present in PTL C. PTLs B and C also show a distinct banded structure, with PTL C displaying two distinct regions: first being open areas with larger pores and sparsely populated with carbon fibers, and the other being contained with relatively smaller pores and higher density of carbon fibers.

Solid and pore distributions were generated based on the porosimetry tests on PTLs A and B and are shown in figure 4.3. For PTL C, experimental porosimetry data was

Figure 4.2: Images of the PTLs used in simulations

not available, but based on the alternate bands of highly porous and dense regions, an artificial realization was generated to imitate the characteristics of the PTL. For this purpose, the pore-size distribution of PTL B was selected and the PSD was split into four distinct regions. The dense region of the PTL was populated such that 80% of the pores were selected from the regions with smallest radius and the remaining pores were selected from each successive region with pore fraction decreasing in step of 20%. Similarly for the sparse region, 20% of the pores were selected from the region with smallest radius and the fraction of pores increased in steps of 20% as the

(a) PTL A

(b) PTL B

Figure 4.3: Pore Size Distribution of the PTLs used

Figure 4.4: Generation of density modulated PTL realization

Figure 4.5: Schematic of the simulation domain

pore radius increased. After the regions were populated, the pores were randomized. A similar process was applied for the solid phase region, with solid cylinders with smaller radii in the sparse region and larger radii cylinders in the dense region. The schematic representing this process is shown in Figure 4.4.

4.5 Network Modeling

The schematic of 2D computational domain (Figure 4.5) is representative of one half of single channel fuel cell. In this work, only the transport in the PTL is simulated. The width of the gas channel is 0.75mm and the width of lands on either side is 0.375mm. The width of the PTL is 1500 m and is same for all PTLs. The simulation domain is discretized uniformly based on the pore lengths of the individual PTLs and the total number of pores and nodes vary accordingly.

4.5.1 Thermal transport

To study the thermal transport in the PTL (no water), the The temperature is set constant at the upper edge of PTL and equal to the gas channel temperature, while a symmetric boundary condition is set at the left and right edge of the PTL. A constant heat flux is applied at the bottom edge of the PTL. Thus heat transfer occurs only in the through plane direction. The heat flux corresponds to a fuel cell operating condition of 1.5 A/cm² at 0.6V, with 50% of the heat passing through the PTL (cathode side). For the uniform compression study, the entire PTL is compressed with uniform strain. For these tests, the presence of land/channel configuration is not important as the boundary condition of constant temperature is applied at the top side of the PTL. Water is not introduced in the pores of the PTL and pores are filled with air.

For the non-uniform compression studies, PTL under the lands are compressed at different levels. Compression results in decrease in the thickness of the PTL under the lands. To prevent a step change in the PTL at the interface between the gas channel and the land, the compression parameter is varied linearly between 3 pores. The boundary conditions are kept similar to the case with no compression.

4.5.2 Permeability study

For the permeability study, the boundary conditions for the thermal transport remain the same as described in the previous section. Liquid water is injected from the bottom side (constant flux boundary condition). Symmetric boundary conditions are applied to left and right side as well as under the lands for liquid and vapor transport. Under the channel, open boundary is set with the pressure set to the atmospheric pressure. When water reached the gas channel, the simulations are stopped. Simulations were run at 20, 50, and 80°C and at 20, 50 and 80% relative humidity. The current density was varied between 1-2 A/cm^2 at 0.4V. All the generated water was passed through the the PTL while half of the generated heat was transferred to the PTL. Only the cathode side was simulated.

Two scenarios arise with the density modulated PTL with the sparse region located under the lands or the sparse region under the channels. Thus in all, four different cases were tested. In the subsequent sections, PTL C1 corresponds the case with the sparse region of the PTL under the lands, whereas in PTL C2, the sparse region lies under the channel.

4.6 Permeability based Performance metric

In the simulations, the liquid water percolates through the pores of the PTL and the rate, and location of the pores saturated with water depends upon the pore-size distribution and the specified operating parameters such as temperature, relative humidity, current density, etc. The information of the pores filled with water is saved during the course of the simulations. For the permeability simulations, the pores filled with water are considered to be closed. The simulations are re-run with the reversal of the location of the source and the sink. The top of the PTL, with pores open to the gas channel acts as the source and the catalyst layer side of PTL is considered to be the sink with air as the fluid. The pores that are filled with water are updated at different times of the simulations and the pressure differential across the PTL is calculated. The permeability is calculated from the Darcy's law:

$$B(t) = \frac{\mu h \bar{V}}{A \Delta P(t)} \quad (4.7)$$

where $B(t)$, $\Delta P(t)$, μ , h , $\bar{V}$, A , and t represents the transient permeability, transient pressure differential, gas viscosity, PTL thickness, volumetric flow rate of gas, area of simulation and the time respectively.

Table 4.1

Effective thermal conductivity from the pore network model with uniform compression.

Strain (%)	Toray TGP-H-060	Toray TGP-H-090 (W/mK)
0	0.36 ± 0.02	0.42 ± 0.03
5	0.45 ± 0.03	0.52 ± 0.03
10	0.63 ± 0.03	0.66 ± 0.04
15	0.83 ± 0.04	0.85 ± 0.04

4.7 Results

4.7.1 Compression

Figure 4.6 shows the temperature profile in PTL B under 0, 5 and 10% compression of original thickness. With an increasing compression, the effective thermal conductivity of the PTL increases which results in lower operating conditions. No variation in thermal profile exist along X-direction as symmetric boundary conditions are applied to left and the right edge and no thermal gradient is present across these two edges.

Table 4.1 shows the effective thermal conductivity values from the network simulations for the two PTLs. The pore network simulations compare well to the experimental data. This shows that the method of determining material properties from extrapolating experimental data and applying it to the unit cylinder model can be used to model the solid phase of the PTL.

Non-uniform

In the fuel cell, the lands of the bipolar plates compress the PTL whereas no compression occurs under the gas channel. To simulate these conditions, The PTL under the lands of the bipolar plate (Figure 4.7) was compressed to 5 and 15% of its original thickness. Temperature profile in the PTL with compression under lands of bipolar plate shows the temperature profile when compression of the PTL occurs under the lands of the bipolar plate. Lower temperatures are seen in the PTL under the lands while the area under the gas channel operate at a higher temperature. Such a variation in the temperature can significantly affect the water transport dynamics in the

Figure 4.6: Temperature Profile in Freudenberg H2315 under Different Compression Under the Lands

fuel cell. Lower temperatures under the lands can favor water vapor condensation and can result in local flooding while the area under the gas channel can dry up.

4.7.2 Permeability

Figure 4.8 shows the percolation of liquid water in the PTL at three different temperatures. At 20°C, PTL A shows the largest accumulation of liquid water, whereas the accumulation of water in PTLs B and C is comparatively smaller. In both cases of PTL C, the water follows a preferential path through the large pores (sparse region). However, in the case of PTL C2, the sparse region lies directly under the channel

Figure 4.7: Temperature Profile in Freudenberg H2315 under Different Compression Under the Lands

which results in much faster breakthrough with the least portion of the PTL being filled with liquid water. PTL C2 was simulated at 2 A/cm^2 without flooding. In PTL A there exists a layer of water that spans from the left to the right which is an indicator of the flooding of the PTL as no passage exists for the reactant gases. Note that the bottom layers is used to apply the boundary condition of constant flux. For the permeability calculations, 2 layers from the bottom are ignored.

As the temperature increases, the rate of evaporation increases and hence the saturation of the PTLs decreases 4.8. The trends appear to be similar with the exception that water continues to accumulate in under the lands of PTL C1 where the sparse region exists.

As the temperature is further increased, the rate of evaporation increases. All of the PTLs operate in a quasi-steady state, i.e., the rate of evaporation is matched by the rate of water generation. None of the PTLs flood at the high temperature at the relative humidity of 80%. Even high current rates of 2 A/cm^2 , none of the PTLs indicate flooding.

Table 4.2 shows the maximum permeability as obtained by applying Equation 4.7 across the PTL. Maximum permeability occurs at the beginning of the simulation with none of the pores filled with liquid water. The relative permeability at other time steps is obtained by normalizing the instantaneous permeability with the initial permeability Figure 4.9 shows the variation in the permeability of the PTL as the

Figure 4.8: Percolation at 70% RH and 20°C after 300 seconds. All PTLs at 1 A/cm^2 except PTL C2 (2 A/cm^2)

time progresses. Flat lines indicate that the breakthrough has occurred at which point the simulations are stopped as the path of least resistance for water transport is obtained when the liquid water reaches the channel. Flooding occurs when there is no path available for the gas to transfer to the catalyst layer side from the gas channel side. This is marked by a drop in the permeability to zero. For the cases tested in this study only PTL A shows flooding at low temperatures (20-50°C). However as the temperature increases, the permeabilities of the PTLs become more or less equal

Figure 4.9: Transient gas permeability of the PTLs. All PTLs at 20°C and 70% RH

Table 4.2
Maximum gas permeability of the PTLs tested

PTL	Permeability (m^2) $\times 10^{-11}$
PTL A	3.1 - 3.5
PTL B	2.5 - 2.8
PTL C1	2.4 -3.0
PTL C2	2.4 -3.0

except PTL C2 which continues to show a higher permeability. Based on the results, the configuration of PTL C2 benefits the low temperature performance of the PTLs. However, the same cannot be said with certainty when the PTL is running at normal operational temperatures (70-80°C). High permeabilities might results in drying up of the PTL and the catalyst layers which adversely affect the performance as the convective transport becomes dominant at high permeabilities [57].

4.8 Conclusion

The morphology of the PTLs plays a dominant role in the water removal properties, especially at low temperatures. Even at low saturation, the water present in the PTL may result in the formation of a barrier which hinders the transport of the gases from the channel to the catalyst layer. By manipulating the structure of the PTL, performance limitations due the flooding can be overcome. From the pore network simulations, a PTL with banded porosity was found to have the least likelihood of flooding at low temperatures. The banded structure allows the liquid water to permeate through the larger pore while keeping the smaller pore relatively open for gas transport, thereby allowing a mode for gas transport. At higher temperatures, water is present primarily in vapor form which minimizes flooding. Superior thermal transport under the lands of the bipolar plate, however, create a non-uniform thermal distribution which results in lower temperature under the land due to a reduction in the contact resistance.

Chapter 5

Surface Plasmon Resonance

Microscopy

Surface Plasmon Resonance (SPR) reflectance microscopy can characterize the properties of thin films in a region of about 200 nm from the metal surface. SPR detects the changes in the refractive index (RI) of the test medium due to concentration, temperature, and phase change. This change in the RI is observed as a loss in the intensity of incident beam of light. SPR microscopy is used commonly in biological applications to detect proteins.

The surface of metals are characterized by abundance of free electrons. When the free electrons are excited by photons, the electrons oscillate producing a charged density

wave which propagates along the surface of the metal which is referred to as surface plasmons (SP). The Surface Plasmons are therefore electromagnetic waves that propagate parallel to the interface between a metal and a dielectric medium. Surface plasmons are also termed as surface plasmon wave, surface plasmon oscillations and surface plasmon polaritons [58, 59]. In 1902, Wood first observed the phenomenon of surface plasmons when he noticed narrow dark bands in the light spectrum on diffraction gratings which he referred to as anomalies [60].

For a given metal-dielectric interface, there exists a characteristic momentum that is needed to excite the surface plasmons. This excitation can be provided by the transfer of momentum and energy by incident photons under specific conditions. For the plasmons to be excited by the photons, the necessary condition is that the wavevector for the incident photons and the plasmons must be equal in magnitude and direction. In a simple two layer configuration consisting of a metal film and a dielectric with the light waves incident on the metal through the dielectric, the surface plasmons cannot be excited for any incident angle and wavelength as the resonance condition is never met.

Otto [61] and Kretschmann [62] demonstrated experimental techniques to establish the excitation of surface plasmon using attenuated total reflection. These breakthrough configurations were then later employed in characterization of thin films. Figure 5.1 shows the schematic described by Otto and Figure 5.2 shows the Kretschmann

Figure 5.1: Otto Configuration. Thin metal layer on glass plate separated by a spacer

Figure 5.2: Kretschmann Configuration. Thin metal layer on prism

configuration. Otto's configurations places a restriction on the thickness of the test medium. Also it is difficult to precisely control the spacing between the prism and the metal. For these reasons Kretschmann's configuration is widely used in SPR microscopy due to the inherent ease of the setup.

5.1 Kretschmann's Three-Layer Configuration

When light wave is incident on the prism-metal interface and undergoes total internal reflection, an evanescent wave is generated which propagates along the thickness of

the metal. For sufficiently thin films, this evanescent wave penetrated the thickness of the metal and interacts with the surface plasmons at the metal-dielectric interface. The energy required to excite the plasmons is provided by the incident light on the prism-metal surface. Under resonance, this means that the reflected light will have less energy which is characterized by a decrease in reflectance. When the surface plasmons are excited, they travel along the surface of the metal with the wave propagation number β_{sp} ,

$$\beta_{sp} = \frac{\omega}{c} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \quad (5.1)$$

where ϵ represents the dielectric constant, c and ω represents the velocity and frequency of light. The subscripts m and d represent metal and the dielectric. The amount of light reflected, R , is calculated by applying the Fresnel theory to the prism-metal-dielectric configuration.

$$R = |r_p|^2 \quad (5.2)$$

$$r_p = \frac{r_{pm} + r_{md}e^{(2ik_{mx}d)}}{1 + r_{pm}r_{md}e^{(2ik_{mx}d)}} \quad (5.3)$$

where k_{mx} is the wavevector component perpendicular to the interface in medium x .

The parameters in the above equation are calculated as:

$$k_{mx} = \sqrt{\left(\frac{\omega}{c}\right)^2 \epsilon_i - k_z^2} \quad (5.4)$$

$$k_z = \epsilon_d^{0.5} \frac{\omega}{c} \sin(\theta) \quad (5.5)$$

$$r_{md} = \frac{\epsilon_d k_{mx} - \epsilon_m k_{dx}}{\epsilon_d k_{mx} + \epsilon_m k_{dx}} \quad (5.6)$$

$$r_{pm} = \frac{\epsilon_m k_{px} - \epsilon_p k_{mx}}{\epsilon_m k_{px} + \epsilon_p k_{mx}} \quad (5.7)$$

$$k_x = \frac{2\pi}{\lambda} n_p \sin(\theta) \quad (5.8)$$

In the above equations, d , θ represents the thickness of metal and angle of incidence.

The subscripts m , d , and p represent metal, dielectric and the prism. The refractive index and the dielectric constant are related as:

$$n_i = \sqrt{\epsilon_i} \quad (5.9)$$

From the above equations, for a four-layer system, which consists of the prism, gold film, the thin test medium and the bulk medium (usually air) above the test medium, the resulting reflectance is obtained as

$$R = \frac{r_1[1 + \exp(-2ik_2d_2)] + [r_1r_2 + \exp(-2ik_2d_2)]r_3\exp(-2ik_3d_3)}{1 + r_1r_2\exp(-2ik_2d_2) + [r_2 + r_1\exp(-2ik_2d_2)]r_3\exp(-2ik_3d_3)} \quad (5.10)$$

where r_i represents the coefficient of reflection between the i th and $(i + 1)$ layer, k represents the wavevector in each medium and d represents the thickness of each medium. Subscripts 1,2 and 3 represents the glass slide (or prism) (BK7), gold film (50 nm) and the test. Thickness of the prism and the bulk medium are not present in the equation as they considered to be infinite.

5.2 Film Thickness Measurement During Droplet Coalescence under Condensation

Experiments were performed to detect and visualize the thin film formation during droplet coalescence under condensation. In the experiment, a droplet of water was placed on the gold layers. An ITO (Indium Tin Oxide) coated glass slide was placed 3-4mm above the gold film and a bridge was formed between the gold and the ITO slide. The ITO slide was heated, resulting in the evaporation of the water and a subsequent condensation on the gold film adjoining the initial droplet. The SPR angle was set at 43.8° and the images were captured at 1500 frames per second. The sequence of images and the measured film thickness is shown in Figure 5.3. Dark and bright regions correspond to air and water, respectively. The original drop is moving to the left leaving a bare gold film. Condensation quickly (μ seconds) reappears on the gold film as a thin liquid water film. The increase in the thickness of water film along a horizontal dashed line is calculated through changes in reflectance intensity. A 12 nm change in thickness occurs between the retracting drop interface (2 nm thick) and the new condensation layer (14 nm thick). This thickness is measured using the SPR reflectance equation 5.10.

High-Speed Surface Plasmon Resonance (SPR) Reflectance Imaging of Drop Coalescence during Condensation and Evaporation

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Drop condensation and coalescence is visualized using high-speed Surface Plasmon Resonance (SPR) reflectance microscopy. SPR microscopy is a label-free technique that can characterize thin films (less than $1\mu\text{m}$) by detecting the changes in the refractive index of the test medium. The sensing surface is a 50 nm thick gold film on a 2.5 nm thick Ti layer is deposited on a borosilicate substrate. P-polarized monochromatic light (632 nm) is incident on the gold film in a total internal reflection mode. Free electrons in the gold film are excited by the incident light when a resonance condition is met. The result is a decrease in the reflected intensity. Resonance depends upon wavelength, incident angle, and refractive index of prism and test medium. To induce condensation, a water bridge is created between the SPR gold film and an ITO coated glass slide. When the ITO coated slide is heated water evaporates from the bridge and condenses on the gold film. The sequence of images on the process of droplet deposition and drop coalescence are captured at 1500 frames per second. Experiments were conducted at an SPR angle of 44° , which is slightly above the minimum intensity angle for air at 43.8° . Therefore, the brightest and darkest regions correspond to the areas on the gold film covered with bulk water and a very thin film of water, respectively. The thickness of the film is proportional to the intensity of reflected light.

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Figure 5.3: Film thickness measurement during droplet coalescence under condensation

Chapter 6

Conclusion and Recommendations

A model to study the thermal transport in the thin porous media of PEM fuel cells has been developed. The model utilizes a separate network to simulate the heat transfer through the solid-phase of the PTLs. The distribution in the thermal resistances for the pore network model is not random but directly tied to the pore size distribution. Material constants for heat conduction, which are independent of compression are extracted from experimentally derived effective properties. Further the change in the effective thermal conductivity during compression is captured in the presented model. A large change in temperature profile in the PTL is observed as the areas under the lands of the bipolar plate are compressed. Simulations performed to estimate transient permeabilities show a high dependence of morphology of the PTL on the operation of the PTL. A control on the structure of the PTL can yield better performance during

cold startup.

In addition to the computational model, a high-speed capable surface plasmon resonance microscope was built which utilizes long distance Kohler illumination. The microscope can detect small changes in the RI of the thin film (approx. 200nm) and characterize material properties. The phenomenon of droplet coalescence during condensation was visualized and the thickness of the films during droplet motion was measured. This experimental system can be utilized to study the characteristics of water transport in thin nafion films.

The list of contributions to research from the current work are summarized below:

- † A methodology to couple multiple networks (representing pore-phase and solid-phase) within pore network model was developed. This methodology can be further expanded and applied to model transport in other media such as catalyst layer.
- † A comprehensive methodology was developed to generate the parameters of the solid-phase of the porous transport layers.
- † A high-speed imaging capable automated surface plasmon resonance (SPR) microscope was developed which was used to observe and measure several phenomena at the nano-scale. This setup can be used to perform several qualitative and quantitative measurements which are applicable to both fuel cells and other

physical phenomena.

6.1 Recommendations

The modeling efforts presented herein are still in developmental stages. Currently, there exists a lack of experimental characterization that can be used to verify or provide values for the variables used in the simulations.

The following is a list of tasks that can be further developed:

- † Experimental characterization of the thermal capacitance of the PTLs need to be performed which can be used to tune the thermal transport model.
- † The data on the variation of the pore size distribution during compression of the PTLs is not readily available. This variation needs to be included in the model as the water distribution in the PTLs in the compressed state can change from the uncompressed state.
- † PTLs are only a small component of a fuel cell system. A larger model that integrates all the components, from the electrochemistry to the control system needs to be developed.
- † The droplet coalescence on different surfaces can be studied by coating the gold

film with suitable monolayers.

† Diffusion in the nano-scale Nafion films can be measured using the SPR system.

The results can be incorporated into a model of the catalyst layers of PEM fuel cells.

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