Effective Thermal Conductivity of Gas Diffusion Layers Used in PEMFC: Measured with Guarded-Hot-Plate Method and Predicted by a Fractal Model

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An experimental setup to determine thermal conductivity and thickness of a gas diffusion layer (GDL) as a function of compression was developed and calibrated. The actual thermal conductivities, based on compressed thickness, of plain Toray TGP-H gas diffusion layer (GDL) at compression pressures of 0.04 to 1.5 MPa and over temperature range of 25 °C to 75 °C are reported in this paper. The thermal conductivity of TGP-H GDL was found to decrease with temperature and to increase with compression. An effort was made to numerically account for the effective thermal conductivity by using theoretical models. Krischer model was found to be able to match with the experimental data, but this model relied on a priori knowledge of the thermal properties of the solid matrix. A new analytical model based on fractal analysis of GDL microstructure is proposed to account for GDL thermal conductivity as well as its variation with compression without using any empirical parameter.

Introduction

Gas diffusion layer (GDL) is one of the critical components in a proton exchange membrane fuel cell (PEMFC). It has a heterogeneous, fibrous structure with fiber diameters on the order of 10 µm. The thickness of GDL is usually in the range of 200-400 µm. The main functions of a GDL include uniform distribution of reactant gases to the catalyst layer, removal of product water from the catalyst layer, electrical conduction between the catalyst layer and bipolar plates, and mechanical support for the membrane-electrode assembly, as well as dissipation of waste heat to the cooling channels.

Heat transfer through a GDL is complex because of the existence of both solid and fluid phases, and also due to the random pore morphology. The mode of heat transfer, in terms of conduction, convection and radiation, varies for different pore structures. In a porous medium, heat transfer due to convection occurs when there is a flow within the pores. The effect of convective heat transfer is more apparent in the case of large pore sizes, but can be neglected for small pores (<100 µm) at lower temperatures because of the lack of intense fluid circulation in the pores (1). Heat transfer due to radiation is significant only for pores of sizes greater than 10 µm and for pore temperatures above 1000 K (2), while the operating temperature of a PEMFC is generally below 373 K. Accordingly, conduction is the predominant mode of heat transfer in a GDL.
Thermal conductivity is an important material property in modeling the heat transfer through heterogeneous porous GDL. Accurate determination of GDL thermal conductivity is therefore of critical importance. However, only a few studies related to experimental measurement of GDL thermal conductivity have been reported in literature (3-7). Vie et al. (3) determined the thermal conductivity of fuel cell membrane and GDL in an operating fuel cell. Khandelwal et al. (4) used a steady state method to measure the thermal conductivity of GDL as a function of compression and PTFE content. The same method was also used by Ramousse et al. (5), Nitta et al. (6) and Karimi et al. (7) to determine thermal conductivity of various GDLs. All these measurements reported the thermal conductivity based on the non-compressed GDL thickness. However, in a fuel cell stack the GDL thickness is significantly reduced due to the compression, and the thermal conductivity based on the compressed thickness is more realistic. Hence, there is a need to account for thickness changes with compression in thermal conductivity measurement.

The objective of the present work is to develop an apparatus to measure the actual thermal conductivity of GDL as a function of temperature and compression. An additional goal of this work is to develop a sound theoretical model to predict the thermal conductivity of GDLs.

Measurement of GDL Thermal Conductivity

Guarded-Hot-Plate Method

Guarded-hot-plate method (8) is the most widely used method to determine the thermal conductivity of low thermal conductivity materials in which the heat flow is steady and unidirectional. In this method, two identical samples are placed on both sides of a flat heater comprising of a main heater and an annular guard heater (see Figure 1). The main and guard heaters are maintained at the same temperature by individually controlling their power supplies to prevent radial heat loss. GDL samples and the heaters are then sandwiched between two heat sinks (copper plates in this work) which are maintained at a fixed temperature with a constant temperature circulating bath. At steady state condition, the heat flux from the heater is transferred across the samples and thermal conductivity \( k \) of the samples is calculated using Fourier heat conduction equation:

\[
k = \frac{Q L}{2 A \Delta T}
\]

In this equation, \( Q \) is the heat transfer rate through the GDL, \( L \) is the GDL thickness, \( A \) is the heat transfer area, and \( \Delta T \) is the temperature difference across the GDL. The factor 2 in the denominator is used because the heat flux is assumed to be equally divided between the two samples.
Plain Toray TGP-H (0 wt.% PTFE) GDLs were investigated to measure the thermal conductivity under various temperature and compression pressures. Two GDL samples TGP-H-060 (190 µm, manufacturer data) and TGP-H-120 (370 µm) were used in the experiment. The experimental setup is shown in Figure 2. The assembly of heaters, GDL samples and cold plates was compressed by using the loading clamp to a set pressure in the range of 0.04 to 1.5 MPa. These compressive forces are representative of those commonly used in fuel cell stacks. The applied compression was monitored with a load cell (LC304-5K, Omega) which was placed between the loading clamp and the top cold plate. The temperatures of the main heater, the guard heater and the cold plates were precisely measured by using ultra thin thermocouples (TT-K-36, Omega) inserted at multiple locations of each component. The thermocouples were calibrated using a two point calibration scheme, with the ice point and the boiling point of water being the two fixed temperatures. After calibration, an accuracy of ±0.1 °C was obtained. All the temperatures and the compression pressure were recorded through a data acquisition system (NI-SCXI, National Instruments) controlled by a LabVIEW program developed in-house.
Accurate measurement of GDL thickness is critical to determine the thermal conductivity of a GDL at a given compression. In this work, the thicknesses of GDL samples placed between the heater and the cold plate were measured with a digital microscope (VHX-500, Keyence). Figure 3 shows the change of GDL thickness as a function of compression for TGP-H-060 and TGP-H-120 GDLs. A large reduction in thickness is observed at the beginning of the compression, followed by a linear decrease at higher compressions for both samples. The initial dramatic reduction of GDL thickness upon small compression, resulting from the loose fibers on GDL surface, makes it difficult to determine the actual uncompressed GDL thickness. In this work we define a zero-load GDL thickness \( (L_0) \), which was obtained by extrapolating the linear part of thickness-compression plot to zero compression, as the uncompressed thickness. We believe that the GDL thermal conductivity based on the zero-load thickness is more meaningful. Table 1 displays the comparison between the zero-load thickness and the free-standing thickness reported by manufacturer for Toray GDLs.

![Figure 3. Plot of GDL thickness versus compression for TGP-H-060 and TGP-H-120 samples. The inset plot displays the method to determine the zero-load GDL thickness.](image)

After the actual GDL thickness was determined, the thermal conductivity was calculated from Eq. 1. During the experiments, two different thicknesses of the same sample were tested in order to unravel the bulk thermal conductivity from the effects of contact resistance. This is because, in actual thermal measurement, the experimentally accessible variable is the total thermal resistance \( (R_{\text{total}}) \), which contains the contribution from the contact resistance, and can be written as:

\[
R_{\text{total}} = \frac{\Delta T}{(Q/2)} = R_b + 2R_c
\]  

where \( R_b \) is the bulk thermal resistance of the samples and \( R_c \) is the contact resistance between the sample and the copper plate.
Table 1. Comparison of the zero-load thickness obtained in this work to the thickness provided by manufacturer for TGP-H-060 and TGP-H-120 GDLs.

<table>
<thead>
<tr>
<th>GDL</th>
<th>Zero-load thickness (μm)</th>
<th>Thickness by manufacturer (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGP-H-060</td>
<td>182 ± 3</td>
<td>190</td>
</tr>
<tr>
<td>TGP-H-120</td>
<td>340 ± 3</td>
<td>370</td>
</tr>
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</table>

By assuming that the contact resistances between two GDLs of different thicknesses and the copper plate are the same, the thermal conductivity of GDL can be obtained by combining Eqs. 1 and 2:

$$k = \frac{L_1 - L_2}{(R_{total1} - R_{total2}) A} \tag{3}$$

where $L_1$ and $L_2$ are the actual thicknesses of the two samples under compression; $R_{total1}$ and $R_{total2}$ are the measured total thermal resistances of the two samples.

The test apparatus was validated before the GDL thermal conductivity measurements were carried out. PTFE sheets of known thermal conductivity and having two different thicknesses were used for calibration. The system was operated for at least 30 minutes before the actual measurements in order to ensure steady state in which the temperature fluctuation was kept within 0.1 °C. The validation test was performed at room temperature (~ 26 °C) and the thermal conductivity obtained for PTFE sheet was 0.329 W/m.K, which is in close agreement with literature data of 0.33 W/m.K (9) and 0.32 W/m.K (10).

The measurements of GDL thermal conductivity were carried out over temperatures from 25 °C to 75 °C and under compressions of 0.04 MPa – 1.5 MPa. These conditions were relevant to real fuel cell operation. The uncertainty in the thermal conductivity measurements was analyzed to be about 8.8%.

Thermal Conductivity of Plain TGP-H GDL

Figure 4 shows the variation of thermal conductivity with temperature for plain Toray TGP-H GDL at a compression of 0.04 MPa. It was observed that the thermal conductivity of this GDL decreased with temperature. This is in agreement with the measurement by Khandelwal et al. (4). Their data are also plotted in Figure 4 for comparison. The decrease of Toray thermal conductivity with increasing temperature may be attributed to the presence of the binder which is carbonized thermo-setting resin. Thermal conductivity of the resin was found to decrease as temperature increases (4,11).
Figure 4. Plot of thermal conductivity of Toray TGP-H GDL versus temperature at compression of 0.04 MPa.

The effect of compression on thermal conductivity of Toray sample measured at 58 °C is plotted in Figure 5. It was found that the thermal conductivity increases with compression. This can be accounted for by the reduction of porosity upon compression. Under a compression force, the carbon fibers in the GDL are compressed leading to a reduction in the pore space. This reduction in the porosity results in an increased GDL thermal conductivity. The apparent thermal conductivities calculated on the basis of the zero-load GDL thickness are also plotted in the figure. It was found that the apparent thermal conductivities were higher than the actual thermal conductivity and deviated significantly from the actual conductivity at higher compressions. This reinforces that the GDL thickness variation under compression has to be considered when determining the thermal conductivity.

Although the contact resistance between GDL and copper is intentionally eliminated in derivation of the GDL thermal conductivity, it can be back calculated from the thermal conductivity data by using the following equation:

$$R_c = \left(\frac{2 \Delta T_1}{Q_1} - \frac{L_1}{kA}\right) \frac{A}{2}$$

Where $L_1$, $Q_1$, and $\Delta T_1$ are the thickness, heat transfer rate and the temperature drop, respectively, corresponding to the sample with thickness $L_1$; $k$ is thermal conductivity of the sample; $A$ is the heat transfer area. Figure 6 shows the contact resistance of a GDL-copper interface as a function of compression for Toray GDL. The contact resistance was found to decrease with increasing compression. This is expected because of the better contact between the GDL fibers and the copper surface under compression, thereby leading to lower resistance to the heat flow.
Figure 5. Thermal conductivity plot as a function of compression for Toray TGP-H GDL at 58°C.

Figure 6: Plot of contact resistance of a GDL-copper interface versus compression for Toray TGP-H sample.

Models to Predict GDL Thermal Conductivity

Theoretical Models Based on Idealized Structures

Theoretical model prediction of thermal conductivity (13-15) is generally carried out by using theoretical expressions derived based on idealized geometries. For example, layer structure is used in parallel, series and Krischer model and sphere shape is used in effective medium theory model. Table 2 lists some of these models.
Table 2: Effective thermal conductivity models from idealized structures.

<table>
<thead>
<tr>
<th>Model</th>
<th>Structure Schematic</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel</td>
<td><img src="image" alt="Parallel" /></td>
<td>$k_{eff} = c_k f_s + c_f k_f$</td>
</tr>
<tr>
<td>Series</td>
<td><img src="image" alt="Series" /></td>
<td>$k_{eff} = \frac{1}{\frac{1}{k_f} + \frac{1}{k_s}}$</td>
</tr>
<tr>
<td>Krischer (Parallel-Series)</td>
<td><img src="image" alt="Parallel-Series" /></td>
<td>$k_{eff} = k_f + k_s - 2(k_f - k_s)c_L$</td>
</tr>
<tr>
<td>Maxwell-Eucken (M-E)</td>
<td><img src="image" alt="M-E" /></td>
<td>$k_{eff} = k_f + k_s - 2(k_f - k_s)c_L$</td>
</tr>
<tr>
<td>Effective Medium Theory (EMT)</td>
<td><img src="image" alt="EMT" /></td>
<td>$c_k f_s k_f + c_f k_f k_s - 2k_f c_L = 0$</td>
</tr>
</tbody>
</table>

In these models, the effective thermal conductivity of GDL is estimated from the respective properties of the solid and fluid phases and their respective volumetric fraction. The thermal conductivity of fluid (air, $k_f$) is well known, with a value of 0.026 W/m.K. However, prediction of the thermal conductivity of the solid phase ($k_s$) is difficult due to the anisotropic fiber orientation. This explained why a wide range of GDL thermal conductivity, varying from 0.2 W/m.K to 65 W/m.K, was encountered in literature (5). Although carbon fibers are highly conductive in the axial direction ($k_{fiber} = 120$ W/m.K), the thermal resistance of a GDL in the transverse direction depends mostly on the quality of contact between fibers and a significantly smaller value than 120 W/m.K is expected. Ramousse et al. (5) estimated the transverse thermal conductivity of carbon felt GDLs and obtained a value in the range of 0.21 – 12 W/m.K. Shi et al. (16) modeled the effective thermal conductivity of GDLs with $k_s = 8$ W/m.K.

In this work, in order to evaluate these theoretical models, an arbitrary value of $k_s = 8$ W/m.K was selected. Figure 7 shows the comparison of the effective thermal conductivities predicted from these models with the experimental data. In this figure, porosity (x-axis) denotes the compressed GDL porosity ($\epsilon$), which was derived by assuming that the change in GDL volume under compression is merely due to reduction in the pore spaces (17), as given by:

$$\epsilon = \frac{\epsilon_0 - CR}{1 - CR}$$  \[5\]

where $\epsilon_0$ is the initial GDL porosity; $CR$ is the compression ratio and is defined as $CR = \frac{L - L_c}{L}$, with $L$ and $L_c$ being the uncompressed and compressed GDL thickness, respectively.

It is seen from Figure 7 that parallel and series models predict the respective upper and lower bounds of effective thermal conductivity and other models lie in between them. Carefully comparing the measured thermal conductivities with model predictions, it was found that Krischer model with $f = 0.0015$ ($f$ is a distribution factor and is obtained from non-linear regression) provided a close match with experimental data at different compressed porosities, as seen from the inserted enlarged view in Figure 7. The
predictions from parallel model are close to those from Krischer model at high porosity. However, at lower porosities, the difference between these two models is quite significant as seen in Figure 7.

Although Krischer model is able to predict the effective thermal conductivity of Toray GDL, there are several drawbacks with this model. First, it requires \textit{a priori} knowledge of the thermal conductivity of the solid matrix. Second, it includes an empirical parameter $f$, which cannot be determined mechanistically from the physical structure of GDLs. Lastly, this model (as well as other models in Table 2) simply considers the volumetric fraction of solid and fluid phases, and the microstructures of the porous media are largely ignored. Therefore, we do not advocate such an approach. Instead, a more analytical and mechanistic approach based on fractal analysis is proposed to predict GDL thermal conductivity in the next section.

![Fractal Model of Effective Thermal Conductivity](image)

**Figure 7.** Comparison of the measured thermal conductivity of TGP-H GDL and the effective thermal conductivity calculated by different theoretical models versus porosity. The inserted figure displays the enlarged view in the porosity range of 0.75 to 0.8.

**Fractal Model of Effective Thermal Conductivity**

Recent studies have shown that microstructures and pore-size distribution of the GDL have a fractal characteristic (16,18,19). Several studies have focused on the application of the fractal method to the prediction of thermal conductivity of porous media (16,20). In this work, the fractal model is modified to incorporate the GDL compression. In addition, a new treatment of the thermal resistance of the solid phase is proposed.

Heat is conducted in a GDL through both the carbon paper substrate and the fluid phase. The fluid flow paths in porous media are usually described as the tortuous capillaries which consist of pores with different sizes, and these pores are randomly distributed in solid phase. The tortuous paths through porous GDL ($L_t$) are statistically self-similar fractals and can be characterized by fractal analysis as (21)
\[ L_t(\lambda) = \lambda^{1-D_t} L_0^{D_t} \]  \[ N(L \geq \lambda) = \left( \frac{\lambda_{\text{max}}}{\lambda} \right)^{D_f} \]

where \( D_t \) (1 < \( D_t < 2 \) for two dimensions) is the fractal dimension for tortuosity, \( L_0 \) is the straight capillary length, and \( \lambda \) is the pore diameter.

Similarly, it has been shown that the size distribution of pores in porous media follows the fractal power law (21)

\[ \epsilon = \left( \frac{\lambda_{\text{min}}}{\lambda_{\text{max}}} \right)^{2-D_f} \]

In this equation 2 is provided for two-dimension pore area.

On the basis of the above fractal description of the GDL, the heat transfer through the fluid phase (air) can be simplified as transport through parallel channels, whose length depends on respective pore diameter (as Eq. 6). The thermal resistance of gas phase in the porous media is described as (20)

\[ R_g = \frac{4L_0^{D_t}(D_t-D_f+1)}{\pi k_g D_f^2 \lambda_{\text{max}}^{D_f+1} (1 - \frac{\lambda_{\text{min}}}{\lambda_{\text{max}}} D_t-D_f+1)} \]

The thermal resistance of the solid matrix is dictated by the quality of the contacts between fibers. Its thermal resistance can be expressed as

\[ R_s = \frac{L_0}{k_c A_{s,c}} \]

Sadeghi et al. (22) used an idealized “basic cell” model, consisting of uniformly sized equally spaced cylindrical fibers immersed in air, to represent the fibrous media and to calculate the contact area dimensions as well as the effective thermal conductivity of carbon cloths. The similar geometrical model is also used in this work to describe the structure of TGP-H GDLs, as shown in Figure 8. In carbon paper GDLs like Toray TGP-H, the fibers are bound together by binders (see Figure 8 (a)). The thermal conductivity of the solid matrix is mostly decided by the quality of the binders. To estimate the total contact area between fibers, the fiber network model of Nam and Kaviany was used (23). In this model the GDL is composed of a stack of interwoven fibers (Figure 8) with equal spacing in three directions. Considering the presence of binder in the contacting region, the use of fiber diameter as contact dimension is recommended until detailed information.
on the actual resistance can be derived from microscopic studies in the future. For simplicity the fibers are allowed to intersect. The unit cell in this model has dimensions of S+D in all three directions. The fraction of the contact area to the unit cell is obtained as:

\[ \frac{A_{SC}}{A} = \frac{D^2}{(S+D)^2} = \frac{1}{(1+\frac{S}{D})^2} \]  \[11\]

The parameter S/D can be solved from porosity based on the relation

\[ \epsilon = \frac{S^2}{(S+D)^2} = \frac{(\frac{S}{D})^2}{(1+\frac{S}{D})^2} \]  \[12\]

As a result, the thermal resistance from the fiber matrix is obtained to be

\[ R_S = \frac{L_0}{Ak_c} \cdot \frac{1}{(1-\epsilon^{0.5})^2} \]  \[13\]

where \( k_c = 120 \text{ W/m.K} \) is the thermal conductivity for the contacts between fibers.

Thus, the effective thermal conductivity \( (k_{eff}) \) of GDL can be obtained as

\[ k_{eff} = \frac{L_0}{R_cA} = \frac{L_0}{A} \left( \frac{1}{R_s} + \frac{1}{R_{g,f}} \right) \]  \[14\]

In order to model the actual thermal conductivity under compression, the straight capillary length \( (L_0) \) is further expressed as

\[ L_0 = L_{0,0} \frac{1-\epsilon}{1-\epsilon_0} \]  \[15\]

where \( L_{0,0} \) is the uncompressed straight capillary length, \( \epsilon_0 \) and \( \epsilon \) are the uncompressed and compressed porosity, respectively.

By substituting Eqs. 9, 13 and 15 into Eq. 14, the effective thermal conductivity under compression is obtained as:

\[ k_{eff} = \frac{k_g(2-D_f)}{(D_t-D_f+1)} \cdot \left( \frac{\lambda_{\text{max}}}{L_0} \right)^{D_t-1} \cdot \epsilon (1-\epsilon)^{1-D_t} \left( 1 - \epsilon \frac{D_t-D_f+1}{2-D_t} \right) + k_c(1-\epsilon^{0.5})^2 \]  \[16\]

This equation is then used to predict the effective thermal conductivity of GDL under compression. The parameter values used in this model are listed in Table 3. Figure 9 shows the comparison between the model calculation and the experimental measurement. A very close agreement within 2.5% between model and measurement is obtained.

The above fractal model has the following merits: (1) every parameter in the model has a clear physical meaning, unlike the Krischer model; (2) due to the consideration of the disordered characteristic and the particular microstructures as well as the compression effect, this fractal model is more realistic in comparison with the normal volume-average
models and other fractal model; (3) the fractal model deduced above can be easily adjusted to predict the transport properties in three-phase porous media (20). This last point is particularly useful for modeling thermal conductivity of GDL in a PEMFC where liquid water provides additional heat transfer paths.

Figure 8. (a) Cross section image of Toray TGP-H GDL (12). (b) Schematic diagram of fiber structure used to determine the fiber contact areas in Eq. 11. \( S \) denotes the spacing between fibers and \( D \) is the fiber diameter.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>100 ( \mu \text{m} )</td>
<td>Maximum pore diameter</td>
</tr>
<tr>
<td>( \epsilon_0 )</td>
<td>0.79</td>
<td>Uncompressed GDL porosity, ref. (12)</td>
</tr>
<tr>
<td>( L_0^0 )</td>
<td>182 ( \mu \text{m} )</td>
<td>Uncompressed GDL thickness</td>
</tr>
<tr>
<td>( D_t )</td>
<td>1.25</td>
<td>Tortuous fractal dimension, ref. (18)</td>
</tr>
<tr>
<td>( D_f )</td>
<td>1.9</td>
<td>Pore area fractal dimension, ref. (18)</td>
</tr>
<tr>
<td>( k_g )</td>
<td>0.026 W/m.K</td>
<td>Thermal conductivity of air</td>
</tr>
<tr>
<td>( k_c )</td>
<td>120 W/m.K</td>
<td>Thermal conductivity of fiber contacts</td>
</tr>
</tbody>
</table>
Figure 9. Comparison of the effective thermal conductivity of TGP-H as a function of compression between experimental measurement at 58 °C and that predicted by the proposed fractal model. The calculation with Krischer model is also plotted in this figure.

Conclusion

In the present work, a guarded-hot-plate method was developed to measure the thermal conductivity of plain Toray TGP-H GDL. The GDL thickness at different compressions was first measured to obtain the actual thermal conductivity. The GDL thermal conductivities were determined under the compression range of 0.04 to 1.5 MPa and over the temperature range of 25 to 75 °C. The thermal conductivity of TGP-H sample was found to decrease with increasing temperature. This was attributed to the resin binders used in this type of GDL. The GDL thermal conductivities were observed to increase with compression and were accounted for due to the reduction in GDL porosity caused by compression.

The effective thermal conductivity and its variation with compression could be modeled by a Krischer model. However, an empirical constant – distribution factor $f$ – has to be used for the model and a priori knowledge of the thermal properties of the solid matrix is required. This made the Krischer model less plausible. A new fractal model (as shown in Eq. 16) is proposed in this work to predict the effective thermal conductivity of GDL without using any empirical constant. The prediction from the proposed model was found to match very well with the measured thermal conductivity within 2.5%. This fractal model is more realistic in comparison with the normal volume-average models and other fractal model due to the consideration of the disordered characteristic and the particular microstructures of GDL as well as the compression effect.
Acknowledgments

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References