

Available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/he

Measurement of the through-plane thermal conductivity of carbon paper diffusion media for the temperature range from -50 to $+120$ °C

Nada Zamel^a, Efim Litovsky^b, Xianguo Li^{a,*}, Jacob Kleiman^b

^a20/20 Laboratory for Fuel Cell and Green Energy RD&D, Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, Ontario, Canada

^bIntegrity Testing Laboratory Inc., Markham, Ontario, Canada

ARTICLE INFO

Article history:

Received 27 March 2011

Received in revised form

31 May 2011

Accepted 17 June 2011

Available online 20 July 2011

Keywords:

Through-plane thermal conductivity
Temperature dependence
PEM fuel cells
Carbon paper diffusion media

ABSTRACT

Carbon paper, a fibrous material, is often used as the gas diffusion layer in polymer electrolyte membrane (PEM) fuel cells, which are being vigorously developed as a zero-emission power source for transportation applications. The temperature field and heat transfer in this material is determined by its thermal conductivity and diffusivity, which are directly dependent on the operating temperature. In this work, we use a quasi-steady method known as the thermal capacitance (slug) method to experimentally measure the through-plane thermal conductivity of TORAY carbon paper for a temperature range from -50 to $+120$ °C. The effects of compression and PTFE loading on the overall thermal conductivity are also investigated. Compression leads to a decrease in thermal resistance between the carbon fibers; hence, an increase in the overall thermal conductivity. However, it is also found that this thermal resistance is highly dependent on the temperature and the PTFE loading. In contrast with our in-plane thermal conductivity measurements from a previous study, the through-plane thermal conductivity is found to increase with an increase in temperature in this study. This finding suggests that the thermal expansion of the carbon fibers is a direction dependent quantity.

Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The temperature field and heat transfer in thin anisotropic porous materials are often determined by their apparent thermal conductivity and diffusivity, which are directionally dependent properties. Carbon paper is an example of such materials and it is widely used as the gas diffusion layer (GDL) in polymer electrolyte membrane (PEM) fuel cells. Carbon paper is a fibrous material that is composed of carbon fibers and held together by a carbon binder. The properties of the

carbon material can take on that of carbon or graphite depending on the heat treatment it undergoes [1]. To assist in liquid water removal and to increase its mechanical durability, PTFE is often added to the carbon composite to increase the hydrophobicity of the resultant carbon paper. Due to its manufacturing process, the resultant structure is strongly anisotropic and highly porous. Typical operating temperatures of PEM fuel cells lie in the range of -30 to $+120$ °C. In this temperature range, the thermal physical properties of the carbon paper can be used to determine its thermal durability.

* Corresponding author.

E-mail address: xianguo.li@uwaterloo.ca (X. Li).

Knowledge of the thermal properties at subzero temperatures is especially important during the cold start of the fuel cell. At these conditions, the heating process of the fuel cell can directly affect the start up mechanisms [2–4]. Numerical simulations are often utilized to investigate the temperature rise during the cold start process. This process is transient; hence, the effect of temperature on the thermal conductivity is of crucial importance for the accuracy of the numerical simulation.

To-date, experimental efforts have been tailored to understanding the effect of compression on the through-plane thermal conductivity using the guarded heat flux meter method. With this method, Khandelwal and Mench [5] measured the effect of temperature in the range of +26 to +73 °C on the thermal conductivity of TORAY carbon paper. They reported a decrease in the thermal conductivity with temperature. Their measurements were reported at a compression pressure of 2 MPa. This compression pressure marks the pressure at which the contact resistance is minimized. In the same study, they also measured the effect of Teflon treatment on SIGRACET carbon paper and showed that the addition of PTFE to carbon paper drastically reduces its thermal conductivity. The effects of compression and addition of PTFE on the overall thermal conductivity of carbon paper by various manufacturers were also investigated in [6–13]. The general trend observed was that the through-plane thermal conductivity increases with the increase in compression pressure, which is mainly attributed to the decrease of the overall contact resistance between carbon fibers. In the study by Burheim et al. [8], they investigated the effect of compression, thickness, PTFE and liquid water on the through-plane thermal conductivity of carbon paper. In their study, they reported that the addition of PTFE results in the decrease of the overall thermal conductivity, while compression and liquid water resulted in the increase of this property. Further, one of their main observations was that TORAY papers with differing thicknesses exhibited different thermal conductivity. They attributed this finding mainly to the manufacturing process of this carbon paper. Through SEM imaging of this paper, they hypothesized that the thicker samples were manufactured by stacking thinner samples together. In the study by Nitta et al. [13] it was reported that the thermal conductivity of TORAY carbon paper was found to be independent of the compression pressure despite applying pressures up to 5.5 MPa. They argued that this trend was mainly caused due to heat transfer through the air despite its low thermal conductivity in comparison to that of the solid carbon fibers. It is important to note here that according to the material specification [14], the through-plane thermal conductivity of TORAY carbon paper is 1.7 W/K m at room temperature despite the thickness of the paper. There is no published information on the method of measurement used by TORAY. Further, there is much discrepancy in the published literature about the compression pressure needed to obtain this value. For instance, according to the studies by Khandelwal and Mench and Burheim et al. [5,8], the compression pressure has a significant effect on the overall thermal conductivity, whereas, this is not the case as seen in Ref. [11–13].

Although much work has been done to experimentally measure the thermal conductivity of various carbon papers, much of the work is tailored to the measurement of this value

in a small range of temperature. Hence, a more comprehensive understanding of the effect of temperature on this important property is still needed. The present study is an extension of our previous study on the measurement of the in-plane thermal conductivity of carbon paper [15]. In our previous study, we used the method of monotonous heating [16–19] to measure the in-plane thermal conductivity for a temperature range of –20 to +120 °C and for four PTFE loadings (0, 5, 20 and 50 wt.%). This measurement technique allowed for the investigation of the effect of phase change due to the addition of Teflon on the thermal conductivity. In this same study, we found that the in-plane thermal conductivity decreases with an increase in temperature for all samples. However, the slope of decrease for the untreated sample was much more pronounced. In other words, Teflon was found to be the main contributor to the thermal resistance once it is introduced to the sample.

The evaluation of the thermal physical properties of a material, such as carbon paper, is necessary also in the through-plane direction due to the anisotropic geometry of such a material. Further, as we have shown in our previous study [15], it is crucial to establish the dependency of the thermal conductivity on temperature. However, experimental measurements for a wide range of typical operating temperature encountered in PEM fuel cells are still lacking. The use of the standard steady state methods requires long testing periods. Hence, the objective of this study is to experimentally measure the effect of temperature, compression and Teflon on the through-plane thermal conductivity in a time-efficient manner. The experimental measurements can be considered as development of thermal capacitance (Slug) calorimeter ASTM E2584-07 [20], which is based on a quasi-steady measurement technique and will be described in more detail in the next section. New reference data are important for the further development of the GDL of PEM fuel cells and the validation of theoretical predictions.

2. Slug calorimeter method for thermal conductivity measurement

The basic operational principle of this method is the use of a slug that is manufactured from a thermally conductive material [20]. The material of choice for the slug must have a thermal conductivity substantially higher than that of the tested material (carbon paper in this study). When the outer surface of the test samples is exposed to a heating element, heat will pass through the test material causing the temperature of the slug to rise. The temperature rise through this slug is controlled by three elements, the rate of heat conducted through the slug's surface, its mass and its heat capacity. Hence, the rate in temperature rise of the slug is directly proportional to the heat flux entering it. Under these conditions, the slug becomes a flux-gauging device; hence, the thermal conductivity of the sample can be calculated directly. This technique can be used to measure the thermal conductivity of a wide range of geometries and the design of the slug will be directly influenced by the geometry of the test material. In this study, the tested materials (carbon paper) have a rectangular shape; hence, the slug also is of a rectangular shape.

Since this testing technique is based on the monotonous heating of the specimens, it is very useful for the problem at hand. In this study, our interest is to measure the thermal conductivity of the carbon paper samples for a wide range of temperatures, specifically for the range -50 to $+120$ °C. As we mentioned in our earlier study [9], using traditional steady state methods, measurements for this wide range of temperature could take up to weeks. However, using the thermal capacitance calorimeter, measurements of the thermal conductivity for this wide range of temperature will only take 1–2 h. Further, with the test set up, we are also able to investigate the effect of compression, which is governed by calibrated gaskets. This method was developed for measuring the thermal conductivity of silica insulation under compression [19].

The experimental technique utilized in this study along with the experimental conditions and the error associated with this technique are discussed in the next sections of this paper.

3. Experimental

3.1. Experimental technique and apparatus

In this study, the through-plane thermal conductivity of TORAY carbon paper was measured at Integrity Testing Laboratory (ITL) using a thermal capacitance (Slug) calorimeter (ASTM E2584-07). This method has been used extensively in other studies to measure the thermal diffusivity [16,21]. The method was developed for measurement of thermal conductivity of refractory, plastics and of compressed fiber insulation materials in the general temperature range 20 – 1700 °C [16–19].

A schematic drawing of the method and the setup used for the measurements in this study are shown in Fig. 1. According to Ref. [20] this method is based on the assumption that the heat flow through the carbon paper sample is one-dimensional. In other words, the temperature distribution in the carbon paper sample depends on the spatial coordinate x shown in Fig. 1(a) and time t ; that is $T = T(x, t)$. In this study, the solution to the one-dimensional problem is determined using a similar analysis as that used in [22]. Here, the temperature of the surfaces of the carbon paper samples exposed to the aluminum plates is increasing at a constant rate. In this study, the analysis is done using a pair of carbon paper samples each having a thickness L , as shown in Fig. 1, and with the initial condition that the temperature is constant throughout the thickness of the specimen and the slug, that is, $T(x, 0) = T_i$. At the mid-plane of the steel slug plate, the adiabatic boundary can be considered due to symmetry. Hence, only one half of the steel slug plate is considered. With the assumption that the properties are constant, the temperature in the specimen must satisfy the one-dimensional Fourier's law of conduction:

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (1)$$

where $\alpha = k_{\text{sample}}/\rho_{\text{sample}}C_{\text{sample}}$ is the thermal diffusivity in (m^2/s), k_{sample} is the thermal conductivity of the carbon paper samples in ($\text{W}/\text{m K}$), ρ_{sample} is the density of the carbon paper

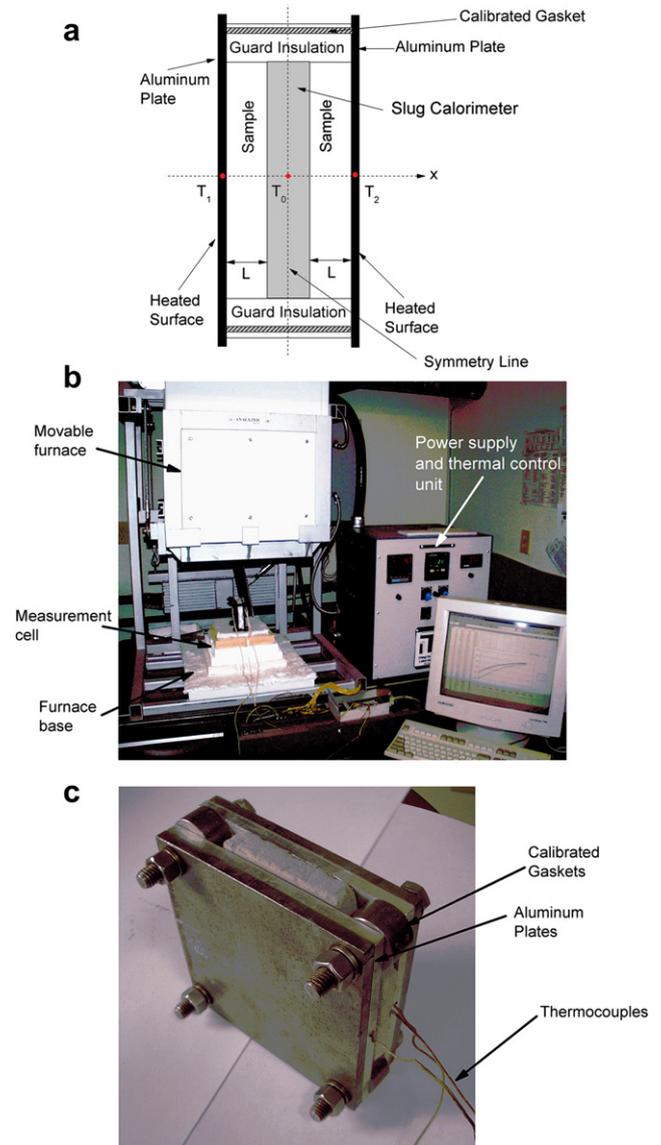


Fig. 1 – Experimental apparatus for measuring the through-plane thermal conductivity of the carbon paper GDL. (a) Schematic of the thermal conductivity test method; (b) photo of test apparatus; and (c) photo of measurement cell.

samples and C_{sample} is the heat capacity of the carbon paper specimens.

If the rate of heating is maintained constant, say, $\partial T/\partial t = b$ during the experiment, then the right-hand side of Eq. (1) will be a constant; Eq. (1) can be integrated with the solution in the form of second order polynomial in x ,

$$T(x, t) = \frac{b}{2\alpha} x^2 + c_1 x + c_2 \quad (2)$$

Hence, two boundary conditions are required to determine the integration constants c_1 and c_2 . Considering the left sample shown in Fig. 1a without loss of generality, the boundary condition at the left surface of the sample can be written as

$$\text{At } x = 0: T(0, t) = bt + T_i = T_1 \quad (3)$$

where b is the heating rate, maintained constant during the present experimental measurement, it has the unit (K/s); and T_1 is the temperature at $x=0$ and is measured in this study as well.

To determine the second boundary condition at the right surface of the left sample in Fig. 1a, consider energy balance for the left half of the steel slug in the middle of Fig. 1a: heat conducted in through the sample carbon paper on the left must equal the heat absorbed by one half of the steel slug plate. Since the thermal conductivity for the steel slug is much larger than that of the sample carbon paper, the steel slug, having an equivalent Biot number of much less than 0.1, essentially maintains a uniform temperature distribution. Therefore, the energy balance for the steel slug will result into the second boundary condition at the right surface of the left sample as

$$\text{At } x = L : k_{\text{sample}} \frac{\partial T}{\partial x} + Hb = 0 \quad (4)$$

where

$$H = \frac{M_{\text{slug}} C_{\text{slug}}}{2A} \quad (5)$$

is the thermal capacity of the slug plate per unit surface area ($\text{J}/\text{m}^2\text{K}$), M_{slug} is the mass of the slug (k), C_{slug} is the heat capacity of the slug (J/kgK), and A is the cross-section area of the slug, which is also the same as the surface area of the sample carbon paper in this study, as shown in Fig. 1a, and is equal to $6 \text{ cm} \times 6 \text{ cm} = 36 \text{ cm}^2$ in this study.

With the boundary conditions given by Eqs. (3) and (4), the solution given in Eq. (2) becomes:

$$T(x, t) = \frac{b\rho_{\text{sample}} C_{\text{sample}}}{2k_{\text{sample}}} x^2 - \left(\frac{Hb + Lb\rho_{\text{sample}} C_{\text{sample}}}{k_{\text{sample}}} \right) x + T_1 \quad (6)$$

With the above solution for the temperature distribution across the carbon paper sample, the temperature difference across the sample can be written as:

$$\Delta T = T(0, t) - T(L, t) = \frac{bL}{k_{\text{sample}}} \left(H + \frac{L\rho_{\text{sample}} C_{\text{sample}}}{2} \right) \quad (7)$$

Hence, the thermal conductivity of the carbon paper sample can be found as:

$$k_{\text{sample}} = \frac{bL \left(H + \frac{L\rho_{\text{sample}} C_{\text{sample}}}{2} \right)}{\Delta T} \quad (8)$$

using Eq. (5) for H and factoring out the cross-sectional area, A , Eq. (7) can be rewritten as:

$$k_{\text{sample}} = \frac{bL(M_{\text{slug}} C_{\text{slug}} + M_{\text{sample}} C_{\text{sample}})}{2A\Delta T} \quad (9)$$

where $\Delta T = T_1 - T_0$, and both T_1 and T_0 , as shown in Fig. 1a, are measured in this study. Then the thermal conductivity of the carbon paper sample is evaluated at an average temperature, which is equal to the average of the mean slug temperature and the exterior specimen temperature; that is, $T_{\text{ave}} = 1/2(T_1 + T_0)$.

As illustrated in Fig. 1, the main elements of the system are the measurement cell, moveable furnace, thermocouples connected to the Data Acquisition System (DAQ), power

supply, thermal control unit and computer. The moveable furnace is shown in its upper position. When the experiment is running the furnace is lowered to its base. The temperature is increased at a constant rate, which is assured by an automatic thermal control unit. Time-dependent thermal voltage signals are measured by three K-type thermocouples and registered by the DAQ system. In order to obtain measurements of the thermal conductivity at sub zero temperatures, the calorimetric system and samples were cooled in liquid nitrogen before heating.

3.2. Experimental conditions

In this study, the experiment is carried out using a sample composed of 6 layers of TORAY carbon paper TPGH-120 with each layer having a thickness of $370 \mu\text{m}$; hence, the total thickness of each sample is 2.22 mm . The experimental conditions encountered in this study under which the through-plane thermal diffusivity was measured are summarized as follows.

1. The effect of temperature on the through-plane thermal conductivity was investigated for the temperature range from -50 to $+120 \text{ }^\circ\text{C}$ for all the samples under study.
2. The effect of Teflon treatment on the through-plane thermal conductivity was determined for two different loadings (0 and 60 wt.%). The Teflon is added using the dipping technique and the drying process is slow to ensure that the Teflon is evenly distributed along the carbon paper sheet.
3. The effect of deformation on the through-plane thermal conductivity was measured for two different deformation percentages (1% (low) and 16% (high)). The thickness of the samples, L , was ensured by using stainless steel gaskets calibrated with a tolerance of $\pm 0.01 \text{ (mm)}$.

All measurements were made under atmospheric pressure.

3.3. Uncertainty analysis

In this study, the through-plane thermal conductivity, as shown in Eq. (9), is a function of the following parameters:

$$k_{\text{sample}} = f(b, \Delta T, L, A, \rho_{\text{sample}}) \quad (10)$$

Hence, the uncertainty associated with determining the thermal conductivity depends on these five parameters. It should be pointed out here that the mass of the carbon paper sample depends on its volume (area \times thickness) and volumetric density. The main uncertainty in the experiments comes from the variation of the heating rate, b with a maximum error of 5%. The maximum error associated with any variation in the thermocouples is 3% and with the thickness and the area is 1%. The error associated with the density measurements is 2.5%. The density of the samples was measured in our previous study [15]. Hence, the uncertainty for the thermal conductivity can be calculated from [23]:

$$\frac{\delta k_{\text{sample}}}{k_{\text{sample}}} = \sqrt{\left(\frac{\delta b}{b}\right)^2 + \left(\frac{\delta \Delta T}{\Delta T}\right)^2 + 2\left(\frac{\delta L}{L}\right)^2 + 2\left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta \rho_{\text{sample}}}{\rho_{\text{sample}}}\right)^2} \quad (11)$$

For the present study, the maximum uncertainty is estimated to be $\pm 7\%$.

4. Results and discussion

4.1. Effect of deformation

Deformation of the carbon paper GDL in the direction of its thickness (through-plane direction) is very common during the assembly of the cell. The compression pressure has an effect on the change in thickness of the carbon paper sample as given in Fig. 2. As it can be seen, the PTFE loading has a direct effect on the elasticity of the carbon paper sample. Further increases in the PTFE loading result in the sample reaching a plastic deformation region at high compression pressure. When studying the effect of deformation on the thermal conductivity, it is believed that a compressive force will result in the decrease of contact resistances between these components; hence, facilitating heat conduction as shown in Fig. 3. As the compression level increases, regardless of the PTFE content of the carbon paper, the thermal conductivity increases.

At low deformation, the through-plane thermal conductivity increases with an increase in temperature. This increase can be attributed to the thermal expansion of the graphitized carbon fibers. Due to the increase in temperature, the contact resistance between the fibers is decreased; hence, the overall conductivity of the fibers is increased. This trend is especially interesting when considering the change of the in-plane thermal conductivity with temperature. As was shown in our earlier study [15], the in-plane thermal conductivity of TORAY TGP-H-120 carbon paper decreases with an increase in temperature; in other words, the thermal expansion in the in-

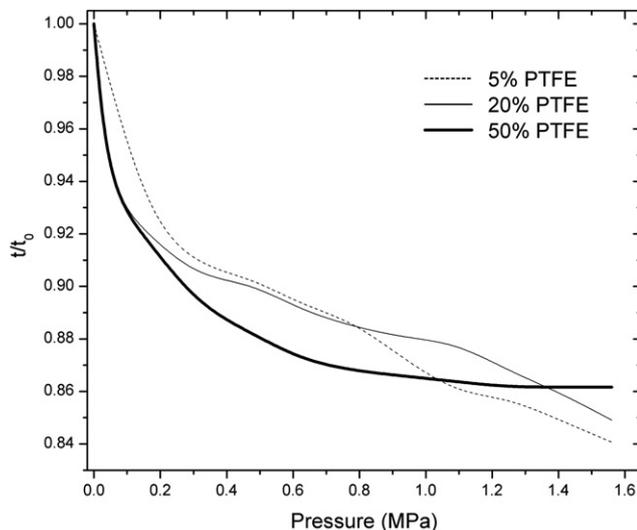


Fig. 2 – Change in thickness of TORAY TGP-H-120 carbon paper with compression pressure for samples with PTFE loading of 5, 20 and 50 wt.%.

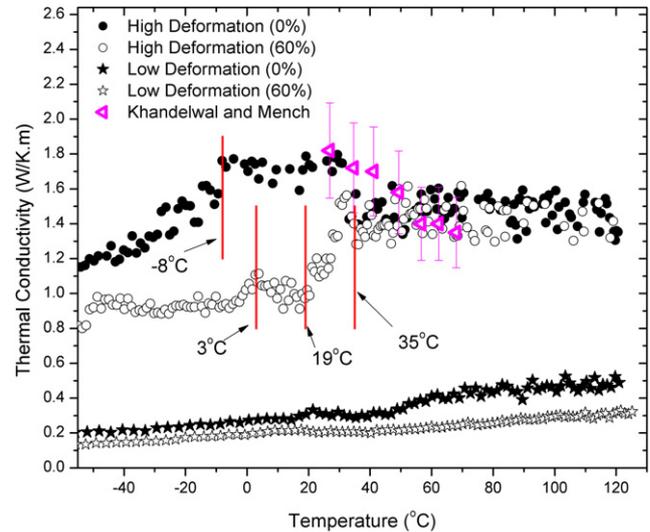


Fig. 3 – Effect of deformation and PTFE on the through-plane thermal conductivity of TORAY TGP-H-120 carbon – other experimental measurements taken from Ref. [5].

plane direction is negative. Hence, the findings of this work and our previous work suggest that the coefficient of thermal expansion of carbon paper is directionally dependent. This is in agreement with the measurements of the thermal expansion of graphite in [24]. Further, this change in trend with temperature could be related to cracks in the carbon binder, which usually exist in the through-plane direction and lead to thermal resistance. This phenomenon is discussed in more detail in the next sections of this paper.

As it can be seen from Fig. 3, at low deformation, the change in the thermal conductivity is proportional to the temperature. However, that is not the case once the deformation level is increased. First, let us consider the untreated carbon paper sample (PTFE content is 0%). As it can be seen, at temperatures lower than -8°C , the thermal conductivity increases with the increase in temperature. At higher temperatures, the change in thermal conductivity with temperature is not as pronounced. There is a slight decrease in thermal conductivity at temperatures higher than -8°C until reaching a temperature of 35°C , after which the thermal conductivity reaches a constant value. Taking experimental errors into consideration, the results of this study and that of Khandelwal and Mench [5] are in agreement. In the case where Teflon is added to the sample, the thermal conductivity of the carbon paper increases with temperature and reaches a constant value at a temperature of around 35°C , as seen in Fig. 3. This temperature value corresponds to the temperature at which PTFE transitions from the partially ordered to the very disordered phase [25]. Further, another two instances where a phase change occurs were measured for the 60% sample at 3°C and 19°C . In [25], they detected an expansion step for a pure PTFE sample at 19.2°C that was attributed to a partially ordered phase. This expansion resulted in a decrease in the thermal conductivity of the PTFE sample. A similar analogy can be used to explain the sudden decrease in thermal conductivity of the 60% sample at about 19°C . The

measurements of the thermal expansion of Teflon in [25] showed that a transition area exists between 19.2 °C and 35.4 °C. In this area, the thermal expansion changes from negative to positive with a very steep slope. This transition is very comparable in trend to that measured in this study.

4.2. Effect of PTFE loading

The effect of PTFE loading on the through-plane thermal conductivity is investigated for two different loadings (0 and 60 wt.%) at both deformation levels (low and high) as given in Fig. 3. As it can be seen, the general trend at both deformation levels is the same in that the thermal conductivity of the carbon paper GDL decreases with an increase in Teflon loading. This decrease is generally attributed to the low thermal conductivity of PTFE, which increases the overall thermal resistance. This trend was also observed earlier for the in-plane thermal conductivity [15]. Further, it is interesting to point out that the through-plane thermal conductivity of both samples (0% and 60%) at high deformation is comparable at temperatures higher than 35 °C. As mentioned earlier, this temperature is denoted as a temperature where a phase change in PTFE occurs. Further, from Fig. 3, it can be seen that at high deformation levels, the thermal conductivity of both samples is scattered around an average value. The thermal conductivity of both samples under high deformation lies in the range of $1.3 \leq k_{\text{sample}} \leq 1.6$ W/K m, with the average thermal conductivity around 1.45 W/K m. This finding suggests that the thermal conductivity is no longer dependent on the PTFE content in the carbon paper sample. This is similar to the trend we have observed for the in-plane thermal conductivity [15]. In addition, the change in the PTFE structure at high temperatures, coupled with the high deformation, might be resulting in a contact area between the carbon fibers as that of the untreated sample.

4.3. Estimating the effect of temperature and compression on the thermal resistance between fibers

In reality, cracks in the carbon binder can form during the manufacturing process and will result in thermal contact resistance between the fibers. Studying the scanning electron microscope (SEM) images of the treated and untreated carbon paper, Fig. 4, the cracks in the carbon composite binder are observed. As it can be seen, the amount of Teflon in the sample has a direct effect on the geometry and shape of the crack. The cracks appearing in the 0% sample are sharp; whereas the gaps in the binder of the 60% sample look more like tears.

Theoretically, the thermal conductivity of a porous medium can be represented as an average of the various mechanisms contributing to the heat transfer in the medium. In other words, the thermal conductivity of carbon paper may be written as a function of [16,21]:

$$k_{\text{sample}} = Mk_{\text{solid}}f_1(\epsilon) + k_{\text{gas}}f_2(\epsilon) + k_{\text{rad}} + k_{\text{conv}} \quad (12)$$

where M is a complicated function taking into account the heat barrier resistance between fibers in the materials and depends on the geometry of contact area and mismatch

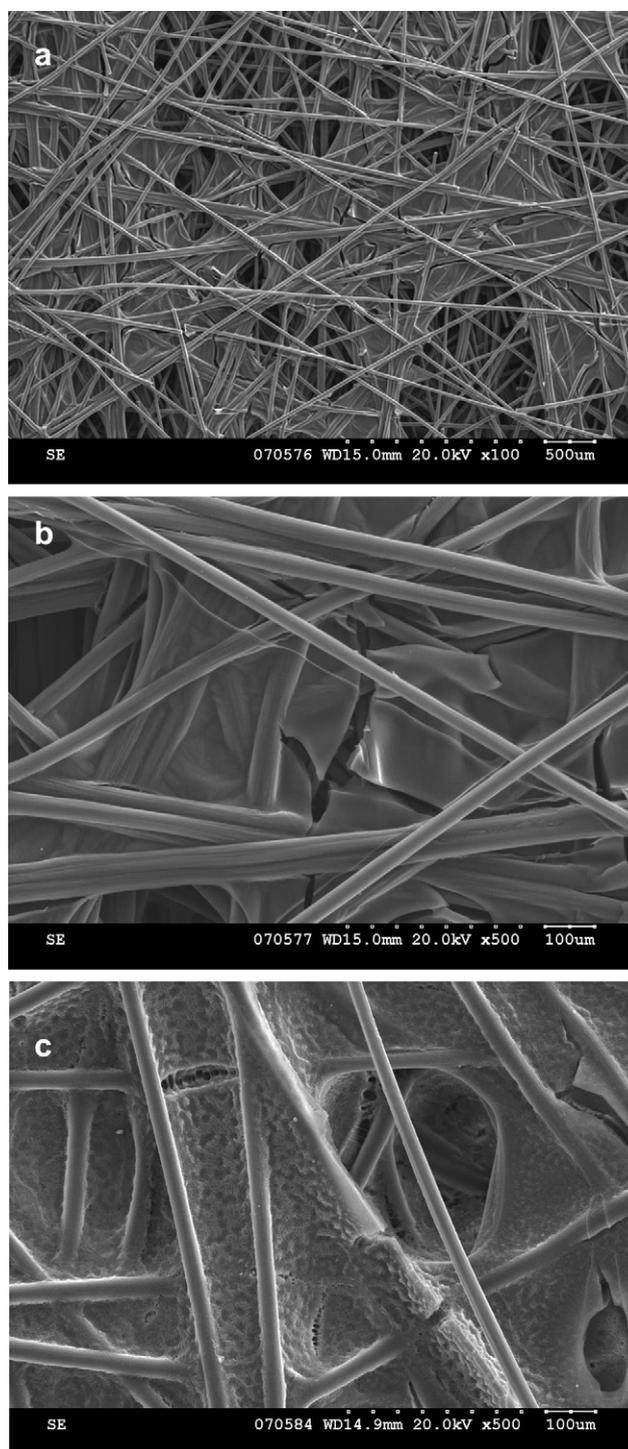


Fig. 4 – SEM image of TORAY-TPGH-120 with (a) 0% PTFE – low magnification [15]; (b) 0% PTFE – high magnification; and (c) 60% PTFE.

between grains and fibers [16,21], k_{solid} and k_{gas} are the thermal conductivity of fibers and gas, respectively, $f_1(\epsilon)$ and $f_2(\epsilon)$ are functions taking into account the effect of the porous structure and the density of the material using the porosity, ϵ , as the independent variable. k_{rad} is the heat radiation component of the apparent thermal conductivity, k_{conv} is the convection component of the apparent thermal conductivity.

In this study, the contribution of the gas, radiation and convection to the overall thermal conductivity is negligible; hence, the thermal conductivity can be written as:

$$k_{\text{sample}} = Mk_{\text{solid}} f_1(\varepsilon) \quad (13)$$

where the value of the heat barrier resistance coefficient, M , is dependent on the resistances of the crack and the contact layer of inter-grain material, the micro-crack thickness, the distance between the micro-cracks and the effective radii of the contact area and of the grain boundary. The variation in the value of M can be influenced by the micro- and nano-cracks between the fibers. The change of the area between grains could lead to the change during the heating of the carbon paper sample and can explain the decrease and increase in the thermal conductivity of the sample under deformation.

In order to estimate the contact resistance coefficient, M , the function $f_1(\varepsilon)$, the solid conductivity and the through-plane effective thermal conductivity are needed. The function $f_1(\varepsilon)$ generally takes the following form [16,21]:

$$f_1(\varepsilon) = (1 - \varepsilon)^{1.5} \quad (14)$$

Using the measurements of our earlier study [15] for the in-plane thermal conductivity, the thermal conductivity of the solid fibers can be estimated. From our previous study we were able to obtain an empirical relation of the in-plane thermal conductivity versus temperature for an untreated TORAY carbon paper and is written as:

$$k_{\text{eff}}^{\text{in}} = -7.166 \times 10^{-6} T^3 + 2.24 \times 10^{-3} T^2 - 0.237 T + 20.1 \quad (15)$$

where T is the temperature in degrees Celsius and $k_{\text{eff}}^{\text{in}}$ is the in-plane thermal conductivity in W/m K.

In the in-plane direction, the carbon fibers are considered without cracks (continuous fibers) or boundaries with interfaces; hence, the heat barrier resistance coefficient, M , may be set equal to 1. Using $M=1$ and Eqs. (12)–(14), the thermal conductivity of the carbon fibers, k_{solid} can be estimated as:

$$k_{\text{solid}} = \frac{-7.166 \times 10^{-6} T^3 + 2.24 \times 10^{-3} T^2 - 0.237 T + 20.1}{(1 - \varepsilon)^{1.5}} \quad (16)$$

where $(1 - \varepsilon)^{1.5} = 0.103$ for the untreated, uncompressed sample, used for the measurements of the in-plane thermal conductivity, which has a porosity of $78 \pm 2.0\%$. The porosity was measured using the method of standard porosimetry as described in our earlier study [15]. With Eq. (16), the thermal conductivity of the solid carbon fibers is evaluated as 195 ± 14 W/K m at a temperature of 0°C . The thermal conductivity of graphitized carbon is highly influenced by the treatment process it undergoes and by its crystal structure as seen in [26,27] with its value between 117 and 350 W/K m at 0°C . With this type of analysis, the effect of direction on the thermal conductivity of the solid is taken into account through the coefficient M [16,17,28]. This coefficient takes into account the effect of the thermal conductivity of the inter-grain material. In this case, this material can possess properties of graphite and carbon.

Using Eqs. (13), (14) and (16), the heat barrier resistance in the through-plane direction for the untreated sample can be estimated for both deformation levels as given in Fig. 5. It is

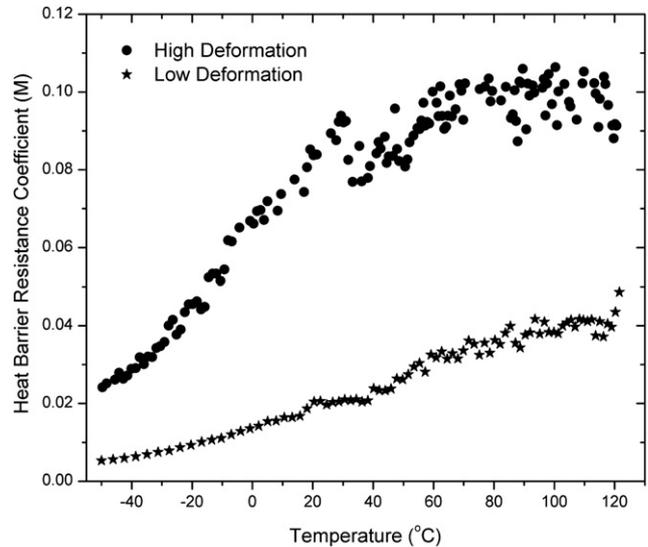


Fig. 5 – Effect of temperature and deformation level on the heat barrier resistance coefficient, M .

interesting to observe that M is smaller under low deformation. This is mainly attributed to the higher resistance between the fibers. In other words, compression of the carbon paper will facilitate in heat conduction between fibers. Further, it is clear that M increases with an increase in temperature. This finding suggests that heating of the carbon fibers could result in their expansion, minimizing surface contact resistance.

5. Conclusions

In this study, the thermal capacitance slug calorimeter was used to experimentally measure the through-plane thermal conductivity of TORAY carbon paper in the temperature range of -50 to $+120^\circ\text{C}$. The combined effect of temperature, deformation and PTFE loading was also investigated. An increase in the compression was found to drastically increase the thermal conductivity of both treated and untreated carbon paper. This increase is mainly attributed to the decrease in the overall contact resistance between the carbon fibers. The addition of Teflon resulted in the decrease of the overall thermal conductivity. However, at high deformation levels, the thermal conductivity of both treated and untreated carbon paper was found to be approximately the same and to remain constant at temperatures higher than 35°C . This temperature marks a phase change in the structure of pure PTFE. Further, using the experimental measurements of our previous study along with the experimental data of this study, the thermal resistance due to cracks and gaps between fibers was estimated.

Acknowledgements

The financial support by the Natural Sciences and Engineering Research Council (NSERC) of Canada is gratefully acknowledged.

REFERENCES

- [1] Mathias M, Roth J, Fleming J, Lehnert W. Diffusion media materials and characterization, handbook of fuel cells-fundamentals. Technology and applications, vol. 3. John Wiley and Sons; 2003.
- [2] Tajiri K, Tabuchi Y, Wang CY. Isothermal cold start of polymer electrolyte fuel cells. *J Electrochem Soc* 2007;154: B147–52.
- [3] Tajiri K, Tabuchi Y, Kagami F, Takahashi S, Yoshizawa K, Wang CY. Effects of operating and design parameters on PEFC cold start. *J Power Sources* 2007;165:279–86.
- [4] Jiao K, Li X. Cold start analysis of polymer electrolyte membrane fuel cells. *Int J Hydrogen Energy* 2010;35:5077–94.
- [5] Khandelwal M, Mench MM. Direct measurement of through-plane thermal conductivity and contact resistance in fuel cell materials. *J Power Sources* 2006;161:1106–15.
- [6] Ramousse J, Didierjean S, Lottin O, Maillet D. Estimation of the effective thermal conductivity of carbon felts used as PEMFC gas diffusion layers. *Int J Therm Sci* 2008;47:1–6.
- [7] Burheim O, Vie PJS, Pharoah JG, Kjelstrup S. Ex situ measurements of through-plane thermal conductivities in a polymer electrolyte fuel cell. *J Power Sources* 2010;195: 249–56.
- [8] Burheim OS, Pharoah JG, Lampert H, Vie PJS, Kjelstrup S. Through-plane thermal conductivity of PEMFC porous transport layers. *J Fuel Cell Sci Technol* 2011;8:021013-1–021013-11.
- [9] Karimi G, Li X, Teerstra P. Measurement of through-plane effective thermal conductivity and contact resistance in PEM fuel cell diffusion media. *Electrochim Acta* 2010;55:1619–25.
- [10] Sadeghi E, Djlali N, Bahrami M. Effective thermal conductivity and thermal contact resistance of gas diffusion layers in proton exchange membrane fuel cells. Part 1: Effect of compressive load. *J Power Sources*; 2010. doi:10.1016/j.jpowsour.2010.06.039.
- [11] Sadeghi E, Djlali N, Bahrami M. Effective thermal conductivity and thermal contact resistance of gas diffusion layers in proton exchange membrane fuel cells. Part 2: hysteresis effect under cyclic compressive load. *J Power Sources* 2010;195:8104–9.
- [12] Radhakrishnan A, Lu Z, Kandilkar SG. Effective thermal conductivity of gas diffusion layers used in PEMFC: measured with guarded-hot-plate method and predicted by a fractal model. *ECS Trans* 2010;33:1163–76.
- [13] Nitta I, Himanen O, Mikkola M. Thermal conductivity and contact resistance of compressed gas diffusion layer of PEM fuel cell. *Fuel Cells* 2008;8:111–9.
- [14] TORAY Carbon Paper Specification Sheet, www.fuelcell.com/techsheets/TORAY-TGP-H.pdf.
- [15] Zamel N, Litovsky E, Shakhshir S, Li X, Kleiman J. Measurement of in-plane thermal conductivity of carbon paper diffusion media in the temperature range of –20 to +120°C. *Appl Energy*; 2011. doi:10.1016/j.apenergy.2011.02.037.
- [16] Litovsky E, Puchkelevitch N. Thermophysical properties of refractory materials, Reference book. Moscow: Metallurgy; 1982.
- [17] Volohov GM, Kasperovich AS. Monotonic heating regime methods for the measurement of thermal diffusivity. In: Maglic KD, Cezairliyan A, Peletsky VE, editors. Compendium of thermophysical property measurement methods: recommended measurement techniques and practices, vol. 2. New York and London: Plenum Press; 1989. pp. 429–454.
- [18] Platunov ES. Instruments for measuring thermal conductivity, thermal diffusivity, and specific heat under monotonic heating. In: Maglic KD, Cezairliyan A, Peletsky VE, editors. Compendium of thermophysical property measurement methods: recommended measurement techniques and practices, vol. 2. New York and London: Plenum Press; 1989. pp. 347–374.
- [19] Litovsky E, Issouпов V, Kleiman J, Latham R, Kotrba A, Olivier K. Thermal conductivity of mechanically compressed fiber insulation materials in a wide temperature range: new test method and experimental results. In: International thermal conductivity conference, ITCC 29/ITES 17 conferences, Alabama, June 24–27, 2007.
- [20] ASTM – Designation: E2584-07. Standard practice for thermal conductivity of materials using a thermal capacitance (Slug) Calorimeter. This practice is under the jurisdiction of ASTM Committee E37.
- [21] Litovsky E, Gambaryan-Roisman T, Shapiro M, Shavit A. Heat transfer mechanisms governing thermal conductivity of porous ceramic materials. *Trends Heat Mass Moment Transf Res Trends* 1997;3:147–67.
- [22] Bentz DP, Flynn DR, Kim JH, Zarr RR. A slug calorimeter for evaluating the thermal performance of fire resistive materials. *Fire Mater* 2006;30:257–70.
- [23] Taylor JR. An introduction to error analysis: the study of uncertainties in physical measurements. 2nd ed. Sausalito, US: University Science Books; 1997 [chapter 3].
- [24] Tsang DKL, Marsden BJ, Fok SL, Hall G. Graphite thermal expansion relation for different temperature ranges. *Carbon* 2005;43:2902–6.
- [25] Blumm J, Lindemann A, Meyer M, Strauser C. Characterization of PTFE using advanced thermal analyses technique. NETZCH, http://www.netzsch-thermal-analysis.com/download/P-022_315.pdf; 2010.
- [26] Powell RW, Schofield FH. The thermal and electrical conductivities of carbon and graphite to high temperatures. *Proc Phys Soc* 1939;51:153–72.
- [27] Buerschaper RA. Thermal and electrical conductivity of graphite and carbon at low temperatures. *J Appl Phys* 1944; 15:452–4.
- [28] Mar JD, Litovsky E, Kleiman J. Modeling and database development of conductive and apparent thermal conductivity of moist insulation materials. *J Build Phys* 2008;32:9–31.