Measurement of thermal conductivity and heat pipe effect in hydrophilic and hydrophobic carbon papers

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1. Introduction

Carbon papers are porous materials that are widely applied in a variety of engineering applications, such as batteries, heat transfer devices, fuel cells, multi-stage filters, high-temperature thermal insulators, and friction/wear applications. Carbon papers are non-woven fibrous media, based on carbon fibers, and are commercially available. Carbon fibers possess excellent properties of stiffness, strength, conductivity, and light weight, and can be made from polyacrylonitrile (PAN), heavy fractions of oils or coals, cellulose, or others. In fabrication, the raw carbon fibers are carbonized at high temperature in inert environment to reduce other elements (such as nitrogen, oxygen, and hydrogen), yielding fibers with high carbon content and strong mechanical strength. In the papermaking process, the chopped carbon fibers are dispersed in water with binders, such as polyvinyl alcohol, to produce carbon paper roll. Binder content in carbon papers usually ranges from 5% to 15% by weight. The paper’s porosity can be 80% or higher, e.g. Toray carbon papers. This type of carbon papers has a mean pore size of about 20 μm. Their pore network provides passages for fluid flow or species transport, while the solid matrix enables electric current conductance or heat transfer [1,2].

Carbon paper’s surface property plays an important role in two-phase flow occurring inside the medium. This property can be modified through adding Polytetrafluoroethylene (PTFE), nanostructures, or other chemical agents. Applying PTFE loading is widely adopted in PEM fuel cell development. In this method, carbon papers are dipped into aqueous PTFE suspensions or by spraying. The wet papers are then placed in an oven for drying to remove the residual solvent. High temperature above 300 °C will sintet PTFE and fix it to the fiber surface. Higher PTFE content yields a more hydrophobic property. Adding PTFE, however, reduces the media’s porosity and possibly the mean pore size.

Thermal conductivity is an important property of carbon papers, particularly in thermal and power applications. Though carbon fibers are highly conductive, the effective conductivity can be low when the porosity is high. The effective conductivity is also dependent on compression, PTFE loading, solid matrix’s tortuosity, and the fluid materials in the void space. Various experimental methods have been employed to measure thermal conductivity [3], and can be extended to carbon papers. Khandelwal and Mench [4] measured carbon papers and Nafion membranes for PEM fuel cell. They reported a thermal conductivity of 0.22 ± 0.04 W/m °C for Sigracet® 20 wt.% PTFE carbon paper and 1.80 ± 0.27 W/m °C for Toray papers. Zamel et al. [5] measured the through-plane thermal conductivity of dry Toray papers in a range of 50–120 °C. They reported about 0.8–1.8 W/m °C conductivity at high deformation and 0.2–0.4 W/m °C at low deformation. Burheim et al. [6]
2. Heat transfer and heat pipe effect in carbon papers

In carbon papers, the carbon fibers are randomly aligned in the lateral direction. In the presence of static air or hydrogen gas in the void space, a major portion of heat flow is through the solid matrix of fibers because of its high conductivity. The solid matrix’s structure therefore plays an important role in heat transfer through the carbon papers.

2.1. Carbon paper microstructure

Carbon papers consist of randomly aligned carbon fibers bound by carbonized thermoset resin, see Fig. 1(a). The fiber diameter is usually around 5–10 μm. The paper’s fiber structures can be reconstructed through imaging or stochastic modeling. The former uses imaging techniques, such as the X-ray Tomograph or magnetic resonance. The material is repeatedly sectioned and imaged. The images are used in software to reconstruct the detailed material’s 3-D structure. The latter method is based on the knowledge of the material’s structure and stochastic theory. It is cost effective and fast, and its resolution is usually limited by the reconstruction mesh. Fig. 1(b) displays the reconstructed solid matrix of a carbon paper [10], showing a highly tortuous solid matrix due to the lateral alignment of its carbon fibers. Direct simulation results revealed that the through-plane heat conduction occurs via a route combining the lateral path along fibers and through-plane one at the contact points, see Fig. 2(a), resulting in a value of about 13 for the tortuosity of the solid matrix [10], and a complex distribution of temperature, see Fig. 3. The effective conductivity can be evaluated by accounting for the volume fraction of individual phase:

\[ k_{\text{eff}} = k_f(1-\varepsilon) + k_g \varepsilon \tau \]

where \( \tau \) is tortuosity. In the occasion that the fibrous matrix is much more conductive than the fluid in the void, the effective conductivity can be approximated by only accounting for the solid content:

\[ k_{\text{eff}} = k_f(1-\varepsilon) \]

Adding PTFE changes the carbon paper’s surface properties, and it also alters the medium’s porosity, and possibly its thermal conductivity. Fig. 1(c) and (d) display the carbon papers with 0 and 30 wt.% PTFE loadings, respectively.

2.2. Vapor-phase diffusion and heat pipe effect

The pore size of commercial carbon papers such as Toray papers usually ranges from 10 to 100 μm with the mean size of about 20 μm [2]. Due to the small dimension, phase equilibrium generally holds true between vapor and liquid phases in local pores. Under an isothermal condition, this equilibrium ensures a uniform vapor partial pressure throughout the medium. In a non-isothermal environment, i.e. temperature varies spatially, local vapor-partial pressure differs spatially, leading to vapor-phase diffusion. Using a 1-D case as example, the presence of a temperature gradient will cause the following vapor-phase diffusive flux [8]:

\[ -D_{g,\text{eff}}^\text{v} \frac{dc_g^\text{v}}{dx} = -D_{g,\text{eff}}^\text{v} \frac{dc_{g,\text{sat}}(T)}{dT} \frac{dT}{dx} = -D_{g,\text{eff}}^\text{v} \frac{dc_{g,\text{sat}}}{dT} \frac{dT}{dx} \]
where $C_{\text{sat}}(T)$ represents the saturated water concentration, and its profile is displayed in Fig. 4 as a function of temperature. The diffusion coefficient is dependent on temperature and pressure:

$$D_w = D_w^0 \left( \frac{T}{353} \right)^{3/2} \left( \frac{1}{P} \right).$$  \hspace{1cm} (4)

The vapor phase contains the latent heat of evaporation, and therefore its diffusion delivers heat. This is realized by water vapor at hotter sites, vapor diffusion through the interstitial spaces, and subsequent condensation at cooler sites. This mode of heat transfer is conventionally referred to as the heat pipe effect. In another word, the heat pipe effect here is driven by the concentration difference of water vapor imposed by a temperature difference. It involves a coupling phenomenon between transport of heat and mass. Assuming the vapor diffusion is the limiting factor in heat pipe effect, the delivered heat flux can be estimated as follow:
The above derivation indicates the heat pipe effect can be described using an apparent thermal conductivity \( k_{hp} \). This conductivity is a function of temperature, pressure, and pore structure. Fig. 4 displays the saturation vapor concentration and its derivative, showing both rapidly increase with temperature. Fig. 5 displays the apparent conductance \( k_{hp} \) at different temperatures, calculated from Eq. (5), showing a similar trend of \( k_{hp} \) with temperature: the heat pipe effect is weak (<0.05 W/m°C) at <20°C, and increases to 0.7 W/m°C at 80°C for the water–air system and porosity of 0.8. Because water vapor in hydrogen gas has a higher diffusivity, the heat pipe effect is stronger, about 1 W/m°C versus 0.4 W/m°C for the water–air system at 80°C. Because the vapor-phase diffusion occurs in the void space, the heat-pipe heat transfer is parallel to that in the solid matrix. Thus, the apparent heat conductance can be directly added to local intrinsic thermal conductivity.

2.3. Capillary flow

In addition to vapor-phase diffusion, the heat-pipe conductance is also limited by the capillary liquid flow and phase-change rates.
The phase-change rate is determined by the local mass-transfer coefficient, effective surface area, and others. In carbon papers, e.g., Toray papers with their mean pore size around 20 μm, the interfacial area between the liquid and vapor phases is large, resulting in rapid phase change. The capillary flow, however, can be slow, and become a limiting factor in the heat pipe performance. The capillary flow flux \( j^0 \), driven by the capillary pressure \( P_c \) and gravitational force, can be expressed as [11]:

\[
\begin{align*}
\hat{j}^0 &= \frac{\sigma}{\cos\theta} K [\nabla P_c + (\nabla \rho - \nabla \rho^0)] \\
P^0 - P^0 &= P_c = \sigma \cos(\theta) (s)^{1/2} \frac{j}{s}
\end{align*}
\]

where \( \sigma \) is the surface tension, \( \theta \) the contact angle, \( v \) the kinematic viscosity, \( \lambda \) the phase mobility, \( K \) the permeability, and \( s \) the liquid saturation. The Leverett-J function \( J(s) \) for hydrophilic media is given by:

\[
J(s) = 1.417(1 - s) - 2.120(1 - s)^2 + 1.263(1 - s)^3 \quad \text{for} \; \theta_c < 90
\]

It should be pointed out that the above Leverett function was originally developed to describe liquid–water transport in soils; as such, it is not directly applicable to the liquid water transport in carbon papers due to their unique fibrous characteristics. Kumbar et al. [12] showed the above Leverett function exhibits significant deviation from their experimental data, and developed new Leverett functions that better fit with the data. Gostick et al. [13] proposed a new correlation for the capillary pressure for fibrous porous media as well. In addition, the capillary flow in hydrophobic media can be different. Though continuum models were proposed for hydrophobic carbon papers, the actual two-phase flow is usually highly dynamic, and difficult to predict. Several studies visualized liquid water flow through hydrophobic media, showing liquid flows via preferred routes when the breakthrough pressure is reached. Before reaching the breakthrough pressure, liquid water is stuck inside the medium and remains static. The stuck water is similar to the irreducible residual liquid that is bound inside the pores by surface tension force and hence cannot be removed by drainage but only by evaporation.

3. Experimental

To measure the thermal conductivity of carbon papers and heat pipe effect, the experiment was designed as shown schematically in Fig. 6. The experimental setup consists of housing for the carbon paper sample, a gasket for seal, a cooling plate for heat removal, a hot plate, and an insulation enclosure to prevent heat loss during measurement. The cooling plate is made of aluminum with grooved mini serpentine channels for cooling flow fed by a self-designed high-precision flow injector. The cooling flow rate is injected under control with uncertainty as low as 0.01 mL/min. By measuring the inlet and outlet flows’ temperatures, the heat removal rate, i.e., the heat flow across the sample and gasket, can be obtained. A micro channel was machined in the housing plate to enable liquid injection by a high-precision syringe with an accuracy of 0.002 mL (equivalent to ~5% saturation in samples). Four thermocouples were used to measure the temperatures of the two sample surfaces with an uncertainty of 0.05 °C. The uncertainty of conductivity measurement is about 0.03 W/m·°C [11]. In testing, we use Toray papers (TGP-H60) with 0 and 30 wt.% PTFE, respectively. Fig. 1(c) and (d) show these two media; and Fig. 7 displays the droplet shapes at the medium surfaces, through which the contact angles were measured to be about 66° and 128°, respectively. In the experiment, the two media were compressed by 15 ± 3% and 18 ± 3% in thickness, respectively. We choose to use the compression ratio instead of the compaction pressure because a PTFE gasket is used to seal the sample. The portion of the compaction pressure acting on the sample is therefore unknown and difficult to determine. Several studies investigated the relative compression ratio, compaction pressure, and effective thermal conductivity of GDL materials [1,5,7,14], which may provide a way to estimate the compaction pressure over the sample. Readers who are interested in these subjects are referred to these articles. The entire device is insulated by insulation foam with 1 cm thickness. The sample through-plane conductivity is calculated via Fourier’s law using the measurements of the heat flow through the sample, the surface temperatures, and the sample area and thickness. Several materials with known thermal conductivity, such as printing papers and PTFE sheets, were tested using the device, showing good accuracy. (Table 1) lists several major experimental parameters.

In the experiment, the contact resistance between the sample and plates and among fibers can be large upon insufficient compression due to the use of gasket. Fig. 2(d) shows the fibers and their contact with a plate: the contact resistance arises not only between the carbon paper and plate which is the conventional meaning of contact resistance, but also among the constituent fibers. A high compression will yield a better contact or a large contact area both between the sample and plate, and among papers. As explained before, the fiber-to-fiber contact area can be a limiting factor for the through-plane conductivity. We assume the contact resistance distributes uniformly throughout the sample. In other words, the sample’s intrinsic conductivity is dependent on the pressure imposed over its surface. This is similar to unsolidified packed beds, whose conductivity increases with compression due to the enhanced contact among particles. Using spherical particles as example, a compressed state exhibits higher overall thermal conductivity than a loosely packed state, because the contact among particles is tighter in the former case. If this holds true for the carbon paper, the presented contact resistance then has no effect on the measurement of heat pipe effect and liquid water influence because the contact resistance is cancelled out when comparing the dry sample’s measurement with the wet one, to be discussed later in this section. To change the sample temperature, external heated flow is fed in the hot flow plate. It took up to one hour for the device to reach steady state. Measurement was taken when no temperature change was observed in 10 min.

In the experimental procedure, measurement was conducted first on a dry sample. Neglecting the air’s contribution to conductance, the overall effective conductivity can be expressed by:

\[
k_{eff} = k' (1 - \epsilon)^2
\]
After the dry sample is measured, a controlled amount of liquid water was then injected into the sample without disassembling the device. The wet sample conductivity can then be expressed by:

\[ k_{\text{eff}}^{\text{wet}} = k_s (1 - \varepsilon) + \varepsilon \omega k_l + k_{hp} \]  

(9)

The above takes into account the added thermal conductance due to liquid water presence \( \varepsilon \omega k_l \) and heat pipe effect \( k_{hp} \). Added liquid can influence the overall thermal conductivity in several ways, such as liquid location (e.g. near the fibers joints) and shape (e.g. contact angle). Burheim et al. [7] presented a discussion on the contribution of liquid water. Those factors can be lumped in the parameter of tortuosity, which characterizes the transport path. Comparing the two measurements yields:

\[ k_{\text{eff}}^{\text{wet}} - k_{\text{eff}}^{\text{dry}} = \varepsilon \omega k_l + k_{hp} \]  

(10)

In addition, the contact resistance between the sample and plate and among fibers enters both measurements. Because the two measurements were conducted without disassembling the device, the contacting conditions are identical such as the compartment pressure and temperature, and hence the contact resistance is the same. Because the contact resistance is assumed to be spread uniformly throughout the medium, the subtraction on the left side of Eq. (10) cancels the contact resistance. Further, in the above equation the last term on the right is small at low temperature, and changes rapidly with temperature, while the first term on the right remains almost constant, as shown in Fig. 5. Thus, the heat pipe effect can be separated out by comparing the measurements at high and low temperatures.

4. Results and discussion

Fig. 8 presents the measured thermal conductivities of the hydrophilic carbon paper (0 wt.% PTFE loading) at different temperatures and liquid water saturations. The data show that the measured thermal conductivity for the dry case decreases with temperature: at 35 and 80 °C the measurements are about 0.6 and 0.4 W/m °C, respectively, smaller than that under well compression [3]. This value is between the measurements at low and high deformations [5], and along the line with Burheim et al. [7]. As to the decreasing trend, one reason is that the contact resistance between the fibers and the plate and among fibers is included in the measured data. It is difficult to eliminate it because of its dependence on compression pressure and the use of gasket. As temperature increases, the contact resistance may change as a result of the non-uniform thermal expansion of other components.
The measured thermal conductivity of the hydrophilic carbon paper sample (0 wt.% PTFE loading).

Fig. 9 shows the added heat conductance due to liquid water presence inside the hydrophilic paper, i.e. Eq. (10). The measurement shows increasing conductivity with temperature in most cases. At 35 °C, Fig. 5 shows a weak heat pipe effect (about 0.05 W/m°C for s = 0.4), contributing a portion of the added conductance. The liquid water is conductive, which is another reason for the observed increase. The contribution of bulk liquid can be evaluated using the first term on the right of Eq. (10), \( \varepsilon V_k \). Assuming liquid water follows a morphology between the solid matrix and pore network, the bulk water conductivity of 0.6 W/m°C (see Fig. 5), a tortuosity of 2.0, a saturation of 0.4, and porosity of 0.76 will yield a conductance around 0.055 W/m°C. A smaller tortuosity, i.e. less than 2.0, will yield a larger contribution, which will better match with the experimental data. Note that the solid matrix tortuosity is much larger than 2.0. Despite that in reality liquid water attaches the hydrophilic matrix, liquid may not follow the matrix morphology completely. Instead, it exists preferentially at fiber joints, reducing local thermal resistance, see Fig. 2(b). The solid matrix is made of fibers, which are placed randomly in the lateral direction and touch each other at their contacting points. Our previous study [10] directly simulated pore-level heat transfer, indicating that the through-plane heat conduction occurs via a route combining the lateral path along fibers and through-plane one at the contacting points, see Fig. 2(a). The cylindrical shape of fibers results in a small contacting area and hence large resistance. Consequently, the solid matrix’s tortuosity was found to be over 10. Liquid presence at the contacting area, however, considerably improves local heat transfer by reducing the contact resistance among fibers, see Fig. 2(b).

In addition, the experimental data show the overall heat conductance increases with temperature in most cases, indicative of enhanced the heat pipe effect. A model prediction is also plotted for the liquid saturation of 0.4, showing a similar trend of thermal conductivity change. The model prediction assumes the vapor diffusion is the rate limiting step for the heat pipe effect. The liquid flow rate can be another limiting factor which explains the observed discrepancy between the experimental data and model prediction. This is particularly true for the fiber–matrix system, in which liquid inclines to attach the joint areas between fibers due to the hydrophilic nature of the surface, see Fig. 2(b). At a higher level of saturation, more liquid can be sent back to the evaporation surface, improving the heat pipe effect. Another possible reason for the observed conductance increase is the temperature-dependence of the bulk water conductivity: Fig. 5 shows that about 0.06 W/m°C will be added to water conductivity when temperature changes from 35 to 85 °C, which accounts for a minute portion of the increased thermal conductivity.

The wetting property of carbon paper is an important factor governing two-phase flow, see Fig. 2(b), (c), (e), and (f). Thus, a hydrophobic carbon paper likely exhibits a different heat-pipe effect. Fig. 10 displays the experimental data of a hydrophobic carbon paper with 30 wt.% PTFE loading. In this case, a slightly higher compression ratio 18 ± 3% was applied. This, along with the PTFE addition, may result in less change of thermal conductivity with temperature, as seen from the data of the dry sample. When liquid water is added, the overall thermal conductivity is slightly increased. For this medium, two liquid saturations, 0.2 and 0.4, were considered in the experiment because a larger uncertainty may arise when injecting high-content water in the nonwetting medium. However, the conductance increase with temperature is small.

Fig. 11 plots the added thermal conductivity due to liquid water presence. At 45 °C where heat pipe effect is relatively weak, the added conductance appears small in comparison with the hydrophilic one, with about 0.08 versus 0.16 W/m°C. One possible reason is due to the distinct morphologies of liquid presence in the two media: liquid tends to form isolated bulk droplets at a hydrophobic surface whereas it tends to form a film at the hydrophilic surface, see Fig. 2(e) and (f). Isolated droplets contribute smaller conductance; however, the droplet morphology makes it easier to link neighboring fibers, reducing tortuosity, see in Fig. 2(c). The final effect is determined by the balance of the two factors. Another possible reason is heat pipe effect, which is likely active only in a portion of the hydrophobic paper, to be detailed later. From 45 to 85 °C, the thermal conductivity is slightly increased by about 0.05 W/m°C, which again is much lower than that of the hydrophilic paper. This value is close to the increment of bulk water conductivity in the range of temperature increase, see Fig. 5. We also plot in the figure the liquid water conductivity from 45 to 85 °C with a liquid saturation of 0.3 (the average of the two experimental
saturations) using the Bruggeman correlation. Bulk liquid with the tortuosity of 1.5 contributes about 0.08 W/m°C to the conductivity at a temperature point. A higher tortuosity 2.0 gives a lower value, around 0.05 W/m°C. For both tortuosities, the temperature dependence of liquid thermal conductivity is negligible, less than 0.01 W/m°C increase is indicated when temperature changes from 45 to 85°C. In addition, the heat pipe conductance predicted by Eq. (5) is much larger than the observation: the equation gives an increase of about 0.4 W/m°C in the apparent conductivity from 45 to 85°C. A much small increase observed in the hydrophobic medium is possibly due to the lack of liquid flow back to the evaporator side: several experiment reported that a breakthrough pressure [15–18] is required to enable liquid water flow through hydrophobic carbon papers. Fig. 12 visualized droplet formation at the surface of a hydrophobic carbon paper [18]. The liquid droplets result from liquid water transport through the medium.

5. Conclusion

This paper presented an experimental study of the thermal conductivity of carbon papers with/out liquid presence and the heat pipe effect. An experimental setup was designed and measurement was carried out for both hydrophilic and hydrophobic carbon papers. We found that the overall conductivity is improved when liquid water is added to the carbon papers, and the overall conductivity in wet media increases with temperature. By separating out the thermal conductivity of dry carbon papers, the added conductivity due to liquid water presence was obtained. For the hydrophilic paper, the measured data showed an increase of conductivity at 35°C, which is larger than that of the predicted heat pipe effect. It is possibly due to the fact that liquid is presented preferentially at the contact area among fibers, which greatly reduces the local resistance. For the hydrophobic carbon paper, the increase is smaller than the hydrophilic because of difference in either liquid morphology or heat pipe effect. Under high temperature, heat pipe effect becomes significant, improving the overall thermal conductivity of the hydrophilic papers. The added conductance increases rapidly with temperature with about 0.4 W/m°C from 35 to 85°C. The model prediction showed a similar trend as the experimental data. The heat pipe effect is smaller for the hydrophobic carbon paper, which is likely due to its nonwetting surface: liquid water only flows back to the evaporation surface via preferred routes at the breakthrough pressure. As a result, the heat pipe effect is active in part of the hydrophobic medium, yielding a reduced increase in added thermal conductivity with temperature.

References


