IMPROVING THE TRANSIENT PLANE SOURCE METHOD FOR MEASURING THERMAL CONDUCTIVITY OF THIN FILMS BY DECONVOLUTING THERMAL CONTACT RESISTANCE WITH APPLICATIONS IN FUEL CELL TECHNOLOGY

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ABSTRACT

A new method is used to eliminate the effects of contact resistance from transient plane source (TPS) measurements of thin films and coatings to obtain accurate values for their bulk thermal conductivity. Nafion membrane, gas diffusion layer (GDL), and ethylene tetrafluoroethylene (ETFE) are tested by the proposed method, and the results are compared to guarded heat flow (GHF) measurements. The proposed method yields thermal conductivity values of 0.174 ± 0.002 $W \cdot m^{-1} \cdot K^{-1}$ for ETFE and 0.243 ± 0.007 $W \cdot m^{-1} \cdot K^{-1}$ for Nafion, while the GHF method yields values of 0.177 ± 0.002 $W \cdot m^{-1} \cdot K^{-1}$ for ETFE and 0.214 ± 0.003 $W \cdot m^{-1} \cdot K^{-1}$ for Nafion. Both methods measured an increase in the thermal conductivity of GDL with increasing compressive load, with about 16% difference between the results of the two methods. Overall, the developed method shows promising results and is proved to be highly reliable, quick, and accurate.

INTRODUCTION

Measurement of the thermal conductivity of thin films is critical to an increasing range of technologies, including polymer electrolyte membrane (PEM) fuel cells for the thermal management of the layers of the membrane electrode assembly (MEA) [1-5]. In the conventional TPS method for testing thin films, inclusion of different thermal contact resistances (TCRs) in the final results leads to deviation of the obtained value of thermal conductivity from the bulk thermal conductivity of tested films and coatings, up to 67% relative difference as will be shown further in this article.

In this work, the TPS method for thin films is modified to deconvolute the effects of TCRs in the test column. The proposed method is used to obtain the bulk thermal conductivity of Nafion membrane and gas diffusion layer (GDLs), which are among the main elements of the MEA in a typical PEM fuel cell, as well as ethylene tetrafluoroethylene (ETFE) which is used in the fabrication of PEM fuel cells catalyst layers.

EXPERIMENTAL METHOD

The thin materials tested include ETFE sheets received from Asahi Glass Co. in thicknesses of 11, 24, 50, 105, and 204 µm; Nafion films prepared in-house at the industrial partner of the project, Automotive Fuel Cell Cooperation Corp. (AFCC), in thicknesses of 10, 16, 26, and 48 µm; and two commercial carbon fiber GDLs, 190 and 280 µm thick when uncompressed, with 5% polytetrafluoroethylene (PTFE) content (GDL 24BA and GDL 34BA) from SIGRACET®, SGL Group. The thicknesses of the samples were measured by a custom-made testbed (TUC_RUC, AFCC) with a resolution of 1 µm.

The thin films are tested with a transient plane source (TPS) thermal constants analyser (Hot Disk TPS 2500S, ThermTest Inc.). The TPS thin film sensor (Sensor 7280, 14.67 mm radius) consists of a 10 µm thick double spiral nickel element sandwiched between two 25 µm thick Kapton layers via some adhesive material [6]. To test thin films, the sensor is sandwiched between two equivalent samples and thick, high thermal conductivity background material, as shown in Fig. 1 [6]. In this study, two stainless steel (SIS 2343) blocks were used as the background material. Also, to ensure an accurate measurement, lack of temperature drift for the nickel probe is ensured by allowing at least 5 min relaxation time prior to each measurement. Overall, each TPS measurement takes ~ 3 min.

Measurements are also performed on the samples with the GHF method described in Ref. [7], and the results of the two methods are compared with each other. The first steady-state test by the GHF testbed takes about 5 hr, with subsequent tests at different pressures requiring ~ 2 hr to reach steady-state condition.

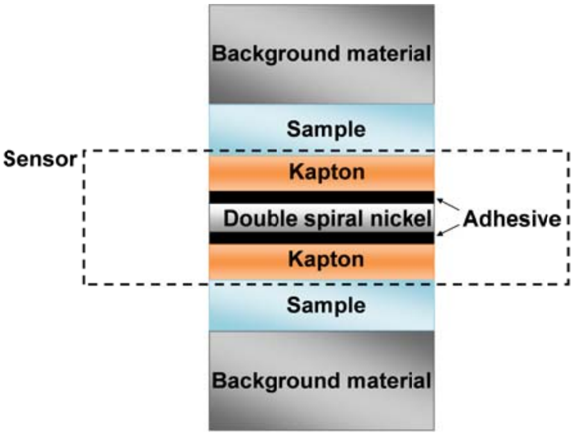

Fig. 1. Schematic of the TPS test column

TPS thin film thermal conductivity measurements

After obtaining the temperature difference between the nickel probe and the background material from the TPS measurements, the details of which can be found elsewhere [6,8-10], the effective thermal conductivity of the materials between the nickel probe and the background material is calculated by:

$$k_{\text{eff}} = \frac{P_0 h_{\text{p-bm}}}{2A\Delta T_{\text{p-bm}}} \tag{1}$$

As per ISO22007-2 [6], the procedure for measuring the thermal conductivity of a thin film is:

1. A reference test with the thin film sensor alone between two slabs of the background material to determine the effective thermal conductivity of the Kapton layer together with the adhesive,
2. An experiment with the sensor sandwiched between two identical pieces of the sample, supported by the slabs, to determine the effective thermal conductivity of the series combination of the adhesive layer, the Kapton layer, and the sample.

Then, according to ISO22007-2 [6], the effective thermal conductivity of the thin film, k_{s}, of thickness, h_{s}, should be found from [6,11]:

$$R_{\text{tot}} = R_{\text{b,s}} + R_{\text{b,Kap\&adh}} \tag{2}$$

or, equivalently, the following relation [6,10]:

$$\frac{h_{\text{Kap\&adh}} + h_{\text{s}}}{k_{\text{eff}} A} = \frac{h_{\text{s}}}{k_{\text{s}} A} + \frac{h_{\text{Kap\&adh}}}{k_{\text{Kap\&adh}} A} \tag{3}$$

However, the ISO22007-2 standard notes that tests on samples of different thicknesses or with different clamping pressures may be necessary to eliminate mathematically the influence of thermal contact resistances [6]. Also, at relatively low contact pressures, TCR between contacting surfaces can be much higher than the bulk resistance of a sample [12,13]. Therefore, the following method for deconvoluting the effects of TCR from TPS thin film thermal conductivity measurements is developed and validated.

Improved TPS thin film method

Deconvoluting the effects of the TCR in the TPS test column is of vital importance for obtaining accurate values of bulk thermal conductivity for thin films. The thermal resistance network of the TPS test column is shown in Fig. 2. Therefore, the total the thermal resistance in the TPS test column is:

$$\begin{aligned} R_{\text{tot}} &= R_{\text{c,bm-s}} + R_{\text{b,s}} + R_{\text{c,s-Kap}} + R_{\text{b,Kap\&adh}} + R_{\text{c,adh-p}} \\ &= \frac{h_{\text{s}}}{k_{\text{s}} A} + \frac{h_{\text{Kap\&adh}}}{k_{\text{Kap\&adh}} A} + TCR \end{aligned} \tag{4}$$

where $TCR = R_{\text{c,bm-s}} + R_{\text{c,s-Kap}} + R_{\text{c,adh-p}}$ is defined as the total contact resistance of the test column. In Eq. (4), the term $R_{\text{b,Kap\&adh}}$ takes the effect of $R_{\text{c,Kap-adh}}$ into account. By comparing Eqs. (2) and (4), it is clear that the effective thermal conductivity found for the sample by Eq. (2) is not the true bulk thermal conductivity of the sample and includes the effects of the TCRs of the TPS test column. In fact, it also includes the effect of TCR between the Kapton layer and the background material due to the performed reference tests, which may induce additional error in the measurements by the standard method because such a TCR does not exist in the measurement of the sample.

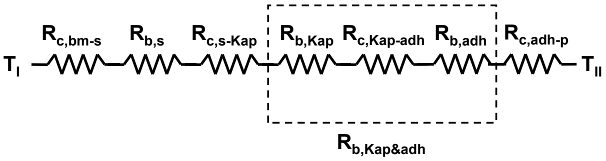

Fig. 2. Thermal resistance network of the TPS test column

For convenience, Eq. (4) is rewritten as follows:

$$R_{\text{tot}} = \frac{h_{\text{s}}}{k_{\text{s}} A} + R' \tag{5}$$

where $R' = h_{\text{Kap\&adh}} / (k_{\text{Kap\&adh}} A) + TCR$. The total thermal resistance in Eq. (5) should be back-calculated by substituting the values of h_{s}, k_{s}, $h_{\text{Kap\&adh}}$, and $k_{\text{Kap\&adh}}$ into Eq. (3). For more clarification, Eq. (3) is rewritten as follows:

$$\begin{aligned} R_{\text{tot}} &= \frac{\left(h_{\text{s}}\right)_{\text{entered into the software}}}{\left(k_{\text{s}}\right)_{\text{reported by the software}} A} \\ &+ \frac{\left(h_{\text{Kap\&adh}}\right)_{\text{entered into the software}}}{\left(k_{\text{Kap\&adh}}\right)_{\text{entered into the software}} A} \end{aligned} \tag{6}$$

After performing measurements for at least two thicknesses of a sample, the bulk thermal conductivity of the sample can be obtained by performing a linear regression between the obtained data of total resistance versus thickness. As shown in Eq. (5), the slope and intercept of such a line will yield the bulk thermal conductivity of the sample and the resistance, R', respectively. The developed method has the following advantages:

1. Accurate measurement of the bulk thermal conductivity of thin films,
2. Elimination of the previously needed reference tests and the possibility of entering any values for h_{s}, $h_{\text{Kap\&adh}}$, and $k_{\text{Kap\&adh}}$ into the software due to the usage of the same values in back-calculation of the total resistance, and
3. Elimination of the unwanted noise of the TCR between the Kapton layer and the background material induced by the standard reference tests.

The downside of the proposed method is the need for performing tests for at least two thicknesses of the same sample, which may not be available.

GHF method

The details of the GHF method and the device can be found elsewhere, see for example [4,7]. The total resistance of a sample measured by the GHF testbed is the summation of the sample bulk thermal resistance and the TCRs between the sample and the fluxmeters, as follows:

$$R_{\text{tot}} = \frac{h_s}{k_s A} + TCR \tag{7}$$

Therefore, similar to the modified TPS method, the thermal conductivity of the sample and the TCR of the test column should be obtained from a linear regression through the data of total resistance versus thickness of the sample.

RESULTS AND DISCUSSION

The bulk thermal conductivities of three thin film materials, ETFE, GDL and Nafion membrane, were measured by TPS and GHF methods. Multiple thicknesses of each sample type were tested, and the data was processed to eliminate the effects of contact resistances from the results.

Thickness measurements by the TUC_RUC device showed no change in the thickness of ETFE and Nafion films under pressure. However, as shown by the TUC_RUC measurements at 10 bar pressure, the thicknesses of GDL 24BA and GDL 34BA can decrease up to 18 % and 14 %, respectively. Accordingly, the expected thicknesses under pressure were used in calculations of the GDL samples.

ETFE results

The measured thermal conductivities at different pressures are shown in Fig. 3 next to the results of the conventional TPS thin film theory. Figure 3 shows a consistent measurement of thermal conductivity of ETFE by the modified TPS method and the GHF method. In addition, comparing the obtained consistent thermal conductivity values from the modified TPS method with the values from the conventional TPS method further uncovers the significant effects of TCR in the results of the conventional method, up to 67% relative difference for the 11 μm ETFE film. As shown in Fig. 3, the TCR effects decrease as the thickness of ETFE increases, the reason of which is decrease in the share of the TCRs in the total resistance with an increase in the thickness of ETFE. The maximum uncertainties (confidence intervals) in Fig. 3 are 6.7% for the proposed modified TPS method and 7.5% for the GHF method. The average value of thermal conductivity of ETFE is 0.174 ± 0.002 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ from the modified TPS method and 0.177 ± 0.002 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ from the GHF method.

Nafion results

The measured bulk thermal conductivity of Nafion at different pressures is shown in Fig. 4. The relative difference between the thermal conductivity results of the two methods, shown in Fig. 4, is about 13.5%. The average thermal conductivity of Nafion measured by the modified TPS method is 0.243 ± 0.007 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, whereas the average value measured by the GHF method is 0.214 ± 0.003 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

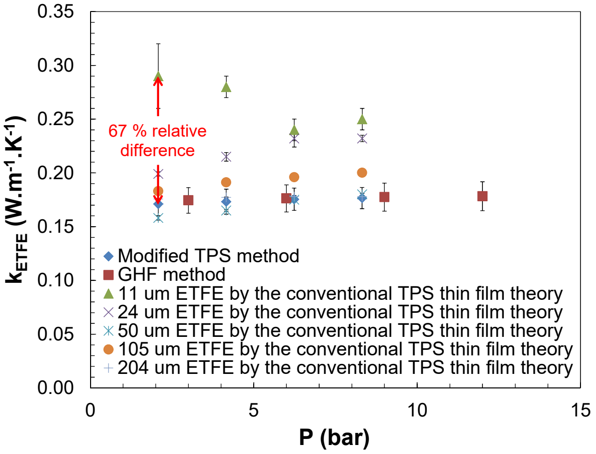

Fig. 3. Thermal conductivity of ETFE versus pressure

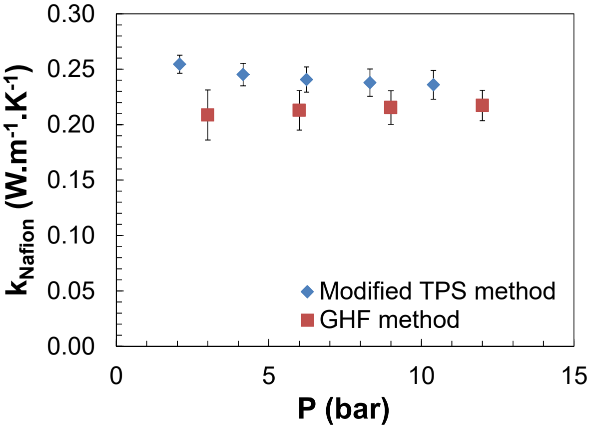

Fig. 4. Thermal conductivity of Nafion versus pressure

GDL results

For GDL, two samples, namely GDL 24BA and GDL 34BA, are measured. The measured bulk thermal conductivity of GDL at different pressures is shown in Fig. 5. As shown in Fig. 5, thermal conductivity of GDL increases with an increase in pressure. The reason for this behavior is given in several studies in literature [4,14,15] and can briefly be restated as increase in the area of point contacts between the carbon fibers in GDL by increasing pressure. The thermal conductivity values of GDL measured by the two methods are about 16% different from each other which could mainly be attributed to hysteresis behavior of GDL materials under compressive load due to their fibrous porous structure as explained in details in Ref. [14]. In the GHF testbed, the fluxmeters undergo a series of thermal expansions and contractions until the device reaches the steady state, whereas in the TPS testbed, these effects are not present, as it is a transient and fast test. Accordingly, GDL experiences some hysteresis effects in the GHF testbed at each pressure increment, whereas the TPS results for GDL are free of such effects. The maximum uncertainties (confidence intervals) in the obtained values of GDL thermal conductivity are 3.4% for the results of the modified TPS method and 6.6% for the results of the GHF method.

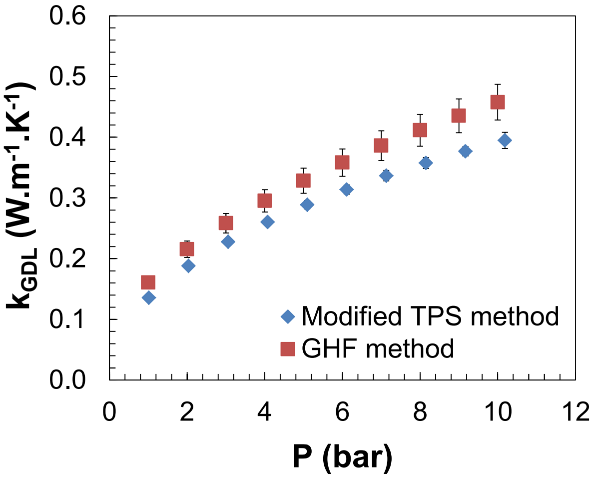

Fig. 5. Thermal conductivity of GDL versus pressure

CONCLUSIONS

In this study, the conventional TPS thin film theory was modified by deconvoluting the effects of TCRs in the TPS test column. The proposed modification can also eliminate the need for conducting any reference tests required by the conventional method. Instead, one should conduct measurements on at least two thicknesses of the same sample. To validate the developed method, ETFE sheets, Nafion films, and GDL samples were tested by both the developed method and the GHF method. Overall, when selecting a measurement method for measuring thermal conductivity of a thin film or coating, the mechanical behavior of the sample should be taken into consideration. However, considering the much longer time required for GHF measurements compared to modified TPS tests, one can conclude that the proposed method is a valuable and efficient tool for accurate measurement of thermal conductivity of thin films and coatings.

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NOMENCLATURE

A	Cross sectional area, m^2
h	Thickness, m
k	Thermal conductivity, W·m^{-1}·K^{-1}
P_0	Constant output power of the sensor, W
R	Thermal resistance, K/W
R'	A combination of bulk and the thermal contact resistances in the TPS test column, K/W
T	Temperature, K
T_I	Temperature of the surface of the background material facing the sensor, K
T_{II}	Temperature of the nickel probe, K
Greek letters	
Δ	Difference operator
Subscripts	
I	Surface of the background material facing the sensor
II	Surface of the nickel probe
adh	Adhesive sticking the Kapton layer to the nickel probe
b	Bulk property
bm	Background material
c	Contact
eff	Effective property
Kap	Kapton insulating layer
p	Probe
s	Sample
tot	Total

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