CHARACTERIZATION OF TRANSPORT PROPERTIES IN GAS DIFFUSION LAYERS FOR PEMFCs

Michael J. Bluemle¹, Vladimir Gurau¹, J. Adin Mann, Jr.¹, Thomas A. Zawodzinski, Jr.¹
Emory S. De Castro², Yu-Min Tsou²
¹Chemical Engineering Department Case Western Reserve University,
Cleveland, OH 44106-7217
²E-TEK division, De Nora North America, Inc., Somerset, NJ 08873

ABSTRACT

Durability of proton exchange membrane fuel cells (PEMFCs) is likely to be significantly influenced by the properties of the gas diffusion layer material. An optimum humidification level and water distribution within the gas diffusion media are required to lower the ohmic resistance and prevent the appearance of hot spots in the catalyst coated membrane. In the same time such optimum humidification level and distribution must minimize reactant mass transport losses in the gas diffusion layer. For proper cell design and water management the transport properties of the gas diffusion media must be evaluated. In this paper we describe techniques for evaluation the through-plane and in-plane viscous and inertial permeability, the internal contact angle to water and the surface energy of macro and micro-porous substrates of gas diffusion layer materials.

INTRODUCTION

In order to meet performance targets for PEMFCs, E-TEK creates new Gas Diffusion Layer (GDL) structures with varying properties (1) such as porosity, permeability and hydrophobicity. Such varying properties are tailored to optimize the following properties for various applications: reactant and liquid water transport in the GDL and a better electrical contact with the catalyst layer.

The convective transport of gas reactants in a porous GDL is characterized by the permeability coefficient, while the capillary transport of the liquid water is determined by the contact angle of water to the material and by the surface energy of the GDL material.

Since GDL materials are highly anisotropic, the permeability is represented by a rank two tensor. Different permeability coefficients describe the fluid transport ‘in plane’ (x, y directions), versus ‘through plane’ (z direction). The ‘in-plane’ permeability is assumed two-dimensional isotropic represented by a single coefficient. A method to determine separately the permeability coefficients in (x, y) and z directions respectively, by controlling the direction of the gas flow through the porous sample is employed at Case. This method is applied initially to the macro-porous substrate of the GDL alone and subsequently to the macro-porous substrate with different micro-porous layers applied on it. The permeability of the micro-porous layer is calculated from the two measurements.
The internal contact angle of water to the fibers of a GDL is determined both by the material and by the pore structure of the GDL. Determining the contact angle of water by measuring the meniscus formed when the GDL is immersed in water (2) accounts only for the GDL material effect. We use a Krüss Processor Tensiometer along with the Owens-Wendt calculation method (3) to determine the internal contact angle of water to the fibers of the GDL and the surface tension of the GDL fibers. The method is applied separately to the macro-porous substrate and the micro-porous sub-layer.

PERMEABILITY MEASUREMENTS

Four GDL materials prepared by E-TEK were subjected to permeability testing. The samples consisted of a carbon fiber cloth (macro-porous substrate) impregnated with a micro-diffusion sub-layer (four combinations of two different types of carbon and two different PTFE loadings). The systems used to determine the through-plane and in-plane permeability coefficients were designed and fabricated at Case.

Through-Plane Permeability Measurements (z-Direction)

The system for the through-plane permeability is shown in Figure 1. In order to prevent in-plane flow a back pressure regulator was adjusted until $P_3$ equaled $P_2$. The thickness of each GDL sample was measured in five points using a digital micrometer. The pressure drop $P_1-P_2$, the pressure $P_2$ and the temperatures $T_1$ and $T_2$ were measured for approximately twenty different flow rates.

![Figure 1](image-url)

Test Apparatus for Through-Plane (z-Direction) Permeability Measurements
The through-plane viscous and inertial permeability coefficients, $k_v [m^2]$ and $k_i [m]$ were then calculated from the Darcy-Forchheimer equation [1] by application of the least squares method (4):

$$\frac{\Delta P}{e} = \frac{\mu}{k_v} + \frac{\rho}{k_i} v^2$$  \[1\]

In equation [1] $e$ is the sample thickness, $\mu$ and $\rho$ are the dynamic viscosity and density of the probe fluid (dry Nitrogen), $\Delta P$ is the pressure difference $P_1 - P_2$ and $v$ is the probe fluid velocity through the sample. The method was applied to the four GDLs and to the macro-porous backbone (same for all GDLs). The viscous permeability coefficients for the micro-porous substrates were calculated with equation [2]:

$$k_{v,\text{micro-porous}} = \frac{e_{\text{micro-porous}}}{e_{\text{entire GDL}} - e_{\text{macro-porous}}} \frac{k_{v,\text{entire GDL}}}{k_{v,\text{macro-porous}}}$$  \[2\]

Table 1 shows the through-plane viscous and inertial permeability coefficients for the four different GDL materials and the viscous permeability coefficients for the macro-porous backbone and the micro-porous substrates that form the GDLs. In the case of the macro-diffusion backbone the inertial resistance to flow was found to be negligible, therefore the inertial permeability coefficient $k_i$ could not be measured with the existing set-up. The inertial permeability coefficients of the GDLs are therefore entirely attributed to the micro-diffusion substrates.

| Sample                        | Entire GDL | Micro-Porous |
|-------------------------------|------------|--------------|
|                               | $k_v \times 10^{12} [m^2]$ | $k_i \times 10^7 [m]$ | $k_v \times 10^{12} [m^2]$ | $k_i \times 10^7 [m]$ |
| 30% PTFE, carbon type 1       | 0.440±0.005 | 3.4±0.8      | 0.118±0.013 | 3.4±0.8      |
| 70% PTFE, carbon type 1       | 2.20±0.06   | 0.80±0.02    | 0.64±0.05   | 0.80±0.02    |
| 30% PTFE, carbon type 2       | 0.79±0.02   | 0.63±0.03    | 0.09±0.02   | 0.63±0.03    |
| 70% PTFE, carbon type 2       | 8.5±0.2     | 1.86±0.02    | 4.9±0.7     | 1.86±0.02    |

Downloaded on 2019-04-28 to IP 207.241.231.82 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
The margins of error shown in the Table 1 represent 95% confidence limit. The results for all batches are based on measurements of four samples. Results show that the samples with a higher PTFE content have the viscous permeability one order of magnitude higher than the corresponding samples with a lower PTFE content. The samples containing carbon type 1 have a lower viscous permeability than the corresponding samples containing carbon type 2.

Figure 2 shows the pressure gradient vs. the superficial velocity plot for one of the samples. The solid line represents non-linear regression best fit. Dotted lines represent the bounds of 95% confidence interval. The parabolic profile indicates that both viscous and inertial permeability are significant.

\[ \text{Figure 2} \]
Pressure Gradient vs. Velocity (entire GDL, 30% PTFE, carbon type 2)

In-Plane Permeability Measurements (x, y directions)

The system for in-plane permeability is shown in Figure 3. An annular GDL sample was clamped between an upper and a lower fixture. The gas entered the upper fixture through an inlet opening and was forced through the GDL into the atmosphere in a radial direction. The upper and lower fixture assembly was placed between the platens of a press. The compression force and the deformation of the sample were measured with a load cell and a strain sensor attached to the upper platen through a support. The thickness...
of each GDL sample was measured in five points using a digital micrometer. For the required interval of flow rates the apparatus correction was determined by measuring the pressure drop in the fixtures without any sample. At different compression levels and for at least five flow rates $Q$ we measured the compression force $F$, the GDL deformation $D_e$, the pressure $P_j$, the temperatures $T_1$ and $T_0$ upstream and downstream of the test fixture. The in-plane permeability coefficients were then calculated from Darcy-Forchheimer equation [3] by application of the least squares method (4):

$$\Delta P = \frac{\mu}{k_v} \frac{Q}{2\pi} \ln \left( \frac{D_2}{D_1} \right) + \frac{P}{k_i} \frac{Q^2}{2\pi e^2} \frac{D_2 - D_1}{D_1 D_2}$$

[3]

In equation [3] $\Delta P$ is the pressure difference $P_j - P_o$, $Q$ is the volumetric flow rate and $D_1$ and $D_2$ are the internal and external diameters of the annular GDL sample.

![Test Apparatus for In-Plane (x, y Directions) Permeability Measurements](image)

The tests showed that the in-plane inertial resistance to flow was much lower than the viscous resistance and therefore the inertial permeability could not be determined. The in-plane viscous permeability was in this case determined using a linear, non-iterative form of the least squares method. The in-plane viscous permeability coefficient $k_v$ at different compression rates and for each GDL is presented in Table 2. The margins of error shown in the table represent 95% confidence limit. The results are based on measurements of four samples for each batch. The in-plane permeability for all four GDLs has the same order of magnitude. Materials with higher PTFE content have a higher permeability. Materials with carbon type 1 have a lower permeability than materials with carbon type 2. The same trend was observed for the through-plane permeability.
Table 2
In-Plane Viscous Permeability Coefficient as a Function of Compression Load

| Load [psi] | $k_v \times 10^{12} [m^2]$ (entire GDL) |
|------------|------------------------------------------|
|            | 30% PTFE, carbon type 1 | 70% PTFE, carbon type 1 | 30% PTFE, carbon type 2 | 70% PTFE, carbon type 2 |
| 51         | 2.6±0.5                        | 3.3±0.6                    | 3.8±0.7                    | 4.7±0.9                    |
| 102        | 2.4±0.4                        | 2.9±0.5                    | 3.2±0.6                    | 4.0±0.7                    |
| 153        | 2.0±0.4                        | 2.7±0.5                    | 3.0±0.6                    | 3.6±0.7                    |
| 203        | 1.6±0.3                        | 2.6±0.5                    | 2.6±0.5                    | 3.3±0.6                    |
| 255        | 1.3±0.3                        | 2.5±0.5                    | 2.2±0.5                    | 3.2±0.6                    |
| 305        | 1.0±0.3                        | 2.3±0.5                    | 1.9±0.5                    | 3.0±0.6                    |

An equation similar to [2] may not be used to determine the in-plane permeability coefficient for the micro-porous substrate. However, it may be assumed that all the gas flows through the macro-porous backbone alone and the permeability measured for the GDL is entirely attributed to the macro-porous layer alone.

Figure 4
Pressure Gradient vs. Flow Rate (entire GDL, 30% PTFE, carbon type 1, 153 psi)
Figure 4 shows the pressure vs. flow rate plot for one of the samples. The solid line represents linear regression best fit. Dotted lines represent the bounds of 95% confidence interval. The graph shows a linear variation of pressure with flow rate, indicating that only the viscous in-plane resistance to flow is significant for the range of flows used in the experiments.

WETTABILITY MEASUREMENTS

Same four gas diffusion materials used for permeability measurements were subjected to wettability measurements. A schematic of a Kriiss Processor Tensiometer used to determine the internal contact angle of water to the fibers of the GDL and the surface tension of the GDL fibers is shown in Figure 5. The GDL sample is held by a metal clamp, which is attached to a sensitive balance. The test liquid is placed on a platform on a precise screw-type motor. The motor raises the test liquid until the balance detects the contact of the diffusion layer material to the liquid’s surface. A computer records the mass of liquid absorbed by the GDL as a function of time. The GDL sample is first tested with N-hexane (assumed to have a zero contact angle to the GDL pores) and the capillary constant of the material is determined from the Washburn equation (5):

\[ c = \frac{m^2}{t \cos \theta \cdot \rho^2 \gamma_{LV}} \]  

In equation [4] \( c \) is the capillary constant of the GDL sample, \( m \) is the mass of liquid absorbed by the sample in time \( t \), \( \eta \), \( \rho \) and \( \gamma_{LV} \) are the liquid viscosity, density, and surface tension and \( \theta \) is the contact angle, assumed to be zero for N-hexane. The capillary constant \( c \) is material dependent and is a function of the pore structure of the GDL. With the capillary constant determined, contact angles against at least four different wetting liquids (methanol, acetone, diiodomethane, toluene, benzyl alcohol) are measured using mass squared versus time data and equation [4]. The contact angle against water and the surface tension of the GDL material are next calculated from the previously determined contact angles using Owens-Wendt equation (3):

\[ (1 + \cos \theta)(\gamma_{LV}^p + \gamma_{LV}^d)/2\sqrt{\gamma_{LV}^d} = \sqrt{\gamma_{SV}^p + \gamma_{SV}^d/\gamma_{LV}^d} \]  

In equation [5] \( \gamma_{LV}^p \) and \( \gamma_{LV}^d \) are the polar and dispersive components of the liquid surface tension (known) and \( \gamma_{SV}^p \) and \( \gamma_{SV}^d \) are the polar and dispersive components of the solid surface tension.

A plot of \( (1 + \cos \theta)(\gamma_{LV}^p + \gamma_{LV}^d)/2\sqrt{\gamma_{LV}^d} \) versus \( \sqrt{\gamma_{LV}^p/\gamma_{LV}^d} \) for different liquids yields \( \gamma_{SV}^d \) (square of the y-intercept), \( \gamma_{SV}^p \) (square of the slope) and consequently \( \gamma_{SV}^d \).
(νsv = νsvd + νsvd). The plots for the same solid and different liquids are situated on a straight line, therefore for known values of $\sqrt{\gamma_{LV}^p}/\gamma_{LV}^p$ for water, the contact angle between water and solid may be calculated from the ordinate after interpolation. Alternatively, varying the values of $\gamma_{LV}^d$ and $\gamma_{LV}^p$ in a least squares fit analysis of contact angle data will yield the dispersive and polar components of the surface free energy of the solid and consequently $\gamma_{SV}$. This last method was proposed by Mann (4).

The plots for the same solid and different liquids are situated on a straight line, therefore for known values of $\sqrt{\gamma_{LV}^p}/\gamma_{LV}^p$ for water, the contact angle between water and solid may be calculated from the ordinate after interpolation. Alternatively, varying the values of $\gamma_{LV}^d$ and $\gamma_{LV}^p$ in a least squares fit analysis of contact angle data will yield the dispersive and polar components of the surface free energy of the solid and consequently $\gamma_{SV}$. This last method was proposed by Mann (4).

![Figure 5](image.png)

**Figure 5**

Krüss Processor Tensiometer

The contact angles to water and the solid free surface energies with their dispersion and polar components are shown in Table 3. GDL materials containing 70% PTFE have a higher contact angle to water than the materials containing 30% PTFE. The margins of error shown in the table represent 80% confidence limit.

| Sample (entire GDL)                  | $\theta_{H2O}$ | $\gamma_s$ | $\gamma_s^d$ | $\gamma_s^p$ |
|--------------------------------------|----------------|------------|---------------|--------------|
| 30% PTFE, carbon type 1              | 89±3           | 21±2       | 13±1          | 8±2          |
| 70% PTFE, carbon type 1              | 101±3          | 17±1       | 13.8±0.8      | 3.1±0.8      |
| 30% PTFE, carbon type 2              | 88±7           | 22±4       | 14±2          | 8±3          |
| 70% PTFE, carbon type 2              | 96±7           | 19±3       | 14±2          | 4±2          |

Table 3

Internal Contact Angle to Water $\theta_{H2O}$, GDL Surface Energy $\gamma_s$, and its Dispersive and Polar Components $\gamma_s^d$ and $\gamma_s^p$
The results for the capillary constants are based on measurements of five samples for each batch. The results for the internal contact angle to water and for the free surface energy of the material are based on measurements of four or five samples for each batch. Figure 6 shows the Owens-Wendt plot for the 30% PTFE, carbon type 1 sample using five testing fluids.

ACKNOWLEDGEMENTS

This material was prepared with the support of the US Department of Energy, under award number DE-FC04-02AL67606.

REFERENCES

1. B. Mueller, T. Zawodzinski, J. Bauman, F. Uribe, S. Gottesfeld, E. De Castro, M. De Marinis in Proton Conducting Membrane Fuel Cells II, PV 98-27, p. 1, The Electrochemical Society Proceedings Series, Pennington, NJ (1998)
2. C. Lim and C.Y. Wang in Electrochemical Society Meeting, October 20-25, 2002, Salt Lake City, UT
3. D. K. Owens and R. C. Wendt, J. Appl. Polym. Sci. 13, 1791 (1969)
4. J.A. Mann, Jr., in Surface and Colloid Science 13, E. Matijevic and R. J. Good, Editors, p. 213, Plenum Press, New York, (1984)
5. E.W. Wasburn, Phys. Rev., 18, 3 (1921)