

Characterization of transport properties in gas diffusion layers for proton exchange membrane fuel cells

1. Wettability (internal contact angle to water and surface energy of GDL fibers)

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Abstract

This is the first in a series of papers in which we present state-of-the-art methods demonstrated at Case for the estimation of transport properties in gas diffusion layers (GDLs) for proton exchange membrane fuel cells (PEMFCs). Most of the methods used today for measuring wettability properties of GDLs are related to the external contact angle to water. The external contact angle however does not describe adequately capillary forces acting on the water inside the GDL pores. We show as well that the direct method of estimation of the internal contact angle using goniometry on micrographs is impractical. We propose and describe in this paper a method for estimating the internal contact angle to water and the surface energy of hydrophobic and hydrophilic gas diffusion media. The method was applied to GDLs having different contents of hydrophobic agent and carbon types. The method can be applied separately to different components of the GDL including macro-porous substrates and micro-porous layers. The uncertainty estimates using this method are usually within 3% of the measured value.

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1. Introduction

Gas diffusion layers (GDLs) are essential components of polymer electrolyte-based fuel cells, including hydrogen and methanol fueled systems. The role of GDLs within a proton exchange membrane fuel cell (PEMFC) is to allow the gaseous reactants to move towards the catalyst layer areas situated above the ribs between the gas channels. They also provide a path for electrons to flow between catalyst layers and bipolar plates. The GDL also plays a critical role in water management within the cell. Cell humidification and water removal are both achieved through the GDL. GDLs are responsible for an optimum humidification level and liquid water distribution in the catalyst layer. This is required in order to minimize the ohmic resistance of

the ionomer and to prevent the appearance of local hot spots in the catalyst coated membrane. Depending on specific operating conditions, a variety of aspects of the GDL come into play.

At the fuel cell cathode, supersaturated conditions are sometimes encountered. The liquid water produced in the cathode catalyst layer changes the effective porosity of the GDL hindering the ability of oxygen to diffuse towards the catalyst, a phenomenon referred to as ‘flooding’ of the electrode. This is typically the origin of the limiting current for PEM fuel cells. In addition, resulting occlusion of flow channels by liquid water droplets at the GDL/channel interface have recently been implicated in problems with durability in cells. Local reagent starvation seems to lead to substantial local voltage excursions, causing carbon corrosion.

The anode of a hydrogen/air cell, on the other hand, tends to dry out and it may be desirable for the GDL to act to retain water. In a liquid-fed direct methanol fuel cell, the GDL represents an adjustable impedance to reagent delivery. Thus, the wettability

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Nomenclature

a_k	unknown parameters ($k = 1, 2$)
A	vector in Eq. (A.10)
C	matrix in Eq. (A.10)
C_W	Washburn constant (cm^5)
f	functional relationship between dependent and independent variables
F	conditional function
L	weight factor
m	mass absorbed by test sample (g)
n	number of measurements
R	residuals
S	weighted sum of the squares of residuals
t	time (s)
V	vector in Eq. (A.10)
w	weights
x_j	calculated independent variable ($j = 1, 2, 3$)
\bar{X}_j	measured independent variable ($j = 1, 2, 3$)
y	calculated dependent variable
Y	measured dependent variable

Greek letters

γ	surface tension (mN m^{-1})
η	dynamic viscosity (mPa s)
θ	contact angle
ρ	gas density (g cm^{-3})
σ	standard deviation

Subscripts

L	liquid
LV	liquid–vapor interface
SV	solid–vapor interface
SL	solid–liquid interface

Superscripts

d	dispersive component of surface tension
p	polar component of surface tension

characteristics of the GDL are of paramount importance in its function and in overall fuel cell function.

Given the importance of the GDL in fuel cell function, it is somewhat surprising that they have not been the subject of significantly more work. This stems partly from the complexity of media themselves. Significant structural complexity underlying the GDL behavior leads to difficulty in defining a set of easily measurable, rigorously meaningful parameters of description.

Gas diffusion layers are usually constructed from macro-porous substrates coated with one or more micro-porous layers. The morphology of the GDLs for PEMFCs may vary widely depending on the nature and proportion of their constituents. Macro-porous substrates for GDLs may be carbon fiber cloth (Fig. 1) carbon fiber paper (Fig. 2), or non-woven carbon materials. The surfaces of the carbon materials are not so inert as, for example the pure sp^3 bonding of diamond but include structures that provide some polar character to the carbon materials

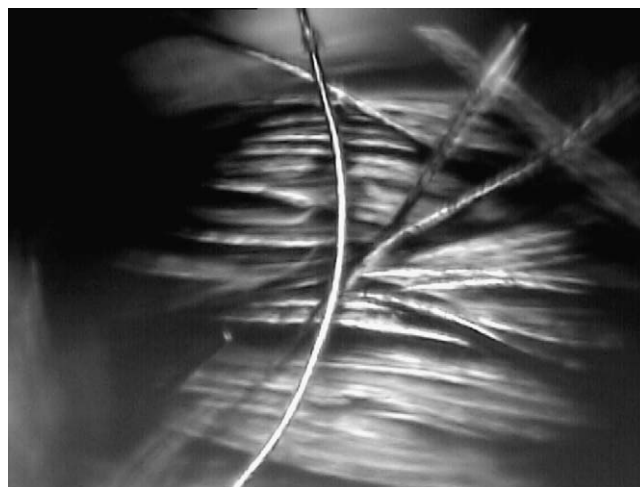


Fig. 1. 200 \times reflected light microscopy image of an ELAT[®] carbon fiber cloth (E-TEK division De Nora North America).

used in GDLs. To increase the contact angle to water and prevent flooding, macro-porous backbones of gas diffusion layers are impregnated with poly(tetrafluoroethylene) (PTFE). Micro-porous layers (amorphous mixtures of carbon and PTFE) are applied on macro-porous substrates in order to improve electrical contact with the catalyst layers and to add a further level of control of water transport. Indeed, the macro-porous layer used alone will tend to fill with liquid water, or flood, at the fuel cell cathode. For a structurally complex medium such as this, defining the factors controlling wetting is extremely difficult. However, advancing the state of the art requires development of rigorous descriptions of these phenomena, supported by the development of rigorous testing methods.

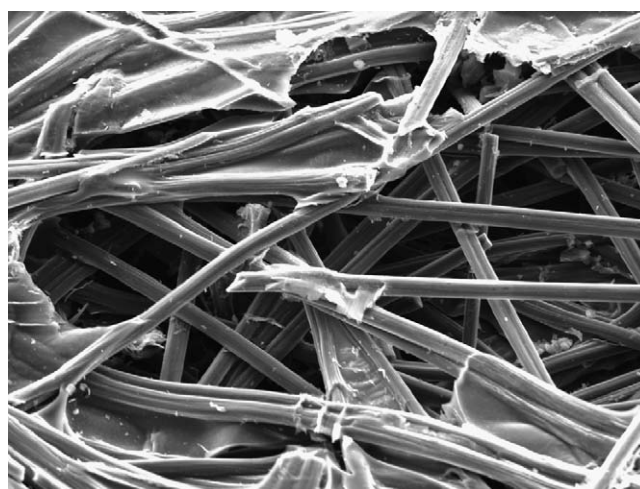


Fig. 2. 500 \times scanning electron microscopy (SEM) image of a Toray[®] carbon fiber paper. The image shows carbon fibers, clusters of PTFE and small particles on the fibers (PTFE or of other origin). At pore (microscopic) level the GDL material may not be considered homogeneous as in a macro-homogeneous model. The internal contact angle to water will depend on the nature of the material the droplet is in contact with. The measured internal contact angle to water must represent a statistical average over the GDL properties at microscopic level.

Liquid water within the GDL is transported by capillary and gas-phase pressure gradients while body forces such as gravity and two-phase drag do not significantly affect its momentum. The properties of the GDL that influence the capillary action are its surface energy and the contact angle to water. To support the research of new candidate materials for GDLs as well as for design considerations one must, at a minimum, be able to provide quantitative estimations of the surface tension and the internal contact angle to water of GDL materials.

Most of the methods used today to estimate the contact angle to water of GDL materials, such as capillary meniscus height, goniometry (sessile drop) or Wilhelmy (plate) are methods for determining the *external* contact angle. Usually values of the external contact angle between 120° and 140° or even higher have been reported [1–3] for different GDL materials. Since the contact angle to water of pure PTFE is only 108° [4] these large values cannot be explained by the presence of the hydrophobic agent inside the GDL pores but rather by the contribution of GDL surface roughness. During an external contact angle measurement water does not experience the molecular force field with the internal pores of a porous material, but the contact with a solid plate having surfaces of a certain roughness. For a rough, structured surface, these measurements do not provide a true measure of the interfacial properties of the material. Instead, structural aspects dominate the observed behavior through such phenomena as droplet pinning. It is well known [5] that surfaces with a roughness above approximately $1\ \mu\text{m}$ generate higher contact angles to water than smooth surfaces and a hysteresis effect when advancing and receding contact angles are measured. While in general the external contact angle may describe only qualitatively the wettability of GDL materials it may not be used as a quantitative estimation for calculations or design purposes.

In contrast, the *internal* contact angle to water of gas diffusion media depends on the surface energy at the pore level. Since at the pore (microscopic) level the structure and composition of gas diffusion media is not homogeneous (see Fig. 2), a meaningful internal contact angle must reflect a statistical average over the material properties at microscopic level. For this reason, direct measurement of internal contact angle using goniometry associated with SEM or other optical techniques is impractical given that it would require the interpretation of a very large number of droplets. Use of the direct method for interpretation of internal contact angles is complicated even further if the contact point between the water droplet and the solid phase in a micrograph is hidden behind the droplet or behind the fiber (see Fig. 3). Even when this is not the case, it has been shown [6] that “micro” and “macro” contact angles measured using goniometry may differ significantly.

An internal contact angle to water reflecting a statistical average over diffusion media properties at the microscopic level can be obtained using the sorption or Washburn method [7]. The Washburn method has been cited in the past in the literature related to gas diffusion media [8] as a possible method to be used to determine the contact angle to water, but no results or even attempts to use it for hydrophobic GDL materials have been reported; this is not surprising considering that sorption methods

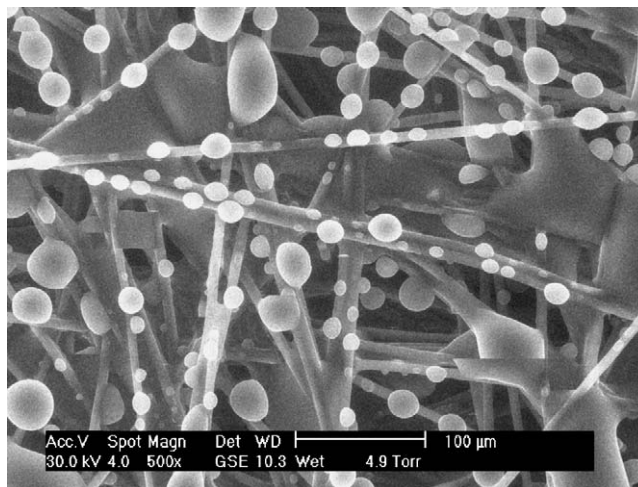


Fig. 3. $500\times$ scanning electron microscopy (SEM) image of a Toray[®] carbon fiber paper. The image shows water droplets formed on the GDL fibers. Despite the large number of droplets, all the boundaries between water and fibers in this image are situated either behind the droplets or behind the fibers, making the interpretation of the contact angle inaccurate.

may not be used with hydrophobic porous media when the test fluid is water.

Mathias et al. [3] refer to the Zisman plot [9] as a method to be used to determine the surface energy of GDL fibers, but once again no results or attempts to use it are reported. Our initial attempt to use this method to determine the surface energy of the GDL fibers and the internal contact angle to water failed. Since Zisman theory is a one component model for the surface energy, it does not emphasize molecular interactions; for this reason it works best with non-polar surfaces, but becomes inadequate when surfaces are even marginally polar [5]. It appears that dipole–dipole and even hydrogen bonding interactions are present between the gas diffusion media and the test fluids. When such polar interactions are possible, other models for surface energy must be employed. It is beyond the scope of this paper to evaluate the various surface chemistry models that have been developed and that are the subject of much discussion in the literature. See Adamson and Gast [5] for some details. From an engineering perspective, the two-parameter model of the surface tension provides a reasonable and practical algorithm for determining the internal contact angle. In this model, the surface tension is represented by the sum of two components: a term that represents the result of dispersion forces and a term that includes all other contributions. The algorithm depends on curve fitting data for different liquids (with different surface energy components) sorbing into the GDL fiber network. In the end the number of points in the sample space of the fitting is the number of liquids that sorb significantly for which the two components of the surface tension have been estimated by other means. Therefore, the number of degrees of freedom for the fit is a small number. As a result the uncertainty estimates are necessarily crude but useful. Note: a fitting function that employs three or more parameters, for example the acid-base model [5], will not allow uncertainty estimates since the data set and therefore the degrees of freedom is too small. Moreover, the purpose

of our experiment and data processing is to provide information that leads to material design criteria for GDL fiber networks. A discussion of the fundamental problem of the molecular level interpretation of the many-parameter partition of the surface energy or the equation of state approach is deferred for future publications.

2. Materials and method

The technique demonstrated at Case for estimating the internal contact angle to water and the surface energy of GDL materials uses the Washburn method [7] for hydrophilic materials and a combination of the Washburn method and the Owens-Wendt two-parameters theory [4] for hydrophobic materials. In the second case, since liquid water cannot be used as test fluid, the Washburn method is conducted with a set of wetting fluids to find their internal contact angle to the GDL material. The Owens-Wendt theory is used next to extrapolate the data obtained with the Washburn method and determine the internal contact angle to water and the surface energy of the GDL material. A least squares fit analysis method [10] is used to interpret the data and provide error analysis.

Four GDL samples were prepared by E-TEK division, DeNora North America (Somerset, New Jersey). The samples consisted of a single-sided carbon fiber cloth (the macro-porous substrate was the same for all samples) impregnated with a micro-porous sub-layer (four combinations of two different types of carbon and 30% and 70% PTFE loading, respectively).

The internal contact angles to water of the GDL materials and their surface tensions were determined at room temperature using a Krüss Processor Tensiometer. In the tensiometer 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, which raises it until the balance detects the contact of the GDL sample to the liquid surface. A computer records the mass of liquid absorbed by the GDL as a function of time. The data acquisition rate was of 10 records per second.

The set of test fluids used with this technique and their surface tension components are summarized in Table 1. All test fluids were obtained from Fischer Scientific and were of HPLC grade.

Table 1
The test fluids and their surface tension with dispersive and polar components

Test fluids	γ_{LV}^d [mN m ⁻¹]	γ_{LV}^p [mN m ⁻¹]	γ_{LV} [mN m ⁻¹]
For Washburn method			
<i>n</i> -hexane	18.4	0.0	18.4
Toluene	26.1	2.3	28.4
Acetone	17.3	6.4	23.7
Benzyl alcohol	30.3	8.7	39.0
Diiodomethane	50.8	0.0	50.8
Methanol	16.0	6.7	22.7
For Owens-Wendt calculation			
Water	19.9	52.2	72.1

Source: Krüss processor tensiometer database.

3. Theory and calculation

3.1. The Washburn method [7]

The Washburn method described below is the first step of the analysis and is used to determine the Washburn constant of the material and the internal contact angle of the test fluids to the GDL material.

The Lucas-Washburn Eq. (1) describes the capillary rise of a liquid in a porous material when inertia and gravity forces are negligible:

$$\cos \theta = \frac{m^2}{t} \frac{\eta_L}{C_W \rho_L^2 \gamma_{LV}} \quad (1)$$

The GDL sample is first tested with *n*-hexane that is assumed to have a zero contact angle to the GDL pores ($\cos \theta = 1$) and the Washburn constant of the material is determined from the Lucas-Washburn equation. In Eq. (1) C_W is the Washburn constant of the GDL sample, m the mass of liquid absorbed by the sample in time t , η_L , ρ_L and γ_{LV} the liquid viscosity, density, and surface tension and θ is the contact angle; the viscosity and density of the gas-phase are ignored. The Washburn constant C_W is material dependent and is a function of the GDL pore structure. With the Washburn constant determined, contact angles against at least four different wetting liquids (see Table 1) are measured using mass-squared-versus-time data and the Lucas-Washburn equation (1). The contact angle against water and the surface tension of the GDL material are next calculated from the previously determined contact angles using the Owens-Wendt equation.

3.2. The Owens-Wendt calculation of contact angle to water and surface energy [4]

According to the Owens-Wendt two-parameter model the surface tensions of the solid–vapor and liquid–vapor interphases consist of two components: a dispersive one accounting for van der Waals and other non-site-specific interactions and a polar one accounting for dipole–dipole, dipole-induced dipole, hydrogen bonding and other site-specific interactions [5]

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \quad (2a)$$

$$\gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p \quad (2b)$$

Combining Good's equation (3) [11] with Young's equation (4)

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 \left[\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \gamma_{LV}^p} \right] \quad (3)$$

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (4)$$

yields

$$(1 + \cos \theta) \frac{\gamma_{LV}^p + \gamma_{LV}^d}{2\sqrt{\gamma_{LV}^d}} = \sqrt{\gamma_{SV}^d} + \sqrt{\gamma_{SV}^p} \times \sqrt{\gamma_{LV}^p / \gamma_{LV}^d} \quad (5)$$

where θ is the contact angle between the test liquid and the pores of the GDL material. The two unknown components of the GDL surface tension γ_{SV}^d and γ_{SV}^p in Eq. (5) can now be determined

from the previously measured contact angles against the test fluids with known values of surface tension components γ_{LV}^d and γ_{LV}^p (Table 1). 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 the dispersive component γ_{SV}^d (square of the y -intercept), the polar component γ_{SV}^p (square of the slope) and consequently the surface tension of the solid–vapor interface γ_{SV} from Eqs. (2a) and (2b). The plots for the same GDL material and different liquids are situated on a straight line; for the known value of $\sqrt{\gamma_{LV}^p/\gamma_{LV}^d}$ for water, the contact angle of the GDL material against water can be calculated from the ordinate after extrapolation.

Alternatively, the adjustment of the values of γ_{SV}^d and γ_{SV}^p in a least squares analysis of contact angle data does yield the dispersive and polar components of the surface tension of the solid–vapor interface and consequently γ_{SV} from Eqs. (2a) and (2b). Moreover, estimates of the uncertainty of the surface energy components and thereby γ_{SV} can be estimated from the Hessian matrix computed in the least squares procedure. Since the degrees of freedom is small, and all of the experimental numbers are uncertain to a significant extent, the least squares algorithm must be carefully formulated. We have discussed the details in Appendix A.

4. Results and discussion

The average Washburn constants of the four GDL materials and the internal contact angles to the test fluids are shown in Table 2 (see also [12]). The Washburn constants were found to be similar among the four GDL samples and repeatable with the largest standard deviation less than 10% for the sample with 30% PTFE and carbon type 2. The results for the Washburn constants are based on measurements of five samples for each batch. The results for the internal contact angles are based on measurements of three to five samples for each batch.

The internal contact angle to water and the surface tension of the four GDL samples with their dispersive and polar component are shown in Table 3. The margins of error shown in the table represent 80% confidence limit. The results for the internal contact angle to water and for the surface tension are based on measurements with four or five test fluids for each batch. Typically uncertainties within 3° are obtained for the internal contact angle when five test fluids are used. Larger uncertainties were obtained for the samples containing carbon type 2 for which only four test fluids were used. The results show that

Table 3

The internal contact angles against water and the surface tensions of the GDL materials with dispersive and polar components

Sample	θ_{H_2O} [°]	γ_{SV}^d	γ_{SV}^p	γ_{SV}
30% PTFE carbon type 1	89 ± 3	13 ± 1	8 ± 2	21 ± 2
70% PTFE carbon type 1	101 ± 3	13.8 ± 0.8	3.1 ± 0.8	17 ± 1
30% PTFE carbon type 2	88 ± 7	14 ± 2	8 ± 3	22 ± 4
70% PTFE carbon type 2	96 ± 7	14 ± 2	4 ± 2	19 ± 3

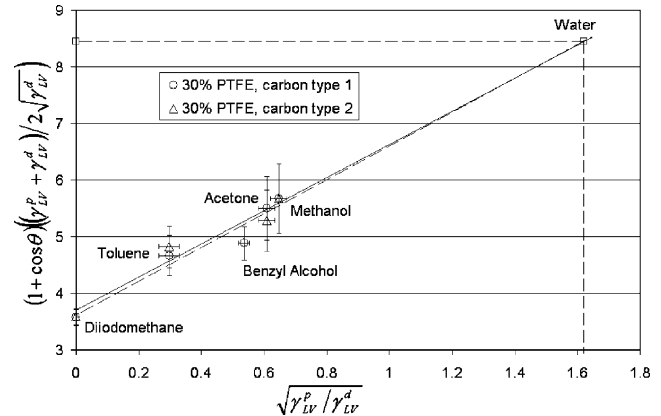


Fig. 4. Owens-Wendt plot for the GDL materials containing, 30% PTFE and carbon type 1 and carbon type 2, respectively.

the materials with the same PTFE content have similar internal contact angles to water and free surface energies. As expected, the GDL materials containing 70% PTFE have a higher internal contact angle to water and lower surface tensions than the materials containing 30% PTFE. All measured contact angles have values less than the contact angle of pure PTFE to water. All samples have similar values for the dispersive component of the surface tension. The polar component of the surface tension is similar for the samples with same PTFE content; it is the polar component which differentiates between the samples containing 30% and 70% PTFE, respectively. This is the reason why the initial attempts to use the one parameter Zisman model for surface tension failed.

Figs. 4 and 5 present the Owens-Wendt plots for the samples obtained with four and five testing fluids.

Remark. While the results shown here were obtained for GDL materials containing both macro-porous substrate and micro-porous layer, we have demonstrated this method at Case for macro-porous substrates separately, for micro-porous layers applied on solid substrates and for catalyst layers.

Table 2
The GDL Washburn constants and the internal contact angles against the test fluids

Sample	Washburn constant ($\times 10^{-5}$ cm ⁵)	Internal contact angle, θ [°]				
		Toluene	(CH ₃) ₂ CO	Benzyl alcohol	CH ₂ I ₂	MeOH
30% PTFE carbon type 1	1.45 ± 0.03	47 ± 3	21 ± 2	68 ± 1	89.9	0
70% PTFE carbon type 1	1.33 ± 0.06	55 ± 1	48 ± 3	71 ± 5	89.4	47 ± 2
30% PTFE carbon type 2	1.4 ± 0.1	43 ± 3	31 ± 4	0 ^a	89.7	0
70% PTFE carbon type 2	1.47 ± 0.04	50 ± 1	39 ± 4	84 ± 4 ^a	89.8	42 ± 4

^a Value not used in subsequent analysis.

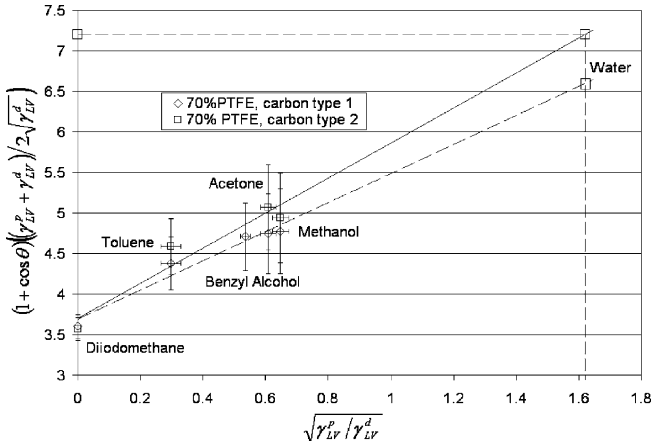


Fig. 5. Owens-Wendt plot for the GDL materials containing 70% PTFE and carbon type 1 and carbon type 2, respectively.

5. Conclusions

The external contact angle to water is not indicative of the capillary forces acting on the water inside the pores of GDL materials. The external contact angle provides information on the wetting phenomena on the external surfaces of the GDL, while the internal contact angle provides information on the wetting phenomena in the GDL pores. The former depends on the surface roughness more than on the material composition (the measured contact angle is outside the range of the contact angles measured for each individual component), while the latter depends on the pore structure and materials at the pore level.

It is not practical to measure the internal contact angle to water using goniometry on micrographs. Since at the microscopic level the GDL materials are not homogeneous, a method for the estimation of internal contact angles must provide contact angles representing a statistical average over the GDL properties at the pore level.

We have demonstrated and presented a method for estimation of the internal contact angle to water and of the surface tension of hydrophobic and hydrophilic GDL materials. The method combines the Washburn technique with the Owens-Wendt two-parameter theory and the method of least squares. The method was applied to four GDL materials containing two different carbon types and 30% and 70% PTFE, respectively. The samples containing 70% PTFE have higher contact angles to water and lower surface tensions. All measured contact angles to water are less than the contact angle to water of pure PTFE. Uncertainties within 3° degrees for the contact angle are usually obtained with this method when at least five test fluids are employed. The method is applicable to macro-porous substrates and micro-porous layers of GDL materials as well as to catalytic layers.

Acknowledgements

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Appendix A

An alternative to the graphical Owens-Wendt method is the method of least squares [10], which provides in addition the standard deviation of the estimated parameters. While there are computer programs that will do a least squares analysis of data fit to a model, the number of degrees of freedom of the GDL contact angle is sufficiently small that the weights must be carefully estimated and uncertainties included in details as we outline next. The fundamental assumption is that the measured quantities obey a Gaussian distribution; the law of large numbers generally assures that this is the case, see for example Mann [10] and citations therein. However, clearly, the number of liquids that are suitable is limited and therefore the degrees of freedom in determining the fits is limited. It is therefore necessary to explain in some detail the algorithm that we used to provides both the estimate of parameters and an estimate of the uncertainty in their values.

The physical law (5) is rewritten as

$$y = \sqrt{a_1 x_1} + \sqrt{a_2 x_2} \tag{A.1}$$

or as a functional relationship between the dependent and independent variables

$$y = f(a_1, a_2, x_1, x_2) \tag{A.2a}$$

where the dependent variable is

$$y = \frac{(\gamma_{LV}^p + \gamma_{LV}^d)(\cos \theta + 1)}{2} \tag{A.2b}$$

the independent variables are $x_1 = \gamma_{LV}^d$, $x_2 = \gamma_{LV}^p$ and the unknown parameters are $a_1 = \gamma_{SV}^d$ and $a_2 = \gamma_{SV}^p$.

The residuals are defined as the difference between the measured and calculated values of the dependent and independent variables, respectively

$$R_{y_i} = Y_i - y_i, \quad R_{x_{j,i}} = X_{j,i} - x_{j,i}, \quad j = 1, 2 \tag{A.3}$$

The weights are defined as the reciprocal of the squares of the measurement uncertainties (standard deviations)

$$w_{y_i} = \frac{1}{\sigma_{y_i}^2}, \quad w_{x_{j,i}} = \frac{1}{\sigma_{x_{j,i}}^2} \tag{A.4}$$

Notice that σ_{y_i} must be computed from Eq. (A.2b), since we can estimate the uncertainties of $\{\gamma_{LV}^d, \gamma_{LV}^p, \theta\}$ from experimental information. A simple calculation with Eq. (A.2b), Mann [10] provides the following formula for the error propagation

$$\sigma_y^2 = \left(\frac{\partial y}{\partial \gamma_{LV}^d} \right)^2 \sigma_{\gamma_{LV}^d}^2 + \left(\frac{\partial y}{\partial \gamma_{LV}^p} \right)^2 \sigma_{\gamma_{LV}^p}^2 + \left(\frac{\partial y}{\partial \theta} \right)^2 \sigma_{\theta}^2 \tag{A.4b}$$

and thereby w_{y_i} can be estimated. Also recognize that since the uncertainty in the $\{\gamma_{LV}^d, \gamma_{LV}^p\}$ must also be included through w_{y_i} .

The method of least squares consists in determining the values of the parameters a_1 and a_2 which minimize the weighted

sum of the squares of residuals

$$S = \sum_{i=1}^n \left(w_{y_i} R_{y_i}^2 + \sum_{j=1}^3 w_{x_{j,i}} R_{x_{j,i}}^2 \right) \quad (\text{A.5})$$

This amounts to a maximum likelihood algorithm for a Gaussian distribution function of noise involved in measuring the various parameters.

The conditional function is defined as

$$F^i = y_i - f(a_1, a_2, x_1, x_2) \quad (\text{A.6})$$

The initial guess of the unknown parameters is a_1^0 and a_2^0 . The initial value of the conditional function is estimated from measurements and the initial guess of the unknown parameters

$$F_0^i = Y_i - f(a_1^0, a_2^0, X_1, X_2) \quad (\text{A.7})$$

The weight factor for each measurement is defined as

$$L_i = \frac{1}{w_{y_i}} \left(\frac{\partial F^i}{\partial y} \right)^2 + \sum_{j=1}^3 \frac{1}{w_{x_{j,i}}} \left(\frac{\partial F^i}{\partial x_{j,i}} \right) \quad (\text{A.8})$$

The optimized values of the unknown parameters are calculated as

$$A = C^{-1} V \quad (\text{A.9})$$

where

$$A = \begin{bmatrix} a_1^0 - a_1 \\ a_2^0 - a_2 \end{bmatrix}, \quad C = \begin{bmatrix} \sum_{i=1}^n \frac{1}{L_i} \frac{\partial F^i}{\partial a_1} \frac{\partial F^i}{\partial a_1} & \sum_{i=1}^n \frac{1}{L_i} \frac{\partial F^i}{\partial a_1} \frac{\partial F^i}{\partial a_2} \\ \sum_{i=1}^n \frac{1}{L_i} \frac{\partial F^i}{\partial a_1} \frac{\partial F^i}{\partial a_2} & \sum_{i=1}^n \frac{1}{L_i} \frac{\partial F^i}{\partial a_2} \frac{\partial F^i}{\partial a_2} \end{bmatrix},$$

$$V = \begin{bmatrix} \sum_{i=1}^n \frac{1}{L_i} \frac{\partial F^i}{\partial a_1} F_0^i \\ \sum_{i=1}^n \frac{1}{L_i} \frac{\partial F^i}{\partial a_2} F_0^i \end{bmatrix} \quad (\text{A.10})$$

The standard deviations for the unknown parameters are estimated by

$$\sigma_{a_k} = \left(\frac{S}{n-2} \right)^{1/2} (C_{kk}^{-1})^{1/2} \quad (\text{A.11})$$

The classical algorithm [10] for determining a_1 and a_2 is the following

1. Collect the data measurements Y_i, X_1, X_2 and the standard deviations $\sigma_{y_i}, \sigma_{x_{j,i}}$;
2. Make the initial guess for the unknown parameters a_1^0 and a_2^0 ;
3. Using the initial guess for the unknown parameters and the measurements, calculate the conditional function (Eq. (A.7)) and its partial derivatives from (Eq. (A.6));
4. Calculate the weight factors (Eq. (A.8));
5. Calculate the elements of matrix C and vector V (Eq. (A.10));
6. Invert matrix C ;
7. Calculate vector A (Eq. (A.10)) and a_1 and a_2 ;
8. Use newly calculated a_1 and a_2 as the initial guesses for step 2;
9. Continue steps 2–8 until the change in a_1 and a_2 is less than a prescribed value;
10. Calculate the standard deviations for a_1 and a_2 (Eq. (A.11));

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