

# CHARACTERIZATION OF WETTABILITY IN GAS DIFFUSION LAYER FOR PROTON EXCHANGE MEMBRANE FUEL CELLS.

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## ABSTRACT

This paper presents a detailed study of the wetting properties of three fuel cell gas diffusion layers (GDL) having different morphologies and different contents of hydrophobic agent. An internal contact angle to water at temperature representative of PEM fuel cell operating conditions was directly obtained using the Washburn method with 66°C water as test liquid. This result shows that the surface of the carbon fibres is hydrophilic under fuel cell operating conditions. The surface energy value of the GDL fibres, determined by a combination of the Washburn method and the Owens-Wendt two parameters theory, was found to be low, indicating that GDL are wet very poorly by most liquids. About 40% of the total surface energy value was related to a polar component allowing dipole-dipole and hydrogen bonding interactions with water. The origin of this polar character is discussed.

## 1. INTRODUCTION

Proton Exchange Membrane fuel cells are undergoing intense development. Many groups work throughout the world in order to improve their performances, efficiency, reliability, manufacturability and cost-effectiveness. One way for studying fuel cells is to develop computational models representing the complex multi-physics transport processes occurring in fuel cells [1]. While much progress has been made in recent years, the understanding of water flow in the gas diffusion layer (GDL) remains an issue, especially because the lack of data for the various fibrous materials forming the diffusion media [2-3].

The GDL allows distribution of reactant gases through the porous matrix and collection of current through the fibres. At the fuel cell cathode, supersaturated conditions are sometimes encountered. When local water and heat management is inadequate, flooding may occur: water condensation takes place hindering the ability of oxygen to diffuse towards the catalyst. In order to avoid this, the GDL are commonly treated with PTFE to impart hydrophobicity and force water droplets to agglomerate at the free surface of the GDL [4]. Thus, the hydrophobic or hydrophilic nature of the GDL has a great impact on the water transport and the wetting properties of the GDL are of paramount importance in its function and in overall fuel cell function.

The GDL consist of an anisotropic fibrous structure, either in the form of carbon fibre cloth, carbon fibre paper or non-woven cloth [4]. Its thickness typically ranges between 170 and 400  $\mu\text{m}$ , whereas the fibre diameter is of the order of 10  $\mu\text{m}$ . Depending on the applications considered, one or several microporous layers (amorphous mixtures of carbon agglomerates and PTFE) may be attached to the fibrous structure, in order to improve the electrical contact with the catalyst layer and the water management [5]. This structural complexity leads to difficulty in defining relevant parameters describing the wetting.

A classic way of characterizing wetting is to use the concept of contact angle, which is the angle  $\theta$  between the solid phase surface and the interface between the two fluids. When the two fluids are liquid water and air, the surface is said to be hydrophilic when this *external* contact angle measured in the water is lower than  $90^\circ$  and hydrophobic when  $\theta$  is higher than  $90^\circ$ . The wetting behaviour of an ideal flat solid is fixed by its chemical composition via the Young's relation, but real solids are rough, which affects their wetting properties [6]. In the case of hydrophobic GDL, the liquid is only in contact with the upper part of the relief: the texture is mainly filled with air, which leads to higher contact angle value than for a flat surface. During the measurement, water experience the contact with a solid plate having surfaces of a certain roughness. Most of the methods used today are related to the measurement of *external* contact angle to water [4;7-9]. *External* contact angle do not describe adequately capillary forces acting on the water inside the GDL pores but wetting phenomena on the external rough surfaces of the GDL.

On the contrary *internal* contact angle may be used as a quantitative estimation for calculations or design purposes because it accounts for a statistical average over the material properties at microscopic level. *Internal* contact angle depends on the surface energy at the pore level. Calculating surface energy of PEM fuel cell components allows to predict the how well this component will be wet by water. A high surface energy means that interfaces between the solid and air are not favourable in a thermodynamic sense. High surface energy solids are therefore wet extremely well by liquids, since liquids wetting eliminates solid/air

interfaces in favour of liquid/solid interfaces. Low surface energy solids are correspondingly wet very poorly by most liquids. Gurau et al. [10] have demonstrated how a combination of the Washburn method [11] and the Owens-Wendt two parameters theory [12] allows an estimation of both the internal contact angle to water and the surface energy of GDL materials.

However a contact angle measured at temperature representative of PEM Fuel cell operating conditions (60 to 80°C) is more relevant for modelling purposes than a calculated contact angle to room temperature water. Lim et al. [9] have used an optically meniscus height measurement method based on Wilhelmy plate gravimetric technique to measure the surface contact angle as a function of the liquid temperature. The contact angle value was found to be a strong function of temperature: increasing temperature was found to decrease the measured surface contact angles to less than 90°, indicating that the GDL surface was hydrophilic under these conditions.

Inspired by these previous works, this paper presents a detailed study of the wetting properties of fuel cell diffusion media. Internal contact angle to water at temperature representative of PEM Fuel cell operating conditions was directly obtained using the Washburn method with 66°C water as test liquid. Then a combination of the Washburn method and the Owens-Wendt two parameters theory was used to determine the surface energy of the GDL fibres. Results for GDL having different morphologies and different contents of hydrophobic agent are presented.

## 2. EXPERIMENTAL

Three GDL (A, B and C) with different carbon-fibre-based diffusion media and PTFE loadings were studied. GDL B and C are single side carbon fibre papers impregnated with a micro-porous sub layer. The PTFE loadings are 5wt% for GDL B and 20 wt% for GDL C, respectively. GDL A is a carbon fibre cloth loaded with 10wt% PTFE. Experiments were performed with square shape samples with dimensions of 2.5cm\*2.5cm.

The capillary rise experiments were performed using a Krüss K100MK2 tensiometer tooled up with a thermostat vessel allowing the monitoring of liquid temperature. Each sample was held by a metal clamp which was attached to the microbalance. The test liquid in a beaker was placed in the thermostat vessel and was raised by a screw-type motor (detection speed usually 4 mm.min<sup>-1</sup>) until the microbalance detected the contact of GDL sample to the liquid surface (minimum detection sensitivity usually 0.005g). The mass of liquid absorbed by the sample was recorded as a function of time through the computer interfaced with the microbalance.

Name, temperature, surface tension with dispersive and polar components, density and viscosity of used test fluids are summarized in Table 1. Temperature corrections were applied to viscosity and surface tension using data from [13-14]. The ratio between polar and disperse part of surface tension was assumed not to be temperature dependent [15] and was calculated according to Kruss processor tensiometer database. All liquids were obtained from Fisher Chemical or Acros Organics and were of For Analysis grade.

Table 1. The test fluids used and their physical properties.

Fluids	Temperature T (°C)	Density $\rho$ (g.cm <sup>-3</sup> )	Viscosity $\eta$ (mPa.s)	Surface tension (mN.m <sup>-1</sup> )		
				total $\gamma$	disperse $\gamma^d$	polar $\gamma^p$
n-Heptane	25	0.684	0.381	19.7	19.7	0
1-Bromonaphthalene	19	1.483	5.11	44.5	44.3	0.2
Toluene	25	0.867	0.519	27.9	25.6	2.3
Benzyl alcohol	21	1.044	6.218	35.4	27.5	7.9
Acetone	20	0.791	0.320	26.0	19.0	7.0
Methanol	17	0.792	0.977	22.7	16.0	6.7
Water	66	0.9799	0.439	64.9	19.4	45.5
Water	25	0.998	1.002	72.8	21.8	51.0

### 3. METHODS

#### 3.1 The Washburn method

Washburn described the dynamic of the capillary rise of a liquid in a porous material [11]. Since it concerns a confined medium, it is generally appropriate to balance the viscous force with the capillary force minus the weight. For short times, the gravity forces are negligible so that the equation becomes:

$$m^2 = t \frac{C_W \rho^2 \gamma}{\eta} \cos \theta \quad (1)$$

Where  $m$  is the mass of liquid absorbed by the sample in time  $t$ ,  $C_W$  the Washburn or capillary constant,  $\eta$ ,  $\rho$  and  $\gamma$  are the liquid viscosity, density, and surface tension and  $\theta$  is the contact angle between the test liquid and the pores of the material. The viscosity and density of the gas-phase are ignored. If liquid of known density, viscosity and surface tension is used, a plot of the mass of liquid squared versus time yields two unknowns: the internal contact angle of the liquid on the solid and the Washburn constant.

The Washburn constant  $C_W$  is dependent on the porous architecture of the solid. Considering a simple parallelepipedic structure of the GDL:

$$C_W = \frac{\bar{r}}{2} (Lef)^2 \quad (2)$$

Where  $\bar{r}$  is the average radius of the mean pore,  $L$  and  $e$  the length and thickness of the GDL,  $f$  the porous fraction of the GDL. However, if a capillary rise experiment is performed with a liquid which is known to have a contact angle of  $\theta = 0^\circ$  ( $\cos \theta = 1$ ) on the solid, then  $C_W$  is the only remaining unknown and can thus be determined. Short straight-chain alkanes, like n-hexane or n-heptane, are generally a good choice as liquids for determining  $C_W$  because of their low surface tension purely attributable to dispersive forces. Once the Washburn constant has been determined, sample can be tested with another liquid and the internal contact angle is calculated using mass-squared-versus time data and Equation (1). In the subsequent analysis the Washburn constant is assumed to be unmodified by the liquid temperature.

#### 3.1 The Owens Wendt calculation of surface energy

Owens-Wendt theory accounts for site specific interactions between solid surfaces and liquids. Surface tension of the solid-vapour,  $\gamma_{SV}$ , and liquid-vapour,  $\gamma_{LV}$ , interphases consist of two components: a dispersive component and a polar component. The dispersive component accounts for Van der Waals and other non-site specific interactions and the polar component accounts for dipole-dipole, dipole-induced dipole, hydrogen bonding, and other site-specific interactions.

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \quad (3a)$$

$$\gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p \quad (3b)$$

Combining Good-Fowkes' equation (4) with Young's equation (5)

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 \left( \sqrt{\gamma_{SV}^d \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \gamma_{LV}^p} \right) \quad (4)$$

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (5)$$

yields the linear relation (6)

$$(1 + \cos \theta) \frac{\gamma_{LV}}{2\sqrt{\gamma_{LV}^d}} = \sqrt{\gamma_{SV}^d} + \sqrt{\frac{\gamma_{LV}^p}{\gamma_{LV}^d}} \times \sqrt{\gamma_{SV}^p} \quad (6)$$

Where  $\theta$  is the contact angle between the liquid and the solid. The two unknown components of the solid surface tension  $\gamma_{SV}^d$  and  $\gamma_{SV}^p$  in equation (6) can be determined from the previous measurements of the contact angles of different liquids with known values of surface tension components  $\gamma_{LV}^d$  and  $\gamma_{LV}^p$  (Table 1).

#### 4. RESULTS AND DISCUSSION

Capillary rise experiments were performed with test liquids listed in Table 1. Figure 1 shows the mass versus time plots and the square root fits of the adsorption tests with n-heptane, methanol and 66°C water for the GDL B. Adsorption data follow a square root law until they reach a plateau. 66°C water was found to wet samples leading to a direct measurement of internal contact angle to water at temperature representative of PEM Fuel cell operating conditions.

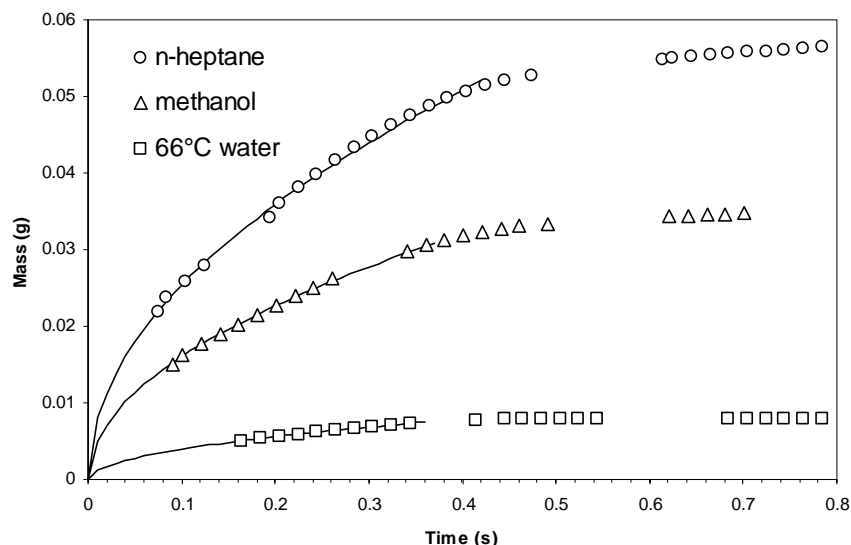


Figure 1. Mass versus time plots and square root fits of the adsorption tests for GDLB with n-heptane, methanol and 66°C – data are normalized to 1 cm wetted.

The Washburn constants of the three GDL materials were determined using n-heptane, with the assumption that the liquid totally wet the samples. All results are based on measurement of at least three samples for each bath. The average capillary constant determined with n-heptane and internal contact angle against test liquids for the three GDL are displayed in Table 2. The capillary constants were found to be similar among the three samples and repeatable with uncertainty of 4% for GDL A and GDL C and of 11% for GDL B. Since arccosine function is sensitive to angle variation close to  $\cos \theta = 1$  ( $\theta = 0^\circ$ ), the deviation of internal contact angle value is more weighty for low  $\theta$  value. Nevertheless the larger deviation on contact angle data observed for GDL B on methanol is partly due to uncertainty on capillary constant. Otherwise the deviation on contact angle data is  $5^\circ$  or less.

Table 2. The GDL capillary constants and internal contact angles against test fluids

Sample	Capillary constant ( $10^{-5} \text{ cm}^5$ )	Internal contact angle $\theta$ ( $^\circ$ )					
		1,Bromo-naphthalene	Toluene	Benzyl alcohol*	Acetone	Methanol	Water (66°C)
GDL A	$1.30 \pm 0.03$	$89 \pm 0$	$0^*$	$87 \pm 3$	$53 \pm 2$	$34 \pm 4$	$89 \pm 0$
GDL B	$1.59 \pm 0.18$	$89 \pm 0$	$58 \pm 10$	$89 \pm 0$	$68^* \pm 3$	$41 \pm 11$	$89 \pm 0$
GDL C	$1.26 \pm 0.05$	$88 \pm 0$	$61 \pm 4$	$87 \pm 1$	$70^* \pm 2$	$28 \pm 6$	$89 \pm 0$

\* Not used in subsequent analysis

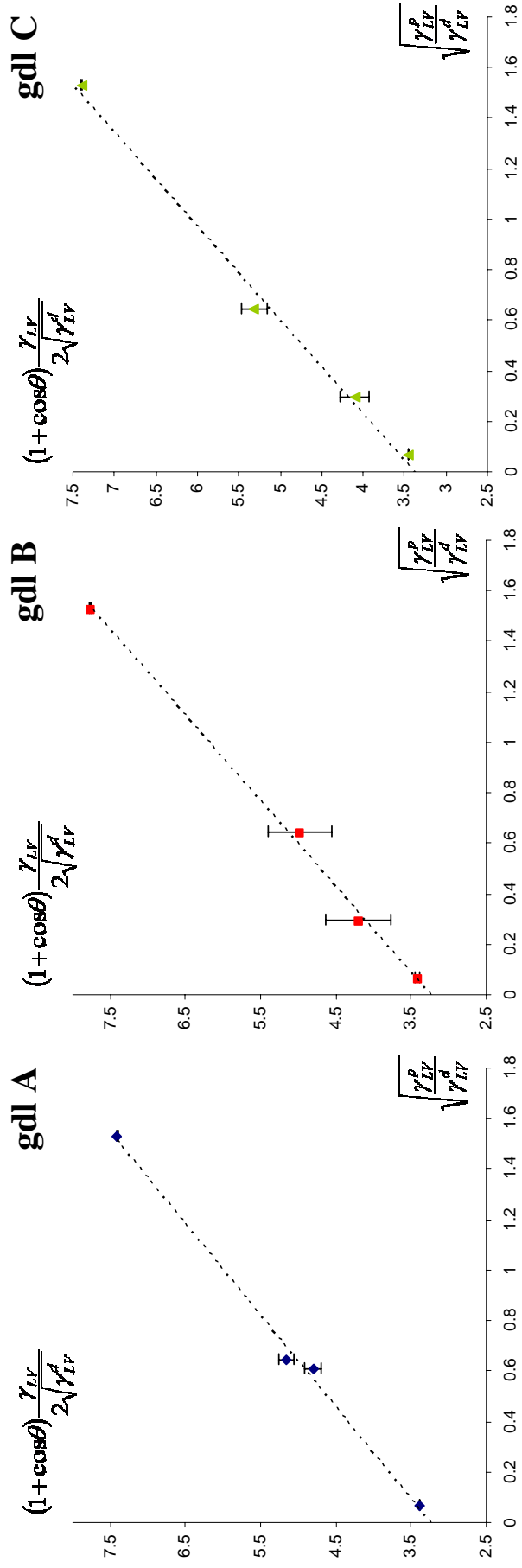


Figure 2. Owens-Wendt plots for GDL A, GDL B and GDL C

Table 3. The internal contact angles against 20°C water and the surface energies of the GDL material with polar and dispersive components.

Sample	$\gamma_{SV}^p$ (mJ.m <sup>-2</sup> )	$\gamma_{SV}^d$ (mJ.m <sup>-2</sup> )	$\gamma_{SV}$ (mJ.m <sup>-2</sup> )	$\theta_{H_2O}$ (°) @20°C
GDL A (10wt%)	7.6 ± 0.7	10.4 ± 0.7	18.0 ± 1.4	93 ± 3
GDL B (5wt%)	8.7 ± 0.7	10.3 ± 0.7	19.0 ± 1.4	90 ± 3
GDL C (20wt%)	7.3 ± 0.9	11.2 ± 0.9	18.5 ± 1.8	92 ± 3

Benzyl alcohol was found to poorly wet the samples. This is not consistent with the surface contact angle data from Kruss database of 78.6° for benzyl alcohol on a PTFE flat surface. This result may be due to relatively high viscosity of benzyl alcohol (6.218 mPa.s) which involve to a slower adsorption process. Thus, benzyl alcohol data were not used for subsequent interfacial surface energy calculation. On the other hand toluene was found to totally wet GDL A. As only liquids which have non-zero contact angles can be used in the Owens-Wendt model, this particular value was not considered for analysis.

Figure 2 presents the Owens-Wendt plots for the three GDL obtained with four test liquids. The linear fits of the experimental data yielded the dispersive and polar components of the surface energy. The surface energy values of the 3 GDL with their dispersive and polar components are displayed in table 3 together with internal contact angle to 20°C water extrapolated from Owens-Wendt plot according to method used in [10]. Surface energy results show that for GDL B and GDL C, the two carbon fibre papers based diffusion media, carbon polar component slightly decreases with increasing PTFE loading and, on the contrary, the dispersive component slightly increases with increasing PTFE loading. The resulting surface free energies values of the three GDL were found to be similar and close to 18 mJ.m<sup>-2</sup>. This value can be compared with the surface energy of pure PTFE. However the calculated contact angle to 20°C water have values lower than 110°, the contact angle value of water on pure PTFE flat surface. PTFE has only a dispersive component and is assumed to be capable of no polar type interactions whereas GDL materials have a polar component (about 40% of the total surface energy). Hammer et al. [16] reports a surface energy value of graphite fibres of 41.1 mJ.m<sup>-2</sup>, with 20% attributable to polar interaction capability. Most of GDL fibres are made from carbonized or graphitized polyacrylonitrile (PAN) fibers. Graphitic surfaces -sp<sup>2</sup> bonded- may include structures that provide some polar character to the carbon materials used in GDL, allowing polar interactions such as dipole-dipole and hydrogen bonding interactions between the GDL and the test fluids. The polar component may also be related to C-O or C-N functional groups attributed to residual material from ineffective graphitization or the result of former surface treatment or physisorbed impurities [16]. Further XPS experiments will allow the study of the surface chemistry its components' chemical states.

## 5. CONCLUSION

A detailed study of the wetting properties of three fuel cell gas diffusion layers having different morphologies and different contents of hydrophobic agent was presented. Internal contact angle to water at temperature representative of PEM Fuel cell operating conditions was directly obtained using the Washburn method with 66°C water as test liquid. The surface energy of the GDL fibres was determined by a combination of the Washburn method and the Owens-Wendt two parameters theory.

- Samples were found to be wetted by 66°C water with a contact angle of 88° indicating that the fibre surface is hydrophilic at temperature representative of PEM fuel cell operating conditions.
- The calculated surface energies were found to be low, close to 18 mJ.m<sup>-2</sup>. About 40% of the total surface energy value was related to a polar component.
- The polar component allows polar interactions such as dipole-dipole and hydrogen bonding interactions between the GDL and the test fluid. This can explain the wetting by water.
- The polar character of the GDL :
  - may be related to sp<sup>2</sup> bonded carbon which may include structures that provide some polar character to the carbon materials used in GDL
  - may be related to C-O or C-N functional groups attributed to residual material from ineffective graphitization or the result of former surface treatment or physisorbed impurities. Further XPS chemical analysis would clarify this point.

## 6. ACKNOWLEDGMENT

Financial support from GIP ANR (project ANR-06-PANH-022-02 “Chameau”) is gratefully acknowledged.

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