Water Management in PEM Fuel Cells

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Abstract

Water management is critical for well-functioning of the proton exchange membrane fuel cells (PEMFC). The gas diffusion layer (GDL) plays an important role in water management since humidification and water removal are both achieved through the GDL. Various numerical models developed to illustrate the multiphase flow and transport in the fuel cell. The accuracy of these models depends on the accurate measurement of the GDL properties such as wettability, surface energy, and porosity. Most of the studies conducted for measuring wettability of GDLs are based on the external contact angle measurements. However, the external contact angle does not describe adequately capillary forces acting on the water inside the GDL pores. In this study, the capillary penetration technique is used to determine the penetration rate of the liquid (into the GDL) from the experimental weight increase. The complete form of the Washburn's equation including gravity and inertial forces is implemented. Using the Newton-Raphson optimization technique, the experimental data is fitted to the theoretical curve (obtained by integrating the Washburn's equation) to find the contact angle, porosity, and average pore size of the porous media. It has been observed that the experimental weight increase is a consequence of two simultaneous processes: the capillary penetration inside the GDL and the formation of meniscus outside the GDL. The weight increase due to the latter is also considered in this study. Finally, the contact angle results are used to determine the surface tension of the GDL using the surface tension components approach.

Introduction

The PEM fuel cell consists of a membrane electrode assembly (MEA) sandwiched between two flow channels. The MEA contains a polymer electrolyte membrane (e.g. Nafion) embedded between two porous gas diffusion electrodes (GDE). The GDE is composed of a platinum catalyst and a gas diffusion layer (GDL) constructed from macro-porous substrates (i.e., carbon fiber or carbon cloth impregnated with polytetrafluroethylene (PTFE)) coated with one or more micro-porous layers (i.e., amorphous mixture of carbon and PTFE). PEM fuel cell technology has come a long way in the last few years. However, the performance of fuel cells still must be improved significantly before they can contribute a viable market. Recent experimental and numerical investigations identify water management as a critical factor in the design of robust and high-efficiency fuel cells. In essence, the ionic conductivity of the electrolyte is dependent on the hydration level of the membrane as water molecules transport hydrogen ions across the electrolyte. However, excessive water vapor condensation, due to lengthy operation or large output current, forms micro-droplets that cover the active sites on the catalyst layers, fill the pores of the GDL, and block the access of reactant gas to the reaction site. Typically, this is the origin of the limiting current for PEM fuel cells. Thus, water management is one of the major problems on the road to commercialization of PEM fuel cells. To enhance water management, it is necessary to study droplet formation and multiphase flow in the

internal network of the fuel cell, especially through the GDL as humidification and water removal are both achieved through this porous medium.

Experimental results obtained from a fluorescence microscopy technique show that water transport in the GDL is dominated by fingering and channeling effects which are dependent on the surface properties of the porous structure [1]. Also, in the models developed recently [2, 3, 4], the effects of the viscous and capillary forces as well as the porosity and wettability of the GDL on liquid water transport were elucidated. However, the wetting properties of the GDL were either approximated or measured using experimental methods such as the goniometry, capillary rise and Wilhelmy plate methods which only determine the external contact angles. The contact angle values of 120° (or even larger) have been reported for different GDLs using the external contact angle methods [4]. Since the contact angle of water on a pure PTFE surface is approximately 108°, these large values of contact angle cannot be due to the presence of the hydrophobic agent (PTFE) inside the GDL pores but rather due to surface roughness of the GDL. In general the external contact angle may describe qualitatively the wettability of the GDL, but it cannot be used as a quantitative estimation for calculations or design purposes. Thus, it is required to find a method that is capable of measuring the internal wettability of the GDL. The capillary penetration technique has been used to understand the relationship between pore structure, internal wettability and capillarity. In a recent study [5], this technique has been used to determine and further control the penetration of liquid into the GDL of the fuel cells. The modified Washburn's equation, which relates the capillary to the viscous forces, was used to measure the internal contact angle from the penetration rate of liquid into the porous media. The results obtained from this approach [5] show that for some testing liquids the values of contact angle are not defined. It has been shown [6] that the effect of gravitational and inertial forces is comparable to that of capillary and viscous forces, especially at the early stage of penetration (see Figure 1).
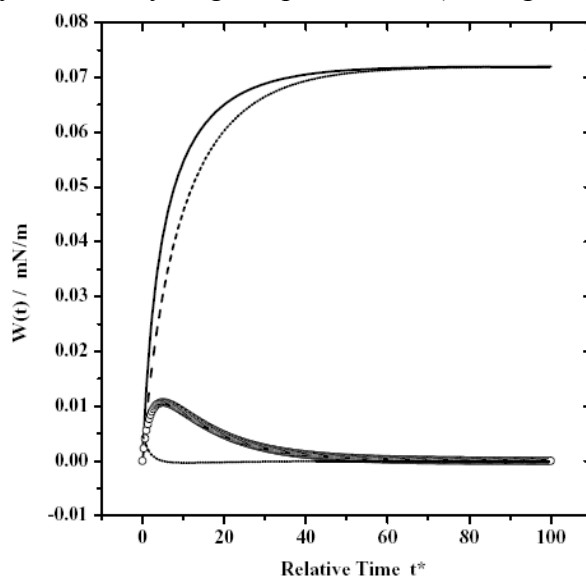

Figure 1. Comparison of the surface tension (-), gravity (- -), viscosity (∘∘∘), and inertial forces as liquid water penetrates into a sample porous medium (obtained from [6])

In this study, the complete form of the Washburn's equation is used. First, the experimental procedure carried out to measure the penetration rate of test liquids into a sample GDL is explained. The internal contact angles of these liquids are determined using an efficient optimization technique described in this paper. In essence, the Newton-Raphson method is used to fit the experimental data

(obtained from the experimental weight increase due to liquid penetration into a sample GDL) to the theoretical curve generated by integrating the Washburn's equation. The best fit will determine the internal contact angle. The results presented here will also show that the experimental weight increase is a consequence of two simultaneous processes: the capillary penetration inside the GDL and the formation of meniscus outside the GDL. The weight increase due to the latter is also presented in this paper. Finally, the internal contact angle results obtained from a variety of test liquids are used to determine the wettability and surface tension of the sample GDL using the surface tension components approach.

Materials and Method

The objective of this study is to find the wettability (i.e. the internal contact angle of water in the pores of the GDL) and surface tension of the porous medium. However, water cannot be used as the test liquid in the capillary penetration technique since the GDL samples are partly hydrophobic. In this approach, the capillary penetration experiments are conducted with a set of wetting fluids to find their internal contact angles in the sample GDL material. Later on, these internal contact angles are extrapolated to determine the wettability and surface energy of the GDL using the surface tension components approach.

The GDL sample was prepared by E-TEK division, DeNora North America (Somerset, New Jersey). The sample consisted of a single-sided carbon fiber cloth impregnated with a micro-porous sub-layer. The weight increase was measured using the 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 liquids used in this study includes pentene, methanol, acetone, cyclohexane, chlorophorm, and toluene. All test liquids were obtained from Fischer Scientific and were of HPLC grade. Figure 2 presents a typical weight increase due to penetration of pentane into the sample GDL.
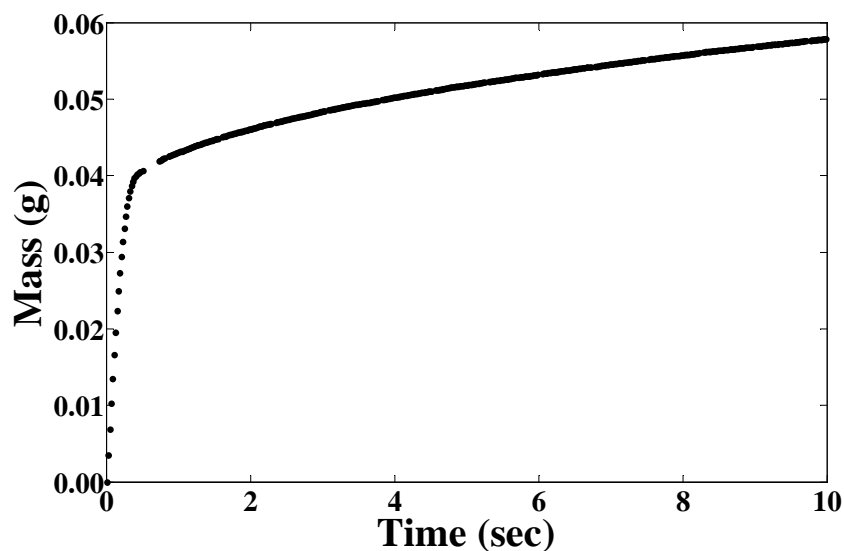

Figure 2. The weigh rise due to penetration of pentane into the sample GDL

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Washburn Method

The modified Washburn's equation, which relates the effect of surface tension and viscous forces without considering gravitational and inertial forces, has been used to find the wettability of porous media in [5, 7, 8]. The integration of the modified Washburn's equation results in a simple relation that predicts a linear behavior when the square of the increase of weight of the porous solid due to the liquid penetration is plotted as a function of the time. Thus, the internal contact angles presented in [5, 7, 8] were obtained by fitting a straight line to only a first few seconds of the mass-squared versus time plot since the deviation of the experimental data from the theoretical Washburn curve grow dramatically after the first few seconds. This significant deviation is because of neglecting the gravity an inertial terms. In this paper, the complete form of the Washburn's equation is used as

$$\underbrace{\frac{2}{R}\gamma_{lv}\cos\vartheta}_{Surface\ Tension} = \underbrace{\frac{g}{\rho A\varepsilon}m}_{Gravity} + \underbrace{\frac{8\eta}{R^2 A^2 \rho^2 \varepsilon^2}m\frac{dm}{dt}}_{Viscosity} + \underbrace{\frac{1}{\rho A^2 \varepsilon^2}\frac{d}{dt}\left(m\frac{dm}{dt}\right)}_{Inertia} \qquad (1)$$

where m and t present the mass of the test liquid penetrated into the porous media and the time, γ_{lv} and θ present the liquid surface tension and internal contact angle, ρ and η present the liquid density and viscosity, R and ε denote the average pore size and porosity of the porous medium, and A denotes the cross-section of the sample that is in touch with the test liquid.

An efficient optimization method (explained in the next section) is used to determine the internal contact angle based on the best fit between the experimental curve (like the curve in Figure 2) and the theoretical curve obtained by integrating the Washburn's equation. The integration is performed using Runge-Kutta method. The second order nonlinear ODE equation (1) is converted into the following set of first order nonlinear ODE equations:

$$\begin{cases} y'_1 = \dfrac{y_2}{y_1} \\ y'_2 = \dfrac{b}{c} - \dfrac{a}{c}y_1 - \dfrac{2}{c}y_2 \end{cases} \qquad (2)$$

where $y_1 = m$ and $y_2 = m(\dfrac{dm}{dt})$. Also, a, b, and c are the optimization parameters defined as

$$a = \frac{R^2 \rho^2 gA\varepsilon}{4\eta} \qquad (3)$$

$$b = \frac{(A\varepsilon\rho)^2 R}{2\eta}\gamma\cos\vartheta \qquad (4)$$

$$c = \frac{\rho R^2}{4\eta} \qquad (5)$$

For known liquid properties (i.e., liquid density, viscosity and surface tension), the best fit between the experimental and theoretical curves will determine not only the internal contact angle but also the average pore size and porosity of the porous media.

Optimization Procedure

To measure the agreement between the experimental weight increase and the theoretical curve (obtained by integrating the Washburn's equation), an objective function, E, is defined as the sum of the individual errors, e_i, given as

$$E = \sum_{i=1}^{N} e_i \qquad (6)$$

$$e_i = (y - Y)^2 \qquad (7)$$

where y and Y present the theoretical and experimental weight, respectively. The objective function, E, is a function of a set of parameters p, with elements p_k, $k = 1, \cdots, M$. The goal is to find the parameter set p that gives the best fit between the experimental points and a Washburn curve. The objective function E will assume a single absolute minimum value at one point in the M-dimensional space of E. In this study, p is the vector of three parameters (i.e., $p = \begin{bmatrix} a & b & c \end{bmatrix}^T$). To find the best fit between the experimental points and the theoretical curve, the objective function must be minimized. The necessary conditions for an extremum in the value of E are

$$\frac{\partial E}{\partial p_k} = \sum_{i=1}^{N} \frac{\partial e_i}{\partial p_k} = 0 \qquad k = 1, \cdots, M \qquad (8)$$

These extremum conditions form a set of algebraic equations in the variables p_k, $k = 1, \cdots, M$. An iterative solution is required to solve for these variables. There exist several methods to solve these systems of equations. There are no general or perfect methods for solving systems of nonlinear equations. Every method has advantages and disadvantages, and the choice of a particular method depends on the characteristics of the problem. The best known and most powerful one is the Newton-Raphson method. This method is very easy to implement and its asymptotic convergence rate is quadratic. In this study, the Newton-Raphson method was used to solve the system of Eqs. (8) since the required partial derivatives can be accurately computed. The iterative procedure of Newton-Raphson method can be expressed as

$$p^{i+1} = p^i - \Delta p^i \qquad (9)$$

where p^i is the vector of unknown variables at the i-th iteration step and Δp^i is a correction vector resulting from the solution of the associated linear system

$$H(p^i) \times \Delta p^i = E(p^i) \qquad (10)$$

The components of the vector $E(p^i)$ are the first partial derivative terms obtained from Eqs. (8) and evaluated at the i-th step. The Hessian matrix $H(p^i)$ is a symmetric matrix whose components are computed as follows:

$$\frac{\partial^2 E}{\partial p_k \partial p_l} = \sum_{i=1}^{N} \frac{\partial^2 e_i}{\partial p_k \partial p_l} \qquad (11)$$

One important advantage of this algorithm is that the value of the objective function and its first and second partial derivatives are all evaluated with the same degree of accuracy, since they can be evaluated analytically in terms of first order ordinary differential expressions that can be integrated numerically. The major limitation of the Newton-Raphson method is that it requires a good initial estimate of the optimization parameters. In this study, the initial values of the parameters are estimated using a Monte Carlo method which alters initial values for $p = \begin{bmatrix} a & b & c \end{bmatrix}^T$ by random amounts over numerous iterations until an error of 10^{-3} has been achieved. To refine each optimization parameters and enhance convergence, the incremental loading method [9] (with c as the loading parameter) was combined with the Newton-Raphson technique. In general, convergence is completed once an error of 10^{-6} or less was achieved.

Results and Discussion

The aforementioned optimization method was used to determine the internal contact angle for the test liquids. Figure 3 presents the result of the experimental weight increase of a GDL sample due to the penetration of a test liquid (i.e., pentane) and the best fitted theoretical curve. The result shows that the Washburn's equation is a correct model for the driving forces in capillary penetration except for the first few seconds of the experiment during which the weight increase is a result of two simultaneous phenomena: the capillary penetration inside the GDL, and the formation of meniscus outside the sample [10]. In this paper, both phenomena have been taken into account (see Figure 4). The mass increase due to both phenomena were calculated separately and combined. The total mass increase fits very well to the experimental weight increase (see Figure 5). The full fit represents the contact angle of the test liquid in the GDL.

The above procedure was repeated for different test liquids to calculate their internal contact angles. These results are summarized in Table 1.
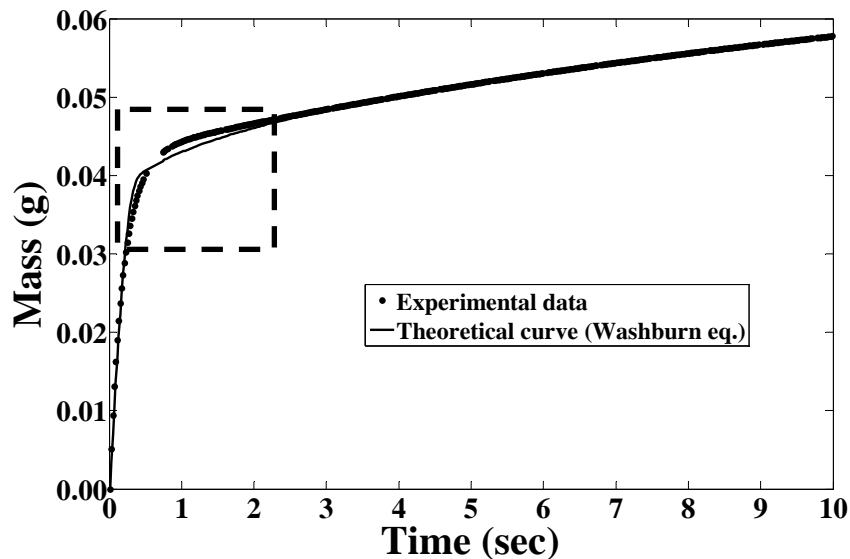

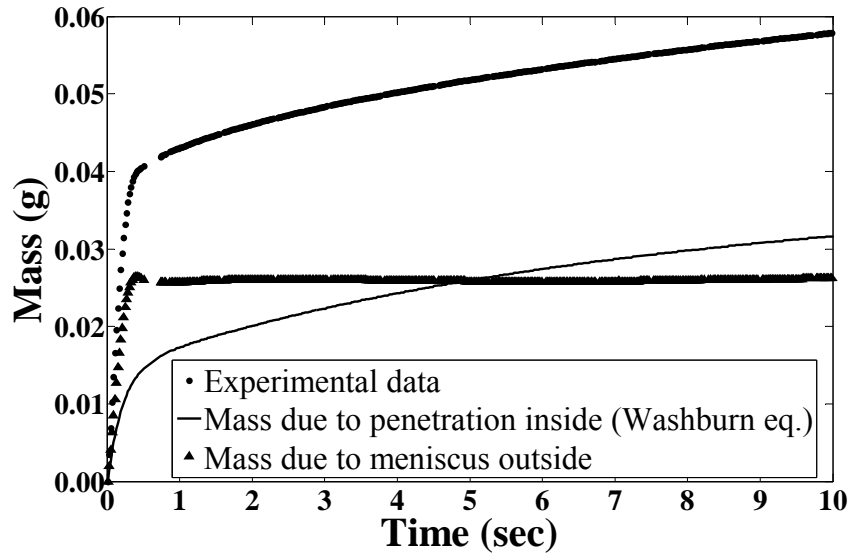**Figure 3.** The experimental weight increase and the best fitted Washburn's equation

Figure 4. The effect of the meniscus outside and the liquid penetration inside the GDL
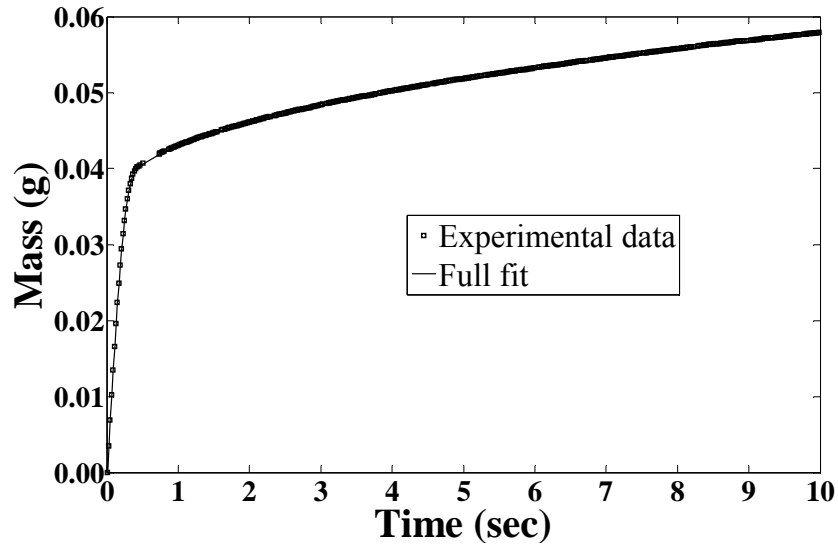

Figure 5. The combined effect of the meniscus outside and the liquid penetration inside the GDL

Table 1. Internal contact angle values for different test liquids

Test Liquid	γ_{lv}^{P} (mJ/m²)	γ_{lv}^{d} (mJ/m²)	γ (mJ/m²)	ρ (g/cm³)	η (mPa.s)	θ (deg.)
Pentane	0.0	15.4	15.4	0.626	0.224	0.0
Methanol	6.7	16.0	22.7	0.792	0.577	34.3
Acetone	6.4	17.3	23.7	0.791	0.326	29.2
Cyclohexane	0.0	25.5	25.5	0.779	0.980	41.2
Chloroform	0.0	27.2	27.2	1.483	0.568	47.5
Toluene	2.3	26.1	28.4	0.867	0.590	50.8

The internal contact angle values presented in Table 1 were used to calculate the wettability and surface energy of the sample GDL using the Owens-Wendt surface components approach (Eq. (12)). According to the Owens-Wendt two-parameter model, liquid and solid surface tensions consist of two components: dispersive and polar parts. In Eq. (12), the two unknown components of the GDL surface tension ($\gamma_{sv}^d, \gamma_{sv}^p$) can be determined from the previously measured contact angles against the sample liquids with known values of surface tension components ($\gamma_{lv}^d, \gamma_{slv}^p$).

$$\underbrace{(1 + \cos\theta)\left(\left(\gamma_{LV}^p + \gamma_{LV}^d\right)\Big/ 2\sqrt{\gamma_{LV}^d}\right)}_{Y_{OW}} = \underbrace{\sqrt{\gamma_{SV}^d}}_{A} + \underbrace{\sqrt{\gamma_{SV}^p}}_{B} \cdot \underbrace{\sqrt{\gamma_{LV}^p\Big/\gamma_{LV}^d}}_{X_{OW}} \tag{12}$$

A plot of Y_{OW} versus X_{OW} for different liquids yields the dispersive components 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 GDL. For the known value of $\sqrt{\gamma_{LV}^p/\gamma_{LV}^d}$ for water, the internal contact angle of water in the GDL pores can be calculated from the ordinate after extrapolation. Figure 6 represents the results obtained using this method. The internal contact angle of water and surface energy of the sample GDL determined in this study are 20.7 mJ/m^2 and 97.5°, respectively.
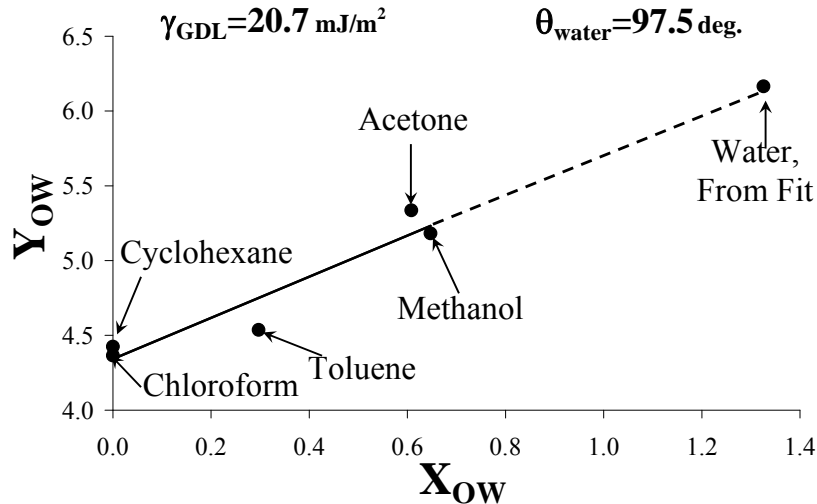

Figure 6. The wettability and surface tension of the GDL using the surface components approach

Summary

The knowledge of the surface properties of the GDL is of utmost importance in the study of water management in PEM fuel cells. Most studies conducted on the wettability of the GDL measure the external contact angle which is not indicative of the capillary forces acting on the water inside the pores. These methods depend on the surface roughness more than on the material composition of the GDL, i.e., a mixture of carbon and PTFE. As a result, the measured contact angle is larger than the contact angle of water on a pure PTFE surface. In this paper, the average internal contact angle and surface energy of a sample GDL were determined using the complete Washburn equation in conjunction with the surface components approach. Unlike the values obtained using external contact angle measurement techniques, the contact angle value calculated here is less than the contact angle of water on a pure PTFE substrate.

References

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