



Short communication

Measurement of water transport rates across the gas diffusion layer in a proton exchange membrane fuel cell, and the influence of polytetrafluoroethylene content and micro-porous layer

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ABSTRACT

Water management in a proton exchange membrane (PEM) fuel cell is one of the critical issues for improving fuel cell performance and durability, and water transport across the gas diffusion layer plays a key role in PEM fuel cell water management. In this work, we investigated the effects of polytetrafluoroethylene (PTFE) content and the application of a micro-porous layer (MPL) in the gas diffusion layer (GDL) on the water transport rate across the GDL. The results show that both PTFE and the MPL play a similar role of restraining water transport. The effects of different carbon loadings in the MPL on water transport were also investigated. The results demonstrate that the higher the carbon loading in the MPL, the more it reduces the water transport rate. Using the given cell hardware and components, the optimized operation conditions can be obtained based on a water balance analysis.

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1. Introduction

Water management in a PEM fuel cell significantly affects fuel cell performance and durability. The membrane electrode assembly (MEA), the key component in a PEM fuel cell, can only perform with proper water management, and poor water management can result in considerable durability loss. The hydration level of a proton exchange membrane is the major factor that determines its proton conductivity. If the amount of water in the membrane is low, the proton conductivity of the membrane will drop, as will the fuel cell performance. Low membrane hydration is usually associated with a high membrane degradation rate, due to attacks from radicals formed electrochemically or chemically during fuel cell operation. In some extremely dry conditions physical damage to the membrane may occur. Ideally, the membrane should be kept fully hydrated. But excessive water in the MEA could very possibly result in flooding of the catalyst layer, the gas diffusion layer, or even the flow field channels, which will result in dramatic mass transport loss and lead to a drop in fuel cell performance. Whenever flooding occurs in a PEM fuel cell, a series of events may occur, such as uneven electrochemical reaction, local heat build-up, cell

reversal, etc., all of which may seriously harm the durability of the fuel cell.

The gas diffusion layer (GDL) plays a key role in the delicate water balance required for the MEA. The GDL needs to keep sufficient water in the membrane and remove excessive product water away from the catalyst layer to avoid flooding of the catalyst layer and the GDL. The water transport rate across the GDL is thus vitally important for the GDL to fulfill this function, and depends heavily on the GDL's structure. Information about the effects of this structure on the water transport rate under different fuel cell operation conditions can be very important in designing a GDL with superior water management for a PEM fuel cell.

A GDL is usually made of a carbon fiber paper or carbon cloth treated with PTFE, then coated with a thin micro-porous layer (MPL). A great deal of effort has gone into investigating the effects of GDL structure, such as PTFE content, porosity, and permeability, on water transport capability and fuel cell performance. It was demonstrated that hydrophobic PTFE (e.g., Teflon[®]) treatment of the carbon fiber paper modifies the wetting characteristics of the GDL, which leads to improved water management [1,2]. Suitable PTFE content helps to effectively remove the liquid water from the GDL to the flow channels. Park et al. [3] intensively investigated the effects of PTFE content in GDLs on PEM fuel cell performance. They found that increasing PTFE content in the GDL lowers the liquid water ejection rate from the electrodes to the flow channels via the

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GDL. Wang et al. [4] found that a GDL with 15 wt% PTFE content had better electrochemical performance within the range of their investigations into different PTFE contents in the GDL.

Many researchers [5–13] have reported that an MPL can significantly improve the performance and durability of PEM fuel cells. An MPL is usually a very thin coating of carbon/PTFE composite on the GDL facing the catalyst layer, with loadings from a fraction of a milligram to several milligrams per square centimeter. The different types of carbon particles [5,9,12], carbon loadings [2,7,14], and PTFE contents [6,7,15,16] used in an MPL can influence PEMFC performance significantly. Qi and Kaufman [7] recommended an optimal loading of 35 wt% PTFE and 2.0 mg cm^{-2} carbon based on their study. Park et al. [16] investigated the effects of PTFE content in the MPL on water management in PEM fuel cells. The results indicated that PTFE in the MPL increases the resistance of the water flow across the GDL.

In our previous work we reported a simple technique for easily measuring the water transport rate across the GDL in a PEM fuel cell, along with our measurement results under different fuel cell operating conditions based on the established measurement technique. In this study, by applying the same measurement technique we further investigated the effects of both PTFE content and the application of a MPL to the GDL on the water transport rate across the GDL. The effects of carbon loading in the MPL on water transport were also studied. Using the given cell hardware and components, the optimized operation conditions can be obtained based on a water balance analysis.

2. Experimental

The experimental setup and water flux calculations are similar to those described in our previous report [17]. The cell was operated by a home-made fuel cell test station which allowed the control of air flow rate, air temperature, and coolant temperature. Air was fed to the cathode side of the cell with controlled humidity through a Fideris® bubbler humidifier (Fideris, USA). The water content of the humidified air that emerged from the humidifier at controlled dew point settings of 50, 60, and 70°C was measured as 40, 64, and 100% RH, respectively.

The membrane used is Nafion® 211CS from DuPont® (DuPont, USA) with a thickness of $25 \mu\text{m}$, which is the thinnest Nafion® membrane commercially available. On the one hand, the water diffusion rate is very high through this extreme thin membrane. On the other hand, on the “anode” side of the membrane are fed with liquid water, which keeps the membrane fully hydrated all the time. In other words, the membrane serves as a water supply to the “cathode” side. Therefore, by enhancing water diffusion through this thin membrane, water diffusion through the porous GDL becomes the rate-controlling step.

TORAY® TGPB-060 carbon fiber paper ($190 \mu\text{m}$ thick) was used for the GDLs. The GDLs treated with 0, 10, 20, and 40 wt% PTFE were purchased from E-TEK®, USA. To balance the membrane stress from both sides, the plain GDLs (without wet-proofing) were put on the “anode” side. Since the porous plain GDL is hydrophilic, the liquid water can easily transport through the plain GDL to the membrane. The preliminary test results proved that there were no obvious differences between water fluxes with and without a plain GDL on the “anode” side.

To avoid the effects of PTFE content in the GDL, the MPL was screen printed on the plain GDL when we were investigating the role of the MPL on water transport. The PTFE content in the MPL was 20 and 30 wt% and the carbon loadings in the MPL were 1.0 and 2.0 mg cm^{-2} , respectively.

The quantity of water transported across GDLs containing different PTFE content (0, 10, 20, and 40 wt%) and plain GDLs with

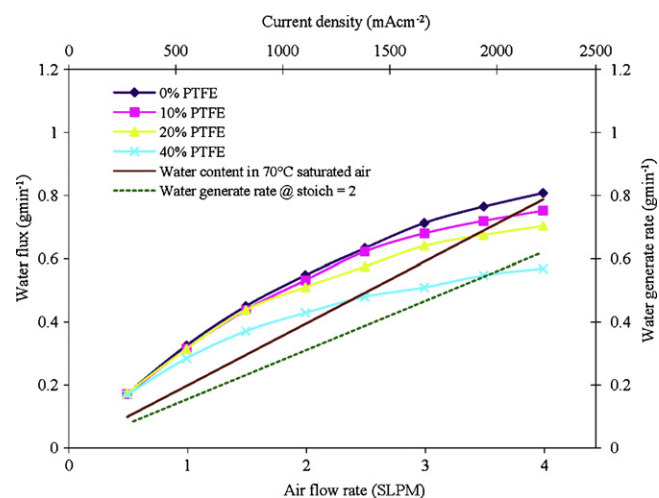


Fig. 1. Water flux through GDLs with different PTFE contents using 70°C dry feed air. PEM: Nafion® 211CS, $7 \text{ cm} \times 7 \text{ cm}$. GDL: TORAY® TGPB-060, 0, 10, 20, and 40 wt% PTFE-treated GDL on the cathode, respectively, and plain GDL on anode. Anode: deionized water; cathode: dry air at 70°C .

different MPLs was measured at different air flow rates (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 SLPM (standard liter per minute)) and under different humidities (0, 40, 64, and 100% RH). The maximum flow rate in our experiment was 4 SLPM, which corresponds to an air stoichiometric ratio of 4.5 at a current density of 1 A cm^{-2} for a 50 cm^2 fuel cell. This flow rate is higher than that of a practical PEM fuel cell cathode (the stoichiometric number is 2–4). A higher stoichiometric ratio is not desirable as it consumes more parasitical power, which decreases the system efficiency. The cell temperature was controlled at 70°C during the measurements.

3. Results and discussion

3.1. Effects of PTFE content in the GDL on the water transport rate

Fig. 1 shows the plots of the water transport rate (water flux measured at 70°C with dry air feed) across the GDLs with different PTFE content (0, 10, 20, and 40 wt%) against the air flow rate, in comparison with the water transport rate by saturated vapor, which is calculated using the saturated vapor pressure at 70°C . To elucidate the water transport and balance scenario in the GDL, the product water generation rate is plotted against the current density in the same figure, assuming the stoichiometry is 2, which is usually used for PEM fuel cells in automotive applications. From Fig. 1, it is clearly seen that the water transport rate decreases with increasing PTFE content in the GDL. The effect is more pronounced at high air flow rates. Thus, it is obvious that the role of PTFE in the GDL is to keep water from crossing the GDL into the flow field channels. This may help keep sufficient water in the membrane to maintain its high conductivity. But with dry air feed, even for the GDL with 40 wt% PTFE the water transport rate across the GDL is still much higher than the water production rate at a stoichiometry of 2. Therefore, at 0% RH operational water balance (i.e., balance between water produced and water transported away) cannot be achieved at the cathode. In other words, it is impossible to realize 0% RH operation simply by modifying the GDL structure with hydrophobic treatment.

If the air flow rate is not too high, the water flux is higher than the saturated vapor carried away by the air. This means that the water crossing the GDL is partially in vapor form and partially in liquid form. It is difficult to tell precisely by this experiment how the PTFE content in the GDL affects the vapor transport rate and the liquid water transport rate. But the results at high air flow rates show that

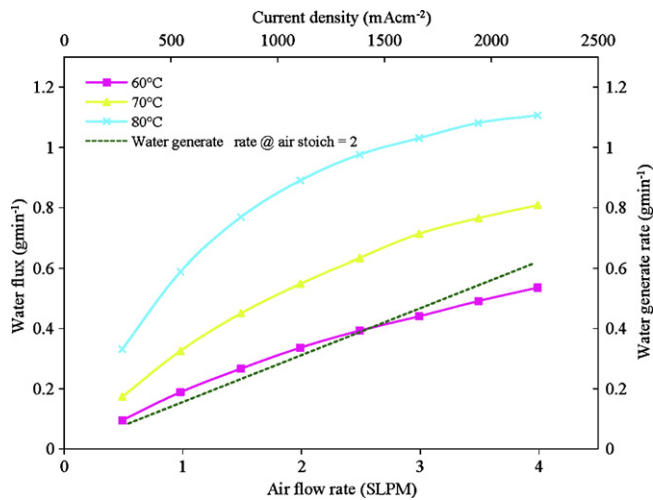


Fig. 2. Water flux through plain GDLs using dry feed air at different temperatures. PEM: Nafion® 211CS, 7 cm × 7 cm. GDL: TORAY® TGPH-060, plain GDL on the cathode and anode. Anode: deionized water; cathode: dry air at 60, 70, and 80 °C.

the water flux is less than the saturated vapor carried away by the air, and decreases with increasing PTFE content in the GDL. It means that the PTFE in the GDL has effect on the vapor transport rate in the GDL. The more PTFE in the GDL, the lower the vapor transport rate across the GDL. It can also be seen that the higher the PTFE content in the GDL, the earlier the water flux curve intercepts with the saturated vapor curve. This means the PTFE in the GDL also has an effect on the liquid water transport rate. The higher the PTFE content in the GDL, the lower the liquid water transport rate across the GDL. In summary, the PTFE in the GDL lowers both the vapor and the liquid water transport rates across the GDL.

3.2. Effects of temperature on water transport across the GDL

Fig. 2 shows the effects of operating temperature on the water transport rate across the GDL. In this experiment, a plain GDL (0 wt% PTFE) was used under dry air feed conditions. It is easy to see that the water transport rate is very sensitive to the operating temperature. The higher the temperature, the greater the water transport rate. The most interesting point to observe from this figure is that a good water balance can be achieved by operating the fuel cell at 60 °C under 0% RH conditions with a GDL of very simple structure (no PTFE, no MPL). This tells us two things. First, 0% RH operation is possible if a suitable GDL and suitable operating temperature are used. Second, when choosing a GDL, its structure and the operating conditions need to be considered simultaneously.

3.3. Effects of the MPL on the water transport rate

To separate the effects of the MPL from those of the PTFE in the GDL, we used a GDL consisting of a MPL coated on a plain GDL (carbon fiber paper only). The carbon loading of the MPL was 2.0 mg cm⁻² and the PTFE content in the MPL was 30 wt%.

The water fluxes measured using the plain GDL and the MPL-coated GDL are compared in Fig. 3. If the air flow rate is less than 1 SLPM, there is no obvious difference in water flux between the two types of GDLs. At air flow rates higher than 1 SLPM, the water flux across the MPL-coated GDL is significantly lower than that across the plain GDL. The effect is more pronounced with increasing air flow rate. As the air flow rate increases, more water is taken up from the membrane to the micro-pores in the MPL, leading to a higher capillary pressure in these pores. Higher capillary pressure decreases the water transport efficiency from the membrane

to the GDL. Although the absolute water flux increases, the rate of increase slows down compared with the rate without the MPL. The phenomenon is quite similar to what occurs with the PTFE-treated GDL. The role of the MPL is also to reduce the water transport rate across the GDL. But adding the MPL to the plain GDL does not bring the water transport rate sufficiently close to the water generation rate to keep the membrane from drying out. In other words, 0% RH operation cannot be achieved just by adding a MPL to the GDL.

Since the pore size in the MPL ranges from 0.1 to 0.5 μm, much smaller than that in the carbon fiber paper, which ranges from 10 to 30 μm, the influence of capillary effects on water transport is more significant in the MPL than in the carbon fiber paper. Thus, the MPL prevents the water from transporting across the GDL. The hydrophobic pores in the MPL, from the PTFE, also contribute to the capillary effect at the interface between the membrane and the GDL. This result is in accordance with that from the multi-phase mixture (M²) modeling done by Pasaogullari et al. [11], who concluded that the MPL reduces the water flux toward the cathode and prevents cathode flooding.

3.4. Effects of the carbon loading in the MPL on the water transport rate

The carbon loading in the MPL also plays an important role in the water transport rate. Different carbon loadings in the MPL lead to different MPL microstructures, as well as variable gas permeability. Fig. 4 shows the effects of carbon loadings in the MPL on water flux. The carbon loadings investigated were 1.0 and 2.0 mg cm⁻², and the PTFE content in the MPL was 20 wt%. The water flux through the GDL with a MPL that has 2.0 mg cm⁻² carbon loading is obviously lower than the flux with 1.0 mg cm⁻² loading at all flow rates. This indicates that a higher carbon loading in the MPL is prone to reduce the water flux. Since a higher carbon loading cause the tighter porous structure of the MPL and less mass transport channels in the MPL, a lower gas permeability could be obtained using the GDL with a MPL, with water passage more difficult as a result.

Generally speaking, to simplify the design of a fuel cell system, a less humidified gas feeding is preferred. However, a drier gas feeding may dehydrate the membrane. Since a higher carbon loading in the MPL could reduce the water transport rate from the membrane to the GDL, in practice, a higher carbon loading may help to hold the

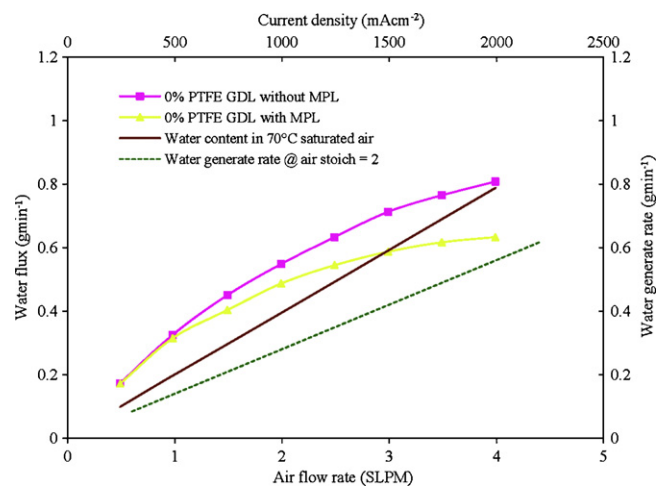


Fig. 3. Water flux through the GDLs with and without MPL using dry feed air at 70 °C. PEM: Nafion® 211CS, 7 cm × 7 cm. GDL: TORAY® TGPH-060, plain GDL or plain GDL with MPL on the cathode and plain GDL on the anode. MPL: 2.0 mg cm⁻² carbon loading in the MPL with 30 wt% PTFE content. Anode: deionized water; cathode: dry air at 70 °C.

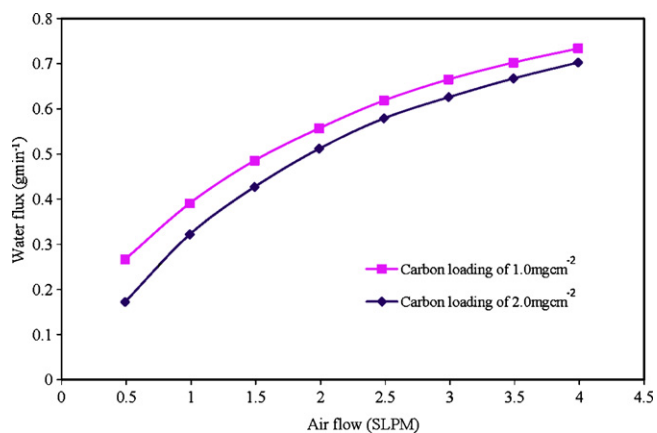


Fig. 4. Water flux through the GDLs with different MPL carbon loadings at 70 °C. PEM: Nafion® 211CS, 7 cm × 7 cm. GDL: TORAY® TGPH-060, plain GDL on the anode; plain GDL with different MPLs on the cathode. MPL: 1.0 and 2.0 mg cm⁻² carbon loading in the MPL with 20 wt% PTFE content. Anode: deionized water; cathode: dry air at 70 °C.

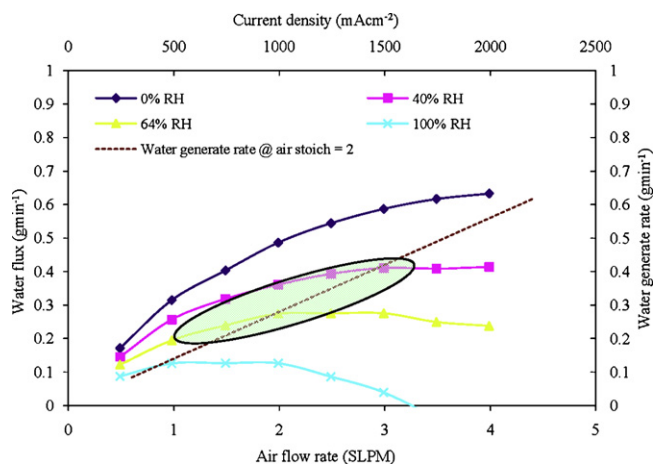


Fig. 5. Water flux through GDLs with MPL using different RH feed airs at 70 °C. PEM: Nafion® 211CS, 7 cm × 7 cm. GDL: TORAY® TGPH-060, plain GDL with MPL on the cathode and plain GDL on the anode. MPL: 2.0 mg cm⁻² carbon loading in the MPL with 30 wt% PTFE content. Anode: deionized water; cathode: different RH airs at 70 °C.

water in the membrane and prevent it from drying out, especially when dry gases are used.

3.5. Effects of RH on the water transport rate

The above results show that at fuel cell operation temperatures of 70 °C and above, modification of the GDL with either hydrophobic PTFE treatment or the addition of a MPL will not bring down the water transport rate across the GDL to close to the water production rate at 0% RH. To maintain water balance in the MEA, a certain level of humidification is still needed when the fuel cell is operated at or above 70 °C. Fig. 5 presents the effects of RH on the water transport rate across a plain GDL with a MPL (30% PTFE content and 2.0 mg cm⁻² carbon loading in the MPL). The solid lines show the actual water flux across the GDL and MPL (not including the water brought in by the feed air) at different air flow rates under the conditions of 0, 40, 64, and 100% RH for the feed air. It can be seen that water flux decreases with increasing RH, as air with higher RH has less capability to remove water. The dashed line is the water production rate as a function of current density at an air stoichiometric ratio of 2. Using the given cell hardware, components, and air stoichiometry, a dry feeding air removes more water from the

cathode than the amount of water generated there, according to Fig. 5. Thus, the membrane is prone to dry out, resulting in poorer proton conductivity and inferior cell performance. If the feed air is 100% humidified, the poor water removal capability of the air flow leads to inadequate removal of the water generated in the cathode when the current density is over 500 mA cm⁻², as can be seen in Fig. 5, which may cause flooding and thus a performance drop or unstable cell performance. Based on the above analysis, the shaded area in Fig. 5 can be marked as the possible water balance operation condition area. If the operating current density is from 500 to 1100 mA cm⁻², a practical fuel cell operating range, the water flux of 64% RH feeding air is very close to the water production rate and therefore the water is easily balanced within the cell. However, if the current density is from 1100 to 1500 mA cm⁻², the 64% RH feeding air will inevitably face the problem of flooding, whereas the 40% RH feeding air is more effective in maintaining the water balance within the cell. Although the data provided here are only quantitatively valuable for the given cell hardware and components, the method we developed can be applied to any cell hardware and components.

Another interesting phenomenon observable in Fig. 5 is that the water flux of 100% RH feeding air is positive if the flow rate is less than 3 SLPM. Apparently, the water activity is 1 on each side of the membrane when 100% RH air is fed, and there should not be a driving force for water transport in either direction. However, the pore size in the MPL ranges from 0.1 to 0.5 μm. In these micro-pores, capillary force plays an important role in the water status. When the saturated water passes through the MPL to the GDL, in which the pore size ranges from 10 to 30 μm, capillary effects have much less influence so the gaseous water might condense as tiny droplets due to the lower saturation pressure compared with that in the MPL. The liquid droplets congregate and are then removed by the air flow. However, if the flow rate is relatively higher, the shearing force might balance the capillary effects in the MPL, resulting in zero water flux.

4. Conclusions

The membrane, the GDL and its properties, and the MPL, together with the operating conditions, determine the water transport rate in the MEA for PEM fuel cells. In this short communication, the water transport rate across GDLs with varying PTFE contents and varying MPLs was measured at different air flow rates, temperatures, and humidification levels. The results show that both PTFE and MPLs play a role in reducing the water transport rate across the GDL. The water transport rate is very sensitive to operating temperature; specifically, increasing operating temperature significantly increases the water transport rate across the GDL. Conversely, increasing the humidification of the feed air significantly decreases the water flux across the GDL. A higher carbon loading in the MPL helps to prevent the membrane from drying out when less humidified feed gases are used in an operating fuel cell.

For the given fuel cell hardware and components in this work, neither dry nor water-saturated feed air is a good choice for operating the cell. Feed airs of about 64% RH and 40% RH are preferable to operate the PEM fuel cell in a current density range of 500–1100 and 1100–1500 mA cm⁻², respectively. To sum up, the method developed in this work could be useful for selecting cell components and their properties and optimizing fuel cell operating conditions.

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