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Water transport in gas diffusion layers of PEM fuels cells in presence of a temperature gradient. Condensation effect.

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ABSTRACT

The gas diffusion layers (GDL) are crucial components as regards the water management in proton exchange membrane fuel cells. The present work aims at clarifying the mechanisms of water transport in GDL on the cathode side using pore network simulations. Various transport scenarios are considered from pure diffusive transport in gaseous phase to transport in liquid phase with or without liquid-vapor phase change. A somewhat novel aspect lies in the consideration of condensation and evaporation processes in the presence of a temperature gradient across the GDL. The effect of thermal gradient was overlooked in previous works. The temperature gradient notably leads to the possibility of condensation because of the existence of a colder zone on the channel side. The pore network simulations lead to phase distributions in qualitative agreement with X-Ray tomography visualizations. The simulations also indicate that the probability of GDL water flooding increases with the distance from the bipolar plate channel inlet.

Keywords: Gas Diffusion Layers, PEM Fuel Cells, Pore Network Simulations, Water Management, Condensation

1. Introduction

The gas diffusion layer (GDL) in PEMFC has several functions, [1]. For instance, the GDL contributes to make more uniform the gas supply to the active layer. The GDL must also contribute to the water management by enabling the water in excess to leave the system on the cathode side without affecting too much the oxygen access to the active layer. A key question in this context is the nature of the water within the GDL, i.e. in gaseous phase or in liquid phase. Obviously, the transfer of the water in excess in vapor phase sounds the best option if the objective is to maintain all pores in the GDL accessible to oxygen. On the other hand, a GDL made hydrophobic generally leads to better performance. A possible effect of a hydrophobic agent makes sense only if water is present in liquid phase in the GDL. If the water transfer is in liquid phase, then as discussed in [2], it is indeed much better to make the GDL

hydrophobic because this favors the formation of liquid capillary fingers occupying a small fraction of the pore space. The complementary fraction, free of water, is therefore available for the oxygen transport. Then it must be pointed out that a PEMFC typically operates at a temperature of about 80°C, which corresponds to a relatively high saturation pressure. Furthermore, as discussed for example in [3], there should be a temperature difference across the GDL with the highest temperature on the active layer side. Since the GDL is colder on the bipolar plate side, water condensation is likely and can be another mechanism leading to the occurrence of liquid water in the GDL. Also, because of the temperature gradient or because the relative humidity in the bipolar plate channel can be lower than 100%, evaporation is also possible. In brief, several options are possible as regards the water transport across the GDL: 1)

transport in vapour phase only, 2) transport in liquid phase only, 3) transport with liquid – vapor phase change.

In this context, the present work discusses different mechanisms of water transport in the gas diffusion layer (GDL) on the cathode side from a combination of simple estimate and two-dimensional pore network simulations in relation with the water management issue.

2. Pore Network simulations

The modeling of transport phenomena in porous media is generally performed within the framework of the continuum approach to porous media. This approach considers volume-average transport equations and relies on the concept of length scale separation, i.e. the averaging volume should be small compared to the size of the porous domain for the Darcy's scale equations to make sense. As discussed for instance in [4], a GDL is only a few pore sizes thick. This is an example of thin porous media [5] in which the length-scale criterion is not satisfied. Furthermore, as also discussed in [4], the scenario of slow liquid invasion in a hydrophobic porous medium leads to a regime called the capillary fingering regime, which is fractal and thus not compatible with the volume-averaged equations. The fact that the continuum approach is highly questionable is a strong argument in favor of an alternate approach. As in several previous works, e.g. [6], [7], [8] and references therein, we use a pore network approach. In the pore network approach, the pore space is represented by a network of pores interconnected by channels. The transport of interest is directly computed at the pore network scale outside the continuum framework. For simplicity, we consider a regular two-dimensional lattice as sketched in Figure 1. The pores correspond to the nodes of the network. The interconnecting channels between two pores correspond to the constrictions or throats of the pore space. The pores are idealized as cubic bodies and the throats are ducts of square cross-section. The pore network is constructed by assigning pore body sizes from a Gaussian distribution in the range $[d_{\min}, d_{\max}]$ with $d_{\min} = 20$ microns and $d_{\max} = 34$ microns. The size of the porous domain is $\ell \times L$ where ℓ is the GDL thickness. As discussed in [4] representative values of L and ℓ are: $L \sim 2\text{mm}$ and $\ell \sim 300$ microns. The lateral size L corresponds to a unit cell containing a rib and two half-channels of the bipolar plate. At the bipolar plate side, one part of the GDL is in contact

with a solid phase, the rib, whereas the other part is in contact with the channel providing the oxygen. The lattice spacing (= the distance between two pores) is equal to 50 microns so that a 40×6 pore network is considered (40 is the number of pores in the lateral (in-plane) direction and 6 the number of pores across the GDL (thus in the through plane direction)).

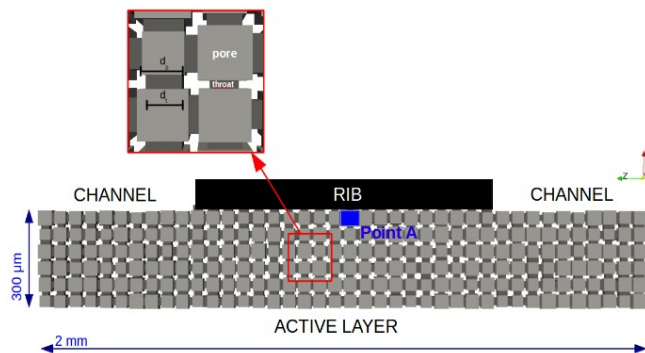


Figure 1: Sketch of GDL as a two-dimensional pore network

3. Water transfer in vapor phase or in liquid phase ?

To discuss the nature of the water transfer within the GDL, we begin with some simple analytical computations. We assume that all the water produced in the active layer as a result of the electro-chemical reaction is directed toward the GDL on the cathode side. This is a conservative estimate since a fraction of the produced water should actually go toward the anode side. The production rate (in mol/s) is classically expressed as a function of the current density in the fuel cell as,

$$Q = \frac{iA}{2F} \quad (1)$$

where F is the Faraday's constant ($F = 96485.34$ C), i is the current density and A the cross-section surface area of the network ($A = 40 \times 50\text{microns} \times 50$ microns with our 2D approach).

Suppose the water transfer takes place in vapor phase by diffusion and consider for simplicity the gas as a binary mixture of oxygen and water vapor. An important parameter is then the relative humidity, denoted by RH , in the channel. The gas at the fuel cell inlet is not dry but humidified. Considering automotive applications, we can take for example $RH = 50\%$ at the inlet. As a result of

water production, the relative humidity is expected to increase along the channel and can even be expected to reach almost 100% RH at the outlet of the fuel cell. Accordingly, we vary in what follows RH from about 50% to 100%. An additional simplification is to suppose that the gas is fully vapor saturated in humidity at the inlet of the GDL (the GDL inlet is the interface between the active layer and the GDL). Under these circumstances, the diffusive transport of the vapor can be expressed as,

$$J = \frac{cA}{\ell} D_{app} (\ln(x_{vsat}(T_{al})) - \ln(RH x_{vsat}(T_c))) \quad (2)$$

with $c = p/RT$ where p is the total pressure ($p \sim 1.5$ bar), R is the gas constant, ℓ is as before the thickness of the GDL ($\sim 6 \times 50$ microns); $x_{vsat}(T_{al})$ is the vapor mole fraction at the active layer - GDL where T_{al} is the temperature at this interface; $x_v = RH x_{vsat}(T_c)$ at the GDL/channel interface where x_v is the mole fraction of vapor and T_c is the channel temperature. When the temperature is considered as uniform over the GDL ($T_{al} \approx T_c$), Eq.(3) can be further simplified as

$$J = -\frac{cA}{\ell} D_{app} \ln(RH) \quad (3)$$

In Eqs. (2) and (3), D_{app} is the apparent diffusion coefficient of the GDL. It differs from the molecular diffusion coefficient because of the presence of the porous microstructure. Using the same method as reported for instance in [9], this coefficient is computed from pore network simulations. D_{app} was actually calculated for two different conditions. The first one (indexed by 1), is a GDL partially blocked by the rib as depicted in Figure 1. The second one (indexed by 2) is when the rib effect is not considered. Thus the GDL is in contact with a gas at specified concentrations over the entire outlet. Repeating the simulations for 10 different realizations of network and ensemble-averaging the results led to $D_{app2} / D = 0.29$ and $D_{app1} / D = 0.19$ where $D = \epsilon D_{wa}$ with ϵ the porosity of the network (~ 0.65) and D_{wa} the molecular diffusion coefficient of vapor ($D_{wa} = 3.08 \cdot 10^{-5} \text{ m}^2/\text{s}$ at 60°C). In our convention, the porosity is taken into account with the molecular diffusion coefficient.

Thus the bending of flux lines due to the presence of the rib

leads to a decrease by a factor of 2 of the apparent diffusion coefficient obtained without rib.

This enables us to define the critical current density i_c beyond which it is not possible to transfer all the produced water by diffusion in vapor phase through the GDL. This current is given by the equation $J = Q$. This yields,

$$i_c = -\frac{2F c}{\ell} D_{app} \ln(RH) \quad (4)$$

The ‘‘critical’’ current i_c is plotted as a function of RH in Figure 2.

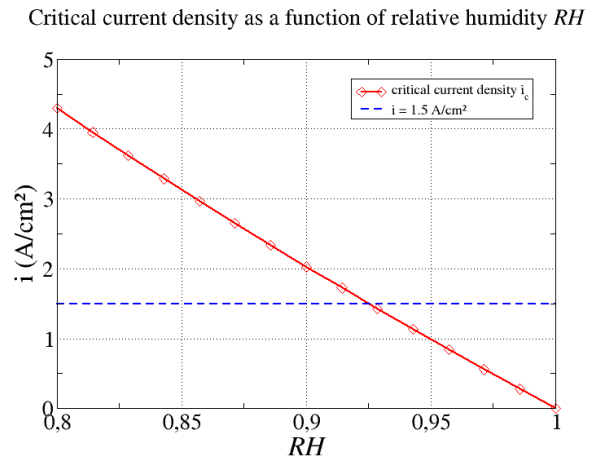


Figure 2: a) Critical current density i_c as a function of relative humidity RH in the channel. The dotted line corresponds to the current density of 1.5 A/cm^2 , which is a typical high current density value in PEMFCs.

The results plotted in Figure 2 suggest that the produced water can be carried away in vapor phase as long as RH in the channel is lower than about 92%. The conclusion of this section is therefore that at least two regions should be distinguished when analyzing the transport of water in the GDL in a fuel cell. In the region sufficiently away from the bipolar plate channel outlet for the relative humidity in the channel to be sufficiently low, the transfer would be in vapor phase only. Closer to the outlet, the transfer is not possible in vapor phase only and thus water should be present in liquid form, at least for sufficiently high current densities. Note, however, that the results shown in Figure 2 were obtained assuming a uniform temperature across the GDL. It is surmised that the existence of a temperature

gradient can change the value of the critical current but not the main conclusion, i.e. the presence of liquid water when the relative humidity is sufficiently high in the channel.

4. Transfer in liquid phase neglecting phase – change phenomena.

Contrary to the assumption made in the previous section, several authors have considered that water enters the GDL directly in liquid phase, e.g. [2], [4], [6], [7], [10], [11] to cite only a few. Further investigations on what really happens in the active layer would be certainly desirable to confirm this scenario. However, we note that such a scenario is consistent with the phase distributions obtained using in Situ X-Ray Tomographic microscopy techniques and reported in [12] and the observation of droplets at the GDL surface. The consideration of this scenario typically leads to a capillary fingering invasion pattern as exemplified in Figure 3. The 3D version of this pattern is qualitatively consistent with the experimental visualizations reported in [12].

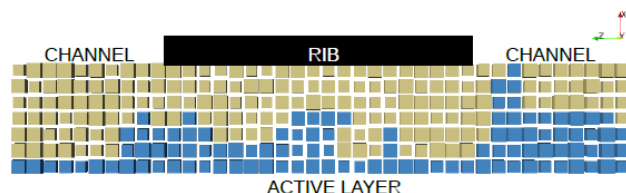


Figure 3. Two-dimensional typical slow invasion pattern in a hydrophobic layer from pore network simulation. Liquid phase in blue, gas phase in white, solid phase in brown.

As discussed in some details in [6], one problem with this type of simulation lies in the boundary condition to be imposed at the inlet. It was argued in [6] that the consideration of independent multiple injection points at the GDL inlet was a better option than the traditional reservoir-like boundary condition. This, however, does not change the main feature of invasion pattern. In other words, both boundary conditions lead to patterns qualitatively consistent with the available visualizations.

5. Transfer by evaporation with partial invasion of the GDL

In section 4, we briefly consider the purely liquid invasion scenario ignoring the possible phase change phenomena.

Since the vapor partial pressure at menisci along the boundary of the invading liquid cluster is the saturation vapor pressure then a transfer by vapor diffusion from these menisci toward the channel (supposed at a lower partial pressure in vapor) is possible.

This kind of situation can be easily simulated using a pore network model. The algorithm we developed for that purpose can be summarized as follows. Initially, the network is only occupied by the gas phase and the liquid/gas interface is supposed to coincide with the GDL/Active layer interface. As for the other cases considered in this article, the medium is supposed to be fully hydrophobic so that the invasion percolation algorithm, [13], can be used for modeling the liquid invasion on the network

- 1) Let $i > i_c$. Determine the flow Q to be transferred from Eq. (1).
- 2) Determine the next throat to be invaded by the liquid using the classical invasion percolation algorithm [13]. Invade the corresponding throat and adjacent pore.
- 3) For the new position of the liquid-gas interface within the network, compute the molar flow J which is transferred by diffusion in vapor phase between the liquid/gas interface and the channel. Thus we impose $x_v = RH x_{v,sat}(T)$ at the GDL/channel interface, a zero-flux condition at the GDL/Rib interface and $x_v = x_{v,sat}(T)$ on each meniscus which are in the system. This part of the algorithm is similar to the one presented in [9] for the calculation of the apparent diffusion coefficient D_{app} .
- 4) If $J < Q$ continue the invasion going back to 2). If $J \sim Q$, the steady-state solution with partial invasion is obtained.

An example of a result obtained with this algorithm is shown in Figure 4.

We are not aware of in-situ visualizations, similar for example to the ones reported in [12], consistent with this scenario of partial liquid invasion with evaporation. It should be noted, however, that a special, very small fuel cell was designed for making possible the visualizations reported in [12]. Thus, further investigations are needed to confirm experimentally the scenario illustrated in Figure 4.

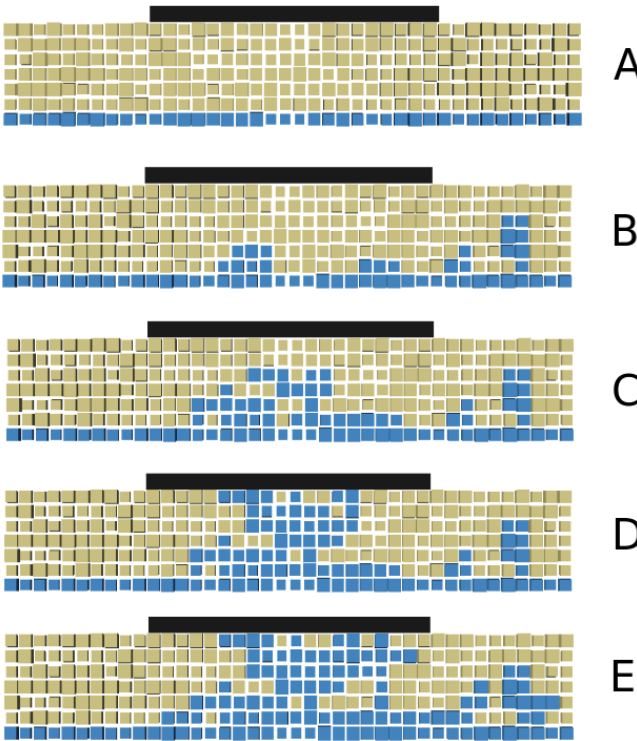
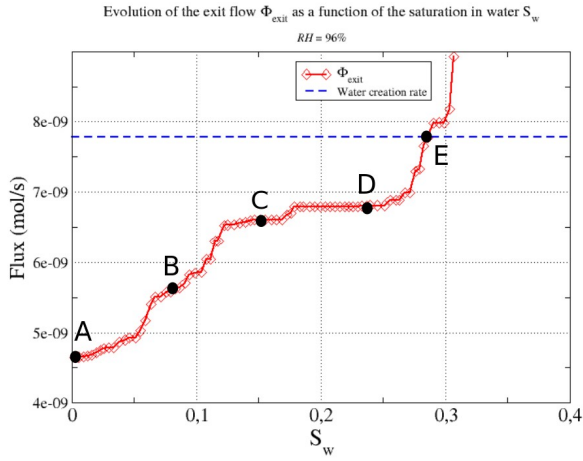


Figure 4. On top is plotted the flux transferred at the exit of the network for several invasion states of the GDL ($T = 80^{\circ}\text{C}$). S_w is the saturation. At the bottom, the invasion patterns are related to the points on the top figure. Steady-state is reached (point E) when evaporation is sufficient along the liquid–gas interface for transferring the produced water after partial invasion of network. Liquid phase in blue, gas phase in white, solid phase in brown.

Interestingly, a partial invasion of the GDL by the liquid water contributes to maintain a better access to oxygen

compared to the situation, depicted in Figure 3, where the evaporation phenomenon is not taken into account or is negligible (which can occur when the relative humidity in the channel is very high, close to 100 % for example).

6. Transfer with condensation phenomenon

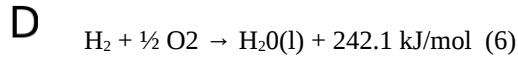
Until now, we have considered the temperature as uniform across the GDL. As mentioned before, authors, e.g. [3] for instance, have shown that a temperature difference of a few K could occur between the hotter active layer and the colder bipolar plate. Given the small thickness of the GDL ($\sim 300 \mu\text{m}$) this represents a significant thermal gradient. These results are supported by the simple estimate that follows.

We express that the temperature difference ΔT is related to the heat flux Φ/A at the GDL/active layer interface due to the reaction. Using Fourier's law yields, the heat flux can be expressed as,

$$\frac{\Phi}{A} = -\frac{\lambda_{eff}}{\ell} \Delta T \quad (5)$$

where A and ℓ are as before the cross-sectional surface area and thickness of the GDL, λ_{eff} is the effective thermal conductivity of the GDL.

The heat released during the exothermic electro-chemical reaction is given by



One can refer to [1] for more details. The corresponding power for a cell producing a current density i is then $\Phi_{vap\ tot} = \Delta H_{vap} i/2F$. The total amount of heat produced by the fuel cell is then expressed as

$$\Phi_{vap} = \Delta H_{vap} i/2F - \Phi_{elec} = (\Delta H_{vap} / 2F - U) i \quad (7)$$

where $\Phi_{elec} = Ui$ is the electrical power and $\Delta H_{vap} = 242.1 \text{ kJ.mol}^{-1}$.

Notice that we have not taken into account the heat flux Φ_{cond} associated with the condensation process if the produced water condenses at the cathode.

Combining Eqs. (5) and (7), gives a relationship between the temperature difference ΔT and the current density:

$$\Delta T = \left| \frac{-\ell}{\lambda_{eff}} \left(\frac{\Delta H_{vap}}{2F} - U \right) i \right| \quad (8)$$

Representative values of thermal conductivity λ_{eff} for a GDL are in the range 0.3 to 0.6 W/(m.K). This value notably increases with the GDL compression rate. Application of Eq. (8) for a representative PEMFC polarization curve leads to a thermal difference ΔT in the range [3.6 K - 7.3 K] in quite reasonable agreement with the results reported in [3].

The first consequence of the temperature difference is that the transfer by vapor diffusion across the GDL is more efficient than for the uniform temperature situation with the same conditions in the channel because the equilibrium molar fraction x_{vsat} on the active layer / GDL interface increases with temperature. In other terms, the critical current plotted in Figure 2 is underestimated when the temperature is not uniform and we consider that the vapor is saturated at the active layer – GDL interface.

The other important consequence of the temperature difference is the possible condensation of the vapor within the GDL because of the existence of the colder region on the channel side.

A first step in the study of the condensation process is to compute the vapor molar fraction field in presence of a thermal gradient in the domain shown in Figure 1. Using again our pore network model, we impose a given vapor molar fraction at the active-layer / GDL interface and a lower vapor molar fraction at the channel / GDL interface and zero flux condition at the rib / GDL interface. This computation is therefore completely similar to the one giving D_{app1} . The result shows that the vapor molar fraction along the outlet of the GDL is located in the middle of the GDL – rib interface. This corresponds to point A in Figure 1. The computation for realistic temperature differences shown that a condensation can indeed occur in the region of point A when the relative humidity is sufficiently high in the channel (the aforementioned computation leads to vapor molar fractions greater than the saturation vapor molar fraction at the corresponding temperature).

Interestingly, this is consistent with the experimental phase distributions reported in [12], which show the presence of a thin liquid layer all over the rib surface in contact with the GDL. Thus, under these conditions, a partial invasion in liquid phase of the GDL is expected from the growth of condensation clusters forming at the GDL/rib interface.

This situation can be simulated from pore network simulations using the following algorithm;

- 1) Determine and label the different water clusters present in the network. If two pores – totally or partially saturated in water – are adjacent, they belong to the same cluster. The first cluster at the very beginning is the pore in the network where the computed molar fraction is the highest above the saturation molar fraction.
- 2) Calculate the vapor molar fraction field x_v imposing the saturated molar fraction at the corresponding temperature along the boundary of each liquid cluster
- 3) Compute the molar flux F_k at the boundary of each cluster
- 4) Determine the throat of larger diameter along the boundary of each liquid cluster
- 5) Compute the invasion time t_k of each cluster k , i.e. the time required to fully invade the pore adjacent to the throat determined in #4 from F_k (step 3) and the volume remaining to invade in the considered pore.
- 6) Compute the time step $dt = \min(t_k)$.
- 7) Fully invade the pore corresponding to dt and update the volume of liquid in the invaded pore in the other clusters
- 8) Go back to step 1 until the water flux at the GDL outlet (GDL –channel interface) reaches a desired value, i.e. the water production rate given by Eq.(1).

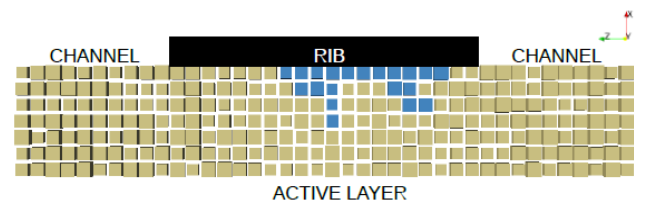


Figure 5: Partial liquid invasion of the GDL by condensation under the rib. Liquid phase in blue, gas phase in white, solid phase in brown.

Figure 5 shows a typical phase distribution obtained with

this algorithm. As can be seen, this leads to an invasion pattern quite different from the ones depicted in Fig.3 and Fig.4. The liquid is moving forward, i.e. toward the bipolar plate, in the scenarios corresponding to Figs. 3 and 4 whereas it is rather moving toward the active layer in the condensation scenario.

Thus, although the condensation algorithm summarized above needs improvements (for example the temperature field is imposed and is not computed taking into account the heat release due to the condensation process), our first simulations, as illustrated in Figure 5, do indicate a quite different liquid invasion scenario of GDL than considered in most previous pore network simulations.

6. Conclusion

The results presented in this article suggest that it is important to distinguish different zones in the GDL along the channel of the bipolar plate on the cathode side in relation with the water management problem. Depending on the distance to the bipolar plate channel exit and for sufficiently high current densities, the different zones would be as follows: a zone where the GDL is dry, a zone with partial liquid invasion and evaporation and finally a zone close to the exit of the channel with significant liquid water invasion coming either directly in liquid phase from active layer or as a consequence of the (evaporation)-condensation process or both from the active layer in liquid phase and as a result of the condensation process.

Further studies are necessary to delineate much more accurately the relative significance of each scenario. This is important in relation with the design of GDL. For example, the analysis of the role of the microporous layer (MPL), which generally improves the performances compared to a GDL without MPL, is different depending on the prevailing scenario. This aspect will be discussed in more details in a future work, notably from 3D pore network simulations.

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