CRITICAL IMPORTANCE OF WATER TRANSPORT TOWARDS THE ANODE IN MINIATURE AIR-BREATHING POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

Simon Hamel*, **Luc G. Fréchette**
Dept. of Mechanical Engineering, Université de Sherbrooke, Sherbrooke, Canada
*Presenting Author: Simon.Hamel@usherbrooke.ca

Abstract: Although water management is known to be critical in miniature Polymer Electrolyte Membrane Fuel Cells (mPEMFCs), this study shows that it is the control of water transport towards the anode that is the determining factor to increase air-breathing mPEMFC performances. An analytical 1D model shows that drying at the anode and flooding at the cathode can happen simultaneously, mainly due to dominant electro-osmotic drag at low temperatures. Experimental results demonstrate that injecting water at the anode, at a rate of 3 times the amount produced at the cathode, should increase the cell performances at high current densities. By this method, the limiting current and maximum power have been raised by 100% and 30% respectively.

Keywords: Water management, Polymer Electrolyte Membrane Fuel Cell, Anode drying, Electro-osmotic drag

INTRODUCTION

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are well suited for small portable applications. Their solid electrolyte, quick start-up and low operating temperature make them ideal candidates to power small portable devices.

Water management is critical in PEMFCs since its ionic membrane needs to be humidified to have a low ionic resistance but the liquid water must not block gas pathways. Because of their low output power, miniature cells (mPEMFCs) can't use external equipment such as pumps or fans to manage water. Therefore, mPEMFCs need to be air-breathing (natural convection) and use a dead-ended anode. Consequently, water management cannot be achieved by using forced gas flows. These restrictions often lead to poor water management in the cell and to low performances of the latter. Because the cathode side has greater activation losses and tends to flood, most research efforts focused on its importance in the water management [1, 2]. Few studies have taken into consideration the anode in their model because it is considered that drying of the anode can't occur simultaneously with flooding at the cathode. Nevertheless, Jung [3] has shown that it is possible to improve air-breathing PEMFC performances by adding a hydrophilic component in the anode. It has been concluded that these results were due to the highest humidification of the anode and not to the water removal from the cathode. Furthermore, Chu [1] has also shown that feeding humidified H_2 to the anode improved slightly PEMFC performances even at low temperatures. This suggests that anode drying happens even at ambient conditions when the cathode is flooding.

In this study, a simple steady-state analytical model of water transport through a mPEMFC is done to capture potential drying at the anode and flooding at the cathode. Results are then validated experimentally by observing the impact of anode humidification on the cell performances.

THEORY & MODELLING

A simple model of an air-breathing mPEMFC is realized to understand the water management phenomena involved. Because the main goal of the model is not to predict precisely the lost of voltage in the cell but to highlight the general trends of water transport inside the Nafion® membrane, some assumptions are made to simplify the model. First, the developed model is steady-state and one dimensional since the water transport phenomena occurs mainly across and perpendicular to the membrane (x axis in Fig. 1). Secondly, the cell is exposed to natural convection leading to evaporation at the cathode, but no flow or evaporation at the anode to represent the dead-ended condition. Thirdly, temperature of a mPEMFC can be easily controlled by its packaging (material, area etc.) [2], so it is considered to be isotherm. Figure 1 shows the different phenomena that the model takes into account. These include water production and consumption at the electrodes, water transport through the membrane, and evaporation from the cathode.

Water Transport in Nafion®

Three water transport phenomena occur in the ionic membrane; permeation, electro-osmotic drag and diffusion. Permeation is the water flow caused by the differential pressure between the anode and the cathode. These pressures are assumed to be the same so permeation is neglected.

The electro-osmotic drag, caused by water molecules carried by crossing protons, is proportional to current I. Total water flux toward the cathode caused electro-osmotic drag, N_{EO}, is computed with
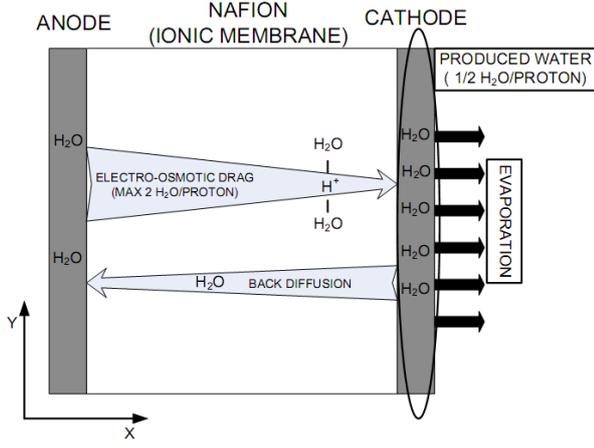
Fig. 1 - Water transport phenomena in a PEMFC showing dominant flux towards the cathode.

Eqn 1 where F is the Faraday number.

$$N_{EO} = N_d \frac{I}{F} \qquad (1)$$

The value of the electro-osmotic drag coefficient N_d varies significantly from one author to another. In this paper, the equations given by Springer [4] are used, expressed as a function of the water content λ which depends on the partial pressure of water P_w and saturation pressure P_{sat}.

$$N_d = \frac{2.5\lambda}{22} \qquad (2)$$

$$\lambda = 0.043 + 17.81 \frac{P_w}{P_{sat}} - 39.81 \left(\frac{P_w}{P_{sat}}\right)^2 \\ + 36.0 \left(\frac{P_w}{P_{sat}}\right)^3 \qquad (3)$$

Because it is assumed that no water is leaving the cell by the anode flow, N_{EO} must counterbalance the back diffusion flux, N_{BD}, to achieve a permanent regime ($N_d = N_{BD}$). The diffusion flux can be written as [5] :

$$N_{BD} = D_w C_f \frac{d\lambda}{dx} \qquad (4)$$

$$D_w = 0.000417\lambda[1 + 161 \exp(-\lambda)] \\ \exp\left(-\frac{2436}{T}\right) \qquad (5)$$

where D_w is the back diffusion coefficient, C_f is the charge concentration in the hydrated membrane and T is the temperature of the cell.

As Eqn 5 shows, the back-diffusion coefficient drops with temperature. Since an air-breathing PEMFC is running at lower temperatures than a standard one, back-diffusion coefficient is lower for an equivalent electro-osmotic drag coefficient (Fig. 2). This causes the membrane to dry more easily on the anode side when the current rises. This drying of the membrane increases its ionic resistivity expressed as :
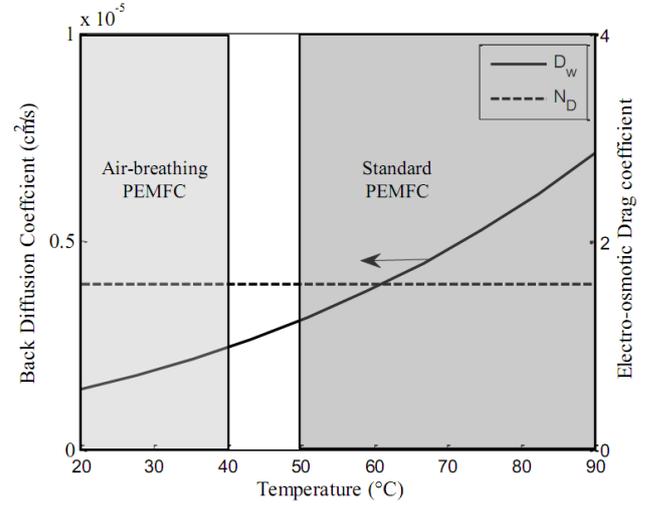

Fig. 2 - Back diffusion and electro-osmotic drag coefficients in function of temperature if membrane is *fully humidified (λ=14)*.

$$\sigma = 0.005139\lambda - 0.00326 \qquad (6)$$

Simple Analytical Cell Model

To define the water content throughout the membrane, Eqns 1 to 6 must be coupled to mass transfer relations at the electrodes. Since natural convection will dominate, the porous electrodes and Gas Diffusion Layers (GDL) are considered as thin layers. Mass transfer from the cathode can be expressed from Maxwell-Stefan relation :

$$\sum_{\beta=1}^{N} (x_\beta \cdot N_\alpha - x_\alpha \cdot N_\beta) = -\Delta x_\alpha \cdot c \cdot h_{m-\alpha} \qquad (7)$$

where x, N and c are respectively the partial pressure, the molar flux and the concentration. Mass transfer coefficients for hydrogen and oxygen ($h_{m-\alpha}$) for a flat vertical surface in a natural convection flow are determined with the relations developed by Pei-Wen Li [6].

Results of the analytical model

To investigate the hypothesis that drying at the anode may be problematic in mPEMFC, the model is applied to a representative configuration. The mPEMFC has an active area of 2 cm^2 with a Nafion® 117 membrane. A stoichiometric flow of 1.5 (with minimal flow of 4 SCCM) of dry hydrogen feeds the cell. The ambient temperature is 22°C with a relative humidity of 50%.

Water contents at the electrodes resulting from this model are shown at Fig. 3. It is possible to see that at normal ambient conditions, the cathode is flooding quickly and that the anode is getting dryer when the current increases.

Three distinct phases appear on Fig. 3 depending on the current. The first section, the wetting zone, is where both electrodes are slowly humidifying and the
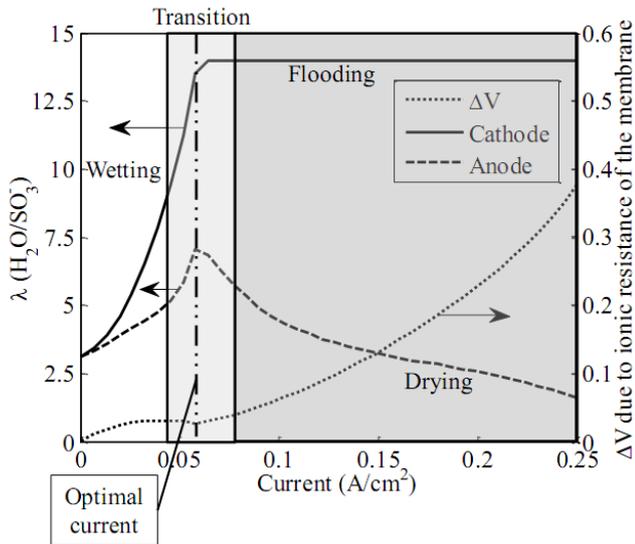
Fig. 3 - Water content of the electrodes depending of current. External temperature = 22°C, RH = 50%.

cell can achieve permanent regime because it can evaporate the water it produces. In the transition zone, the electrodes humidify to their optimal point where the rate of water production is the same as the maximum rate of evaporation. Beyond this point, the GDL on the cathode side accumulates excess water until the oxygen pathways are blocked. On the other side of the cell, the water content at the anode decreases as the electro-osmotic drag flux increases. Because the water content at the cathode is constant at its maximum value during flooding (the excess liquid water is drawn from the surface by the GDL) and that the electro-osmotic drag increases proportionally to current, the total amount of water decreases and the ionic resistance of the membrane rises.

Figure 3 also shows the lost of voltage due to the ionic membrane resistance. Weber [7] explains that under $\lambda = 2$, barely no protons can cross trough the membrane because the conductivity of the Nafion® becomes too low. Figure 3 demonstrates that water content at the anode can go under $\lambda = 3$ at currents higher than 0.3 A/cm^2.

Based on these results, it can be deduced that humidifying the anode will have a positive effect on the performances of the cell even when the cathode is flooding. Of course, water must be removed from the cathode's GDL to allow oxygen diffusion in steady-state operation. Conceptually, these requirements could be satisfied simultaneously by forcing water from the cathode to the anode. By preventing the cathode from flooding and the anode from drying, this approach could lead to high and stable performances of mPEMFCs near ambient temperature.

EXPERIMENTAL SETUP

To validate the fact that cell performances increase by humidifying the anode, even if the cathode is flooding, an experimental characterisation was done with direct injection of water at the anode (Fig. 4).
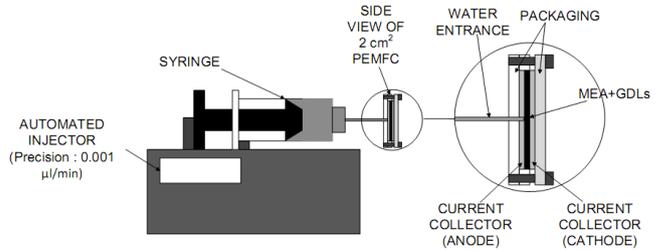

Fig. 4 - Experimental setup for injection of liquid water directly in the anode of the PEMFC while it is running.

Liquid water is injected directly on the anode side of a 1 cm x 2 cm PEMFC by an automated syringe pump while the cell is running. The cell consists of a Nafion NR212 membrane (which is thinner than 117) with 0.3 mg/cm^2 Pt loaded electrodes and 400 µm thick carbon cloth GDLs. The Membrane Electrode Assembly (MEA) is sandwiched between two etched current collectors.

Two different experiences were carried out. First, steady-state VI and power curves of the mPEMFC were done with and without water injection. Secondly, to determine the optimal amount of water that should be redirected towards the anode, water was injected constantly during fifteen minutes with a flow rate of 2.5 to 5 times the water produced by the cell and then stopped.

RESULTS AND DISCUSSION
VI curves

To compare performances of the cell with and without water injection, VI curves are done by fixing the cell current for at least 30 minutes at each point of the polarization curve. The two test series are done with the same external conditions to ensure results compatibility. Figure 5 compares the VI and power curves obtained for the cell without water injection at the anode and with injection of liquid water at a ratio of 5:1 of the produced water by the cell.

The three zones introduced in Fig. 3 are also highlighted in Fig. 5. In the anode wetting and transition zone, injected water do not have significant effects because the voltage drop due to resistance of the membrane is low (Fig. 3). In the anode drying zone, the cell voltage without injection drops rapidly. On the other side, water injection at the anode is shown to significantly increase the cell voltage and power. Two phenomena can explain the voltage drop with no injection: cathode flooding or anode dryout. Indeed, on the cathode side, water droplets begin to be visible meaning that the GDL is saturated and that the oxygen pathways are reduced. Nevertheless, by injecting liquid water at the anode surface, the cell ultimate voltage almost doubles and maximum power increases by 30%. Injected water therefore humidifies the anode which lowers the ionic resistance of the membrane and increases the voltage.
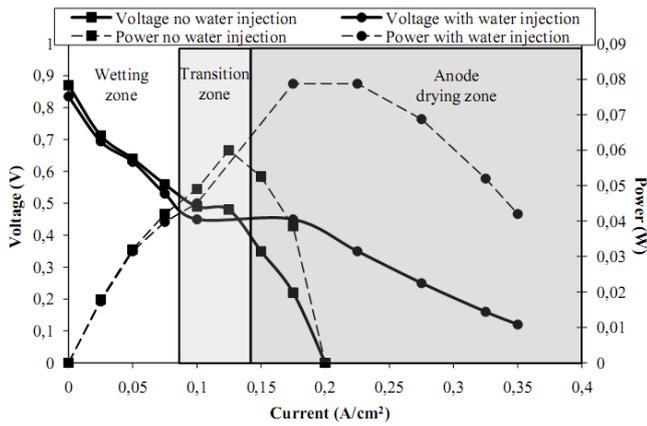
Fig. 5 - VI and power curves of the 2 cm² PEMFC with (circles) and without (squares) injection of water. Dry H₂, st=1.5 (minimum flow = 4 SCCM), Temp = 22 ℃, RH = 50 %.

Optimized water flow

To estimate how much water is needed at the anode to have a significant effect, water injection ratio is varied from 2.5:1 to 5:1, (Fig. 6). A current density of 0.175 A/cm² is chosen because it is where the benefits of injecting liquid water at the anode begin. At this point, water is injected during 15 minutes then stopped. With an injection rate of 2.5:1, the positive effects of injecting water are lower and less durable than at higher injection ratios. At superior rates, the effect of a 15 minutes injection stays for a long period of time. There is enough water injected to humidify the anode GDL and the membrane. At large ratios, however, the anode will eventually flood if water continues to be fed to it. Given this compromise, the optimal water injection ratio appears to be between 2.5:1 and 3:1. This corresponds approximately to the rate of water that is removed from the anode by the electro-osmotic drag plus the water that is evaporated from the cathode surface. This suggests that there is sufficient water available to humidify the anode if all the water at the cathode is redirected by an alternative pathway towards the anode.

CONCLUSION

This work has shown analytically and experimentally that for an air-breathing mPEMFC working at near ambient conditions, flooding of the cathode and drying of the anode are limiting its performances. These two phenomena can happen simultaneously at high current. To increase the ultimate current and power density, water at the cathode could be redirected towards the anode. Water removal from the cathode is required for steady-state operation while water at the surface of the anode humidifies the membrane, decreases the ionic resistance and improves significantly the performances of the mPEMFC. It has been shown that by injecting water directly on the anode, ultimate current can almost be doubled and power can be increased by
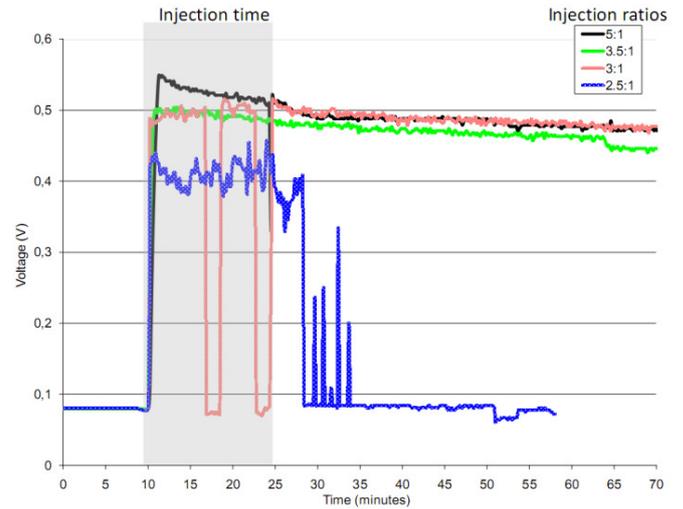

Fig. 6 - Time response of the 2 cm² PEMFC during and after water injection at the specified ratios. Dry H₂, st=1.5 (minimum flow = 4 SCCM), Temp = 22 ℃, RH = 50 %, I = 0.175A/cm².

30%. The next step is to produce a device that would redirect the excess water from the cathode to the anode. In this way, no external water injection would be required.

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