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Operating Proton Exchange Membrane Fuel Cells at a Constant Relative Humidity

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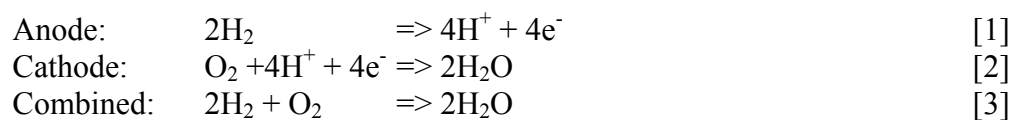# Operating Proton Exchange Membrane Fuel Cells at a Constant Relative Humidity

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This study investigates the possibility of operating a proton exchange membrane fuel cell at a constant humidity of 100% from cathode inlet to cathode outlet. Employing the Engineering Equation Solver (EES), a model has been developed where the cathode channel flow is calculated via the discretized Hagen-Poiseuille equation. The stoichiometric flow ratio such that the decrease in the RH caused by the pressure drop is balanced by the addition of water due to the electrochemical reaction is calculated. Results show that in many cases the calculated stoichiometry is too low to be viable for a straight channel flow field. However, reducing the temperature yields acceptable stoichiometric flow ratios. The channel geometry plays a critical role, and shorter and deeper channels are preferable. In a refined version of the model, the limiting current density is calculated to avoid concerns about the low stoichiometric flow ratios.

Introduction

In proton exchange membrane fuel cells, hydrogen reacts with oxygen from air to generate electric current at high efficiencies. The reaction mechanisms are:

Anode:	$2H_2$	$=> 4H^+ + 4e^-$	[1]
Cathode:	$O_2 + 4H^+ + 4e^-$	$=> 2H_2O$	[2]
Combined:	$2H_2 + O_2$	$=> 2H_2O$	[3]

By-products of the reaction are water and waste heat. While proton exchange membrane fuel cells are being commercialized, there is a need of high power and high current operation to further reduce the capital expenses. As the fuel cell current density is further increased, waste heat removal becomes an issue. Moreover, there has always been a need of proper water management inside the fuel cell, because the proton exchange membrane requires hydration on one side, but on the other side excessive water inside the fuel cell will lead to pore plugging. In early works, Nguyen and White have investigated different methods of providing sufficient water to the cathode or anode inlet stream which requires an external humidifier (1). Later on, Büchi and Srinivasan investigated the possibility to operate fuel cells without the need of external humidification and conducted fundamental consideration concerning the required stoichiometric flow ratio at different cell temperatures (2). Clearly, the cell pressure, cell temperature and stoichiometric flow ratio at both anode side and cathode side of the fuel cell have to be carefully adjusted in order to operate a cell in such a manner that both outlet gas streams are exactly saturated while the inlet gas streams are completely dry. *Dew Point Diagrams* show the dependency of all fuel cell operation parameters and point out the need for an accurate

measurement of the fuel cell water balance (3, 4). By adjusting the anode and cathode inlet temperatures and outlet pressures, PEMFC could be operated in a manner that both outlet streams are exactly saturated if the stoichiometric flow ratios are carefully controlled. In an ensuing computational modeling analysis, it was found out that although the dew point temperatures are independent of the fuel cell current density, the proton exchange membrane has a tendency of dehydrating at elevated current densities due to the higher waste heat production (3). Hence, while both outlet gas streams in the flow channels might be saturated, local membrane dehydration can still exist due to an insufficient thermal management.

Traditionally, carbon fiber papers (CFP) have been used in PEMFC to distribute the reactants and electrons to cell areas covered by land, and to remove the product water which can be in the liquid phase via capillary action. Therefore, the mass transport properties of these carbon fiber papers are very good. On the other hand, the thermal conductivity of these CFP is low, in the range of 0.5 W/mK (5-7), and this can become problematic at high current densities, when the waste heat production can lead to a temperature difference between the membrane and the gas flow channels as high as 10 °C (8). As fuel cell manufacturers are thriving to further increase the operating current densities, there is an increasing focus on thermal management inside the cells. A recent trend has been to replace the CFP by thin, perforated metal sheets where round holes in the order of 80-120 microns are manufactured by a chemical etching technique (9). When perforated metal plates are involved, the micro-porous layer assumes the role of distributing the reactants to the under-the-land areas. However, the MPL is thinner than CFP, typically 30-50 microns, so it is assumed that the land areas should be accordingly smaller. A CFD analysis suggested that the fuel cell operates almost isothermally, and that there is almost no temperature gradient between the membrane and the flow channels (10). In addition, the holes in the metal plates were predicted to remain dry, despite liquid water being in the adjacent micro-porous layer. It seems logic that these fuel cells can only function in the dry regime because if there are flooding conditions, all metal pores will flood coincidentally as the capillary pressure is the same in all uniform pores. However, in previous CFD simulations it as found that even when operating PEMFC according to dew point diagrams, there is liquid water predicted in the middle of the cell, as was also computed by Berg et al. (11), and this suggests that it might not be possible to operate fuel cells with a metal GDL under these conditions. A different question was therefore brought up, similar to early-work research: Can we operate a PEMFC cathode side in a manner that the gas phase remains exactly saturated along the length of the channel? This would mean that the gas is fully saturated both at the inlet and at the outlet. As a consequence of the latter, all product water would be removed from the fuel cell in the vapor phase which has important implications for the thermal management as well. Moreover, if the air stream at the cathode side remains at a relative humidity (RH) of 100%, all product water would locally evaporate and ideally the isothermal fuel cell would remain in the single phase.

In the first place, it appears impossible to let the air enter fully saturated and remain in this state over the length of the cell until the outlet, simply because of the product water, along with the fact that the consumption of oxygen increases the molar fraction of water vapor which alone will lead to an RH above 100%. However, it was pointed out by Berning and Djilali that due to its dependency on the local pressure the RH can decrease in a fuel cell channel with a high pressure drop (12). It has been observed that fuel cells

with perforated metal GDL work best for micro-channels (9). It is therefore the goal of this work to identify operating conditions that would allow both the inlet and the outlet of the cathode side in a PEMFC to be saturated. The main parameter to be determined is the stoichiometric flow ratio, as this is the central parameter that determines the flow velocity at the cathode, hence the pressure drop, and the amount of oxygen/air per product water molecule. In the following, a set of equations will be formulated that relates the stoichiometric flow ratio on the air side to the flow velocity and the pressure drop in the cathode channel. To this end, the Hagen-Poiseuille equation is utilized. By then relating the molar flow rates with the electric current production and enforcing the RH to be unity at both inlet and outlet, the stoichiometric flow ration can be calculated under a variety of operating conditions and geometrical properties.

Model Development

Assumptions

By comparison to models based on computational fluid dynamics, this model is quite coarse, and the simplifying assumptions are:

- The gas is assumed to be ideal.
- All product water exits the cell at the cathode side.
- The flow is assumed laminar to calculate the pressure drop.
- The temperature is assumed constant.
- Oxygen and hydrogen cross-over is negligible.
- The velocity is constant in each control volume.
- The current density is uniform.
- The condensation of water when the RH exceeds 100% is neglected.
- Convective flow in the holes of the perforated plate and the MPL is neglected.

Model with variable current density

In a first approach, the current density was left as a variable and a case-study was conducted. A central equation in this model is the Hagen-Poiseuille equation which relates the velocity and the pressure drop in a circular pipe flow. It is most conveniently written in the following form:

$$\Delta P = 32 \times \mu L_{Ch} u / D_h^2 \tag{4}$$

Where μ is the fluid viscosity, L_{Ch} is the channel length, u is the velocity and D_h is the hydraulic diameter of the channel. The Hagen-Poiseuille equation can be fundamentally derived for a circular pipe, and it requires the flow to be laminar. For a rectangular channel as is the case here, the pipe diameter is replaced by the hydraulic diameter, according to:

$$D_h = 4 \times A_{Ch} / p_{wet} \tag{5}$$

Here, A_{Ch} is the cross-sectional channel area and p_{wet} the wetted perimeter. At the channel inlet, the velocity is given by (13):

$$u_{in} = \lambda \times \left(\frac{i}{nF} \right) \frac{1}{y_{O_2,in}} \times \frac{RT}{P_{in}} \times \frac{A_{MEA}}{A_{Ch}} \qquad [6]$$

Where A_{Ch} is the cross-sectional diameter of the channel and A_{MEA} the active area that is fed by one channel. The geometry is shown in Figure 1 where W_{Ch} denotes the width of a single channel and W_l the land area width. Therefore, the area of the membrane-electrode assembly that is being fed by a single channel is:

$$A_{MEA} = (W_{Ch} + W_l) \times L_{Ch} \qquad [7]$$

And the cross-sectional area of a single channel is:

$$A_{Ch} = W_{Ch} \times H_{Ch} \qquad [8]$$
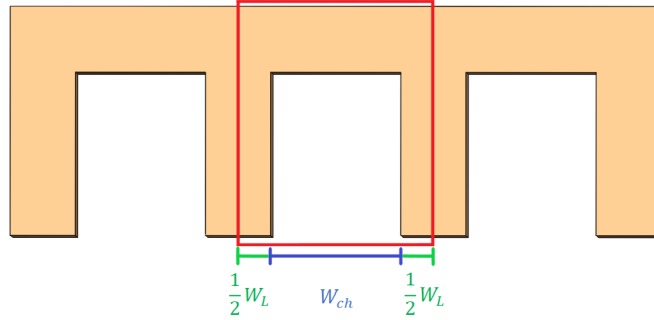
Where H_{Ch} is the channel height.

Figure 1. Geometry used in the current study.

When applying the Hagen-Poiseuille equation, it quickly becomes obvious that in case there is a substantial pressure drop in the down-the-channel direction, the velocity increases because of the density change. Generally, the velocity u is calculated via:

$$u = \dot{m}/(\rho A_{Ch}) \qquad [9]$$

Where the mixture density ρ is calculated out of the local pressure and composition according to the ideal gas law.

$$\rho = \frac{PM}{RT} \qquad [10]$$

Where M is the molecular mass of the mixture, R is the universal gas constant (8.3145 J/mol-K), and T is the temperature. The mixture molecular mass can be calculated out of the molar fractions according to:

$$M = \sum_i y_i M_i \qquad [11]$$

The total mass flow at the inlet is the sum of the mass flow rate of oxygen, nitrogen and water vapor which can be calculated out of the corresponding molar flow rates. The molar flow rate of oxygen at the inlet is:

$$\dot{N}_{O_2,in} = \xi \times \frac{I}{4F} \tag{12}$$

Where ξ is the stoichiometric flow ratio and F is Faraday's constant (96584 C/mole). The corresponding molar nitrogen flow rate is:

$$\dot{N}_{N_2,in} = \xi \times \frac{79}{21} \times \frac{I}{4F} \tag{13}$$

The molar inlet flow of water vapor can be calculated as (3):

$$\dot{N}_{H_2O,in} = \xi \times \frac{x_{H_2O,in}}{1 - x_{H_2O,in}} \times \left(1 + \frac{79}{21}\right) \times \frac{I}{4F} \tag{14}$$

The molar fraction of water vapor can be calculated out of the requirement that the inlet relative humidity is 100%. Employing Dalton's law, we obtain:

$$1 = \frac{p_{H_2O,in}}{p_{sat}(T)} = x_{H_2O,in} \times \frac{p_{in}}{p_{sat}(T)} \tag{15}$$

The saturation pressure can be calculated out of Antoine's equation according to:

$$\log(p_{sat}) = A - \frac{B}{C + T} \tag{16}$$

Where for water A = 5.0768, B = 1657.793, and C = -45.854.

As the cathode air flows down the channel, oxygen is being consumed and replaced by water vapour according to a locally specified current density. In this study the current density was assumed to be constant. At the same time, there is a pressure drop in the down-the-channel direction which can not be neglected in these micro-channels. Therefore, the channel length was discretized and split up into a number of sections with the length Δx. The velocity at the interface between any two elements was calculated based on the updated mass flow rate and an updated pressure that fulfills the Hagen-Poiseuille equation for each control volume with length Δx. The mass flow rate of oxygen and water was updated based on the assumption of a uniform current density in each control volume (CV), and the velocity at the end of each CV was calculated as:
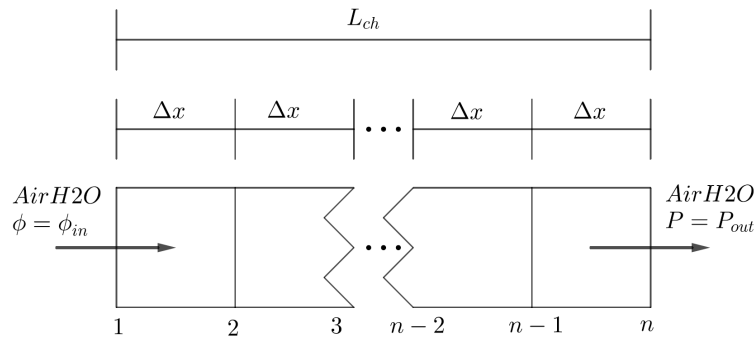
$$u = \frac{\dot{m}}{A_{ch}\rho(P)} \tag{17}$$

Figure 2. Flow channel discretised in *n* nodes and *n-1* volumes of length *Δx*.

With knowledge of the inlet velocity the pressure drop in the first computational cell can be calculated out of the Hagen-Poiseuille equation, then the pressure at the cell outlet and the inlet of the next cell can be updated. Finally, the mixture composition at the cell outlet is updated, and the density at the cell interface is calculated using the updated pressure and mass flow. With that, the velocity at the cell outlet is calculated and is used to calculate the pressure drop. Regardless of the number of discretization volumes, this overall set of equations has as many equations as unknowns and is therefore a solvable problem. In the first version, the current density was employed as an input parameter. With this, the only unknown parameter was the stoichiometric flow ratio, and the calculated values based on the given input current densities will be shown below in the section "Study with variable current density". The software that was used in these calculations was the *Engineering Equation Solver* (EES) (14), a powerful tool to conduct any kind of engineering calculations provided the number of equations is equal to the number of unknowns. In addition, this model was transferred to MATLAB and C-sharp.

Model with limiting current density

In order to obtain a maximum power density these miniature fuel cells should be operated at a current density that is as high as possible. The theoretical limiting current density in a straight-channel flow field is determined out of the diffusion resistance between the bulk flow and the porous media. This was given as (e.g. (15)):

$$i_l = nFD_{eff} \frac{C_B}{\delta}$$ [18]

Here, n is again equal to 4, F is Faraday's constant, D is the diffusion coefficient of oxygen in the porous medium, C_B is the bulk concentration of oxygen in the channels, and δ is the diffusion length. The diffusion coefficient is the effective diffusion coefficient in the porous medium and it has to be corrected by the porosity and tortuosity:

$$D_{eff} = \frac{\varepsilon}{\tau} D_{O_2-air}$$ [19]

In the MPL, the porosity ε was set to 0.75 and the tortuosity τ equal to 3. This effective diffusion coefficient is calculated for the micro-porous layer. In addition, there is the diffusion resistance inside the perforated plate to be accounted for. Here, the porosity is calculated as:

$$\varepsilon_{GDL} = \frac{D_{Hole}^2 \pi}{4\psi^2} \qquad [20]$$

Where the pitch, ψ, is the distance between the center of two holes. The diameter of the holes ranges from 60-110 microns (9) and the land area between the holes is 50 microns, meaning the pitch will be 110-160 microns. The tortuosity is equal to one.

Thus, the total diffusion resistance is calculated as the sum of the resistance in the MPL and the GDL:

$$R_{tot} = R_{GDL} + R_{MPL} = \frac{\delta_{GDL}}{D_{eff,GDL}} + \frac{\delta_{MPL}}{D_{eff,MPL}} \qquad [21]$$

The limiting current density is then calculated as:

$$i_L = \frac{nFC_B}{R_{tot}} \qquad [22]$$

This value is calculated at every computational node and in the end an average value out of the arithmetic average is calculated.

$$i_L = \frac{1}{n}\sum_{j=1}^{n} i_{L,j} \qquad [23]$$

With this, the current density as an input parameter to the model has been eliminated, and the calculated stoichiometry is entirely a function of the operating conditions as well as the geometrical properties of the channels, the GDL and the MPL. It is noted that it does not make sense to operate the cell at the limiting current density as the cell voltage would be by definition zero. However, important insight can be gained because it is desirable to operate these miniature fuel cells at as high a current density as possible.

Model parameters

The input parameters and the geometrical base case parameters in this model are listed in Table 1.

TABLE I. Input parameters.

Parameter	Range	Base Case	Symbol
Channel width	150-300 μm	200 μm	W_{ch}
Channel height	150-300 μm	200 μm	H_{ch}
Channel length	50-200 mm	100 mm	L_{ch}
Land-width ratio	1-3	1	ϕ_{LW}
Cell temperature	60-80 °C		T
Outlet pressure	101.3 kPa		P_{out}
Current density	2.0-6.0 A/cm^2		i

In the first part of this study the current density was used as adjustable parameter. The land-width ratio was defined as:

$$\phi = \frac{W_l}{W_{ch}}$$

[24]

Results and Discussion

Study with variable current density

The first study investigated the possibility of operating a PEM fuel cell at constant inlet and outlet relative humidity, where the cell temperature, the channel dimensions, and the current density were used as input parameters. The question in all these cases was: At which stoichiometric flow ratio will the decrease in relative humidity due to the pressure drop be exactly balanced by the change in molar fractions such that the relative humidity might stay constant?

By comparison to a model that is based on computational fluid dynamics (CFD), the current model is relatively coarse, but it gives an indication about the feasibility. Moreover, the current calculations deliver the boundary conditions that could be used in a CFD model.

The first question concerns the required coarseness of the discretization used in this analysis, i.e. how small the volume elements Δx should be. To this end, the number of nodes was varied between 11, 21, 31, 41 and 51. The calculated relative humidity in the down-the channel direction is shown in Figure 3. The difference between a node number of 21 and 51 was very small. In the current model, calculation time was not important as solutions were always obtained within seconds, but it was still important to understand the effect of the grid on the results.
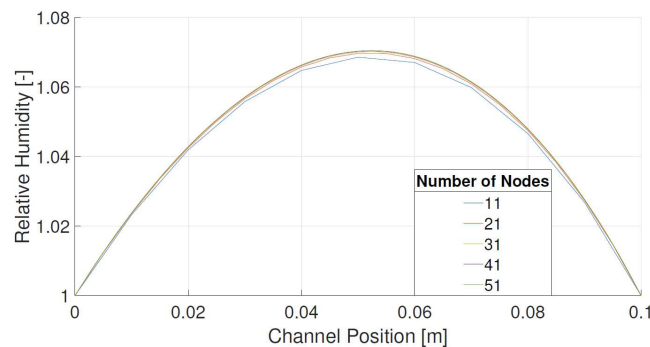

Figure 3. Flow channel discretised in *n* nodes and *n-1* volumes of length Δx.

The calculated stoichiometric flow ratios as function of the current density and channel dimensions are shown in Figures 4-6 for the operating temperature of 60 °C, 70 °C and 80 °C, respectively.
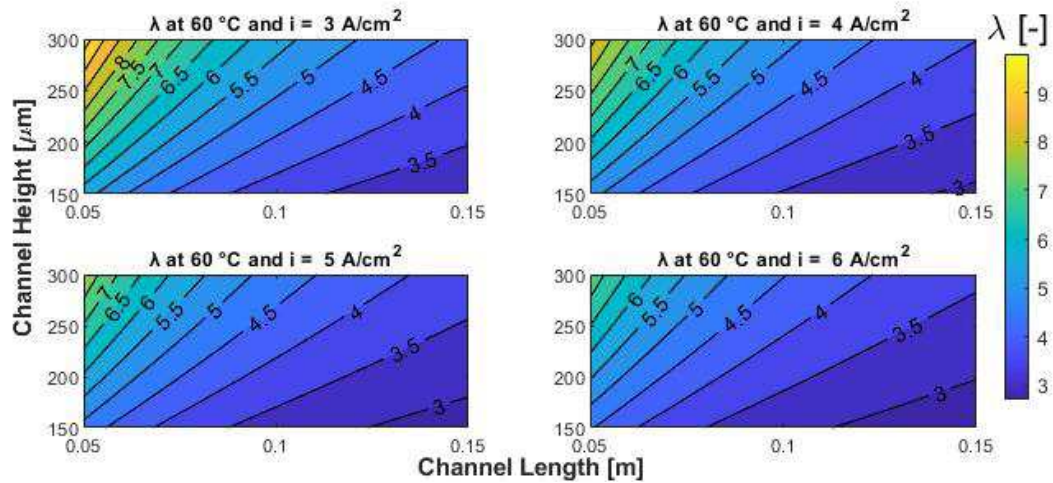
Figure 4. Calculated stoichiometric flow ratios for a cell temperature of 60 °C and varying channel dimensions.
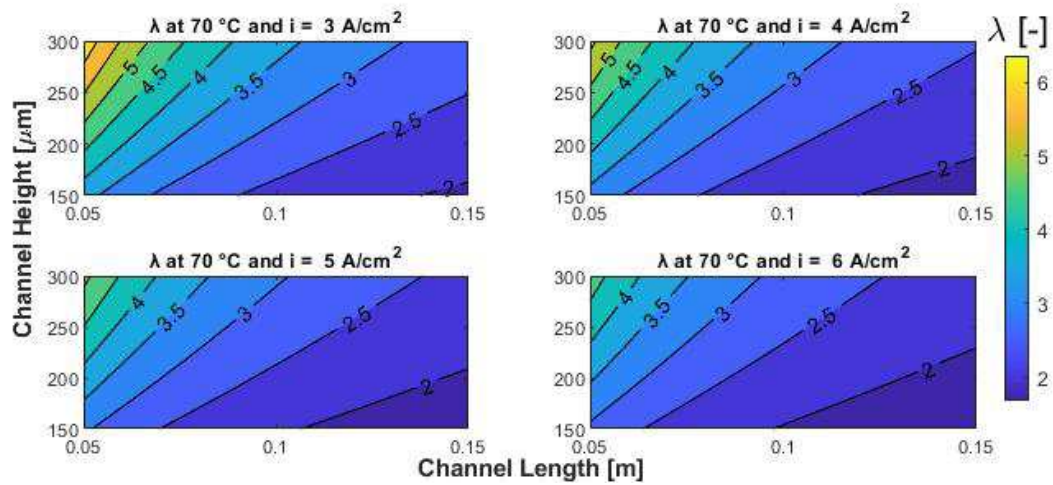

Figure 5. Calculated stoichiometric flow ratios for a cell temperature of 70 °C and varying channel dimensions.
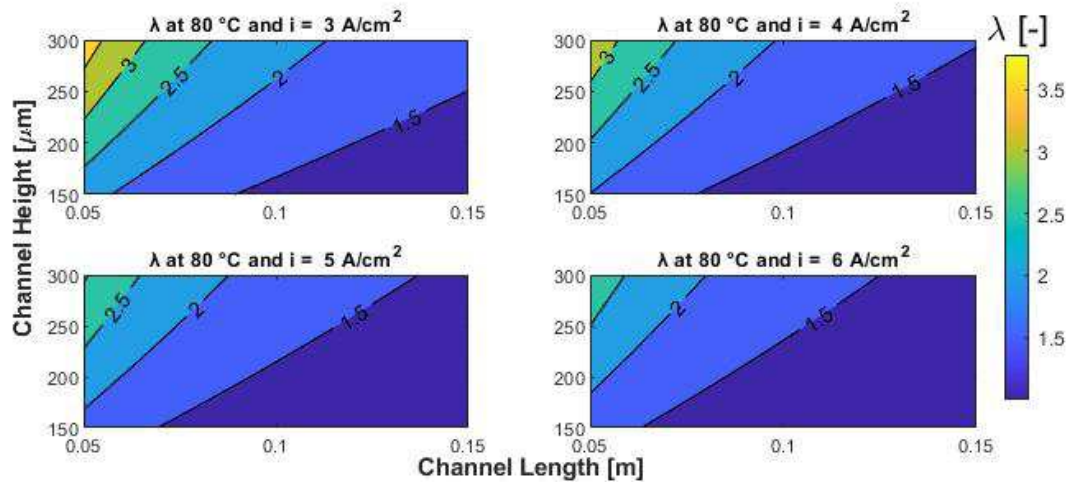

Figure 6. Calculated stoichiometric flow ratios for a cell temperature of 80 °C and varying channel dimensions.

It becomes obvious that it is more feasible to operate the fuel cell at a lower temperature if it is desired to have a uniform relative humidity as the calculated stoichiometric flow ratios at 80 °C are probably too low. It is difficult to see how a fuel cell could successfully be operated at a stoichiometry below $\xi = 2.0$ if the current density is so high. Moreover, a longer channel leads to lower stoichiometric flow ratios while an increase in channel height leads to higher stoichiometries and therefore increases the feasibility of such operation. While the above results list operating conditions such that both the inlet and outlet air is saturated, they do not give insight into the RH distribution inside the cell. In all cases investigated, the relative humidity in the flow channels is higher than 100% in the middle of the channel while it is fixed to 100% by the applied boundary conditions. Therefore, condensation would set in at the channel walls and some of our basic assumptions would be violated. Consequently, the current study only serves as a feasibility analysis and will have to be refined in the future. Figure 7 shows the two cases with the highest and the lowest relative humidity along the channel; all other cases were in between.
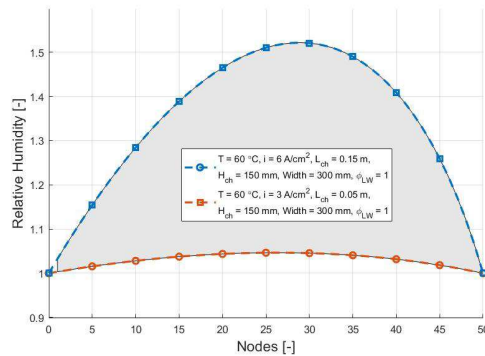

Figure 7. Calculated extreme cases for the relative humidity distribution along the flow channel.

It is, however, not necessarily required to have the air enter the fuel cell in a fully saturated stage. In our model, the inlet relative humidity can be easily adjusted, and we also investigated inlet RH values of 90%, 80% and 70% for two different channel lengths. Due to mass transport limitations for the water vapour transport, the fuel cell membrane can be ideally hydrated even though the gas phase inside the channels is below saturation. Figures 8 and 9 show the resulting relative humidity distribution for three different inlet RH values for a shorter channel of 10 cm and a longer channel of 20 cm. We can conclude that if the goal is to avoid condensation inside the flow channels, shorter channels are preferred. Again it is noted that the resulting stoichiometric flow ratios are very low. If we deem any operation below a stoichiometry of 2 as impossible, the cell temperature should not exceed 70 °C.

On the other hand, it is desirable to operate the cell at as high a temperature as possible for better performance and due to the fact that the metal GDL facilitates better heat transfer and thermal management, thus avoiding temperature peeks. It is the purpose of the current model to help identifying such geometrical parameters that help maximizing the cell temperature. The uncertainty as to whether it is feasible to operate the fuel cell at a stoichiometry of 2-3 can be avoided by including the limiting current density instead of using the current density as a free parameter. The limiting current density itself depends only on geometrical parameters as was seen in equation 22.
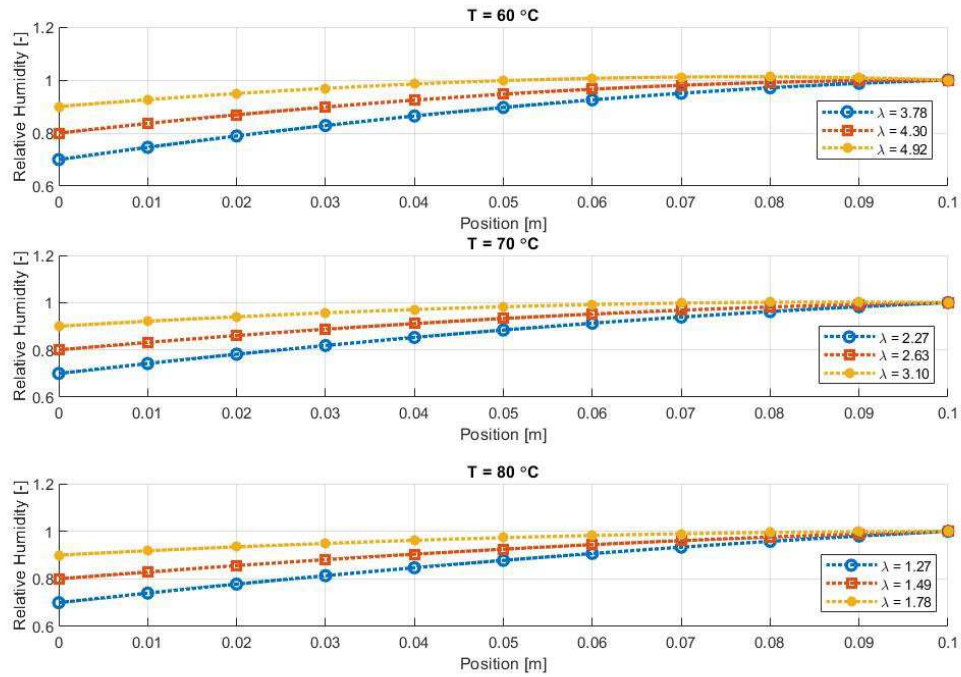
Figure 8. Calculated relative humidity along the channel for a total length of 10 cm at different temperature and inlet relative humidities.
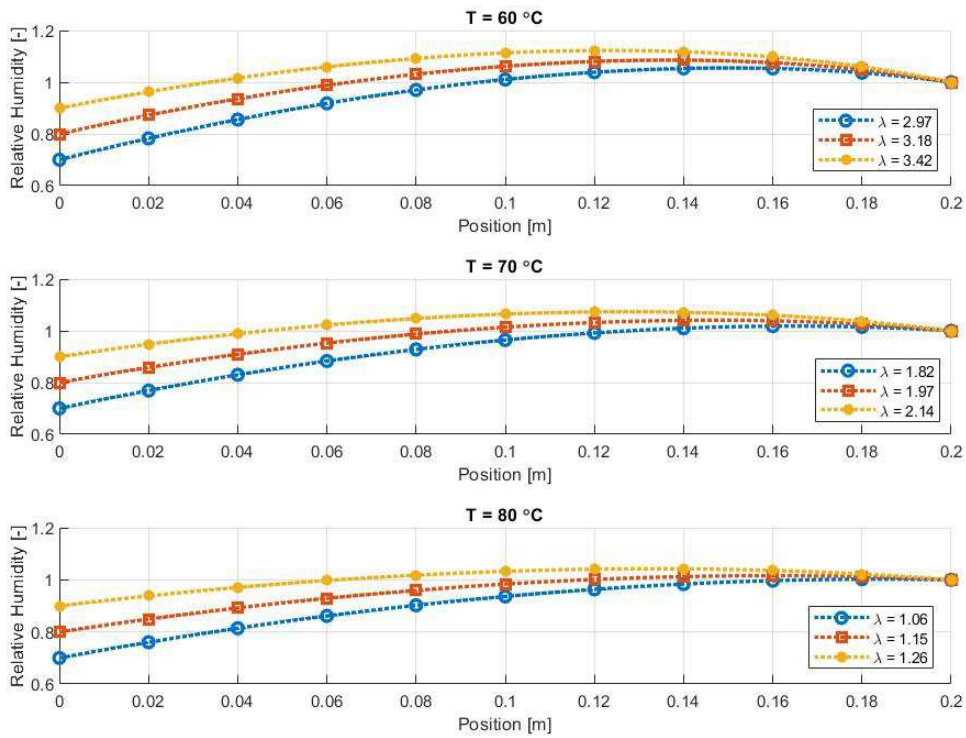

Figure 9. Calculated relative humidity along the channel for a total length of 20 cm at different temperature and inlet relative humidities.

Study with limiting current density

As was described above, the model was refined and an equation was added to calculate the limiting current density out of geometrical properties. From the previous study it was concluded that the channels should be as short as possible, and so the channel length was fixed to the lower end of the spectrum, 50 mm. In addition, the height of the channel was 300 microns and the channel and land area width was 150 microns, respectively. The height of the channels was the maximum value because it would afford the highest stoichiometries owing to the lowest pressure drops.

As the number if input parameters is now very large, only exemplary results can be presented here for the sake of brevity. In an extended version of the model, the cell voltage will be included as well, and consideration of the cell power density compared to the compressor work will be included. Table II lists exemplary results for the chosen cases with the shortest and highest channel.

TABLE II. Exemplary results for the limiting current density study.

Parameter	T = 60 °C	T = 70 °C	T = 80 °C
λ	4.3	2.9	1.8
$I_{l,avg}$ [A/cm^2]	16.8	14.6	10.9
ϕ_{avg} [%]	103.2	100.9	99.32

It is interesting to observe that the limiting current density decreases with increasing temperature. The reason for this is that when the inlet air is nearly fully humidified, the concentration of the oxygen decreases as the temperature increases, resulting in a lower limiting current density. The calculated stoichiometries are still quite low, but this can not be a concern in these calculations because the mass transport resistances are included.

Conclusions

A simplified model has been developed to identify suitable operating conditions such that a miniature fuel cell with a perforated metal GDL can operate at a channel relative humidity at or below 100% while the outlet relative humidity was set to 100%. The goal was to identify geometrical conditions that would keep the channel RH at 100 % so that the holes in the perforated GDL would remain dry. Simulations showed that it is impossible under the given assumptions and the RH will always be higher than 100% in the middle of the cell, but shorter channels and high channels are helpful to reach this goal. The calculated stoichiometries are in many cases fairly low and give reason to concern about mass transport problems. Therefore, the model was refined and included the limiting current density calculations. The overall versatility and usefulness of such a model has been demonstrated, and it can be used to find appropriate boundary conditions for a refined model that uses the methods of computational fluid dynamics.

Acknowledgments

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