Literature study on wettability effects on water management in cathode gas channel and micro/macro porous layer in proton exchange membrane fuel cells (PEMFC)

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ABSTRACT

PEMFCs are subject to many areas of application. A widespread research is going on in different areas of application. In this literature study, a key goal was identified as minimizing auxiliary components such as compressors, humidifiers etc. The key issue is water management and this issue is directly connected to PEMFC function and performance. Since PEMFC and its relative DMFC (direct methanol fuel cells) are subject to miniaturization, there is a need for zero number of auxiliary components. In pursuit of reducing the auxiliary components, wettability was identified as key physical driver. Wettability directly effects the water management of a PEMFC. Many aspects on this are viewed in this article. The conclusions from this article study are that deeper knowledge of the flow and mass transfer is needed in the GDL/MPL/CL by new experimental methods and computer based methods. Design of gas channel should be kept simple and efficient due to the potential high volume manufacturing and low price of PEMFCs. New methods to mange water such as doping the GDL/MPL with PTFE or CL with i.e. SiO3 should be investigated in a complete cell simulation in order to find optimum overall PEMFC design.

NOMENCLATURE

PEMFC Polymer Electrolyte Fuel Cell
RH Relative Humidity
GDL Gas Diffusion Layer
MPL Micro porous layer
OCV Open Circuit Voltage
EDO Electro-Osmatic Drag
PTFE polytetrafluoroethylene
VOF Volume Of Fluid
LBM Lattice Boltzmann Method
CL Catalyst layer
HVM High Volume Manufacturing

INTRODUCTION

Water management in PEMFC is a critical multi-physic issue. In a PEMFC, water is important for the overall function of the fuel cell but if there is too much water then the fuel cell performance will go down as well as if there is too little water. The issue is to keep balance of water in the PEMFC and thereby water management is very important.

Water management issues are not the same for all applications of PEMFC. There are different requirements from different industries due to different operating conditions. In automotive industry, the fuel cell design is different from miniaturized electronic industry. The overall requirement is simplicity such as reduction of auxiliary components i.e. heat exchangers, compressors and heat exchanges [1-2]. When it comes to miniaturized PEMFC then the cathode is supplied with ambient air and then water removal is only due to evaporation [1].

The PEMFC will operate at optimum if the membrane is 100% humid. The topic of membrane hydration is directly related to water management and is affected by thickness and morphology of the membrane, gas diffusion layer, flow-field design, operating current density, gas humidification and cell temperature [3]. The membrane is, as mentioned above, necessary to keep as humid as possible. If the humidity of the inlet gas is not enough then gas humidification is needed. Flooding can occur on the cathode side due to too much water in the gas combined with product water. It is the gas channel and GDL that is flooded and the effect is both drop in cell voltage and an increase in two-phase pressure drop [3].

In this paper, a literature study is performed on water management in PEMFC. Aspects on water management methods, visualization of water in PEMFC and numerical simulation of water management is given. The aim with the literature study is to highlight the effect of contact angle (wettability) on water management. This paper will consider effects of mechanical design, porous material choice and usage of additive to internally change wettability character.

PROBLEM STATEMENT

Water management in PEMFC is essential to handle due to its direct impact on performance. Membrane has highest
performance at 100% RH, if there is no water there is no conductivity.

In order keep the membrane at 100% of RH careful choice of material and PEMFC design has to be accomplished as well as the optimal inlet conditions. There are two extreme situations to mention; flooding and dry out. Flooding will result in blocking the pores in the electrodes or the gas diffusion layer [14]. It is electrochemical and diffusion processes that are the key processes for water management, in Figure 1, these processes are stated.

![Fig. 1. [14] The different water movements to, within, and from the electrolyte of a PEM fuel cell.](image1)

If studying Figure 1, the different types of water production and transfer is visualized. If starting from top there is water production and drag within the cathode and that origin from H+ ions moving from anode to cathode and pulls water molecules with them, this is called electro-osmotic drag [14]. These processes are proportional to current density. Then there is evaporation, back diffusion and external humidification.

It is important to feed the PEMFC with the correct RH of air in order to get high enough RH in the exit, hence feeding the cell with a higher flow rate than necessary [14]. This can be termed as feeding the cell with the stoichiometric rate needed to meet the requirements. Figure 2 show the exit RH to operating temperature at dry inlet air. Then it is obvious that the operating temperature desired, in order to maintain the correct humidity, is around 70 to 80 degrees Celsius. It could be possible to lower the operating temperature but then a higher stoichiometry is required. This will then lead to i.e. higher pressure drop. It is important to notice that operating temperatures above 60 degrees Celsius requires extra humidification for the reactant gases [14]. Figure 2 display the operating temparture and RH as well as stoichiometric curves.

![Fig. 2. [14] A graph of relative humidity versus temperature for the exit air of a PEM fuel cell with air stoichiometry of 2 and 4. The entry air is assumed to be dry, and the total pressure is 1 bar.](image2)

It is clear that improved design of PEMFC is needed on the water management area due to its complexity to handle. In the literature survey below, some methods to improve water management are highlighted from several researchers. Aspects on how to experimentally visualize water management is also investigated.

**LITERATURE SURVEY**

**Survey on impact of water management issues**

Problems related to water management can be hard to detect. In the cases of flooding or dry out, the effects can be shorter life time and low performance. If a PEMFC operate at lower RH than 100% for a long time, it can lead to membrane degradation [13]. The effects of lowering RH are significant on life time. If the RH on cathode side is 70 % (compared to 100%) and RH on anode side is 100% (kept the same in both cases) then the life time reduces from 3300 h to 1100 h [14]. In the case of 100% RH on anode and 0% RH on cathode, the life time reduced to 300 h [14]. It is important to have signals telling if water content is to low or high in the cell even if it is possible to calculate the optimal operating conditions. A way to detect if the RH is too low is by measuring OCV and hydrogen cross-over rates [14]. The problem seems to be that peaks in OCV and hydrogen cross-over rates may be signals on other problems in the PEMFC and not only water content.
Experimental method to measure net water transport

An approach to measure spatially resolved water crossover coefficient was found by [12]. They had an instrumented cell that combines functions such as current collection and gas sampling. It is reported to be capable of measuring current and species distributions simultaneously from a single experiment. Wang et al. use a straight-channel of 10 cm in a co-flow H_2/air cell. Methods to calculate the net water transport coefficient distribution \( \alpha(x) \) are described in [12]. Local current density and mole fraction of water is measured and then net water transport coefficient distribution can be calculated.

[1] carried out experiments on water management in micro air-breathing PEMFCs. By changing the cover opening ratio, it was possible to manage water content in micro-PEMFCs by self-hydration. Water ejection from the cathode side is only by evaporation. Water back-diffusion to anode side was proposed to be removed by a Nafion 112 membrane on the back surface of the anodic room. [1] found for a cell situated in an atmosphere at 10% RH, operating at 0.5 V with 5% opening ration cover led to current densities of 270 mA cm\(^{-2}\). This is similar to 70% RH environment without cover.

[3] conducted experiments on seven evenly spaced flow channels of size 10 cm x 1 mm with bi-polar plate material of hydrophilic nature. The GDL and MPL are loaded with PTFE, the MEA is a Gore membrane. In their experiments it was found that the two-phase front move up towards the inlet as flow stoichiometry decreases at a given current density. [3] define a new parameter walled wetted area ratio to characterize channel flooding and liquid water coverage on GDL. The different types of flow regimes are also identified as; single-phase flow, droplet flow, film flow and slug flow.

Gas channel design and modelling

A u-shaped channel was simulated in [4] and they studied the effects of contact angle (wettability) on gas channel walls and GDL surface. The configuration was a rectangular u-bend and it was compared to a u-bend with a radius turn. This was done to see the effects on channel configuration simultaneously with change of contact angle. [4] showed by quasi-steady state simulation that hydrophilic walls (and hydrophobic GLD surface) improved water management in the gas channel compared to hydrophobic walls. According to the results, water was trapped in the recirculation zones in wall corners and the hydrophilic character of the promoted water transport along channel surfaces or edges with the cost of higher pressure drop. The round shape of u-bend corners distributed the water to the GDL and resulted in blocking of pores. The pressure drop was not significantly larger with sharp u-bend. If the gas velocity inside the channel was increased, the pressure drop increases linearly.

[8] proposed a design of two channels, one primary and one secondary. The primary gas channel is of triangular shape and the secondary channel is designed in order to have capillary forces to dominate. This would result in water droplets are lifted into that secondary channel and transported away. CFD simulations were carried out for two different opening angles, 15° and 30°. Experiments were also carried out to validate the CFD simulations. This type of passive removal of water was found to be most efficient at opening angles larger than 10° combined with hydrophilic walls. [8] claim this method to promote new channel design that is cost efficient for PEMFCs without the need for external water removal components.

On the subject of manifold channel design, [6] found through CFD simulations in Fluent that uneven distribution of water could cause blockage of airflow and uneven distribution of air flow. It was also found that water in the outflow manifold could be blocked by air/water streams from the gas flow channels even at small amounts of water. This will affect the water drainage. Water could be transported back towards the inlet manifold if the water hit the wall facing the inlet. This issue could be solved by converging cross-sectional area in inlet manifold and diverging cross-sectional area in outlet manifold. [6] proposes a manifold design where the inlet flow direction is the same as the outlet flow direction. This is done in order to have the largest amount of water close to the outlet. Regarding wall-adhesion (contact angle), [8] state that keeping contact angle close to 90° would assist water removal. Water removal would be managed by channel design.

A three-dimensional simulation of water droplet dynamics in a PEMFC channel was performed by [16] on a 1000x250x250 μm domain. The droplet dynamics was simulated by a transient 3D CFD code using a VOF method. Effects investigated were; static contact angle of the bottom wall, air inlet velocity, water injection velocity and pore size on the water droplet dynamics. [16] found that droplet emergence in a micro channel is a dynamic and quasi-periodic process that include cyclic formation, deformation, detachment and removal of droplets. If the GDL surface was highly hydrophobic, water removal was promoted in terms of decrease in detachment time, detachment diameter, water saturation and coverage ratio. The drawback is that flow resistance coefficient increase. If the walls were hydrophilic, the water droplets would spread on the wall and coalescence into a liquid film. High inlet velocity promotes water removal in terms of earlier deformation and detachment of water droplet. [16] conclude that water saturation (inside GDL), water coverage ratio, detachment diameter and flow resistance decrease with increased Reynolds number.

Lattice Boltzmann simulations were carried out by [17-18]. Both references used LBM to simulate water transport in gas channel with wettability effects.

Gas diffusion layer design and modelling
Catalyst layer and membrane configuration

[22] added SiO₂ nanosized/sulfonated to the cathode catalyst layer. The effects of adding both nanosized and sulfonated SiO₂ improved hydration of the membrane at low RH. The proton conductivity was improved by adding the sulfonated SiO₂ but the nanosized did not show this improvement. These experiments were conducted in order to be able to decrease the need for auxiliary components.

[23] added hygroscopic γ-Al₂O₃ particles into the catalyst layer that increased the wettability of the anode catalyst layer as well as enhanced the water adsorption of the anode due to back diffusion. This was done in order to improve wettability and performance of PEMFC at low-humidity conditions.

PROJECT DESCRIPTION

A literature study has been conducted on wettability effects of water management in cathode gas channel and macro/micro porous layer in PEMFCs. A linkage between findings in literature of GDL/MEA/CL specialized articles and gas channel design article is to be found in aspect on wettability effects. The findings in the articles will be analysed and viewed from different angles, this in order to find possibilities to have more flexible operating conditions i.e. at low RH or minimizing the need for auxiliary components. Since PEMFCs are promising to be used in miniaturized applications, it is important to highlight the research on this. The focus on wettability is chosen due to its importance in water management which is the most challenging problem to handle. The approach will be top-down from gas channel to membrane on the cathode side. Aspects from experimental correlations found for models along with theoretical findings are included in the discussion.

Top-down introduction

In order to find an optimal design of a PEMFC, some kind of angle of attack has to be found. This article uses the wettability as identifier and then scans the resent research available. It is some work to be done on combining experimental and modelling in order to find this optimal configuration of a PEMFC. Since wettability is chosen as identifier, the main focus is on the water management issue and cathode side of the PEMFC.

If briefly reviewing the structure of the PEMFC starting with the bi-polar plate. The bi-polar plate is basically a piece of some kind of metal in order to conduct electricity in a good way. The bi-polar plate has the freedom to be shaped in order to form the bulk gas channel and manifold. The design of this bi-polar plate has big impact on water management as well as the micro-structure of the inside walls that gives the hydrophobic/hydrophilic behaviour.

Below the gas channel is the GDL/MPL in connection with CL and membrane. The GDL/MPL is basically a porous structure but it has many design parameters as well as doping possibility to change its properties that has great impact on water management. Recently there have been attempts to find out what is happening inside the GDL/MPL [19-21]. The membrane configuration also has great impact on water management and experiments on doping the membrane to be more hydrophilic in low-RH environments have been done [22-23].

How to configure the different components in the PEMFC depends on application.

Wettability effects on gas channel design

The gas channel is a difficult task to design. It is important that the channel distribute the oxygen evenly over the GDL surface. Product water emerging from the GDL has to be transported away in order prevent surface blocking of water that will lead to poor oxygen transport by the GDL to the active zone. [4] simulated a U-shaped channel where the wettability of the walls and GDL was changed together with inflow velocity. [4] only cared about GDL surface wettability but it is important to look into the GDL internal wettability in order to make a good overall design of the cathode side. However, [4] showed interesting conclusions on wettability effects on the walls inside the gas channel as well as design of the u-bend (sharp or rounded). As stated in the literature survey, hydrophilic walls and hydrophobic GDL surface combined with a sharp U-bend resulted in main water collections on the walls of the channel.

There has been an attempt to manipulate the channel geometry by having a capillary channel to transport away the water was done by [8]. This successfully removed the water from the GDL surface. [6] experimented on manifold design in order to have an even distribution to the gas channels and found some conclusions stated in the literature survey.

Judging from [4, 6, 8], there may be ways to handle the water inside the gas channel. If looking at the perspective of manufacturing, it may not be economic to make special designs
of the channels. It may be hard to have high volume manufacturing (HVM) of such cells and miniaturizing those channel designs may by impossible.

[16] performed a 3D CFD simulation in a gas channel on bubble dynamics. Since bubble of water emerge from the GDL surface (due to its hydrophobic character), this is an interesting topic to investigate. [16] found that if the walls in the gas channel are highly hydrophilic, then the bubble will form a liquid film on the walls. They also found that increased velocity (Reynolds number) in the channel promoted water removal. It was not clear in the article if it was pro/con hydrophilic walls in the gas channel. A conclusion can be drawn and it could be appropriate to find a compromise between inlet velocity and wall wettability. The aim is to find the most efficient flow configuration to remove water. If the water can remain in droplet form then it will also promote heat transfer more efficient that a film of water on the walls.

Conclusions from the study on gas channel design are that a channel with optimised wettability on walls, inlet velocity and manifold design will promote economic and efficient water removal. New simulation methods such as LBM [17-18] way assist in better understanding of flow and heat/mass transfer in micro channels.

**Wettability effects on GLD/CL/membrane design**

The GDL design is very important for the function of the PEMFC. Its function is to transport oxygen to the active zone as well as transport product water away from the active zone and at the same time makes sure that the membrane is hydrated to an appropriate level.

When analysing the GDL to reveal the water transport inside it, capillary pressure is used to describe capillary flow in porous material. [15] Capillary pressure is defined as

\[ P_c = P_l - P_g \]  

(1)

where, \( P_l \) is liquid water phase pressure and \( P_g \) is gas phase pressure. Basically, the capillary pressure is a thermodynamic quantity governed by the liquid-gas interface and the properties of the porous medium [15]. This thermodynamic property can be described by the modified Young-Laplace equation [15]

\[ P_c = -\frac{\sigma \cos(\theta)}{R_{\text{eff}}} \]  

(2)

where, \( \sigma \) is surface tension between phases (air/liquid interface), \( \theta \) is contact angle of the air/liquid interface on the porous surface and \( R_{\text{eff}} \) is the effective pore radius. Wettability is defined to be hydrophilic (\( \theta < 90^\circ \)) or hydrophobic (\( \theta > 90^\circ \)). Another important property is liquid saturation (\( S_l \)) in the porous media. Liquid saturation is the fraction of total pore volume occupied by liquid [15]. When having complex porous media with both hydrophilic and hydrophobic character, it is important to look at the capillary pressure/liquid saturation relationship. This means that \( \theta \) and \( R_{\text{eff}} \) in eq. (2) are functions of liquid saturation, \( S_l \) [15]. The liquid saturation is defined in [15]

\[ S_l = \frac{V_{\text{syr}}}{V_{\text{pore}}} \]  

(3)

where, \( V_{\text{syr}} \) is syringe volume (total volume of water) and \( V_{\text{pore}} \) is pore total volume. This is under assumption that the irreducible saturation is less than 5%. Capillary number is also defined in [15]

\[ Ca = \frac{\langle u \rangle \mu_l}{\sigma} \]  

(4)

where \( u \) is the superficial velocity of the invading phase, \( \mu \) is the viscosity of the invading phase and, \( \sigma \) is surface tension between phases (air/liquid interface). It is possible to use the Ca number to predict phase displacement behaviour [15].

The GDL/MPL is difficult to simulate and mostly experimental article was found on the subject. However, this highlights the complexity of the flow inside a porous media. [20] compared different models to simulate the flow inside a GDL and found that both pore-network model and LBM model works for this to some extent.

In most cases, the GDL wettability is only considered on the surface in the gas channel. [19] found interesting relation ship between compression of GDL and capillary pressure. Capillary pressure and viscous forces dominate inside the GDL.

The conclusion from studying GDL design and configuration is that doping the GDL with PTFE improves the water management inside the GDL. When it comes to doping the catalyst layer, application of PEMFC has to be considered. By introduction particles of i.e. \( \text{SiO}_3 \) the wettability of the membrane increased and allow for operation in low-RH environment. A side effect was that sulfonated \( \text{SiO}_3 \) increased proton conductivity in the membrane.

**CONCLUSIONS**

The findings in literature [14] regarding cell operation at low RH highlights the need for optimizing operation to run at maximum life time. Since life time will be a marketing method in the future, it is important to handle those bottlenecks today. It is not only the aspect on running at close to 100 % RH. It is also important to be aware of the fact that GDL and membrane degradation will induce flooding at earlier stages. The porous structure in the GDL can erode due to electrochemical
corrosion [14] and thereby increase liquid water content. This degradation and operating condition might have to be controlled during operation in order to increase life time and thereby market value.

In order to validate numerical models, detailed experiments that can capture i.e. species distribution. Wang et al. [12] engineered an experimental approach to do this for measuring water crossover coefficient. This type of data is very important for developing numerical methods to calculate the protonic related water transport.

Final conclusions on recent findings in articles regarding water management in low-RH environment/design for auxiliary component minimization.

Since PEMFCs are object to miniaturization, it is important to think high volume manufacturing (HVM). It may be unrealistic to have complex design of gas channels as discussed in the article. The conclusion of that is the need for deeper understanding on how to handle water in the layers below the gas channel i.e. GDL/MPL/CL/membrane this in order to have economic and efficient water removal by simple design of the gas channel. Sometimes, it may not be necessary to have auxiliary components attached to the cathode/anode and the water management has to be solved within the cell. If the application allows for auxiliary components, the mission will be to minimize the number of such components.

REFERENCES


