WATER MANAGEMENT STUDIES IN AUTOMOTIVE FUEL CELL

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Abstract

The management of water in a polymer electrolyte membrane (PEM) fuel cell running at a set current is provided in a simplified form. In a two-dimensional slice from the inlet to the exit and across the membrane, the consumption of gases in the flow field channels is associated with the electric potential and water content in the polymer membrane. Particular consideration given to the sensitivity of along-the-channel current density to inlet humidity levels, the make-up of the gas stream, and the stoichiometry of the fuel and oxygen. For proper fuel cell modeling, it is discovered that the parameters defining the nonequilibrium kinetics of the membrane/catalyst interface are crucial. The modeling of nonequilibrium membrane water uptake rates uses a novel parameter. In subsequent runs that compare polarization curves, current density and membrane hydration distributions, water transfer, and stoichiometric sensitivity to the remaining experimental data, four parameters—the exchange current, a membrane water transfer coefficient, an effective oxygen diffusivity, and an average membrane resistance—are fitted to a subset of data and then held constant.

Keywords: Hydrogen energy, fuel cell, electrochemistry, flooding, PEMFC

INTRODUCTION

A popular alternative fixed and mobile power source is the fuel cell, an electrochemical device that converts the chemical energy of a gaseous fuel directly into electricity. They support heat engines, lessen the pervasive reliance on fossil fuels, and hence have important consequences for national security and the environment. As a result, they are being intensively researched for stationary commercial power generation, home uses, and transportation technologies. The use of fuel cells in automobile powertrains is stressed for a variety of reasons, including their significance in terms of worldwide fuel consumption and emission production as well as the fact that ground vehicle propulsion conditions constitute the most difficult control problem. An electrolyte is sandwiched between two electrodes to form a fuel cell. The electrolyte has a unique characteristic that lets protons—positive ions—pass through while obstructing electrons. When hydrogen gas travels over one electrode, known as an anode, it splits into hydrogen protons and electrons with the aid of a catalyst. While the electrons move through an external circuit to produce electricity, the protons move through the electrolyte to the other electrode, known as the cathode.
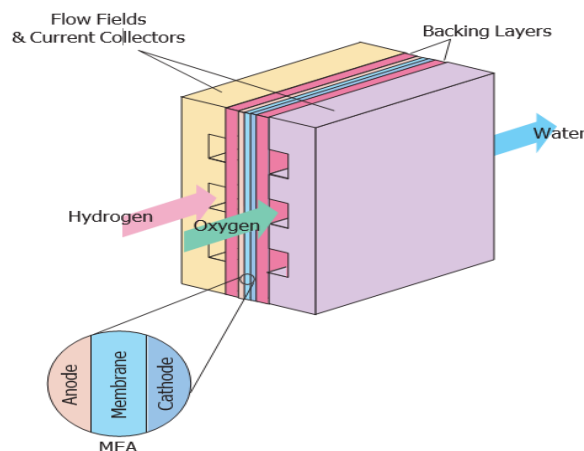
Figure 1: Fuel cell structure

Due to its high efficiency, low noise, and environmental friendliness, the proton exchange membrane fuel cell (PEMFC) is a promising energy conversion technology [1-3]. The performance of PEMFCs is strongly impacted by the challenging and significant issue of water management [4, 5]. A lack of water would cause the membrane to hydrate, which would lower proton conductivity. In the meantime, too much water would cause flooding in the catalyst layer, the gas diffusion layer, and even the flow channel, impeding the transport of the reactants. Various efforts are made to enhance water management in PEMFC [6–9], including improvements to the control system, porous media of the catalyst layer or gas diffusion layer, and the bipolar plate. The main problem with water management in the operation process is striking a balance between dehydration and flooding [10-12]. The membrane's humidity is influenced by the quantity of reactant flow and water fed into the anode and cathode flow streams. High polarisation losses are caused by flooded fuel cells and dry membranes. Water molecules are both created in the cathode and moved from the anode to the cathode by the hydrogen protons as the current is extracted from the fuel cell. Water diffuses from the cathode to the anode as the concentration of water in the cathode rises due to the concentration gradient. Water produced as load increases, changes in the absolute and relative reactant pressure across the membrane, variations in air flow rate, and variations in stack temperature, which alter vapour saturation, are just a few of the factors that can cause fuel cell humidity to shift. There is flooding in PEMFCs, as evidenced by a large body of literature [13]. PEMFC with transparent windows were employed by Lee and Bae [14] to visualise the flow phenomenon in the fuel cell channels. The phenomena of flooding was seen in both single cells and stacks. When Zhan et al. [15] used a high-speed camera to study water transport in a transparent PEMFC, they discovered that if the gas velocity wasn't high enough, liquid water would stick to the channel walls. Soft X-ray radiography was created by Sasabe et al. [16] to view the movement of liquid water inside a PEMFC. According to the findings, there was more liquid water under the rib region than under the channels. Alrwashdeh et al. [17] used neutron radiography to analyse the water distribution in the flow channel with obstacles, and they discovered a significantly more uniform distribution of water there. Using FLUENT with a

volume of fluid (VOF) algorithm and user defined function (UDF), Wang and Zhou [18] investigated the behaviour of liquid water and the flooding process in GDL and reactant flow channels of a PEMFC. It was discovered that the porosity of the porous layer was a crucial element during the water removal process and that the channel design would directly impact the liquid water flooding behaviour. Flooding with water resulted in PEMFC irreparable damage in addition to performance deterioration [19–21]. According to Yang et al. [22] and Kim et al. [23], anode flooding induced significant carbon corrosion in the anode as a result of the shortage of fuel. Kim conducted an experimental investigation on the membrane electrode assembly (MEA) degradation brought on by anode flooding in a PEMFC over an extended period of usage. Due to the large potential of anode flooding that was caused, it was determined that carbon corrosion and carbon oxidation may be primarily blamed for the performance decline. Taniguchi et al. [24] investigated the cell reversal-induced PEMFC deterioration behaviour under air starvation conditions, which may be brought on by start-up, load changes, and water buildup. Chemical investigation revealed platinum sintering and the decrease of cathode catalyst surface area.

Effective water transport and removal techniques are the primary priority of water management to address the issue of floods at PEMFC. Ijaodola et al. [25] studied the mechanisms of water transportation, the effects of water management, various methods for visualising liquid water, and several approaches to prevent water flooding in PEM fuel cells. The study provided a summary of the elements, such as temperature gradient, pressure drop, material mechanical properties, flow field design, etc., that influenced the performance of the cell. The most often used approach to improve water transport in PEMFC among them was the optimisation of flow channel geometry and diffusion medium structure [26–29]. Liu et al.'s [30] numerical simulation was used to investigate how applying a slope turn in a serpentine flow field may improve water removal from the MEA surface. For efficient water removal in PEMFC, Qin et al. [31] developed a modified flow channel produced by placing a hydrophilic plate in a regular flow channel. With the contact angle between the bottom channel surface and the MEA surface, the inserted plate could make the water removal process easier. Using the lattice Boltzmann method, Molaeimanesh and Akbari [32] investigated the impact of GDL with various PTFE contents on water droplet removal. They found that the carbon fibre without PTFE coating prevented the water removal due to the strong interfacial forces, and an appropriate coating method for GDL was the key issue that needed to be resolved in future studies. Additionally, it was investigated how fuel cell system optimisation affected water transportation. Kim et al.'s [33] research of the elimination of water present in the GDL at low temperature by introducing a tiny quantity of hydrogen into the cathode involved this experiment. Condensed water would evaporate and diffuse to the flow channel due to the heat produced by the hydrogen and oxygen interaction at the cathode, demonstrating efficient flooding mitigation in the cathode. A H2/O2 dead-ended PEMFC's capacity to remove water was examined both conceptually and empirically by Wan et al. They discovered that water evacuation was aided by moisture that had collected near the end of the stack. Yu et al. [35] have studied the impact of gravity on various gas intake modes. The highest performance was demonstrated by the air and hydrogen inlets, which were positioned on the upper side of the stack and slanted at a 90° angle. This

result suggests that with suitable design, gravity might aid in the evacuation of water. As previously reported, PEMFC experienced frequent water inundation. With the development of water management strategies, partial flooding is unavoidable, especially near the downstreaming of the flow channel due to the accumulation of water molecules [36], which causes the serious degradation of catalyst layer (CL) at this area [37,38]. Large area flooding can be effectively suppressed during the operation. This study employed theoretical analysis to determine the amount of liquid water in the PEMFC.

THEORETICAL ANALYSIS AND MODELLING

Theoretical Framework

Water is transported through the fuel cell by a variety of processes, including evaporation, condensation, diffusion, electro-osmosis drag and permeation, among others [38]. The humidified reactants introduce water vapour into PEMFC, and the mass flow rate of water vapour at the input might be stated as follows [39].

Anode

$$W_{a, in} = \frac{\lambda n I}{2F} \cdot \frac{\Phi \cdot p_{sat} \cdot T_{an,in}}{p_{an,in} - \Phi \cdot p_{sat}(T_{an,in})} M_{H2O}$$

Cathode,

$$W_{c, in} = \frac{\lambda n I}{4F} \cdot \frac{\Phi \cdot p_{sat} \cdot T_{ca,in}}{p_{ca,in} - \Phi \cdot p_{sat}(T_{ca,in})} M_{H2O}$$

Where,

λ = the stoichiometry,

n = the number of cells in the stack,

I = the current,

F = the Faraday constant,

RH = the relative humidity,

$T_{an,in}$ = inlet temperature at the anode,

$T_{ca,in}$ = inlet temperature at the cathode,

$p_{an,in}$ = inlet temperature at the anode,

$p_{ca,in}$ = inlet temperature at the cathode,

p_{sat} = saturation water vapor pressure and

M_{H2O} = the molecular weight

Similarly, the water vapor mass flow rate at the outlet is shown below.

Anode,

$$W_{a,\,in} = \frac{(\lambda - 1)nI}{2F} \cdot \frac{\Phi \cdot p_{sat} \cdot T_{an,in}}{p_{an,in} - \Phi \cdot p_{sat}(T_{an,in})} M_{H2O}$$

Cathode,

$$W_{c,\,in} = \frac{(\lambda - 1)nI}{4F} \cdot \frac{\Phi \cdot p_{sat} \cdot T_{ca,in}}{p_{ca,in} - \Phi \cdot p_{sat}(T_{ca,in})} M_{H2O}$$

Where,

$T_{an,out}$ = outlet temperature at the anode,

$T_{ca,out}$ = outlet temperature at the cathode,

$p_{an,out}$ = outlet temperature at the anode,

$p_{ca,out}$ = outlet temperature at the cathode

Additionally, the H2/O2 fuel cell can use the aforementioned formulae. Before using the stoichiometry in the case of H2/air, the water vapour mass flow rate at the cathode should be multiplied by a factor of 4.76. Due to the highly fast electrochemical reaction speed and immediate release of heat, the created water during operation initially exists in the form of gas, as stated in the formula below [40].

$$W_{gen,\,H2O} = \frac{\lambda nI}{2F} M_{H2O}$$

The quantity of liquid water present in a PEMFC determines the risk of flooding, and the liquid water flow rate is influenced by the amounts of water vapour present at the intake and exit, the creation of water vapour, and the rate of phase change. The following calculation indicates the likelihood of water flooding by calculating the quantity of liquid water in a PEMFC.

$$W_{H2O} = W_{an,in} + W_{ca,in} + W_{gen,\,H2O} - W_{an,out} - W_{ca,out}$$

Table 1: Thermodynamic Constants Used In Model

Symbol	Variable	Value
P_{atm}	atmospheric pressure	101.325 kPa
T_{atm} γ	atmospheric temperature ratio of	298.15 K 1.4
C_p	specific heat of air	1004 J/(mol·K)
ρ_a	constant pressure specific heat of air air density	1.23 kg/m^3 8.3145 J/(mol·K)
$\bar{R}$	universal gas constant air gas	286.9 J/(kg·K)
$R_a R_{O2}$ R_{N2}	constant oxygen gas constant	259.8 J/(kg·K)
R_v	nitrogen gas constant vapor gas	296.8 J/(kg·K)
R_{H2} M_{O2}	constant hydrogen gas constant	461.5 J/(kg·K) 4124.3 J/(kg·K)
M_{N2}	oxygen molar mass	32×10^{-3} kg/mol 28×10^{-3} kg/mol
M_v	nitrogen molar mass vapor molar mass	18.02×10^{-3} kg/mol
$M_{H2} F$	hydrogen molar mass	2.016×10^{-3} kg/mol
	Faraday number	96485 coulombs

Mathematical Model

The stack voltage, anode flow, cathode flow, and membrane hydration models are the four interacting sub-models that make up the fuel cell stack model. Figure 2 displays a block representation of the stack concept. The stack temperature is considered to remain constant in this model even if we compute the heat produced by the process. In the voltage model, a set of operational parameters, including pressure, temperature, reactant gas partial pressure, and membrane humidity, are utilized to solve an equation to determine stack voltage. The pressure and relative humidity of the reactant gas flow inside the stack flow channels are determined by the cathode and anode flow models using mass conservation and thermodynamic principles. The membrane hydration model illustrates how water is transferred across a membrane.
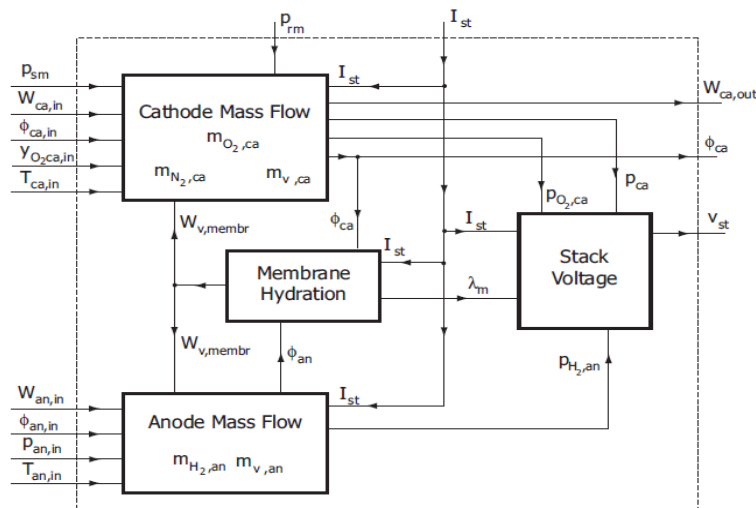

Figure 2: Fuel cell block diagram

Stack Voltage Model

The energy balance between the chemical energy in the reactants and the electrical energy is used to compute the fuel cell's open circuit voltage. There are three primary losses in the fuel cell activation loss, ohmic loss and concentration loss that are taken into account.

Here, cell terminal voltage is given by

$$V_{fc} = E - V_{act} - V_{ohm} - V_{conc}$$

Where

E = Open circuit voltage

V_{act}= Activation loss

V_{ohm}= Ohmic loss

V_{conc}= Concentration loss

Open Circuit Voltage

Chemical energy is instantly transformed into electrical energy by the fuel cell. The change in Gibbs free energy (Δg_f), which is the difference between the Gibbs free energies of the product and the reactants, may be used to determine the chemical energy released by the fuel cell.

$$E = \frac{-\Delta g_f}{2F} = \frac{\Delta g_f^0}{2F} + \frac{RT_{fc}}{2F} ln \left[\frac{p_{H2} p_{O2}^{\frac{1}{2}}}{p_{H_2O}} \right]$$

Activation Loss

The activation loss or activation overvoltage is a result of the need to cause electron transfer and to break and form chemical bonds in the anode and cathode

$$V_{act} = V_0 + V_a(1 - e^{-c_1 i})$$

Where,

V_0 = Voltage drop at 0 current density

V_a, c_1 = Temperature and pressure dependent constant

Ohmic Loss

The polymer membrane's proton transfer resistance and the electrode and collector plate's electron transfer resistance are to blame for the ohmic loss, respectively.

$$V_{ohm} = i \times R_{ohm}$$

Concentration Loss

The change in concentration of the reactants as they are consumed in the reaction leads to concentration loss or concentration overvoltage.

$$V_{conc} = i \left(c_2 \frac{i}{i_{max}} \right)^{c_3}$$

Where, c_2, c_3, and i_{max} are constants that depend on the temperature and the reactant partial pressure and can be determined empirically.

Table 2: Parameters used in simulation

Symbol	Variable	Value
$\rho_{m,dry}$	membrane dry density	0.002 kg/cm^3
$M_{m,dry}$	membrane dry equivalent weight	1.1 kg/mol
t_m	membrane thickness	0.01275 cm
n	number of cell in fuel cell stack	381
A_{fc}	fuel cell active area	280 cm^2
d_c	compressor diameter	0.2286 m
$J_{cp} V_{an}$	compressor and motor inertia anode volume	5×10^{-5} kg·m^2 0.005 m^3
V_{ca}	cathode volume	0.01 m^3
V_{sm}	supply manifold volume	0.02 m^3
V_{rm}	return manifold volume	0.005 m^3
$C_{D,rm}$	return manifold throttle discharge coefficient	0.0124
$A_{T,rm}$	return manifold throttle area	0.002 m^2
$k_{sm,out}$	supply manifold outlet orifice constant	0.3629×10^{-5} kg/(s·Pa)
$k_{ca,out}$	cathode outlet orifice constant	0.2177×10^{-5} kg/(s·Pa)

RESULTS AND DISCUSSION

Effect of Temperature

The consumption of the reactants would result in a rise in the partial pressure of water vapor at the output. The production of water molecules would result in a rise in the relative humidity close to the outflow. Additionally, the fact that liquid water was present in the PEMFC suggested that the exhaust may get saturated at the output. Fig. 3 displays the liquid water flow rate at various temperatures and relative humidity levels. Figure 3 showed that when the relative humidity increased, the flow rate of liquid water also increased. Due to the exhaust's limited capacity for water vapor, any surplus would condense into liquid water, increasing the flow rate of the liquid water. When RH was less than 0.7, the output liquid water flow rate fell as the temperature rose. But when the temperature rose with high relative humidity, it would rise as well. The difference between the amount of water vapor at the inlet and outflow under the same amount of water production was used to calculate the net liquid water flow rate. The reactant's water vapor concentration might rise due to the increasing temperature, making it easier for water vapor to attain saturation. On the other hand, high temperature conditions were helpful in preventing PEMFC flooding at low relative humidity.
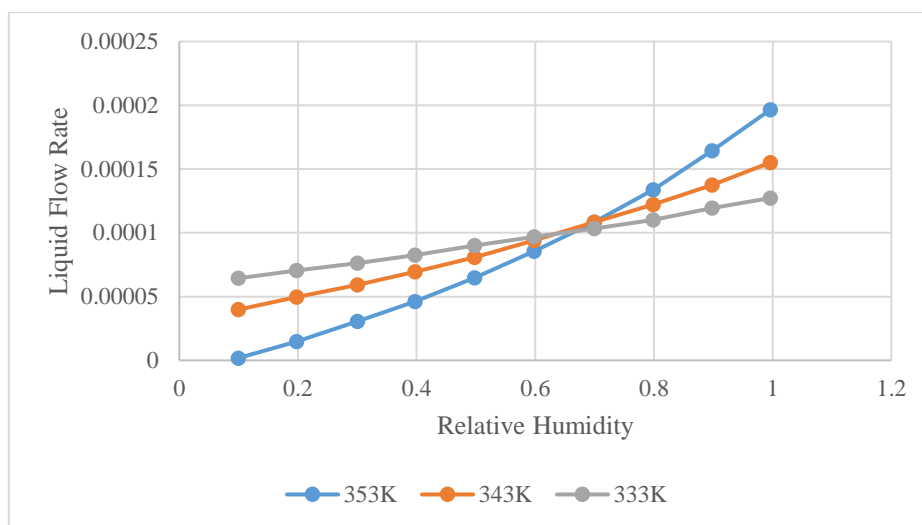
Figure 3: Liquid water flow rate at the outlet (1 A·cm−2)

Effect of Flooding

Fig. 4 depicted the PEMFC's performance during partial inundation. When the catalyst layer and gas diffusion layer were flooded in the rear section by 10% of their volume, the polarization curve nearly corresponded with the original curve, therefore the modest partial flooding had minimal impact on the performance. At 50% flooding of the catalyst layer and gas diffusion layer, the performance significantly degraded. The performance was virtually at the limit value after the back region was almost totally flooded with the percentage reaching 90% or 99%. Increasing the stoichiometry of air supply may generally reduce the phenomena of water flooding [44]. Therefore, in a significant partial flooding condition, unique technology was required for water removal at the down streaming.
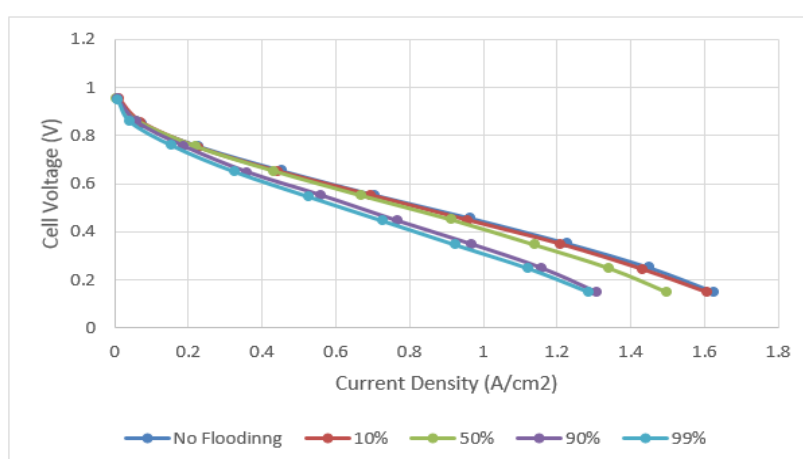

Figure 4: Performance comparison of different flooding extent

CONCLUSION

In this paper, a mathematical model was developed to investigate the effect of flooding on the performance in PEMFC, the following conclusions could be drawn:

1) High temperature conditions were conducive to the suppression of flooding at low relative humidity.

2) Flooding would lead to the deterioration of mass transfer and performance, especially at high current densities. Meanwhile, flooding would cause uneven distribution of current density.

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