Int. Symp. on Convective Heat and Mass Transfer in Sustainable Energy
April 26 – May 1, 2009, Tunisia

ANALYSIS OF THE CATHODE FLOODING IN A PROTON EXCHANGE MEMBRANE FUEL

Faycel Khemili [1,*], Mustapha Najjari[2] and Sassi Ben Nasrallah[1]
[1]Laboratoire d'Etudes des Systèmes Thermiques et Energétiques, ENIM,
Av. Ibn Eljazzar Monastir 5019 Tunisie.
[2]Institut Préparatoire aux études d'Ingénieur, Av. Ibn Eljazzar, Monasir 5019, Tunisia
([*] Corresponding author: khemilifaycel@yahoo.fr)

ABSTRACT. This study investigates the effects of the flooding of the gas diffusion layer (GDL), as a result of liquid water accumulation, on the performance of a proton exchange membrane fuel cell (PEMFC). The transient profiles of the current generated by the cell are obtained using the numerical resolution of the transport equation for the oxygen molar concentration in the unsteady state. The dynamics of the system are captured through the reduction of the effective porosity of the GDL by the liquid water which accumulates in the void space of the GDL. The effects of the GDL porosity, GDL thickness and mass transfer at the GDL–gas channel interface on the evolution with time of the averaged current density are reported. The effects of the current collector rib on the evolution of the molar concentration of oxygen are also examined in detail.

Keywords: Proton exchange membrane fuel cell; Gas diffusion layer; Flooding; Averaged current density.

1. Introduction

One of the most critical aspects of a proton exchange membrane fuel cells (PEMFC) is the water management. There is a delicate balance between membrane hydration and avoiding cathode from flooding. Cathode flooding occurs when water produced exceeds the water removal rate. Flooding in the cathode reduces oxygen transport to reaction sites and decreases the effective catalyst area. In modern fuel cells, cathode (or anode) consists of a; catalyst layer, gas diffusion layer (GDL) and bipolar plates. The GDL is a porous medium electrically conducting. Liquid water that builds up at a fuel cell cathode decreases performances and inhibits operation.

The objective of the present paper is to provide a comprehensive model that describes the evolution of the current density under transient conditions in the presence of a partial flooding of the porous cathode. For this purpose, a two dimensional, transient, single-phase oxygen model is developed. Changes of the molar concentration of oxygen gas-phase with respect to time and liquid water rate production will be derived in terms of an effective GDL porosity.

This article is organized as follows: first we formulate the problem, against the derived model is validated with experimental results. Results concerning the effects of various parameters such as GDL thickness, ribs width and mass transfer at GDL-gas channel interface are presented and discussed.

2. Model development

The present study focus on oxygen mass transport, under transient conditions, taking place in the cathode of a PEMFC. The problem domain under consideration (Fig. 1.) is confined to the porous GDL where the major mass transport limitations occur. The oxygen phase diffuses into the GDL from the humidified air supplied at the inlet of the gas flow channel. The dynamics of the system are captured through the dependence of the effective porosity on liquid water production from the electrochemical reaction at the catalyst layer.

2.1. Effective gas porosity

The presence of liquid water in the porous GDL modifies the effective porosity for oxygen gas transport. The effective gas porosity is determined from the following expression [1,3]:

$$\varepsilon_g = \varepsilon_0 (1 - S) \tag{1}$$

Where ε_0 is the initial porosity of the GDL and S is the liquid water saturation given by:

$$S = \frac{N_p}{N_T} \tag{2}$$

N_T is mass of liquid water corresponding to a complete flooding:

$$N_T = \rho_l \varepsilon_0 h_l w_l M \tag{3}$$

2.2. Oxygen transport: diffusional approach

In this model, we determine the molar diffusion flux of oxygen J_O according to Fick's law:

$$\vec{J}_O = -D_{eff} \vec{\nabla} C \tag{4}$$

Where C is the molar concentration of the oxygen and D_{eff} its effective diffusion coefficient.
The effective diffusion coefficient of oxygen can be termed from the diffusion coefficient in pure gas phase D_0 and the void fraction of the GDL, ε_g using Bruggeman's correction [4]:

$$D_{eff} = (\varepsilon_g)^{3/2} D_0 = (\varepsilon_0 (1 - S))^{3/2} D_0 \tag{5}$$

The basic transport equation for oxygen molar concentration can be stated as:

$$\varepsilon_g \frac{\partial C}{\partial t} = D_{eff} \Delta C \tag{6}$$

The dependence of D_{eff} and ε_g with respect to time is derived from the production of water in the GDL) .

2.3. Boundaries conditions

The GDL is connected to the membrane through catalyst layer CL corresponding to infinitely thin layer and often modelled as interface. The oxygen consumption rate by electrochemical reaction is given by:

$$D_{eff} \left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{i}{4F} \tag{7}$$

The local current density in the catalyst layer is modelled by the Butler-Volmer equation and expressed by Tafel kinetics [5,6]:

$$i = (1 - S) A \, i_0 \delta_c \frac{C(0, y)}{C_{ref}} \exp(\alpha_c F \eta_c / RT) \tag{8}$$

Where i_0 is the reference current density, δ_c the thickness of the catalyst layer, C_{ref} the reference oxygen concentration and α_c the cathode transfer coefficient. In eq. (8), η_c is the activation overpotential corresponding to losses that are associated with the kinetics of the electrochemical reaction

It follows that the boundary condition at the GDL-catalyst layer interface is written as:

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = KC \tag{9}$$

Where

$$K = \frac{(1-S)A_v i_0 \delta_c \exp(\alpha_c F \eta_c / RT)}{4FD_{eff} C_{ref}} \tag{10}$$

The local current density varies with y and is calculated by:

$$i(y) = 4F\,K\;C(0,y) \tag{11}$$

The average current density is then determined from:

$$i_m = \frac{1}{w_l}\int_0^{w_l} i(y)dy \tag{12}$$

Along the GDL-gas channel interface, the boundary condition is obtained from the convective mass transport analysis of gas channel, using heat and mass transfer analogy [7,8]. The corresponding boundary condition is then specified as:

$$-D_{eff}\left(\frac{\partial C}{\partial x}\right)_{\substack{x=h_l \\ 0\le y\le w_c}} = h_m(C(x=h_l, y) - C_0) \tag{13}$$

Where h_m is the convective mass transfer coefficient and C_0 is the molar oxygen concentration in the channel.

At all the remaining faces, impermeable boundary condition is assigned:

$$\frac{\partial C}{\partial x} = 0 \qquad \text{for } x = 0 \text{ and } 0\le y\le w_c \tag{14}$$

$$\frac{\partial C}{\partial y} = 0 \qquad \text{for } y = 0 \text{ and } 0\le x\le h_l \tag{15}$$

$$\frac{\partial C}{\partial y} = 0 \qquad \text{for } y = w_l \text{ and } 0\le x\le h_l \tag{26}$$

2.4. Numerical resolution

The numerical resolution of eq.(12) is based on finite volume method [9]. For the present computations 61 × 51 uniform mesh has been used. Convergence is considered to be reached when the relative changes between successive iterations, at each time step Δt in C field is less than 10^{-5}. $\Delta t = 0.05$ s is chosen for all numerical resolutions.

3. Results and discussions

The developed two-dimensional transient model for the cathode GDL is used to examine the effects of many important factors on the transient phenomena in PEMFC system. Calculations were conducted for a PEMFC in constant voltage discharge mode at ambient pressure. Inlet humidity and temperature are adjusted to 60% and 23°C respectively.

Geometrical and operating parameters are listed in table 1.

3.1. Effects of the initial GDL porosity ε_0

The effects of the initial GDL porosity ε_0 on the evolution of the averaged current density are shown in Fig.2. for three values of ε_0. It is found that the current density is reduced if ε_0 decreases. In fact, a larger porosity ε_0 significantly reduces the resistance of oxygen transport through the GDL and greatly raises the oxygen concentration at the reaction sites due to the increase of effective diffusion coefficient as indicated in eq. (5). However, for large values of ε_0 , more oxygen is consumed and more water is produced. Since, the effects of flooding will be important in this case and the current density decreases with time more and more sharply as ε_0 increases

3.2. Effects of GDL thickness

Fig. 3. shows the influence of the of GDL thickness h_l on the corresponding dynamic results for averaged current density. A thicker GDL leads to a higher resistance for oxygen transport. As a result, the current density is reduced at high values of h_l. However, the current density decreases rapidly with time for a thinner GDL. This is explained by the fact that a thicker GDL signifies a higher value of the void space in the porous GDL. Consequently, the rate of increase in liquid saturation with generated liquid water is smaller in large h_l. With further a decrease in h_l value, the void space is reduced so that the liquid saturation increases sharply. Moreover, due to the filling of pores with liquid water, the oxygen mass-transport to the reaction sites is reduced which leads to a weak current production by the electrochemical reaction.

3.3. Effects of current collector rib

For all preceding results, we have ignored the portion covered by the rib ($w_c = w_l$). In this section, we will consider the presence of a zone covered by the rib, which is represented by an impervious boundary at the GDL-gas channel interface. Presented results have been produced using a constant gas channel width w_c and changing the GDL width w_l. As can be seen in Fig. 4., for high values of w_l, the averaged current density decreases which is the result of the limitation of the oxygen mass transfer at the GDL-gas channel interface. Since the water generation is proportional to current generation, a faster current drop is depicted for low values of w_l.

The current collector rib has a large impact on local current density distribution and on oxygen concentration field as shown in Fig.5. The molar concentration of oxygen has lower values in the portion covered by the rib (Fig. 5.).

4. Conclusions

Excess liquid water in the GDL may dramatically affect cell performance. The purpose of this study is to predict the consequences of flooding on the current generation as well as the reactant concentration. For this purpose, we developed a two dimensional model, based on the resolution of the diffusion equation. The dynamics of the system are captured through the dependence of the effective porosity on liquid water production from the electrochemical reaction at the catalyst layer. Results from the simulations illustrate the evolution of the generated current under the influence of different parameters.

We found that the cell performance may be affected by the flooding at high porosity, thinner GDL and important convective mass transfer of reactant at the GDL-gas channel interface.

We also notice that the presence of the current collector rib can reduce flooding effects however it enhances the resistance to oxygen diffusion.

References

[1] Maggio G, Recupero V, Pino L. Modeling polymer electrolyte fuel cells: an innovative approach. J Power Sources 2001;101(2):275-286.
[2] Roshandel R, Farhanieh B, Saievar-Iranizad E. The effects of porosity distribution variation on PEM fuel cell performance. Renewable Energy 2005;30(10):1557-1572.
[3] Baschuk JJ, Li X. Modelling of polymer electrolyte membrane fuel cells with variable degrees of water flooding. J Power Sources 2000;86(1-2):181-196.

[4] Jeng KT, Lee SF, Tsai GF, Wang CH. Oxygen mass transfer in PEM fuel cell gas diffusion layers. J Power Sources 2004;138(1-2):41-50.

[5] Pasaogullari U, Wang CY. Liquid Water Transport in Gas Diffusion Layer of Polymer Electrolyte Fuel Cells. J Electrochem Soc 2004;151(3):A399-406.

[6] Janssen GJM, Overvelde MLJ. Water transport in the proton-exchange-membrane fuel cell: measurements of the effective drag coefficient. J Power Sources 2001;101(1):117-125.

[7] Chang M-H, Chen F, Teng H. Effects of two-phase transport in the cathode gas diffusion layer on the performance of a PEMFC. Journal of Power Sources 2006; 160:268–276.

[8] You L, Liu H. A two-phase flow and transport model for the cathode of PEM fuel cells. Int J Heat Mass Transfer 2002; 45:2277–2287.

[9] Patankar V. Numerical heat transfer fluid flow. New York: Hemisphere/MacGraw-Hill; 1980.

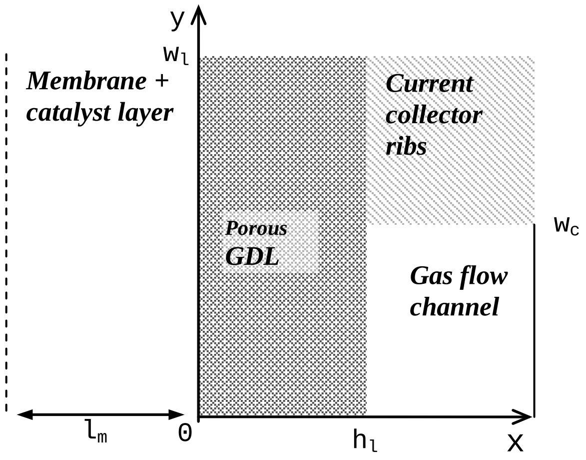


Fig. 1. Schematic of the problem showing coordinates and dimensions of the porous GDL.

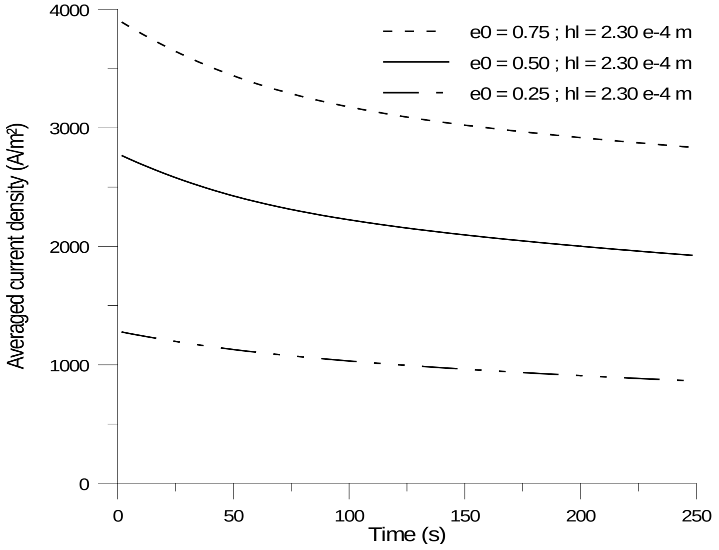


Fig. 2. Effects of GDL porosity on transients profiles of averaged current density

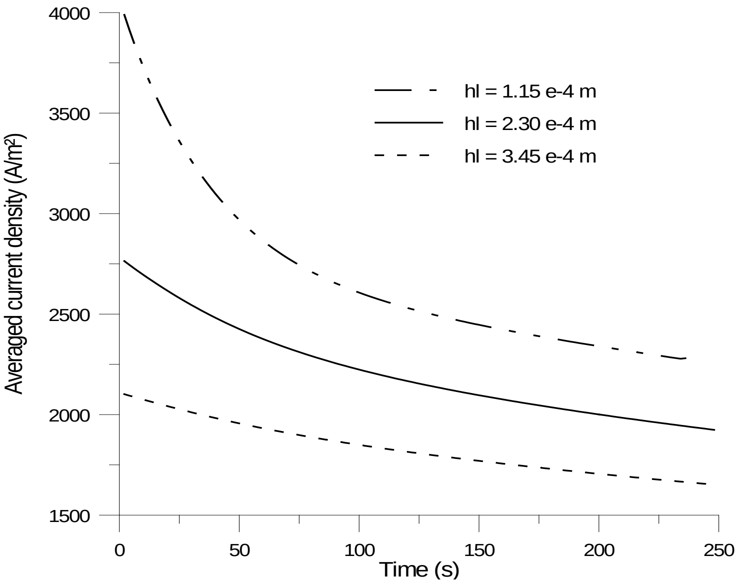


Fig. 3. Effects of GDL thickness on transients profiles of averaged current density. $\varepsilon_0 = 0.5$

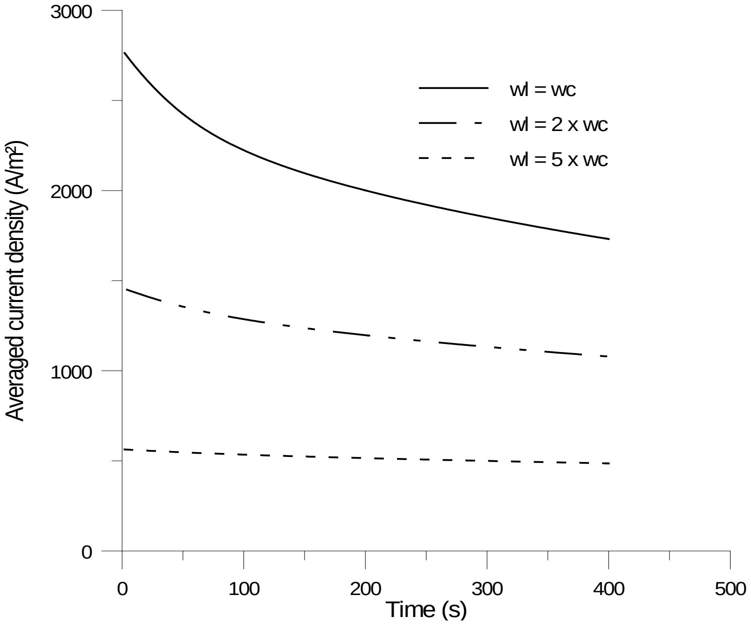
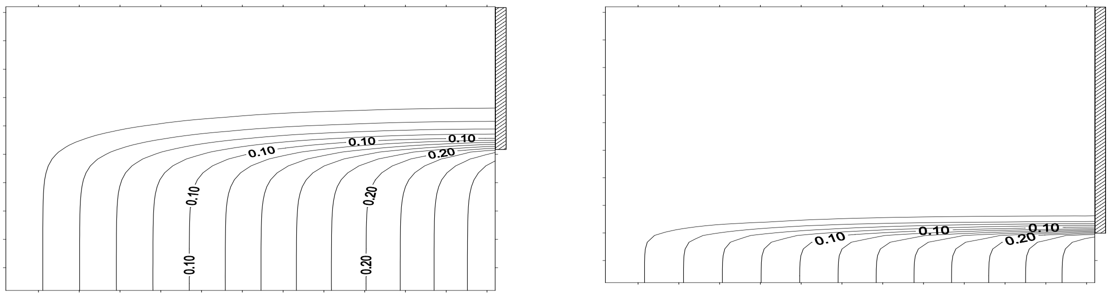


Fig. 4. Transient profiles of averaged current density for different values of gas channel width.



$w_l = 2 \text{ x } w_c$ $w_l = 5 \text{ x } w_c$

Fig. 5. Oxygen molar concentration field for different values of w_l. t = 400 s.

Table 1.

Physical properties and parameters

Parameter	*Value*
Universal gas constant, R (J mol^{-1} K^{-1})	8.314
Water molar weight, M (kg mol^{-1})	0.018
Cell temperature, T (K)	300
Operating pressure, p (Pa)	$1\ 10^5$
Inlet molar fraction of oxygen, x_{O2}	0.21
Oxygen diffusivity in pure gas phase, D_0($m^2.s^{-1}$)	$2\ 10^{-5}$
Air stoichiometry, ξ	2
Relative humidity of inlet gas, RH	60%
Initial GDL porosity, ε_0	0.5
GDL thickness, h_l (m)	$0.23\ 10^{-3}$
Gas flow channel width, w_c (m)	10^{-3}
Convective mass transfer coefficient, h_m (m^2 s^{-1})	$5.395\ 10^{-2}$
Thickness of the catalyst layer, δ_c (m)	$5\ 10^{-6}$

Nomenclature

A	electrode surface area (m^2)
C	oxygen concentration ($mol.m^{-3}$)
C_{ref}	reference oxygen concentration ($mol.m^{-3}$)
D_{eff}	effective diffusion coefficient (m^2s^{-1})
D_0	diffusion coefficient in pure gas phase (m^2s^{-1})
E_r	Reversible cell potential (V)
F	Faraday constant
h_l	GDL thickness (m)
h_m	interfacial mass transfer coefficient (m^2 s^{-1})
i	local current density ($A.m^{-2}$)
i_0	reference current density ($A.m^{-2}$)
i_m	averaged current density ($A.m^{-2}$)
J_o	molar diffusion flux of oxygen
l_m	membrane thickness (m)
M	molar weight of water ($kg.mol^{-1}$))
N_{el}	mass of water produced by electrochemical reaction (kg)
N_{in}	mass of water fed to the cell by humidification (kg)
N_m	mass of water fed to the cathode through the membrane (kg)
N_{out}	mass of water removed by gas convection (kg)
N_p	net mass of water produced (kg)
N_T	mass of liquid water corresponding to a complete flooding (kg)
p	operating pressure (Pa)
R	gas constant
S	liquid water saturation
T	temperature (K)
t	time (s)
V_{cell}	cell voltage (V)
w_c	gas flow channel width (m)
w_l	GDL height (m)
x_{O2}	inlet molar fraction of oxygen
Greek Symbols	

α_c	the cathode transfer coefficient
α	net water transport coefficient through the membrane
δ_c	the thickness of the catalyst layer (m)
ε_0	initial porosity of the GDL
ε_g	effective gas porosity