

NUMERICAL ANALYSIS OF POLYMER EXCHANGE MEMBRANE FUEL CELL WITH GAS CROSS-OVER THROUGH THE MEMBRANE

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ABSTRACT

Transport phenomena through membrane of a proton exchange membrane (PEM) fuel cell have the major role in its performance. Water is transported through the membrane due to diffusion, convection and electro-osmotic drag. Normally in PEM analysis it is assumed that the membrane is impermeable against gases (hydrogen, oxygen and nitrogen). In fact there are some amounts of solvate gases in liquid water which move inside the membrane and reach to the other side. For example oxygen dissolves into water at cathode catalyst. Most of this oxygen reacts with proton (H^+) and produces electricity. But some oxygen molecules diffuse toward anode side and react directly with hydrogen at anode catalyst. This process leads to waste of energy. Here these processes have been studied. We have developed a two-dimensional numerical model using full Navier-Stokes equations and species transport equations of hydrogen, oxygen, water (vapor or liquid). Proton transport equation is also included.

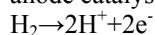
Keywords: Proton exchange membrane fuel cell, Numerical, Gas cross-over through membrane.

1. INTRODUCTION

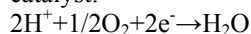
Proton exchange membrane fuel cells (PEMFC) have received most attentions today, since are the important alternative for future vehicles power supply.

The principle of how a PEMFC works is very simple. The primary materials, normally in gas phase, flow in separate channels. Channels are in adjacent with a gas diffusion layer (GDL) which lets the fluid to diffuse inside the cell. Closed to GDL, a polymer membrane is sandwiched. The membrane is a hydrophilic porous media that adsorbs water like a sponge. The adsorbed water is converted to liquid phase, because its partial pressure exceeds saturation pressure. The liquid water performs as a dam against reactant gases and prevents from direct contact between them. The two sides of the membrane are covered with a very thin layer of catalyst to facilitate reactions.

Hydrogen is dissociated to proton and electron at anode catalyst:



The proton has a good conductivity in the hydrated membrane and can migrate to cathode side where oxygen is present. Oxygen reacts with proton on cathode catalyst:



The electrons of above reaction are supplied from anode (as a product of hydrogen dissociation) and are conducted through an electrical circuit. This current is the output DC power. A complete fuel cell consists of several cells connected in series to prepare enough

voltage.

Many efforts have been carried out for study and optimization of PEMFC. Experimental studies represent general insight of what occurs in fuel cells. These methods despite of their reliable results are expensive and involve with numerous measurement limitations.

Detailed information of processes within the fuel cell over a wide variety of operating conditions may be obtained using numerical methods.

Many numerical works have been accomplished during last 15 years. One-dimensional isothermal model of Bernardi and Verbruge [2] which contained only cathode, was a base-frame for the next investigations. Singh et al [3] presented a two-dimensional model considering cross-sectional area normal to membrane as the solution domain. They used Darcy model instead of Navier-Stokes and emphasized on better modeling of mass transfer. Kermani et al [4] investigated importance of energy equation for prediction of liquid water formation. In recent years three-dimensional models have been developed [5-9] to investigate various aspects of processes occurring in cell.

Nearly in all works it is assumed that membrane is an impermeable wall against gas. It means that only water and proton are present in membrane and reactant gases (hydrogen and oxygen) never meet each other. So the only occurring reactions are hydrogen dissociation ($H_2 \rightarrow 2H^+ + 2e^-$) at anode and water production ($2H^+ + 1/2O_2 + 2e^- \rightarrow H_2O$) at cathode.

Impermeability against gas is an ideal property for

membrane as an electrolyte, but unfortunately gases can dissolve into the liquid water at GDL-membrane interface and move to the other side of membrane [10] by diffusion and convection. This effect is more important when speaking about reactant gases, because they can meet each other directly and react at catalysts. We call this phenomenon as “secondary reaction” or “direct reaction”. In fact direct reaction it-self has not a significant influence in fuel cell performance. The notable issue could be loss of fuel (and oxygen if pure oxygen is used).

Direct reaction at anode and cathode depends on amount of oxygen and hydrogen cross-over respectively. Reactant gases solubility in liquid water is small. Diffusion coefficients of gases in dissolved form are a few orders of magnitude less than that in gas phase. Also because of greater value of density and low porosity of media in membrane the velocity is negligible. So it can be concluded that normally the amount of gas cross-over is low and major portion of reaction occurs in indirect form (main reaction) to generate electricity.

Here the importance of cross-over is investigated from point of view of reactant gases consumption.

2. MODEL DESCRIPTION

As figure 1 shows, solution domain contains five regions: gas diffusion layer (GDL) (anode and cathode), catalyst layers (anode and cathode) and membrane. Gas channels and bipolar plates are considered as boundaries.

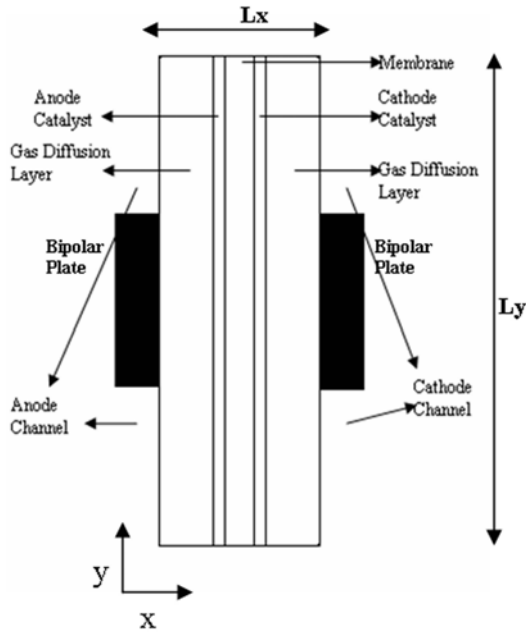


Fig 1. Solution domain

The model is developed under following main assumptions:

- The cell works under steady state conditions.
- The fluid in GDL is ideal gas. Volume of liquid water in this region is negligible and liquid phase has no effect on gas flow.
- The flow all over the cell is laminar.
- Product water is in liquid phase.

- All crossed-over reactant gases are consumed in direct reaction, i.e. neither hydrogen exists in cathode GDL nor oxygen in anode GDL.
- GDL has infinite resistance against proton flow. So all protons generated at anode catalyst migrate to cathode catalyst and react with oxygen.
- Porous media has the same temperature as the fluid.

2.1 Governing Equations

Continuity

$$\frac{\partial(\varepsilon\rho)}{\partial t} + \nabla \cdot [\varepsilon(\rho\bar{u} + \dot{G}^D)] = Su^{mass} \quad (1)$$

\dot{G}^D is defined as diffusive mass flux:

$$\dot{G}^D = \sum_k -D_k \nabla X_k \rho_k \quad (2)$$

Su encompasses mass source/sink terms due to main reactions and electro-osmotic drag as is introduced for source terms of species transport equation:

$$(Su)^{mass} = \sum_k [(Su_k^R + Su_k^{eod}) \rho_k]^{concentration} \quad (3)$$

Momentum

$$\frac{\partial(\varepsilon\rho\bar{u})}{\partial t} + \nabla \cdot (\varepsilon\rho\bar{u}\bar{u}) = -\varepsilon\nabla P + \nabla \cdot (\varepsilon\mu_{eff} \nabla \bar{u}) - \frac{\varepsilon^2 \mu}{K_{hy}} \bar{u} \quad (4)$$

The velocity used in the momentum equation is only due to convective mass transfer and diffusive velocity which originates from chaotic motions of molecules is not included.

Energy conservation

$$\frac{\partial(\rho C_p T)}{\partial t} + \nabla \cdot (\varepsilon\rho C_p \bar{u} T) = \nabla \cdot (k_{eff} \nabla T) + Su^{energy} \quad (5)$$

Energy equation is applied for both porous media and fluid. So, treatment of interactions between these two phases is not needed, but the properties must be calculated as the average value of solid media and fluid. Source term consists of Ohmic losses of proton current, activation over-potential and direct reaction:

$$Su^{energy} = \begin{cases} \frac{i^2}{\sigma} + (V^{act} j + \dot{G}^{Cr} h_{react})_a & \text{anode catalyst} \\ \frac{i^2}{\sigma} & \text{membrane} \\ \frac{i^2}{\sigma} + (V^{act} j + \dot{G}^{Cr} h_{react})_c & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases} \quad (6)$$

i is current density magnitude.

Species transport.

$$\frac{\partial(\varepsilon X_k)}{\partial t} + \nabla \cdot (\varepsilon \bar{u} X_k) = \nabla \cdot (D_k \nabla X_k) + Su_k^{concentration} \quad (7)$$

Subscript k denotes one of species (hydrogen, oxygen, water and probably nitrogen).

There are separate relations for Diffusion coefficient (D_k) of species in various conditions, e.g. gas phase, dissolved form and for water in membrane. In dissolved form we have [10]:

$$D_k^s = c \frac{T}{\mu} \quad (8)$$

μ denotes solvent (water) viscosity. c for each solute gas is a constant. For hydrogen and oxygen D_k^s is considered 1.06×10^{-8} and 7.47×10^{-9} respectively. Generally the source term includes consumption/production of species in main reaction and direct reaction and also specie transport under electro-osmotic drag. Nature of source term concerns to corresponding specie as follows:

Main reaction:

$$Su_{H_2}^R = \begin{cases} -\frac{j}{2FC_{tot}} & \text{anode catalyst} \\ 0 & \text{other locations} \end{cases}$$

$$Su_{O_2}^R = \begin{cases} -\frac{j}{4FC_{tot}} & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases} \quad (9)$$

$$Su_{Water}^R = \begin{cases} \frac{j}{2FC_{tot}} & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases}$$

Direct reaction:

$$Su_{H_2}^{DR} = \begin{cases} \frac{\partial \dot{G}_{H_2}^{Cr}}{\partial x} \\ \frac{\partial \dot{G}_{H_2}^{Cr}}{C_{tot}} & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases}$$

$$Su_{O_2}^{DR} = \begin{cases} \frac{\partial \dot{G}_{O_2}^{Cr}}{\partial x} \\ \frac{\partial \dot{G}_{O_2}^{Cr}}{C_{tot}} & \text{anode catalyst} \\ 0 & \text{other locations} \end{cases} \quad (10)$$

$$Su_{Water}^{DR} = \begin{cases} \frac{2 \partial \dot{G}_{O_2}^{Cr}}{\partial x} \\ \frac{2 \partial \dot{G}_{O_2}^{Cr}}{C_{tot}} & \text{anode catalyst} \\ -\frac{\partial \dot{G}_{H_2}^{Cr}}{\partial x} \\ -\frac{\partial \dot{G}_{H_2}^{Cr}}{C_{tot}} & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases}$$

C_{tot} denotes total volumetric mole of existing fluid. $\dot{G}_{O_2}^{Cr}$ is oxygen flow rates crossing over through membrane and contains both diffusion and convection.

So the term $-\frac{\partial \dot{G}_{O_2}^{Cr}}{\partial x}$ denotes oxygen consumption rate.

Similarly $\dot{G}_{H_2}^{Cr}$ is hydrogen flow rate from anode site to cathode catalyst. Note that the term $\frac{\partial \dot{G}_{H_2}^{Cr}}{\partial x}$ is inherently negative.

Electro-osmotic drag:

$$Su^{eod} = -\frac{\nabla \cdot \vec{i} \cdot n^{eod}}{FC_{tot}} \quad (11)$$

\vec{i} is current density vector indicating both magnitude and direction of protons migration. We can say that its magnitude denotes rate of proton and electron production or rate of primary materials consumption per area of the membrane. It is a good criterion to state fuel cell load.

Dissolving:

When a gas is in contact with liquid, some molecules penetrate in the liquid and are dissolved. Simultaneously some dissolved molecules pass through the liquid surface and escape to gas phase. The value of dissolved gas in liquid surface falls at equilibrium point which the entering rate is equal with exiting rate:

$$C_k^s = \frac{1}{H} X_k^g P \quad (12)$$

where H is Henry's law constant and is equal to 3.2886×10^4 and 2.7426×10^4 for hydrogen and oxygen respectively at temperature of 353 K.

Normally, the species transport equation is solved for 3 species hydrogen, oxygen and water. Nitrogen concentration is then calculated easily:

$$X_{N_2} = 1 - X_{H_2} - X_{O_2} - X_{Water} \quad (13)$$

Phase potential (proton transport)

$$\nabla(\sigma \nabla \Phi) = Su^\Phi \quad (14)$$

where:

$$Su^\Phi = \begin{cases} +j & \text{anode catalyst} \\ -j & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases} \quad (15)$$

The reader is referred to references for fluid properties and electro-chemical quantities.

2.2 Scaling Cross-over

Effect of reactant gases cross-over can be expressed as an equivalent losing current density including anode and cathode losses:

$$i^{loss} = i_a^{loss} + i_c^{loss} = i^{ideal} - i^{ave} \quad (16)$$

$$i_a^{loss} = 4F\dot{G}_{O_2}^{cr} \quad (17)$$

$$i_c^{loss} = 2F\dot{G}_{H_2}^{cr} \quad (18)$$

Superscripts *act* and *ideal* denote to actual and ideal (without losses) cases respectively. In the other hand, i^{loss} denotes additional current density, if the rate of gas cross-over is actually zero.

It is useful to have a quantitative statement for energy efficiency of the cell in terms of impermeability against reactant gases as follows:

For hydrogen:

$$\xi_{H_2}^{imp} = 1 - \frac{\dot{G}_{H_2}^{cr}}{\dot{G}_{H_2}^{cr} + \dot{G}_{H_2}^R} = 1 - \frac{i_c^{loss}}{i_c^{loss} + i^{ave}} \quad (19)$$

For oxygen:

$$\xi_{O_2}^{imp} = 1 - \frac{\dot{G}_{O_2}^{cr}}{\dot{G}_{O_2}^{cr} + \dot{G}_{O_2}^R} = 1 - \frac{i_a^{loss}}{i_a^{loss} + i^{ave}} \quad (20)$$

Overall impermeability efficiency:

$$\xi^{imp} = 1 - \frac{\dot{G}_{H_2}^{cr}}{\dot{G}_{H_2}^{cr} + \dot{G}_{H_2}^R} - \frac{\dot{G}_{O_2}^{cr}}{\dot{G}_{O_2}^{cr} + \dot{G}_{O_2}^R} \approx \xi_{H_2}^{imp} \xi_{O_2}^{imp} \quad (21)$$

2.3 Numerical Procedure

A finite volume code was developed to solve governing equations.

Two grid networks have been used, one for scalar variables and the other (staggered grid) for vector variables (velocity and current density) to enhance the accuracy in calculation of gradients.

Power law scheme was applied for approximation of diffusion/convection fluxes on control volume faces. To decouple equations, SIMPLE [11] algorithm was used and convergence was obtained with iteration. The numerical method converged after 2400-7000 iterations, depending on the case. Very wisely selection of relaxation factors is necessary to prevent divergence.

3. RESULTS AND DISCUSSION

For evaluation of the present model, several test cases were studied. A set of dimensions and operating conditions was selected as a base for comparison of different cases and also validation of the model. Table 1 gives Specifications and operating conditions for the base case.

Figure 2 compares calculated polarization curve of the base case with the experimental data reported by Wang et al for a similar operating conditions [12]. A good agreement can be seen between the present results and experimental data.

Table 1: Specifications and operating conditions for the base case

parameter	Unit	Value
ε in GDL	-	0.4
ε in membrane and catalyst	-	0.25
K_{hy} in GDL	m ²	1.76×10^{-11}
K_{hy} in membrane	m ²	1.8×10^{-18}
Fluid temperature at anode channel	K	353
Fluid temperature at cathode channel	K	353
Pressure at anode channel	atm	3
Pressure at cathode channel	atm	3
RH at anode channel entrance	%	95
RH at cathode channel entrance	%	50
Gas diffusion layers thickness	μm	200
Catalysts thickness	μm	20
Membrane thickness	μm	108
Cell width (Ly)	μm	2000
Bipolar plates width	μm	800

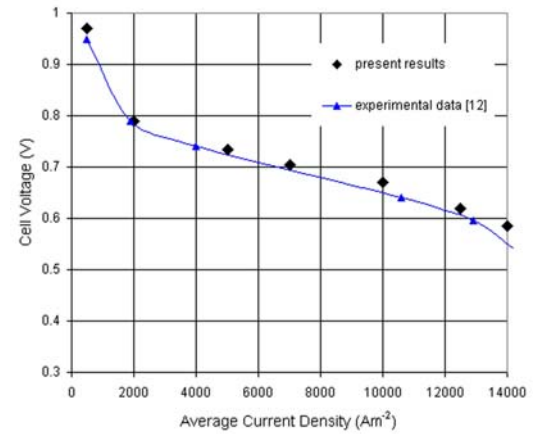


Fig 2. Validation of the present numerical model with experimental data.

In figure 3 hydrogen concentration is displayed. The minimum concentration within the anode GDL is located in adjacent with catalyst, closed to axis $y=Ly/2$ where we have most distance from channels. Since hydrogen should be dissolved in water to enter membrane region, a discontinuity at anode GDL-membrane interface is occurred. Similarly for oxygen, there is a discontinuity where oxygen goes from GDL to membrane. The minimum concentration of oxygen in cathode GDL is located at $y=Ly/2$, next to catalyst boundary. Now we study gas cross-over (direct reaction) contribution in waste of energy. In the first step we consider the effect of current density. For this reason, several tests were carried out with similar conditions of the base case for various current densities. It was found that i^{loss} is decreased as current density becomes more. If current density varies from 1000 Am^{-2} to 14000 Am^{-2} , total value of i^{loss} (i^{loss} at anode plus i^{loss} at cathode) is decreased from 41 Am^{-2} to 32 Am^{-2} . This is due to more

reactant gases consumption at greater current densities. For example hydrogen concentration is decreased at anode side of the membrane if its consumption (dissociation in anode catalyst) is increased, so fewer hydrogen molecules have opportunity to pass through the catalyst and diffuse to cathode.

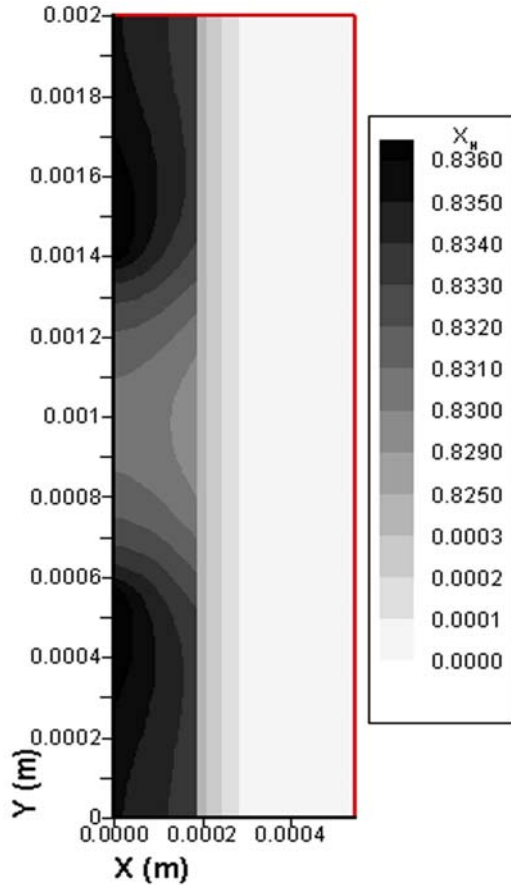


Fig 3. Hydrogen mole fraction within the cell.

In the next step two effective parameters were considered in three cases as listed in table 2. The average current density in all cases was 5000 Am^{-2} . The calculated results are also given in this table.

Table 2: Study cases and corresponding results

case	problem conditions		results		
	Membrane Thickness (μm)	Fluid in Cathode Channel	i_a^{loss} Am^{-2}	i_c^{loss} Am^{-2}	ξ_{imp} %
I	230	Air with 50% relative humidity	5.0	11.3	99.7
II (base)	108	Air with 50% relative humidity	11.7	26.2	99.2
III	108	Pure oxygen with 50% relative humidity	64.2	26.2	98.2

Case I corresponds to the minimum gas cross-over. Comparing with case II (base case) effect of membrane thickness is observed. Thickness of membrane acts as a

resistance against both gases and proton. Consequently with a thicker membrane, the rate of gas cross-over through membrane is decreased and Ohmic loss is increased. It must be noted that even though a thicker membrane leads to more impermeability efficiency, it has more Ohmic losses and this losses usually play a greater role in loss of output power.

From case III it is evident that use of pure oxygen as oxidant instead of air leads to a significant rise in oxygen cross-over and strengthens anode direct reaction in comparison with cathode side. It can be seen that a 380% increase in oxygen concentration from mole fraction of 0.191 (case II, standard air with RH=50%) to 0.915 (case III, pure oxygen with RH=50%) has led to a 450% increase in oxygen cross-over. In this case rate of energy loss has almost amounted to the considerable value of 2%.

4. CONCLUSIONS

A comprehensive study was performed to investigate the effect of gas cross-over (or direct reaction) through the membrane in waste of energy. It was found out that although direct reaction is negligible at high current density conditions for cells with thick membrane, in some cases it is considerable, especially at low current density conditions which are very common in fuel cells operation. In fact even if the cell is at no-load conditions, direct reaction won't be stopped and even is intensified. In the other hand, when the cell is working at a low current density, it gives more voltage, so with a distinct equivalent losing current density, power losses (i.e. product of equivalent losing current and voltage) is increased.

The following items are concluded:

- As the membrane is thinner, direct reaction is increased.
- Direct reaction occurs mainly at cathode catalyst when air is used as the oxidant. With pure oxygen, direct reaction at anode is obviously increased.
- Direct reaction becomes more important at low current density conditions.

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6. NOMENCLATURE

Symbol	Meaning	Unit
a_w	water activity	(-)
C	concentration	(mole m ⁻³)
C_p	specific heat capacity	(Jkg ⁻¹ K ⁻¹)
D	mass diffusion coefficient	(m ² s ⁻¹)
F	faraday constant	(C mole ⁻¹)
GDL	gas diffusion layer	
\dot{G}	mass flux	(kg m ⁻² s ⁻¹) or (mole m ⁻² s ⁻¹)
H	Henry’s law constant	(Pa m ³ mole ⁻¹)
h_{reac}	liquid water enthalpy of formation	(J mole ⁻¹)
\vec{i}	current density vector	(Am ⁻²)
i^{loss}	equivalent losing current density	(Am ⁻²)
j	transfer current density	(Am ⁻³)
k	thermal conductivity	(W m ⁻¹ K ⁻¹)
K_{hy}	hydraulic permeability of	(m ²)

L_x, L_y	porous media dimensions, see figure 1.	(m)
n_{eod}	electro-osmotic drag coefficient	(-)
P	pressure	(kPa)
R	gas constant	(Jmole ⁻¹ K ⁻¹)
RH	relative humidity	(-)
S_u	non-homogeneous source term	
T	temperature	(K)
\vec{u}	velocity vector	(m s ⁻¹)
X	concentration (mole fraction)	(-)
x, y	coordinates	(m)
ε	porosity	(-)
ϕ	phase potential	(V)
μ	viscosity	(kg m ⁻¹ s ⁻¹)
ρ	density	(kg m ⁻³)
σ	proton conductivity	(Ω^{-1} m ⁻¹)
ξ^{imp}	impermeability efficiency	(-)

superscripts

D	diffusion
DR	direct reaction
eod	electro-osmotic drag
g	gas
R	main reaction
S	solute, dissolution

subscripts

a	anode
c	cathode
eff	effective
k	species (hydrogen, oxygen, water or nitrogen)
tot	total