

Numerical analysis of gas cross-over through the membrane in a proton exchange membrane fuel cell

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Abstract

Mass transport phenomena through the membrane have the major role in performance of a proton exchange membrane (PEM) fuel cell. Water is transported through the membrane due to diffusion, convection and electro-osmotic drag. Normally it is assumed that the membrane is impermeable against gases. Strictly speaking there are some amount of solute gases in liquid water which move within the membrane and reach to the other side. For example, oxygen dissolves into the water at cathode catalyst. Most of this oxygen reacts with proton 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 since direct reaction releases energy in form of heat. In this paper 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 and water. It was found that cross-over of reactant gases has a considerable effect on cell energy efficiency in some common cases.

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1. Introduction

Fuel cell study deals with many physical and theoretical issues. The fluid is a mixture, containing various species with completely different properties. The species movement is governed by several mechanisms. Diffusion and convection are common transport mechanisms for all. For water, electro-osmotic drag within the membrane is very important. At liquid–gas phase interfaces we have dissolution of gases such as hydrogen, oxygen and nitrogen.

Moreover chemical reactions, which occur in a very thin layers (catalysts) together with changes in porous media properties, affect the flow pattern, concentrations and hence fluid properties especially in regions closer to catalysts.

Strong coupling between flow parameters is another issue. For instance concentration field of species depends on fluid velocity. In the other hand, local mechanical properties of fluid such as density are a weighted function of species properties and hence depend on each specie concentration.

In such complex problem analytical models can not be so popular. Their scope of work is limited to give estimation in very simplified cases neglecting many effective aspects. It must be mentioned that analytical methods have their own rank since they give parametric results.

In the other hand, experimental methods can give reliable results. However, they have drawbacks such as high costs and measuring limits. Many local quantities can not be measured inside the cell, because the dimensions are so small and the cell performance is intensely sensitive to sensors.

Considering above mentioned limitations of analytical and experimental methods, Numerical methods have received most attention in fuel cell researches. These methods can give various information in a wide variety of operating conditions.

Many numerical works have been accomplished during last 15 years. One-dimensional isothermal model of Bernardi and Verbruge [1] which contained only cathode was a base-frame for the next investigations. Singh et al. [2] 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 modelling of mass transfer. Kermani et al. [3] investigated importance of energy equation for prediction of liquid water formation.

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Nomenclature

a_w	water activity
C	concentration (mole m^{-3})
C_p	specific heat capacity ($J kg^{-1} K^{-1}$)
D	mass diffusion coefficient ($m^2 s^{-1}$)
E^0	open circuit cell voltage
F	faraday constant ($C mol^{-1}$)
GDL	gas diffusion layer
\dot{G}	mass flux ($kg m^{-2} s^{-1}$) or ($mol m^{-2} s^{-1}$)
\dot{G}^{cr}	mass flux of gas crossing over through the membrane ($mol m^{-2} s^{-1}$)
H	Henry's law constant ($Pa m^3 mol^{-1}$)
h_{reac}	liquid water enthalpy of formation ($J mol^{-1}$)
\vec{i}	current density vector (Am^{-2})
i^{cr}	cross-over equivalent current density (Am^{-2})
j	transfer current density (Am^{-3})
k	thermal conductivity ($W m^{-1} K^{-1}$)
K	permeability of porous media (m^2)
L_x, L_y	dimensions see Fig. 1 (m)
M	molar weight ($kg mol^{-1}$)
M_m	membrane molar weight ($kg mole^{-1}$)
n_{eod}	electro-osmotic drag coefficient
P	pressure (kPa)
P_{sat}	saturation pressure of water (kPa)
R	gas constant ($J mol^{-1} K^{-1}$)
RH	relative humidity
R_{O-N}	volumetric ratio of O_2 to N_2
Su	non-homogeneous source term
Sp	homogeneous source term
T	temperature (K)
\vec{u}	velocity vector ($m s^{-1}$)
V^{cell}	actual cell voltage (V)
V^{act}	activation over-potential (V)
X	concentration (mol fraction)
x, y	coordinates (m)
ε	porosity
ϕ	phase potential (V)
λ	water content (mol water/mol SO_3^{2-})
μ	viscosity ($kg m^{-1} s^{-1}$)
ρ	density ($kg m^{-3}$)
ρ_m	dry membrane density ($kg m^{-3}$)
σ	proton conductivity ($\Omega^{-1} m^{-1}$)
ξ^{imp}	impermeability efficiency

superscripts

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

subscripts

a	anode
c	cathode
eff	effective
f	fluid
k	species (hydrogen, oxygen, water or nitrogen)
s	solid media

In recent years three-dimensional models have been developed [4–9] 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).

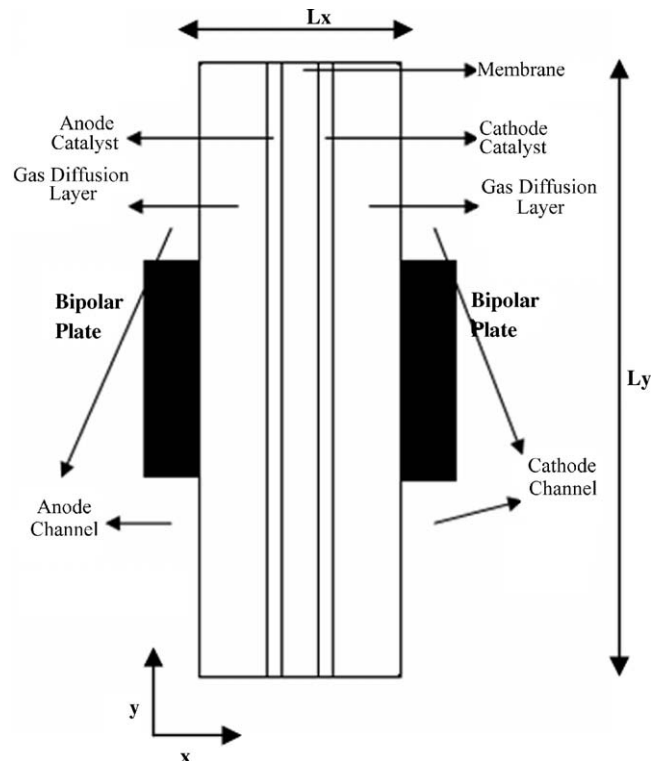


Fig. 1. Solution domain.

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 Fig. 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.

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

2.1.1. Continuity

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

\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 indirect reactions and electro-osmotic drag as is introduced for source terms of species transport equation:

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

2.1.2. Momentum

$$\frac{\partial(\varepsilon\rho\vec{u})}{\partial t} + \nabla \cdot (\varepsilon\rho\vec{u}\vec{u}) = -\varepsilon\nabla P + \nabla \cdot (\varepsilon\mu_{\text{eff}}\nabla\vec{u}) + Sp^d \quad (4)$$

Sp^d is source term modelling friction between fluid and porous media (Darcy's model):

$$Sp^d = -\frac{\varepsilon^2\mu}{K_{\text{hy}}}\vec{u} \quad (5)$$

It is worth saying that the velocity used in the equations is only due to convective mass transfer and diffusive velocity which originates from chaotic motions of molecules is not included.

2.1.3. Energy conservation

$$\frac{\partial(\rho CpT)}{\partial t} + \nabla \cdot (\varepsilon\rho Cp\vec{u}T) = \nabla \cdot (k_{\text{eff}}\nabla T) + Su^{\text{energy}} \quad (6)$$

Energy equation is applied for both porous media and fluid. Consequently, 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:

$$Su^{\text{energy}} = \begin{cases} \frac{i^2}{\sigma} + (V^{\text{act}}j + \dot{G}^{\text{Cr}}.h_{\text{react}})_a & \text{anode - catalyst} \\ \frac{i^2}{\sigma} & \text{membrane} \\ \frac{i^2}{\sigma} + (V^{\text{act}}j + \dot{G}^{\text{Cr}}.h_{\text{react}})_c & \text{cathode - catalyst} \\ 0 & \text{other locations} \end{cases} \quad (7)$$

i is current density magnitude.

2.1.4. Species transport

$$\frac{\partial(\varepsilon X_k)}{\partial t} + \nabla \cdot (\varepsilon\vec{u}X_k) = \nabla \cdot (D_k\nabla X_k) + Su_k^{\text{concentration}} \quad (8)$$

Subscript k denotes one of species (hydrogen, oxygen, water and probably nitrogen). Generally the source term includes consumption/production of species in main reaction and direct reaction and also specie transport under electro-osmotic drag or dissolution effects. Nature of source term concerns to corresponding specie as follows:

Main reaction:

$$Su_{\text{H}_2}^R = \begin{cases} -\frac{j}{2FC_{\text{tot}}} & \text{anode catalyst} \\ 0 & \text{other locations} \end{cases}$$

$$Su_{\text{O}_2}^R = \begin{cases} -\frac{j}{4FC_{\text{tot}}} & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases} \quad (9)$$

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

Direct reaction:

$$\begin{aligned} Su_{H_2}^{DR} &= \begin{cases} \frac{\partial \dot{G}_{H_2}^{Cr}/\partial x}{C_{tot}} & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases} \\ Su_{O_2}^{DR} &= \begin{cases} -\frac{\partial \dot{G}_{O_2}^{Cr}/\partial x}{C_{tot}} & \text{anode catalyst} \\ 0 & \text{other locations} \end{cases} \\ Su_{Water}^{DR} &= \begin{cases} \frac{2(\partial \dot{G}_{O_2}^{Cr})/(\partial x)}{C_{tot}} & \text{anode catalyst} \\ -\frac{(\partial \dot{G}_{H_2}^{Cr})/\partial x}{C_{tot}} & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases} \end{aligned} \quad (10)$$

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 $-(\partial \dot{G}_{O_2}^{Cr})/(\partial x)$ denotes oxygen consumption rate. Similarly $\dot{G}_{H_2}^{Cr}$ is hydrogen flow rate from anode site to cathode catalyst. Note that the term $\partial \dot{G}_{H_2}^{Cr}/\partial x$ is inherently negative.

Electro-osmotic drag:

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

i is current density vector indicating both magnitude and direction of protons migration.

Dissolving:

When a gas is in contact with liquid some molecules penetrate in the liquid and dissolve. The rate of dissolving is proportional to gas partial pressure:

$$\dot{G}^{in} = K_1 P_k = K_1 X_k^g P \quad \left(\frac{\text{mol}}{\text{m}^2 \text{s}} \right) \quad (12)$$

P_k denotes partial pressure of specie k . superscript g is for emphasis on gas phase.

Simultaneously some dissolved molecules pass through the liquid surface and escape to gas phase. This can be formulated as follows:

$$\dot{G}^{out} = K_2 C_k^s \quad \left(\frac{\text{mol}}{\text{m}^2 \text{s}} \right) \quad (13)$$

superscript s denotes the concentration of dissolved form and C_k^s is the concentration of dissolved specie in liquid adjacent to gas interface.

The value of dissolved gas in liquid surface falls at equilibrium point which the entering rate is equal with exiting rate:

$$K_1 X_k^g P = K_2 C_k^s \Rightarrow C_k^s = \frac{1}{H} X_k^g P \quad (14)$$

Where $H = K_2/K_1$ is Henry's law constant.

Instead of direct calculation of concentration in liquid (above equation), dissolution can be considered numerically as a source term:

$$Su^S = \frac{K_1 X_k^g P - K_2 C_k^s}{C_{tot} \Delta x} \quad (15)$$

Δx is length of corresponding control volume in x direction. This term is present at gas–liquid interface and shows the rate of matter leaving gas region and entering liquid so it has a negative value in gas phase region.

It is evident that the dissolution source term is applied only for hydrogen and oxygen (and nitrogen if its transport equation is included).

Species transport equation is solved for three species hydrogen, oxygen and water. Nitrogen concentration is then obtained knowing that the summation of all concentrations is equal to unity:

$$X_{N_2} = 1 - X_{H_2} - X_{O_2} - X_{Water} \quad (16)$$

2.1.5. Phase potential (proton transport)

$$\nabla(\sigma \nabla \Phi) = Su^\phi \quad (17)$$

where:

$$Su^\phi = \begin{cases} +j & \text{anode catalyst} \\ -j & \text{cathode catalyst} \\ 0 & \text{other locations} \end{cases} \quad (18)$$

2.2. Boundary conditions

At $x=0$ (anode channel-GDL interface):

$$X_{Water}(0, y) = \frac{RH_a \cdot P_{sat}}{P(0, y)} \quad (19)$$

$$X_{H_2}(0, y) = 1 - X_{Water}(0, y) \quad (20)$$

$$X_{O_2}(0, y) = X_{N_2}(0, y) = 0 \quad (21)$$

At $x=Lx$ (cathode GDL-channel interface):

$$X_{Water}(Lx, y) = \frac{RH_c \cdot P_{sat}}{P(0, y)} \quad (22)$$

$$X_{O_2}(Lx, y) = (1 - X_{Water}(0, y)) \times \frac{R_{O-N}}{1 + R_{O-N}} \quad (23)$$

$$X_{N_2}(Lx, y) = (1 - X_{Water}(0, y)) \times \frac{1}{1 + R_{O-N}} \quad (24)$$

$$X_{H_2}(Lx, y) = 0 \quad (25)$$

At bipolar plates interfaces we have zero mass flux.

For energy equation convective heat flux was considered at channel interfaces.

For phase potential equation, GDL was excluded from solution domain. As the proton flux at GDL-catalyst interface is zero we have:

$$\left. \frac{\partial \Phi}{\partial x} \right|_{\text{GDL-catalyst interfaces}} = 0 \quad (26)$$

At top-end and bottom-end of the cell, periodic boundary conditions were used for all equations:

$$A(x, 0^+) = A(x, Ly) \quad (27)$$

$$A(x, Ly^-) = A(x, 0) \quad (28)$$

where A is an arbitrary variable.

2.3. Fluid properties and electrochemical quantities

Density:

$$\rho = C_{\text{tot}} \sum_k X_k M_k \quad (29)$$

Viscosity:

$$\mu = \frac{\rho_k \mu_k}{\rho} = \frac{\sum_k X_k M_k \mu_k}{\sum_k X_k M_k} \quad (30)$$

effective viscosity for porous media is [9]:

$$\mu_{\text{eff}} = \left[\frac{1.5(1 - \varepsilon)}{\varepsilon} \right]^2 \mu \quad (31)$$

Thermal conductivity:

Effective thermal conductivity is calculated as a combination of fluid and porous solid thermal conductivities:

$$K_{\text{eff}} = -2K_S + \frac{1}{\varepsilon/(2K_S + K_f) + (1 - \varepsilon)/3K_S} \quad (32)$$

$$K_f = \sum_k X_k K_k \quad (33)$$

Heat capacity:

Heat capacity is also considered as the average value of fluid and porous solid heat capacities:

$$\rho C_p = \varepsilon(\rho C_p)_f + (1 - \varepsilon)(\rho C_p)_s \quad (34)$$

$$(\rho C_p)_f = \sum_k \rho_k C_{p_k} = C_{\text{tot}} \sum_k X_k M_k C_{p_k} \quad (35)$$

Mass diffusion coefficients:

For gas phase we have:

$$D_k^g = D_k^{\text{ref}} \left(\frac{T}{T^{\text{ref}}} \right)^{1.5} \left(\frac{P^{\text{ref}}}{P} \right) \quad (36)$$

In dissolved form diffusion coefficient obeys another relation [11]:

$$D_k^s = c \frac{T}{\mu} \quad (37)$$

μ denotes solvent (water) viscosity. c for each solute gas is a constant.

For liquid water¹ [5,7]:

$$D_{\text{water}}^l = D_i e^{2416((1/303)-(1/T))} \quad (38)$$

¹ The D_i expression for $3 < \lambda \leq 4.5$ has been corrected here. In some references (for example [5] and [7]), the values of D_i in this range are in contradiction with the original equation:

$$D_w = \begin{cases} 3.1 \times 10^{-7} \lambda (e^{0.28\lambda} - 1) e^{-234.6T} & 0 < \lambda < 3 \\ 4.17 \times 10^{-8} \lambda (1 + 16e^\lambda) e^{-234.6T} & 3 < \lambda \end{cases}$$

$$D_i = \begin{cases} 10^{-10} & \lambda < 2 \\ 10^{-10}(-3 + 2\lambda) & 2 < \lambda \leq 3 \\ 10^{-10}(6.5 - 1.167\lambda) & 3 < \lambda \leq 4.5 \\ 1.25 \times 10^{-10} & 4.5 \leq \lambda \end{cases} \quad (39)$$

λ is water content in membrane.

Proton conductivity [4,6]:

$$\sigma = (0.5139\lambda - 0.326) e^{1268((1/303)-(1/T))} \quad (40)$$

Water content in membrane [4,5]:

$$\lambda = \begin{cases} 0.043 + 17.18 a_w - 39.85 a_w^2 + 36.0 a_w^3 & 0 < a \leq 1 \\ 14.0 + 1.4(a_w - 1) & 1 \leq a \leq 3 \\ 16.8 & 3 < a \end{cases} \quad (41)$$

Activity of water:

$$a_w = \frac{X_{\text{water}} P}{P_{\text{sat}}} \quad (42)$$

Water concentration in membrane:

$$C_{\text{water}} = \lambda \frac{\rho_m}{M_m} \quad (43)$$

Total mole of matter per volume:

In gas phase:

$$C_{\text{tot}} = \frac{P}{RT} \quad (44a)$$

In liquid phase:

$$C_{\text{tot}} = \frac{C_{\text{Water}}}{X_{\text{Water}}} \quad (44b)$$

Electro-osmotic drag coefficient [5,7]:

$$n^{\text{eod}} = 0.0029\lambda^2 + 0.05\lambda - 3.4 \times 10^{-19} \quad (45)$$

Current density in membrane:

$$\vec{i} = -\sigma \nabla \Phi \quad (46)$$

Transfer current density:

$$j_a = j_a^{\text{ref}} \left(\frac{C_{\text{H}_2}}{C_{\text{H}_2}^{\text{ref}}} \right)^{0.5} (e^{V_a^{\text{act}} \alpha_a^{\text{F/RT}}} - e^{V_a^{\text{act}} \alpha_a^{\text{F/RT}}}) \quad (47)$$

$$j_c = j_c^{\text{ref}} \left(\frac{C_{\text{O}_2}}{C_{\text{O}_2}^{\text{ref}}} \right) (e^{V_c^{\text{act}} \alpha_c^{\text{F/RT}}} - e^{V_c^{\text{act}} \alpha_c^{\text{F/RT}}}) \quad (48)$$

Cell voltage:

$$V^{\text{cell}} = E^0 - \left(\int_a^c \frac{i_x}{\sigma} dx + V_a^{\text{act}} + V_c^{\text{act}} \right) \quad (49)$$

2.4. Scaling cross-over

The amount of reactant gases cross-over can be expressed with an imaginary current density named cross-over equivalent current density, i^{cr} :

$$i^{cr} = i_a^{cr} + i_c^{cr} \quad (50)$$

$$i_a^{cr} = 4F\dot{G}_{O_2}^{cr} \quad (51)$$

$$i_c^{cr} = 2F\dot{G}_{H_2}^{cr} \quad (52)$$

i_a^{cr} shows rate of oxygen, passing from cathode to anode through the membrane. In the other hand if all crossing over oxygen reacts with proton at cathode catalyst instead of direct reaction at anode catalyst, then we will produce i_a^{cr} with this amount of oxygen. Similar statement can be said for hydrogen and i_c^{cr} .

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:

$$\xi_{H_2}^{imp} = 1 - \frac{\dot{G}_{H_2}^{cr}}{\dot{G}_{H_2}^{cr} + \dot{G}_{H_2}^R} = 1 - \frac{i_c^{cr}}{i_c^{cr} + i^{ave}} \quad (53)$$

For oxygen:

$$\xi_{O_2}^{imp} = 1 - \frac{\dot{G}_{O_2}^{cr}}{\dot{G}_{O_2}^{cr} + \dot{G}_{O_2}^R} = 1 - \frac{i_a^{cr}}{i_a^{cr} + i^{ave}} \quad (54)$$

Overall impermeability efficiency:

$$\xi^{imp} = 1 - \frac{\dot{G}_{H_2}^{cr}}{\dot{G}_{H_2}^{cr} + \dot{G}_{H_2}^R} - \frac{\dot{G}_{O_2}^{cr}}{\dot{G}_{O_2}^{cr} + \dot{G}_{O_2}^R} \approx \xi_{H_2}^{imp} \xi_{O_2}^{imp} \quad (55)$$

2.5. Numerical procedure

A finite volume code was developed to solve governing equations.

Power law scheme was applied to approximate diffusion/convection terms. The SIMPLE algorithm with staggered grid system was adopted to solve the equations.

3. Results and discussion

For evaluation of the present model, several test cases were studied. The physical parameters are listed in Table 1. A base case with operating conditions and dimensions listed respectively in Tables 2 and 3 was studied for comparison the simulated results with experimental data and also for overview of species transport.

Fig. 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.

Fig. 3 gives current density contours of the base case. This figure illustrates that the current density in x-direction is approximately 10 times greater than that in y-direction. It means that protons almost move straight toward the cathode catalyst.

Table 1
Properties^a and physical parameters

parameter	Unit	Value
ε in GDL	–	0.4
ε in membrane and catalyst	–	0.25
Volume fraction of membrane in catalyst	–	0.5
K in GDL (permeability to air)	m ²	1.76×10^{-11}
K in membrane (hydraulic permeability)	m ²	1.8×10^{-18}
ρ_m	kg m ⁻³	1840
M_m	kg mol ⁻¹	1.1
j^{ref} at anode	A m ⁻²	5×10^8
j^{ref} at cathode	A m ⁻²	1×10^2
T^{ref}	K	353
p^{ref}	kPa	101.325
h_{reat}	J kg ⁻¹	-285830
R	J kg ⁻¹ K ⁻¹	8.314
F	C mol ⁻¹	96487
$D_{H_2}^{ref}$	m ² s ⁻¹	1.1×10^{-4}
$D_{O_2}^{ref}$	m ² s ⁻¹	3.2×10^{-5}
D_{Water}^{ref}	m ² s ⁻¹	7.35×10^{-5}
$D_{H_2}^S$ at 353 K	m ² s ⁻¹	1.06×10^{-8}
$D_{H_2}^S$ at 323 K	m ² s ⁻¹	3.40×10^{-9}
$D_{O_2}^S$ at 353 K	m ² s ⁻¹	7.47×10^{-9}
$D_{O_2}^S$ at 323 K	m ² s ⁻¹	2.43×10^{-9}
$H_{H_2} = \left(\frac{K_1}{K_2}\right)_{H_2}$ at 353 K	Pa m ³ mol ⁻¹	3.2886×10^4
$H_{H_2} = \left(\frac{K_1}{K_2}\right)_{H_2}$ at 323 K	Pa m ³ mol ⁻¹	2.7426×10^4
$H_{O_2} = \left(\frac{K_1}{K_2}\right)_{O_2}$ at 353 K	Pa m ³ mol ⁻¹	2.0265×10^4
$H_{O_2} = \left(\frac{K_1}{K_2}\right)_{O_2}$ at 323 K	Pa m ³ mol ⁻¹	1.0387×10^4

^a Values for gases dissolution and diffusivity in water have been adopted or calculated from [11], porous media properties are from [9] porosity in membrane has been assumed according to [12].

Table 2
Operating conditions for the base case

parameter	Unit	Value
R_{O-N} at cathode channel entrance	mol mol ⁻¹	0.266
Fluid temperature at anode channel	K	353
Fluid temperature at cathode channel	K	353
Pressure at anode channel entrance	atm	3
Pressure at cathode channel entrance	atm	3
RH at anode channel entrance	%	95
RH at cathode channel entrance	%	50

In Fig. 4 hydrogen concentration is displayed. The minimum concentration within the anode GDL is located in adjacent with catalyst, closed to axis $y = Ly$ 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. Fig. 5 shows oxygen concentrations. Simi-

Table 3
Dimensions and corresponding grids for the base case

Region	Length (μ m)	Number of allocated grids
Gas diffusion layers thickness	200	17
Catalysts thickness	20	1
Membrane thickness	108	10
Cell width (L_y)	2000	61
bipolar plates width	800	–

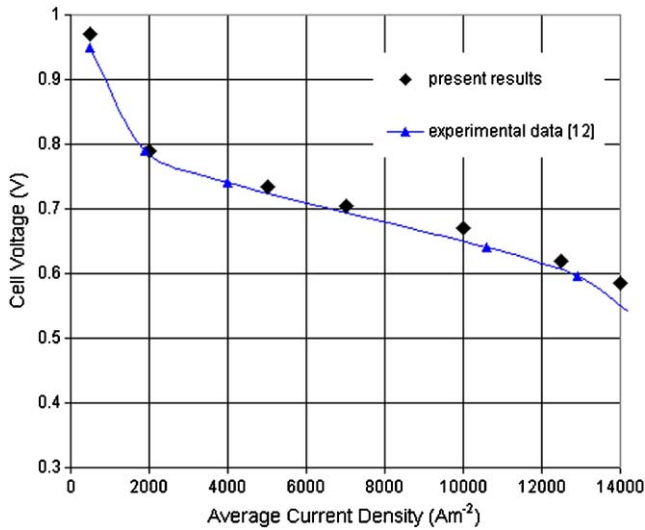


Fig. 2. Comparison of numerical results with experimental data.

larly a discontinuity is observed when oxygen goes to membrane at cathode catalyst. The minimum concentration of oxygen in cathode GDL is located at $y = Ly$, next to catalyst boundary.

With the above background in proton transport and reactant gases distribution, we can 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

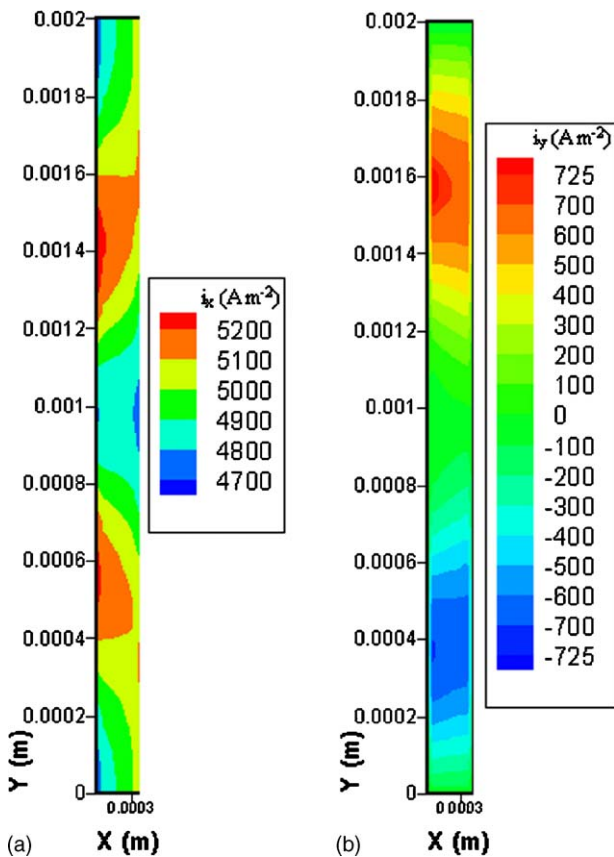


Fig. 3. Current density within the membrane in (a) x-direction (b) y-direction.

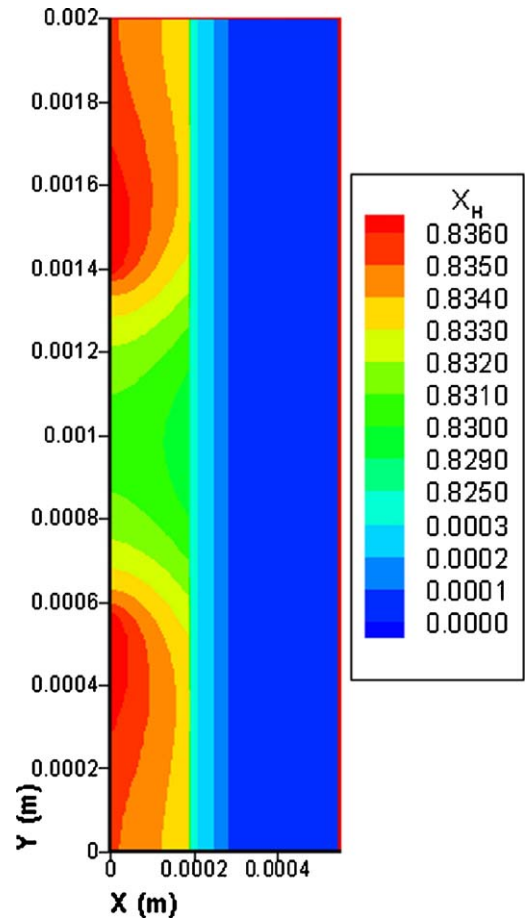


Fig. 4. Hydrogen concentration (mol fraction).

of the base case for a wide range of current densities. The results are presented in Fig. 6. According to this figure, i^{cr} decreases as current density increases. This is due to more reactant gas consumptions 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.

In the next step three effective parameters were considered in four cases as listed in Table 4. The average current density in all cases is 5000 Am^{-2} . The calculated results are also given in this table.

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 decreases and ohmic loss increases. 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 increase in oxygen cross-over and strengthens anode direct reaction in comparison with cathode side. It can be seen that a 380% increase in oxygen

Table 4
Study cases and corresponding results

Case	Problem conditions			Results		
	Membrane thickness (μm)	Fluid in cathode channel	Channels fluid temperature (K)	$i_a^{cr} (\text{Am}^{-2})$	$i_c^{cr} (\text{Am}^{-2})$	$\xi^{imp} (\%)$
I	230	Air with 50% relative humidity	353	5.0	11.3	99.7
II (base)	108	Air with 50% relative humidity	353	11.7	26.2	99.2
III	108	Pure oxygen with 50% relative humidity	353	64.2	26.2	98.2
IV	108	Pure oxygen with 50% relative humidity	323	75.4	19.7	98.1

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%.

Case IV highlights the effect of temperature. Temperature affects two main parameters in gas transport through membrane: solubility and diffusivity. As the solubility of gases in liquid water is greater in lower temperatures, their diffusivity becomes smaller. The resulting cross-over can increase or decrease depending on contribution of each parameter. In case IV the amount of hydrogen cross-over is less than that of case III, but due to greater oxygen cross-over, the total losing current density has slightly grown.

Although direct reaction is negligible at high current density conditions for cells with thick membrane, we observed that in some cases it is considerable, especially at low current density conditions which are very common in fuel cells operation. In fact

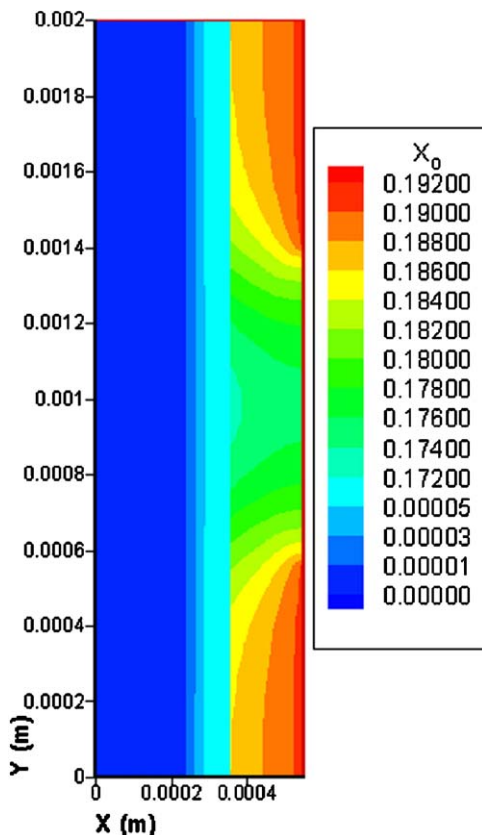


Fig. 5. Oxygen concentration (mol fraction).

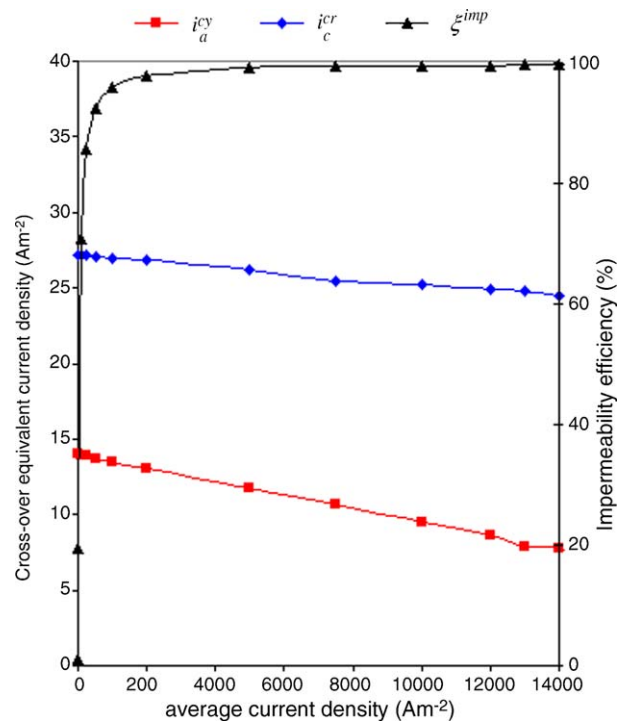


Fig. 6. Cross-over equivalent current density and impermeability efficiency versus current density.

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 cross-over equivalent current density, power losses (i.e. product of equivalent losing current and voltage) increases.

4. Conclusions

A comprehensive study was performed to investigate the effect of gas cross-over through the membrane in waste of energy. It was found out that this effect is not always negligible especially in calculation of cell efficiency. The following items are concluded:

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

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