Analysis and optimization of PEM fuel cell biphasic model

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Abstract: - The optimal operation of proton exchange membrane fuel cell (PEMFC) requires good water management which is presented under two forms vapor and liquid. Moreover, fuel cells have to reach higher output require integration of some accessories which need electrical power. In order to analyze fuel cells operation and different species transport phenomena a biphasic mathematical model is presented by governing equations set. The numerical solution of these conservation equations is calculated by Matlab program. A multi-criteria optimization with weighting between two opposite objectives is used to determine the compromise solutions between maximum output and minimal stack size. The obtained results are in good agreement with available literature data

Key-Words: - PEM Fuel Cell, specie transport, biphasic model, simulation, optimization

1 Introduction
In stationary applications and transportation, PEM fuel cells have to reach efficiency equal or higher than 40% [3]. However, because the efficiency decreases as the output power increases [1], i.e. to reach a great power, they require more energy consumption in auxiliaries systems. Since early models of Springer et al. [2] and Bernardi et al. [3] until the model adopted in our previous work [13] which consider only mono-phase flow, these models give an acceptable approximation in limited current interval. The tendencies are directed towards the biphasic models like that used by Siegel et al. [4], Y. Wang et al. [5], but generally these models are more complicated and need high computing capacity. The present model is less complicated which is based on the study developed and validated by Nguyen and White [6]. In addition to the assumptions enumerated in ref. [6], this model does not take account of flow space variations. Moreover, the water balance was modified, so that it will be valid when liquid water and vapour are presents. The first step consists with model derivation which is used for optimization. This model should be precise, while choosing the reduced form in order to take account of repeated calculations to lead an optimal solution.

2 Mathematical procedures
2.1 Mass balance
an elementary PEM fuel cell, with parallel gas channels at anode and cathode, is composed of collector plate, gas diffusion layer (GDL) and catalyst layer at both side anode and cathode. The polymeric membrane is sandwiched in the center. In this reduced model, we neglect variables space dependency in flow channels. Essentially, we control vapour, liquid water and gases flows. Consequently, governing differential equations will be reduced to algebraic equations. For a given current density, hydrogen and oxygen mass balances are calculated using the difference between inlet flow and consumed flow by the chemical reaction:

- Hydrogen mass balance :
  \[ M_{H_2} = M_{H_2}^{\text{in}} - \frac{\alpha_i}{V} \] (1)

- Oxygen mass balance :
  \[ M_{O_2} = M_{O_2}^{\text{in}} - \frac{\alpha_i}{V} \] (2)

Nitrogen is assumed as inert gas, so does not participate in chemical reaction, i.e. inlet flow is equal to outlet flow:
In channels, inlet reactant flows are determined according to consumed flows by chemical reaction and stoichiometric ratio. Hydrogen and air flows are respectively expressed as:

\[
M_{H_2} = M_{H_2, in} \tag{3}
\]

\[
M_{O_2} = M_{O_2, in} \tag{4}
\]

Water flows with presence of both vapour and liquid water are affected by the following factors [4, 5, 9, and 10]:
- In cathode, water production by electrochemical reaction,
- Water transport from anode to cathode by electro-osmosis drag,
- Upstream water diffusion from cathode toward anode,
- Condensation and evaporation of water.

In anode side, water balance is formulated by equation (4) which shows that inlet water vapour in anode channel exhausts as vapour or condensed liquid or passes across membrane to the cathode:

\[
M'_{w,a} = M_{w,a, in} - M_{w,a} - \alpha \frac{d_i}{e} \tag{6}
\]

With \( \alpha \) is net water molecules ratio passes across the membrane reported to protons flux.

In fuel cells operation, there are two cases which present at anode channel:

**First case**: if both liquid and vapour phases of water are present in anode channel, i.e. \( M_{w,a} \neq 0 \), so outlet vapour is saturated and outlet vapour flow is expressed as:

\[
M'_{w,a} = M_{w,a, in} - M_{w,a} - \alpha \frac{d_i}{e} \tag{7}
\]

Outlet liquid water from anode channel, \( M'_{w,a} \), is the difference between inlet and outlet flows which is expressed by the following equation:

\[
M_{w,a} = M_{w,a, in} - M_{w,a} - \alpha \frac{d_i}{e} \tag{8}
\]

Second case: if liquid water doesn’t exist in anode channel, i.e. \( M_{w,a} = 0 \), so there isn’t equilibrium between liquid and vapour phases. Outlet vapour \( M'_{w,a} \) is calculated as follow:

\[
M'_{w,a} = M_{w,a, in} - \alpha \frac{d_i}{e} \tag{9}
\]

As the same method, we analyse the situation at cathode side, so the water balance in this channel take account for outlet flows of vapour and liquid water, water vapour coming from anode to cathode and water produced by electrochemical reaction at cathode. The overall balance at cathode is expressed as follow:

\[
M'_{w,c} = M_{w,c, in} - M_{w,c} + \alpha \frac{d_i}{e} \tag{10}
\]

First case: if both liquid and vapour phases of water are present in cathode channel, i.e. \( M_{w,c} \neq 0 \), so water vapour is saturated and outlet vapour flow is expressed as:

\[
M'_{w,c} = M_{w,c, in} - M_{w,c} + \alpha \frac{d_i}{e} \tag{11}
\]

Outlet liquid water from cathode channel, \( M'_{w,c} \), is the difference between inlet and outlet flows which is expressed by the following equation:

\[
M_{w,c} = M_{w,c, in} - M_{w,c} + \alpha \frac{d_i}{e} \tag{12}
\]

Second case: if liquid water doesn’t exist in cathode channel, i.e. \( M_{w,c} = 0 \), so there isn’t equilibrium between liquid and vapour phases. Outlet vapour \( M'_{w,c} \) is calculated as follow:

\[
M'_{w,c} = M_{w,c, in} + \alpha \frac{d_i}{e} \tag{13}
\]

Inlet water vapour at anode channel is calculated according to hydrogen relative humidity:

\[
M_{H_2, in} = \frac{\gamma_{H_2, in}}{1 - \gamma_{H_2, in}} M_{H_2, in} \tag{14}
\]

\[
\gamma_{H_2, in} = R H_{H_2} \frac{P_{H_2}}{P} \tag{15}
\]

Also, inlet water vapour at cathode channel is calculated according to air relative humidity:

\[
M_{O_2, in} = \frac{\gamma_{O_2, in}}{1 - \gamma_{O_2, in}} M_{air, in} \tag{16}
\]

\[
\gamma_{O_2, in} = R H_{O_2} \frac{P_{O_2}}{P} \tag{17}
\]
\[ y_{w.a.in} = RH_{Air} \frac{P_{sat}}{P} \] (19)

With \( y_{w.a.in} \) and \( y_{w.c.in} \) are respectively vapour molar fractions for inlet humid gas at anode and cathode channels, \( P \) is the pressure of gas vapour mixture in channels.

Vapour saturated pressure (atm) is expressed according to temperature (T °C) as follow [10]:

\[ P_{sat} = 10^{-2.158-2.158 \times 10^{-5} T-9.19 \times 10^{-5} T^2+1.44 \times 10^{-7} T^3} \] (20)

For determining fuel cells outlet flows, we should calculate the coefficient \( \alpha \) which represents the net ratio of water molecules passes across the membrane. It is the difference between coefficients of electro-osmotic drag and back diffusion of concentration gradient [2]:

\[ \alpha = n_d - n_b \]

Electro-osmotic coefficient is expressed according to water activity:

\[ n_d = 0.0049 + 2.024a - 4.53a^2 + 4.09a^3 \]

Water activity at anode cathode and are obtained respectively by the following relations [10]:

\[ \alpha_a = \frac{M_{w.a}'}{M_{w.a} + M_{H_2}O} P_{sat} P_{W} \]
\[ \alpha_c = \frac{M_{w.c}'}{M_{w.c} + M_{H_2}O + M_{H_2}O} P_{sat} P_{W} \]

Back diffusion coefficient of water concentration gradient [3]:

\[ n_b = \frac{F}{J} D_w (c_{w.c} - c_{w.a}) \]

Diffusion coefficient in the membrane is expressed as [9]:

\[ D_w = n_d D_t \exp \left[ 2416 \left( \frac{1}{303} - \frac{1}{273 + T} \right) \right] \]

Water concentrations at anode and cathode membrane interfaces are expressed by the following relations [10]:

\[ c_{w.a} = \frac{\rho_{m, dry}}{M_{m, dry}} (0.300 + 10.8a_2 - 16.0a_2^2 + 14.1a_2^3) \]

With \( \rho_{m, dry} \) and \( M_{m, dry} \) are respectively density and molar mass of dry membrane.

2.2 Fuel cell electrochemistry

Fuel cells effective voltage is expressed as the difference between reversible thermodynamic voltage and different overvoltage losses:

\[ V_{cell} = V_{rev} - V_{act} - V_{ohm} - V_{con} \] (21)

Reversible thermodynamic voltage: this voltage is based on Nernst equation [29].

\[ V_{rev} = \frac{R(273 + T)}{2F} \ln \left( \frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2}O} \right) \]

With \( V \) is open circuit voltage.

Activation overvoltage represents loss due to reaction rate at electrodes surface, this overvoltage is assumed that mainly occurs at cathode side [9]:

\[ V_{act} = \frac{I}{0.5F} \exp \left( \frac{I}{I_0 P_{O_2}} \right) \]

With \( I_0 \) is exchange current density.

Ohmic overvoltage represents voltage loss due to resistance against protons flow in the electrolyte [9].

\[ V_{ohm} = \frac{I_t}{\sigma_m} \]

With \( t \) is the membrane thickness.

Membrane resistance \( \sigma \) is expressed as follow [10]:

\[ \sigma_m = \left( 0.00514 \frac{M_{m, dry}}{\rho_{m, dry}} \left( a_2 - 0.00324 \right) \exp \left( \frac{1}{303} - \frac{1}{273 + T} \right) \right) \]

With \( \lambda \) is membrane water content.

In literature, we find different approaches used for determining membrane water content. Golbert1 et al. [11] take it as anode water content, L. Wang et al. [12] calculate with the same value at cathode and Pukrushpan [7] use mean activity value between anode and cathode. In this work, we adopt the last approach:

\[ \bar{a}_m = \frac{a_a + a_c}{2} \]
Water content is expressed as the relation given by Springer et al. [2]:

$$\lambda_m = 0.043 + 17.81a_m - 39.85 a_m^2 + 36.0 a_m^3$$

Concentration overvoltage represents voltage loss due to mass transport limitation [15]:

$$V_{con} = \beta I \ln \left( \frac{I}{I_L} \right)$$

With $\beta I$ is mass transport amplification term linked with the overvoltage, expressed as voltage unity, and $I_L$ is limiting current density. With substituting the different terms in equation (21) we obtain the expression of fuel cell voltage:

$$V_{cel} = V_{ocep} + \frac{8}{25} \frac{(I_{cell}+2)}{I_{cell}} \ln \left( \frac{P_{H_2} P_{air}}{P_{H_2} P_{air2}} \right) - \frac{8(I_{cell}+2)}{25} \ln \left( \frac{I}{I_L} \right) - \frac{1}{25} \frac{I_{cell} + 2}{I_{cell}}$$

$$V_{tel} = V_{cel} = \beta I \ln \left( \frac{I}{I_L} \right)$$

(22)

2.3 System efficiency

For evaluating the performance of fuel cells stack, generally we use the efficiency as indicator. System efficiency is defined as ratio between stack net output power and self fuel heating:

$$\eta = \frac{W_{stak}}{W_{fuel}}$$

Self fuel heating:

$$W_{stak} = n_{cel} \xi_H N_H \frac{LH}{25}$$

With LHV is lower heating value of hydrogen, and $n_{cel}$ is number of cells. In calculation we take $n_{cel} = n$, so the area $A$ represents all MEA active area.

Stack output power [8]:

$$W_{stak} = n_{cel} A I$$

(25)

Parasite power is the sum of consumed power by air compressor and others accessories of humidification and cooling [8]:

$$W_{prs} = W_{comp} + W_{other}$$

(26)

Consumed power by air compressor $W_{comp}$ [8]:

$$W_{comp} = \frac{\xi_H N_H}{\eta_{ pneum}} \left( \frac{P_{H_2}}{P_{in}} \right)^{0.68} - 1 \right) m_{air}$$

(28)

With $m_{air}$ is air mass flow [8]:

$$m_{air} = 3.57 \times 10^{-7} n_{cel} \xi_{air} A L$$

(29)

Others power losses $W_{other}$ are taken by Pei et al. [14] equal to 2 kW based on output fuel cells of 62.5 kW. Instead of this value, we assumed $W_{other}$ as 5% of stack nominal output power. Efficiencies of compressor and electric motor are constants, as the approach adopted by others authors [8]:

$$W_{other} = 0.05W_{std}$$

(30)

2.3 System optimization

The approach presented in our previous work [16] shows that PEM fuel cells size (MEA active area) and system efficiency are two opposed objectives which should be optimized. The first objective function (MEA total active area) should be minimised, but the second objective function (system efficiency) should be maximised. Multi-objective optimization is equivalent to resolve the problem defined as follow:

$$\left\{ \begin{array}{l}
\min f_1(x), \\
\max f_2(x), \\
\end{array} \right\}$$

With:

Function $f_1$ is active area "A"

Function $f_2$ is efficiency " $\eta$ "

The variables are:

$x_1$: current density " $i$ "

$x_2$: cells pressure " $P$ "

$x_3$: hydrogen stœchiometric ratio " $\xi_{H_2}$ "

$x_4$: air stœchiometric ratio " $\xi_{air}$ "

$x_5$: hydrogen relative humidity " $RH_{H_2}$ "

$x_6$: air relative humidity " $RH_{air}$ "

The goal of this optimization is to find solutions which represent a compromise between efficiency and size in order to realize conception of PEM fuel cells system for insuring required power. Optimal solutions set present a compromise between two objectives, is called Pareto set. Weighting method is adopted for determining this Pareto set.
The variables bounds are fixed according to common values used in practice [8 - 9]. Bounds of air relative humidity are taken from meteorological statistics of Ouargla city (in south of Algeria). Superior bound of hydrogen relative humidity is slightly reduced. Variables bounds became as follow:

\begin{align*}
0.11 & \leq x_1 \leq 1.3 \\
1.2 & \leq x_2 \leq 5 \\
1.1 & \leq x_3 \leq 10 \\
1.1 & \leq x_4 \leq 10 \\
0.25 & \leq x_5 \leq 0.60 \\
0.50 & \leq x_6 \leq 0.80
\end{align*}

### 3 Numerical procedures

Calculation Steps start by the determination of inlet reactants flows. Further more, the calculation of outlet flows with corresponding voltages. Numerical solution of governing equations is calculated by a Matlab program and the optimization is achieved using "Toolbox". Genetic algorithm method (GA) is chosen for program execution. For each introduced \( \omega \) value, obtained solution is taken as initial point for continuing program execution with Quasi-Newton method. Computing precision is fixed at relative error of 1.e-5. Physical parameters used in the model and base case conditions are presented in Table 1.

#### Table 1: Parameters and base case conditions [9]

<table>
<thead>
<tr>
<th>Designation</th>
<th>Value</th>
<th>Unity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplification constant (( \beta ))</td>
<td>0.085</td>
<td>V/cm²A⁻¹</td>
</tr>
<tr>
<td>Exponent of amplification constant (k)</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Density of limiting current (( I_1 ))</td>
<td>1.4</td>
<td>Acm⁻²</td>
</tr>
<tr>
<td>Lower heating value of hydrogen(LHV)</td>
<td>24 x 10⁴</td>
<td>Jmol⁻¹</td>
</tr>
<tr>
<td>Exchange current density at cathode (( I_0 ))</td>
<td>0.01</td>
<td>Acm⁻²</td>
</tr>
<tr>
<td>Open circuit voltage (( V_{oc} ))</td>
<td>1.1</td>
<td>V</td>
</tr>
<tr>
<td>Coefficient of water diffusion in the membrane (( D_b ))</td>
<td>5.5 x 10⁻⁷</td>
<td>cm²s⁻¹</td>
</tr>
<tr>
<td>Density of dry membrane ( \rho_{m,dr} )</td>
<td>2</td>
<td>gcm⁻³</td>
</tr>
<tr>
<td>Molar mass of dry membrane ( M_{m,dr} )</td>
<td>1100</td>
<td>gmol⁻¹</td>
</tr>
<tr>
<td>Membrane thickness (( t_m ))</td>
<td>5 x 10⁻³</td>
<td>cm</td>
</tr>
<tr>
<td>Compressor efficiency (( q_c ))</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>Compressor inlet temperature (( T_i ))</td>
<td>15 °C</td>
<td>°C</td>
</tr>
<tr>
<td>Compressor inlet pressure (( P_i ))</td>
<td>1</td>
<td>atm</td>
</tr>
<tr>
<td>Electric motor efficiency (( q_m ))</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>Calorific capacity of air (( s_p ))</td>
<td>1004</td>
<td>JK⁻¹kg⁻¹</td>
</tr>
<tr>
<td>Operating temperature ( T )</td>
<td>80</td>
<td>°C</td>
</tr>
<tr>
<td>Relative humidity at anode/cathode</td>
<td>100/5</td>
<td>%</td>
</tr>
</tbody>
</table>

### 4 Results and discussions

#### 4.2 Curve of Pareto set

Figure 1 shows optimal solutions for 50 kW PEM fuel cells. Base case solution (green point) is inside the convex space limited by Pareto curve, therefore this point represents a dominated situation. Optimal solutions are compromise solutions between the efficiency and MEA active area. The curve is composed of all designs which are optimal in the Pareto sense. The highest point (in top on the right) in figure 3 represents the optimal solution for \( \omega = 1 \), which corresponds to the problem with simple optimization objective which consists in maximizing the output of the system without taking account of stack size. This solution is 23% more efficient but the size is 107% larger than the base case. This design requires operation with low current density (thus, at higher voltage), with higher pressure, and with small hydrogen and air stoechiometric ratios compared to the base case. Consequently, it reaches higher efficiency with low fuel consumption. However, the parasitic loss is higher due to pressure increase.

![Figure 1: Pareto set and base case](image)

#### 4.3 Objectives evolution

The optimal values of relative humidity and hydrogen stoechiometric ratio are 0.8 and 1.1 respectively, remaining without variation for all \( \omega \) weights.

Figure 2 shows optimal values of the objectives according to current density. At low current densities, we note that solutions which have big size and high efficiency form the branches at right-hand
sides. Conversely, left branches contain the solutions which are characterized by small size and low efficiency, corresponding to high current density. Generally, according to current density, MEA area, stack efficiency and voltage decrease.

During optimization, some variables bounds are violated particularly lower bound of current density, pressure upper bound, and hydrogen stoichiometric ratio bounds. Concerning lower bounds of current density and hydrogen stoichiometric ratio, we note that current density less than 0.11 and hydrogen stoichiometric ratio less than 1.1 A cm⁻² are not used in practice.

Figure 2: Objectives evolution

5 Conclusion
Optimization stochastic methods are used in this complicated objective function to reach the global minima. But, it requires refining operation by deterministic method. The obtained results indicate that output and stack size are opposed objectives, because for reaching high efficiency, the system must operate at low current density. The low current density coincides with low power density that means we need a greater system characterized by wide area to improve stack power. An optimization study is carried out to examine at which operating pressure level and until which humidification reduction we can go down, in order to have high power and low parasitic consumption (humidifiers, pump, compressor,........).

References: