One dimensionel Simulation of water management in the membrane of PEM Fuel Cell

B. Dokkar, N. Settou, O. Imine, B. Negrou, N. Saifi, N. Chennouf

Abstract— The proton exchanging membrane fuel cell (PEMFC), is the most used cell, but it requires a good water management for its optimal operation. The polymeric membrane plays the principal role in water transport and proton exchange in the cells. In order to analyze this phenomenon, one-dimensional mathematical model is presented by a governing equation. The membrane is regarded as a homogeneous structure. The conservation equation is discretized using the finite volumes method and the numerical solution is calculated by a program conceived with FORTRAN language. The nature of species transport and ionic conductivity in the membrane are illustrated using various curves. The obtained results are in good agreement with those found in literature.

Index Terms— PEM Fuel Cell, polymeric Membrane, water management, ionic resistance.

I. INTRODUCTION

THE fuel cell transforms chemical energy into electric power. This mode of energy production becomes more attracting because it has environmental advantages (very low emissions of acoustical and chemical pollutants). The PEM fuel cell is characterized by a fast starting which lead to wide uses on vehicles. However, it remains with well controlling certain aspects like cost and operation such as the water management in the various layers of fuel cell. Among these layers we distinguish the membrane which constitutes cell electrolyte and ensures the protonic conduction from anode towards cathode under the influence of an electric field. Several water flows pass by the membrane which requires a good regulation to maintain a suitable level of water content in order to ensure a better protonic conduction. By analyzing recent models available in literature concerning species transport and water management in the membrane, we generally note that models differ in the expression of diffusion coefficient. The models of N. R. Siegel [1], Y. Wang and Al [2] and P. H. Lee [3] use an exponential function which often depends on the cell temperature water content. In contrast, C Sui and Al [4] avoid the use of the exponential form and choose a simple differential expression containing the terms of water activity and water content. In this work we choose this last form of diffusion coefficient which presents well the phenomenon. In addition, it is more

B. Dokkar, Laboratoire de Génie des Procédés chimiques (LGPC), Département de Génie des Procédés Faculté des Sciences des l'Ingénieur Université FERHAT ABBAS – SETIF, 19000, Algérie.

adapted to simulation by the fact that it does not contain any exponential function which leads to reduce computing time.

II. MATHEMATICAL MODEL

figure (2.1) shows the membrane which is located at the cell middle between anode and cathode in which it reigns a balance of water flow resulting from the effect of several sweeping forces: the electrosmosis phenomenon which attracts the water molecules from anode towards cathode, the gradient of water concentration which involves the molecules from cathode towards anode and a very weak effect due to pressure gradient.
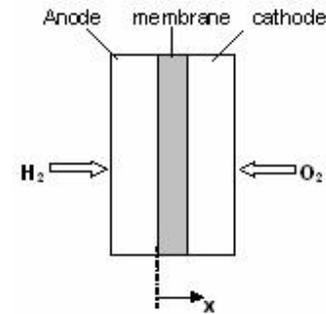

Fig. 2.1 : cell scheme

A. Hypothesis

- Homogeneous and isotropic membrane structure.
- Water in the membrane is in molecular form.
- Steady state.
- Cell temperature remains constant.
- Water in electrodes is in vapour phase.
- Computational domain is one-dimensional

B. Governing equations

The generalized equation of water transport in the phenomenological model is written:

$$J = \frac{n_d}{F} i - \frac{\rho_m}{M_w} D_w \nabla \lambda - \frac{\kappa}{\mu} \nabla p \qquad (2.1)$$

In general, the permeability of water in the membrane is much smaller than drag and diffusion terms, thus we can neglected the term of pressure and by rewriting equation (2.1) in the form of conservation, we obtains:

$$\nabla J = \frac{i}{F}\nabla n_d - \frac{\rho_m}{M_w}\nabla(D_w\nabla\lambda) \qquad (2.2)$$

Drag coefficient n_d is expressed as a linear function of water content λ [5]:

$$n_d = \frac{2,5}{22}\lambda \qquad (2.3)$$

Replacing n_d in equation (2.2) and for steady state we obtain:

$$\frac{2,5}{22}\frac{i}{F}\nabla\lambda - \frac{\rho_m}{M_w}\nabla(D_w\nabla\lambda) = 0 \qquad (2.4)$$

To avoid Schröder paradox (number of water molecules jump between liquid water and the saturated water vapour), our study is limited in the non saturation interval of the membrane, thus the water content is related to the water activity by an experimental relation [5]:

$$\lambda = 0,043 + 17,81a - 39.85a^2 + 36a^3 \quad 0<a\le1 \qquad (2.5)$$

Diffusion coefficient is given by Springer et al. [5]:

$$D_w = 10^{-10}\left(\frac{\lambda}{(1 + s.c_w)^2\, a}\right)\frac{da}{d\lambda}D' \qquad (2.6)$$

Coefficient D' is expressed in each interval:

$$D' = 0.25\,\lambda, \qquad\qquad 0<\lambda\le2$$
$$D' = 0.5 + 0.8125\,(\lambda - 2), \qquad 2<\lambda\le6$$
$$D' = 3.75 + 0.267(\lambda - 6), \qquad 6<\lambda$$

Membrane protonic conductivity is given by Springer et al. [5]:

$$\sigma = (0.005139\lambda - 0.00326)\exp\left(1268(\frac{1}{303} - \frac{1}{T})\right) \qquad (2.7)$$

Membrane resistance is calculated as follow:

$$R = \int_0^{x_m}\frac{1}{\sigma}dx \qquad (2.8)$$

C. Boundary conditions

The computational domain is extended along membrane thickness on x axis direction. By knowing current density, equation (2.4) can be solved with Neumann boundary conditions but usually the water flow is not known, therefore we choose Dirichlet boundary conditions which present water content at catalyst/membrane interfaces. By knowing the cell operating temperature and pressures in cathode and anode sides, we can determine the values of water content at the borders by the following steps:

Water activity at the borders is expressed by the relation given by B. Cheng and Al [6]:

$$a = y_v\frac{p}{P_{sat}} \qquad (2.9)$$

Vapour saturation pressure is expressed the relation given by Y. Wang [7]:

$$\log_{10} P_{sat} = -2,1794 + 0,02953(T - 273,15)$$
$$-9,1837\text{x}10^{-5}(T - 273,15)^2 + 1,4454\text{x}10^{-7}(T - 273,15)^3$$
$$(2.10)$$

Vapour molar fraction y_v is expressed as a function of relative humidity φ:

$$y_v = \frac{\varphi.P}{P - \varphi.P_{sat}} \qquad (2.11)$$

1) Cathode side ($x=x_m$): At this boundary, water production by chemical reaction will take place, therefore the value of relative humidity is rather high. By fixing the value of relative humidity φ_c we can calculate water activity by the relation (2.9), and then we calculate λ using the equation (2.5).

2) Anode side ($x=0$): At this boundary, is carried out proton supply coming from hydrogen reduction. In this case, we fixed φ_a at very low in order to show the impact of diffusion coefficient on numerical results. By fixing the value of the relative humidity we can calculate the water activity by the relation (2.9), and then we calculate λ using the equation (2.5).

III. NUMERICAL RESOLUTION

The conservation equation is discretized using finite volumes method [8] with centred difference scheme. Numerical solution is calculated by a program conceived with FORTRAN language. In calculation of diffusion coefficient we introduce small linear interpolation to determine the inverse function of equation (2.5). The value of water content λ at curve inflexion point is determined by using the formula of exact solution. The algorithm of Gauss-Seidel is used to carry out the iterations on the variable λ, after 16269 iterations the program converges with a relative error of 10^{-5}. The parameters of basic case and the constants are presented in table 3.1.

Table 3.1: Values of base case parameters

symbol	designation	value	unity
F	Faraday constante	96487	C/mol
I	Average current density	10000	A/m
M	Equivalent weight of dry membrane	1,1	kg/mol
s	Swelling facteur	0,126	
P	Pressure (anode and cathode sides)	1,5	bar

T	Cell temperature	353,0	°K
X_m	Membrane thickness	5x10⁻⁵	m
ρ	Density of dry membrane	2000	kg/m³
φ_a	Relative humidity of water vapour at membrane/catalyst anode interface	0,03	
φ_c	Relative humidity of water vapour at membrane/catalyst cathode interface	0,75	

IV. RESULTS AND DISCUSSIONS

A. Water content profile in the membrane

The curve obtained on the figure (4.1) represents water content in the membrane; it shows a good agreement with the results obtained by P. C. Sui [4]. The water content λ increase along the positive direction x axis, therefore along the curve λ we do not find any maximum or minimum except the minimal value at anode border and the maximum value at cathode border. In the interval x = [0, 0.3] we notice a weak increase in the water capacity but beyond this interval the value of λ increases quickly that is due to fast increase in diffusion coefficient.

Fig. 4.2: Effect of membrane thickness

C. Effect of current density

The figure (4.3) shows the profiles of water content calculated on the range of current density (5000, 10000, 15000 A/m²), while keeping the same boundary conditions of base case. By increasing current density, drag force term carries on diffusion term in the governing equation. Consequently, water content profile shifts towards cathode side.

Fig. 4.1: Water content in membrane.

Fig. 4.3: Effect of current density.

B. Effect of membrane thickness

The figure (4.2) shows the profiles of water content calculated on the range of membrane thickness (50, 100, 175 μm) while keeping the same boundary conditions of base case. Therefore, by increasing membrane thickness, diffusion term decrease and drag force term remains constant in the governing equation. Consequently, water content profile shifts towards cathode side.

D. Ionic conductivity

Ionic conductivity characterizes membrane permeability to allow the passage of protons; it is expressed by relation (2.7). Figure (4.4) presents the curve of ionic conductivity according to x-coordinates, it shows a similar pace to the curve of λ, in addition its variation according to the variable λ takes nearly a linear form, (see figure 4.5).
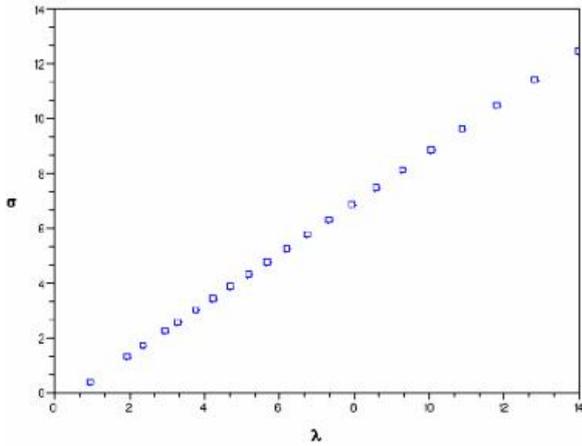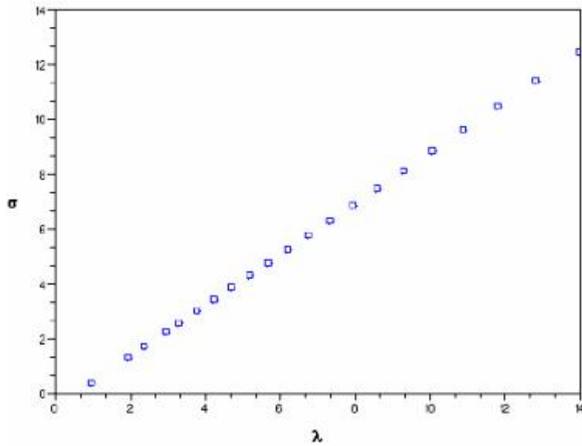
Fig. 4.4: Conductivity variation with x

Fig. 4.5: Conductivity variation with λ

E. Ionic resistance

Ionic resistance (ohmic falls) limits cell operating at high current density and it is mainly associated with the membrane (ratio of thickness to ionic conductivity) [4], therefore we substitute equation (2.7) in equation (2.8) we obtain resistance expression:

$$R = \int_0^{x_m} \frac{dx}{(0.005139\lambda - 0.00326)\exp\left(1268(\frac{1}{303} - \frac{1}{T})\right)}$$

The variable λ also varies according to x-coordinate, so it complicates the expression of resistance R. Therefore, for integral calculation we use a numerical integration which gives a value R $=$ 1,586x10^{-5} Ω. m.

V. CONCLUSION

One dimensional model presents a good approximation of the multidimensional phenomenon of water management in the membrane.

While choosing a condition of very low water content at the anodic boundary we notice that the diffusion coefficient causes a high increase of water content beyond x=0,3 of the membrane x-coordinate, also as increasing current density, diffusion term dominates and consequently water content profile shifts towards cathode side. In addition, it is noted that by increasing membrane thickness, diffusion term decrease which causes a shift of water content profile towards cathode side. The shape of ionic conductivity curve according to x-coordinate gathers with water content curve and calculation of ionic resistance of membrane Nafion 112 gives a relatively low value (R = 1,586x10^{-5} Ω.m).

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Authors

Dokkar Boubekeur[1*], Grade : maitre assistant

SETTOU Noureddine[1], Grade : Proffesseur

Imine Omar[2], Grade : Proffesseur

Negrou Belkhir[1], Grade : maitre assistant

Saifi Nadia[1], Grade : maitre assistant

Chennouf Nacerddine[1], Grade : maitre assistant

[1] Laboratoire de Valorisation et de Promotion des Ressources Sahariennes (LVPRS), Kasdi Merbah university, Ouargla, Algeria,

*E-mail: boubekeur.ogx@gmail.com,

[2] Mechanical engineering department, Mohammed Boudiaf University (USTO), Oran, Algeria