Effect of temperature and water content on the performance of PEM fuel cell

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Abstract—A fuel cell is a promising energy conversion system that will eventually become the first-choice for producing power because of its clean or zero-emission nature. A steady-state, two-dimensional mathematical model with a complete set of governing equations valid in different components of a PEM fuel cell was developed to illustrate the temperature and water content effects on proton exchange membrane (PEM) fuel cell performance. This model considers the transport of species and water along the porous media: gas diffusion layers (GDL) anode and cathode, and the membrane of PEMFC fuel cell.

Keywords— PEM Fuel Cell, Temperature, Mathematical model, Performance

I. INTRODUCTION

Proton exchange membrane (PEM) fuel cells are electrochemical devices that directly convert the energy from the chemical reaction into electricity. Useful features such as high power density, simple, safe construction and fast start-up make those particularly suitable for home appliance, vehicles and transportation tools [1]. Generally, A PEMFC has a working temperature from 60 to 100 $^{\circ}$C and an efficiency of about 50%, such that the remaining 50% is waste heat. The waste heat must be discharged efficiently from the fuel cell to protect the proton exchange membrane [2]. It is well known that the operating temperature has a significant influence on PEM fuel cell performance. The increase in the operating temperature is beneficial to fuel cell performance since it increases reaction rate and higher mass transfer rate but usually lowers cell ohmic resistance arising from the higher ionic conductivity of the electrolyte membrane [1]. Useful mathematical models can provide powerful tools for the analysis and optimization of fuel cell performance [3].

In the early 1990s, the pioneering work on PEM fuel cell model development was done by Bernardi and Verbrugge [4], and Springer et al.

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[5] who formulated one-dimensional and isothermal models for the gas-diffusion layer, active catalyst layer and ion-exchange membrane. Only the direction perpendicular to the membrane was considered. The model employed water diffusion coefficient, electro-osmotic drag coefficients and membrane conductivities to predict the change of membrane resistance with current density. The temperature was assumed to be constant and these models were unable to simulate the flow behavior along the channels.

Compared with one-dimensional model, a two dimensional mathematical model is preferred for water and heat management analysis, as the temperature, pressure and water varies along the channel as well as across the membrane [1]-[6]. D. Singh et al. [7], present a model for a two-dimensional isothermal complete cell, the results indicate that the loss of potential of the cathode, due to the slow reaction of O_2, is dominant at all current densities. The simulations also show that the 2-D model to a significant effect on water management and some aspects of cell performance. S.H.Ge et B.L.Yi [8], present a two-dimensional model for a PEM cell where the transport of water in the membrane by electro-osmotic drag, diffusion and pressure difference are considered. The results show that a higher pressure of the cathode can be used to reduce the problem of dehydration, and water content of the membrane and the performance increases with decreasing the thickness of the membrane. The model of NP Siegel et al. [9] reflects the influence of numerous parameters on cell performance including geometry, porous of material of, the surface active, properties of the polymer, and the composition of the catalyst layer.

P. Costamagna [10] developed a model based on the study of charge transport, mass, momentum and energy in the PEMFC; it is validated by the experimental data. The temperature and water content must be chosen carefully to obtain satisfactory performance.

In the present study, a steady-state, two-dimensional mathematical model with operating temperature and water content effects, on a single PEM fuel cell performance were investigated in details.
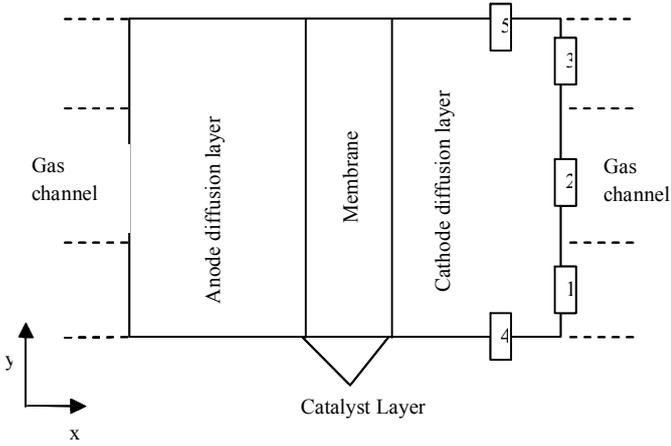
Fig.1. Schematic diagram of PEM fuel cell modeling regions.

II. DESCRIPTION OF THE MODEL

A typical sandwich construction of a PEM fuel cell is shown in Fig. 1. The model regions consist of a proton exchange membrane, two catalyst layers and electrodes at cathode and anode.

The x-axis is normal to the membrane. The hydrogen ions and some water molecules transport from anode to cathode along this x-direction. At the anode, humidified hydrogen gas is supplied at a given excess coefficient into the flow anode channels. Hydrogen gas diffuses through the porous electrode and reaches the anode catalyst layer, then the chemical reaction, $2H_2 \rightarrow 4H^+ + 4e^-$, releases electrons and creates hydrogen ions which pass through the membrane and reach the cathode. At the cathode, humidified air or pure oxygen with a given excess coefficient flows along the cathode channels, then diffuses through the electrode layer and meets with hydrogen ions, the reaction, $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$, occurs. Water vapor is produced along the cathode channels and at the same time electrical energy and heat are released.

A. Basic assumptions

In the present model, the following assumptions were employed:
- stationery model,
- single phase model,
- isotropic and homogeneous electrodes and membrane,
- the membrane is considered impermeable for the gas phase,
- negligible contact resistance,
- catalyst layers as reactive boundaries.

B. Governing equations

In this model, the form of mathematical equations of transport and source terms presented may change from one component to another of the fuel cell, that is to say each item has its own equation. The governing equations are presented below:

- Continuity:

$$\tilde{N}\left(er\,\overline{U}\right)= 0 \tag{1}$$

- Momentum (Darcy's law):

In the gas distribution electrodes, Darcy's law is used to model the flow in this porous media with the pressure gradient as the driving force. In a porous structure, the global transport of momentum by shear stresses in the fluid is negligible because the pore walls impede transport of this momentum to the fluid outside the individual pores. Since a detailed description at the resolution of a pore is not practical in most models, homogenization of the porous and fluid media is a common approach. Darcy's law is based upon homogenization of the porous and fluid media into one single medium and does not require a detailed geometrical description of the pore structure [11].

Darcy's law states that the velocity vector is determined by the pressure gradient, the fluid viscosity, and the structure of the porous media represented with the following equation:

$$\vec{U} = -\,\frac{k_p}{me}\tilde{N}\,P \tag{2}$$

- Species conservation:

$$\tilde{N}\left(e\overline{U}C_k\right)= \tilde{N}\left(D_k^{eff}\tilde{N}\overline{C_k}\right)+ S_k \tag{3}$$

The source S_k term is the rate of consumption or production of each species; the effective diffusion coefficients are obtained using the Bruggemann correction [12]:

$$D_k^{eff} = D_k\,e^{1.5} \tag{4}$$

D_k : Diffusion coefficient, depending on the temperature and pressure S.Um et al. [13]:

$$D(T)= D_0\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{P_0}{P}\right) \tag{5}$$

- Equation of energy

$$e_{cat}\,r\,c_p\left(U\frac{\partial T}{\partial x} + V\frac{\partial T}{\partial y}\right)= k^{eff}\left(\frac{\partial^2 T}{\partial x^2}+ \frac{\partial^2 T}{\partial y^2}\right)+ S_T \tag{6}$$

Detailed expressions of source terms for species conservation and energy are given in Table I.

Table I. Source terms for species conservation and energy equations in various regions.

	S_k	S_T
Backing layers	0	0
Catalyst Layers	$S_{H_2} = -\dfrac{1}{2F}J_a$	$i\,h + \dfrac{i^2}{s_{ct}}$
	$S_{O_2} = \dfrac{1}{4F}J_C$	
	$S_{H_2O} = -\dfrac{1}{2F}J_c$	
Membrane	0	$S_T = \dfrac{i^2}{s_m}$

The term source of heat in the energy equation in the catalytic layers:

$$S_T = i\,h + \frac{i^2}{s_{ct}} \tag{7}$$

In which the first term is the heat produced by the activation overvoltage and the second term is the heat produced by Joule effect.

The energy is transported by convection and conduction in the three areas of the membrane (polymer, liquid, gas). The effects of ohmic losses in the membrane are taken into account by an additional source term in energy equation.

The source term S_T of the ohmic resistance is given by:

$$S_T = \frac{i^2}{s_m} \tag{8}$$

The conductivity of the membrane, expressed as a function of temperature and water content.

$$s_m = s_{m303} \exp\left[268\left(\frac{1}{303} - \frac{1}{T}\right)\right] \tag{9}$$

s_{m303}: The conductivity of the membrane at 303 ° C,

$$s_{m303} = 0.5139\,l_{H_2O/SO_3} - 0.326 \quad pour \ l_{H_2O/SO_3} \geq 1 \tag{10}$$

C. Cell potential

The cell potential is expressed as:

$$V = V_{OC} - h_{act} - h_{ohm} - h_{conc} \tag{11}$$

where

Voc is the thermodynamic open circuit potential,

h_{act} is the cell activation over potential,

h_{ohm} polarisation ohmique and h_{conc} Polarisation de la concentration.

V_{OC} it is equal to zero on the anode but is a function of temperature on the cathode and is calculated using the Nernst law [13]:

$$V_{c,OC} = (0.0025 \times T) + 0.2329 \tag{12}$$

the cell activation and concentration over potential are calculated as:

$$h_{act} = A\ln\left(\frac{i}{i_0}\right) \tag{13}$$

$$h_{conc} = -B\ln\left(1 - \frac{i}{i_l}\right) \tag{14}$$

Where i_0 is the exchange current density.

The polarisation ohmique is defined as:

$$h_{ohm} = i'\,R \tag{15}$$

The membrane resistance is:

$$R = \int_0^{l_m} \frac{1}{s\,(l)}\,dy \tag{16}$$

D. Boundary conditions

As shown in Fig. 1, at the inlet, boundaries 2 is the Dirichlet type boundary condition a:

$f = f_0$ For faces 1, 3, 4 and 5 the Neumann condition was chosen as: $\dfrac{\P f}{\P n} = 0$

E. Solution procedure

The model equations are solved by numerical method. A set of differential equations is replaced by algebraic equations based on the finite difference method. Gauss Seidel method is used to solve the equations system.

III. RESULTS AND DISCUSSIONS

The operating temperature has a significant effect on the performance of the cell. Various transport properties such as protonic resistance of membrane, the diffusivities of gases… depend on temperature. Fig.2 represents the influence of temperature on the performance of the pile where we can see that performance increases with temperature.
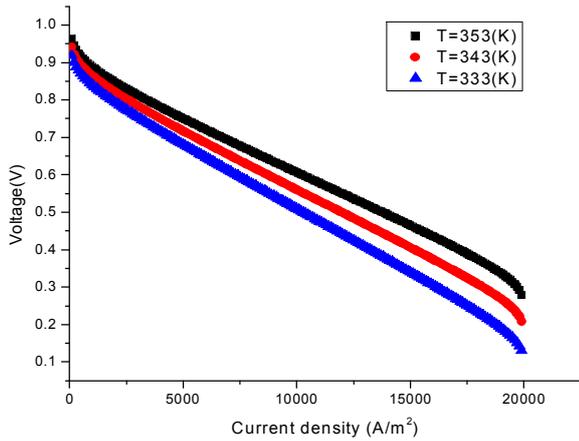
Fig.2. Polarization curve at different values of temperature.

Fig.4. Proton conductivity of the membrane in different values of the water content.

Fig.3 shows the influence of temperature on proton conductivity of the membrane. The conductivity of the membrane (s_m) increases with increasing temperature and leads to greater diffusion of hydrogen protons within the membrane, so the resistance of the membrane which means higher temperatures, the electrochemical reaction is faster, increases the production of water in the cathode and hydrates better membrane, and thus the ionic resistance is reduced.

The proton conductivity of a membrane depends strongly on its rate of hydration, and the fig.4. illustrates this dependence. Indeed, the proton conductivity is an increasing function of its water content λ:

$$s_m = s_{m303} \exp \left[268 \left(\frac{1}{303} - \frac{1}{T} \right) \right]$$

$$s_{m303} = 0.5139 l_{H_2O/SO_3} - 0.326 \; pour \; l_{H_2O/SO_3} ñ1$$

Thus, if the membrane is not sufficiently humidified, the resistivity of the cell increased, thus decreasing performance. Moreover, the drying of the MEA leads to increases activation overvoltage. Indeed, the drying phase electrolyte in the active layer makes certain catalytic sites inoperative due to the ionic resistance. It is therefore essential to ensure a good level of hydration in the cell.

The polarization curves and power density for different temperatures are shown in the fig.5. where the performance increases with increasing the temperature.

Fig.3. Proton conductivity of the membrane for different values of temperature.

The influence of water content (l_{H_2O/SO_3}) on the conductivity of the membrane is shown in fig.4.
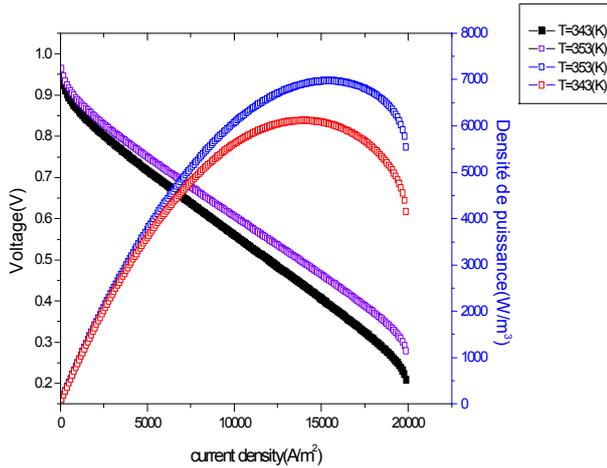
Fig.5. Effect of temperature on the polarization curve of the PEM fuel cell.

Fig.6. shows the influence of water content in the membrane on the polarization curve. Since the proton conductivity of the membrane increases with increasing water content, the ohmic losses in the membrane decreases with increasing water content. Thus, better performance is achieved with higher water content.
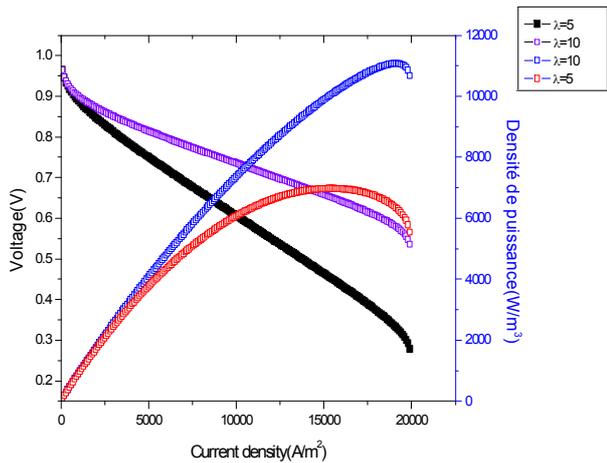
Fig.6. Effect of water content on the polarization curve of the PEM fuel cell.

IV. CONCLUSIONS

A two-dimensional, steady-state model is developed for membrane electrode assembly (MEA) in the PEMFC. The model is used to study the effects of temperature and water content on polarization curve. Based on this study, the following conclusions can be drawn:

- To improve the kinetics of electrochemical reactions at the electrodes and thus reduce the activation overvoltage,

- Increase the gas diffusion electrodes,
- Reduce the drop ohmic, especially in the proton conductive membrane through an increase in ionic conductivity,
- The electrochemical performance of a fuel cell will be strongly depend temperature and water content.

References

[1] J. Peng, S.J. Lee, "Numerical simulation of proton exchange membrane fuel cells at high operating temperature", *Journal of Power Sources* 162 (2006) 1182–1191.

[2] C.Y. Wen, G.W.Huang, " Application of a thermally conductive pyrolytic graphite sheet to thermal management of a PEM fuel cell", *Journal of Power Sources* 178 (2008) 132–140.

[3] B. Zhou, W. Huang, Y.Zong, A.Sobiesiak, "Water and pressure effects on a single PEM fuel cell", *Journal of Power Sources* 155 (2006) 190–202.

[4] D.M.Bernardi, M.W.Verbrugge, "A mathematical model of the solid-polymer-electroyte fuel cell", *Journal of Electrochemical Society* 139 (1992) 2477-2491.

[5] T.E.Springer, T.A.Zawodzinski, S.Gottesfeld, "Polymer electrolyte fuel cell model", *Journal of Electrochemical Society* 138 (1991) 2334-2342.

[6] L.You, H.Liu, A two-phase flow and transport model for the cathode of PEM fuel cells, *International Journal of Heat and Mass Transfer*, 45 (2002) 2277–2287.

[7] D. Singh, D.M. Lu, N. Djilali, "A two-dimensional analysis of mass transport in proton exchange membrane fuel cells", *International Journal of Engineering Science* 37 (1999) 431-452.

[8] S.H.Ge, B.L.Yi, "A mathematical model for PEMFC in different flow modes", *Journal of Power Sources* 124 (2003) 1–11.

[9] N.P. Siegel, M.W. Ellis, D.J. Nelson, M.R. von Spakovsky, "A two-dimensional computational model of a PEMFC with liquid water transport", *Journal of Power Sources* 128 (2004) 173–184.

[10] P.Costamagna, "Transport phenomena in polymeric membrane fuel cells", *Chemical Engineering Science* 56 (2001) 323-332.

[11] G.H. Guvelioglu, H.G. Stenger, "Computational fluid dynamics modeling of polymer electrolyte membrane fuel cells", *Journal of Power Sources* 147 (2005) 95–106.

[12] B.Cheng, O. Minggao, Y.Baolian, "Analysis of Water Management in Proton Exchange Membrane Fuel Cells", *Tsinghua Science and Technology* 11 (2006) 54-64.

[13] S.Um, C.Y.Wang, K.S.Chen, "Computational fluid dynamics modeling of proton exchange membrane fuel cells", *Journal of Electrochemical Society* 147 (2000) 4485-4493.