Short communication

Modeling and simulation of proton exchange membrane fuel cell systems

Abdellah Beicha *

Jijel University, Faculty of Sciences and Technology, Department of Process Engineering, 18000 Jijel, Algeria

ARTICLE INFO

ABSTRACT

This paper presents an electrochemical model for simulation and evaluation of the performance of proton exchange membrane (PEM) fuel cell. The results of the model are used to predict the efficiency and power of the fuel cell as a function of operational parameters of the cell, like temperature, partial pressures and membrane humidity. The influence of temperature on fuel cell's characteristics is more pronounced than the influence of partial pressures and membrane humidity. The effect of platinum loading on cell performance is examined with Pt loadings of 0.18, 0.38 and 0.4 mg cm^{-2}. The kinetic parameters (electron transfer coefficient, exchange current density) are found to be platinum loading dependent.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Within such perspective PEM fuel cell systems have been showing up as a promising alternative due their high efficiency and low impact to the environment. The theoretical approach with mathematical simulation is very effective for designing and analyzing the performance of the PEM fuel cell.

Some work has been reported in the literature on steady-state fuel-cell modeling (e.g. [1–4], as well as dynamic modeling [5–7]). These studies are mostly based on the empirical equations and/or the electrochemical reactions inside the fuel cell. Also we can find several researches regarding influences of certain operating parameters on fuel cell characteristics [8]. There are many other models have been developed and reported in literature, but they did not focus on the impact of individual operating parameters on fuel cell output characteristics.

This paper presents a simple model of a PEM fuel cell that can be used to analyze the impact of individual fuel cell's operating parameters on cell's performance. Using the present model, it is also possible to determine the activation loss parameters of the PEM fuel cell. The model is well adapted for PEM cell and it incorporates the essential physical and electrochemical processes that happen in cell along its operation.

2. Experimental

2.1. Electrode preparation

For the electrode preparation, a substrate made from carbon cloth "A" with thickness 350 μm, platinum-supported carbon 10 wt% Pt/C, activated carbon black, and Teflon (PTFE) 60 wt% have been used. Two different platinum loadings have been used in preparation of the electrodes. One electrode was with platinum loading 0.18 mg Pt cm^{-2}; while the second was with platinum loading 0.38 mg Pt cm^{-2}. The composition of catalyst layer was 70 wt% Pt/C and 30 wt% Teflon (PTFE). Detailed electrode preparation can be found in Ref. [9].

2.2. Operation of single cell in fuel cell test apparatus

During operation of PEM fuel cells, the following processes take place within the electrode: (i) the reactant gases diffuse through the porous backing layer; (ii) at the gas–electrolyte interface, the gases dissolved and then diffuse to the electrolyte–electrode interface; (iii) electrocatalytic reaction inside the catalyst layer precedes the gas adsorption at the electrode surface; (iv) ionic transport occurs in the electrolyte, but electronic transport takes place in the electrode.

The oxygen and hydrogen were passed through humidifiers before being fed into the cell cells. The hydrogen fed into the anode at a flow rate of 140 ml min^{-1} and 1 atm. The oxygen entered the fuel cell through the cathode at a flow rate of 380 ml min^{-1} and 2 atm. The electrons generated from the anode were connected to a digital multimeter, with an external variable resistance to measure the current and voltage produced by the cell. The electric

* Tel.: +213 771916914; fax: +213 34501189.
E-mail address: abeicha@yahoo.com

Nomenclature

$V_{activation}$	activation voltage drop, V
V_{ohmic}	ohmic voltage drop, V
$V_{concentration}$	concentration voltage drop, V
E	fuel cell's reversible voltage, V
F	Faraday constant, C
i	current density, A cm^{-2}
i_0	exchange current density, A cm^{-2}
i_{0c}	cathode exchange current density, A cm^{-2}
k_c	factor related to reaction speed, A cm^{-2} C^{-1}
i_L	limiting current density, A cm^{-2}
l_d	diffusion layer thickness, cm
l_m	membrane thickness, cm
P_{cell}	fuel cell's power density, W cm^{-2}
P_{H_2}	partial pressure of hydrogen, atm
P_{O_2}	partial pressure of hydrogen, atm
R	universal gas constant, 8.314 J K^{-1} mol^{-1}
r_{ion}	ionic resistance, Ω cm^2
r_{el}	electronic resistance, Ω cm^2
T	temperature, K
V	voltage, V

Greek letters

ψ	electron transfer coefficient
Φ	membrane humidity, %
λ	membrane water content
β	symmetry factor
σ_d	diffusion layer electronic conductivity, A V^{-1} cm^{-1}

conductivity was measured by using resistivity meter (Loresta-GP MCP-T600). The specific resistance of the gas diffusion layer composed of 70 wt% Pt/C and 30 wt% PTFE was measured to be 0.21 Ω cm. The operating parameters of the fuel cells are listed in Table 1.

3. PEM fuel cell modeling

3.1. Basic fuel cell operation

The PEM fuel cell consists of membrane, which is ionic conductor and through which hydrogen ions diffuse from anode to cathode. Beside membrane, fuel cell has two catalyst layers, made of platinum, gas diffusion layers, gas channels and current collectors. The schematic of a PEM fuel cell is shown in Fig. 1.

The hydrogen flows through gas channels on anode side of a fuel cell. It diffuse through diffusion layers catalyst where it oxidizes according to the following reaction:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

The protons are conducted through membrane, which is insulator for electrons. The electrons pass through current collectors and external electric circuit to cathode. On cathode side of a fuel cell, protons, electrons and oxygen that flows through cathode gas channels, react according to the following reaction:

$$2H^+ + 2e^- + \tfrac{1}{2}O_2 \rightarrow H_2O + heat \tag{2}$$
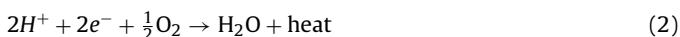
Therefore overall chemical reaction occurring inside PEM fuel cell is

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O + heat + electrical \ energy \tag{3}$$
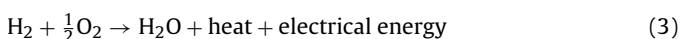
Table 1
Operational parameters of the fuel cell.

Parameters	Value
Temperature, T	298 K
Electrode area	25 cm^2
Membrane thickness, l_m	40 μm
Diffusion layer thickness, l_d	350 μm
P_{O_2}	2 atm
P_{H_2}	1 atm
Diffusion layer electronic conductivity, σ_d	5 Ω^{-1} cm^{-1}

3.2. Model formulation

The output voltage of a single cell can be defined as the result of the following [10,5]:

$$V_{cell} = E - V_{activation} - V_{ohmic} - V_{concentration} \tag{4}$$

In the above equation, E is the thermodynamic potential of the cell and it represents its reversible voltage; $V_{activation}$ is the voltage drop due to the activation of the anode and cathode, a measure of the voltage drop associated with the electrodes; V_{ohmic} is the ohmic voltage drop, a measure of the ohmic voltage drop resulting from the resistances of the conduction of protons through the solid electrolyte and the electrons through its path; and $V_{concentration}$ represents the voltage drop resulting from the reduction in concentration of the reactants gases. The fuel cell's output power density is given by:

$$P_{cell} = V_{cell}i \tag{5}$$

Each one of the terms of Eq. (4) is discussed and modeled separately in the subsections that follow.

3.2.1. Cell reversible voltage

The fuel cell's output voltage is determined by cell's reversible voltage that arises from potential difference produced by chemical reaction and several voltage losses that occur inside a cell. The fuel cell's reversible voltage is a function of temperature and partial
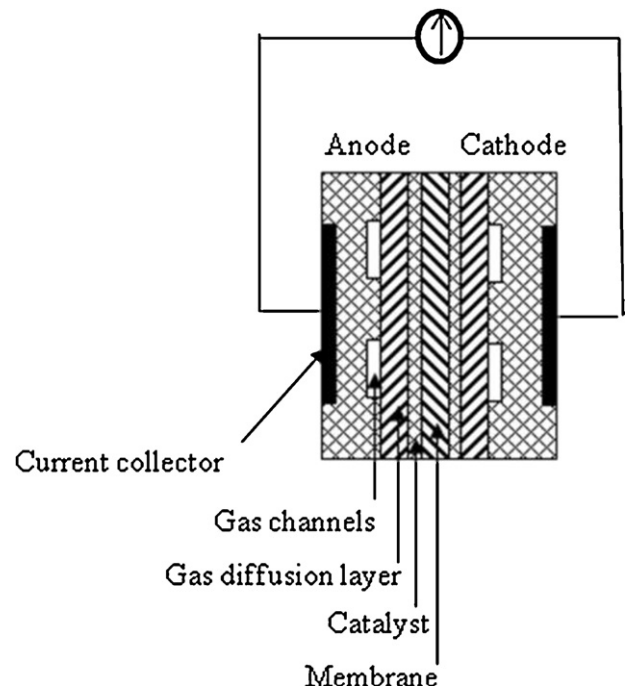

Fig. 1. Schematic of a PEM fuel cell.

pressures of reactants and product as is shown in the following equation:

$$E = \frac{\Delta G}{2F} + \frac{\Delta S}{2F}(T - T_{ref}) + \frac{RT}{2F}[\ln(P_{H_2}) + \tfrac{1}{2}\ln(P_{O_2})] \tag{6}$$

where ΔG is the change in the free Gibbs energy; F is the constant of Faraday; ΔS is the change of the entropy; R is the universal constant of the gases; while P_{H_2} and P_{O_2} are the partial pressures of hydrogen and oxygen, respectively. The variable T denotes the cell operation temperature and T_{ref} the reference temperature. Using the standard pressure and temperature (SPT) values for ΔG, ΔS and T_{ref}, Eq. (6) can be simplified to [10]:

$$E = 1.229 - 0.85 \times 10^{-3}(T - 298.15) + 4.31 \times 10^{-5}T[\ln(P_{H_2})$$
$$+ \tfrac{1}{2}\ln(P_{O_2})] \tag{7}$$

3.2.2. Activation voltage drop

The activation polarization is related to the energy barrier that must be overcome to initiate a chemical reaction between reactants. At low current draw, the electron transfer rate is slow and a portion of the electrode voltage is lost in order to compensate for the lack of electro-catalytic activity. The expression for activation losses is given by:

$$V_{activation} = \frac{RT}{2\psi F} \ln\left(\frac{i}{i_0}\right) \tag{8}$$

ψ is electron transfer coefficient, and is unit less. This value describes the proportion of the electrical energy applied that is harnessed in changing the rate of an electrochemical reaction. It is this value that differs from one material to another. i represents cell's current density, whereas i_0 is exchange current density. i_0 is the value on the Tafel plot when the current begins to move away from zero.

Because of higher anode exchange current density, cathode activation losses are significantly higher so anode activation losses are negligible. The value of cathode exchange current density also depends on operating parameters what is shown by:

$$i_{0c} = 2Fk_c \exp\left(\frac{2.46\beta F}{RT}\right) \tag{9}$$

β and k_c are, respectively, symmetry factor and factor related to reaction speed.

3.2.3. Ohmic voltage drop

The ohmic voltage drop (or "Ohmic polarization") occurs due to resistive losses in the cell. These resistive losses occur within the electrolyte (ionic), in the electrodes (electronic and ionic), and in the terminal connections in the cell (electronic). Since the stack plates and electrolyte obey Ohm's law, the amount of voltage lost in order to force conduction varies mostly linear throughout this region. This is the working region of the fuel cell.

$$V_{ohmic} = i(r_{ion} + r_{el}) \tag{10}$$

We can calculate ionic resistance using the following expression [10]:

$$r_{ion} = l_m \frac{181.6\left[1 + 0.03i + 0.062\left(\frac{T}{303}\right)^2 i^{2.5}\right]}{(\lambda - 0.634 - 3i)\exp\left[4.18\left(\frac{T-303}{T}\right)\right]} \tag{11}$$

The parameter l_m is membrane thickness. The ionic resistance represents PEM fuel cell's membrane resistance to transit of hydrogen ions. This resistance strongly depends on membrane water content. The membrane water content is described by parameter λ

which is influenced by the membrane preparation [11]. The parameter λ can be related to membrane relative humidity Φ [12] by the following expression:

$$\lambda = 0.043 + 17.81\Phi - 39.85\Phi^2 + 36\Phi^3 \tag{12}$$

The electronic resistance can be written as:

$$r_{el} = \frac{2l_d}{\sigma_d} \tag{13}$$

where l_d is diffusion layer thickness and σ_d is diffusion layer electronic conductivity.

3.2.4. Concentration or mass transport voltage drop

The mass transport or concentration polarization results when the electrode reactions are hindered by mass transfer effects. In this region, the reactants become consumed at greater rates than they can be supplied while the product accumulates at a greater rate than it can be removed. Ultimately these effects inhibit further reaction altogether and the cell voltage drops to zero. The expression for fuel cell's concentration losses is given by:

$$V_{concentration} = -\frac{RT}{2F} \ln\left(1 - \frac{i}{i_L}\right) \tag{14}$$

i_L represents limiting current density. This parameter describes maximum current density that can flow through electrode.

4. Results and discussion

The concentration polarization results from restrictions to the transport of the fuel gases to the reaction sites. This usually occurs at high current because the forming of product water and excess humidification blocks the reaction sites. This polarization is also affected by the physical restriction of the transfer of oxygen to the reaction sites on the cathode side of the fuel cell. The concentration polarization can be reduced by using thinner electrodes which shortens the path of the gas to the sites [13,14]. Jordan et al. [14] have observed a dramatic change in slope of the voltage versus current density plot using air oxidant. Such a change, indicative of a diffusion-limited reaction, was not so apparent when pure oxygen is used as the oxidant. The same behavior was also observed by other researchers [15]. This is consistent with the experimental data showed in Fig. 2. Hence, in parameter estimation we have neglected the effect of concentration polarization drop.

4.1. Determination of the activation loss parameters

The experimental data of the cell voltage versus current density (Fig. 2) for the two fabricated electrodes and the commercial electrode E-TECK with Pt loadings 0.18, 0.38 and 0.4 mg cm^{-2}, respectively, are fitted to the present model using a non-linear least squares method. The characteristics of fabricated and commercial electrodes are listed in Table 1. The activation loss parameters, ψ and i_0, are determined and listed in Table 2. Both parameters depend on Pt loading. The increase of Pt loading will cause an increase of ψ and i_0. This can be attributed to the increase of the active sites for hydrogen adsorption.

An inconsistency between the polarization curves for the prepared electrode with Pt loading 0.38 mg cm^{-2} and the commercial on E-TEK with Pt loading 0.4 mg cm^{-2} is observed. The cell voltage in E-TEK dropped slightly faster than the former electrode. Also, the value of i_0 is decreased from 4.95×10^{-8} A cm^{-2} (prepared electrode with Pt loading 0.38 mg cm^{-2}) to 2.86×10^{-8} A cm^{-2} (E-TEK electrode with Pt loading 0.4 mg cm^{-2}). This may be attributed to the fabrication process in the preparation of electrode with Pt loading 0.38 mg cm^{-2}, which creates a better particle distribution of electocatalyst. The localization of platinum in the catalyst layer

Table 2
Variation of the parameters ψ and i_0 with platinum loading at $T = 298$ K.

Parameters	Fabricated electrode 0.18 mg Pt cm^{-2}	Fabricated electrode 0.38 mg Pt cm^{-2}	E-TECK electrode 0.4 mg Pt cm^{-2}
ψ	0.13	0.28	0.3
i_0 (A cm^{-2})	2.94×10^{-9}	4.95×10^{-8}	2.86×10^{-8}

can be improved via the spraying technique [9]. The values of i_0 estimated are lower than that reported by Amphlett et al. [16], which are 107.6×10^{-8} A cm^{-2} at 298 K. From these results, it can be concluded that not only Pt loading will affect the value of i_0.

Typically the value of ψ is in a very narrow range; it ranges from about 0.1 to 0.5 [17]. These minor variations make experimenting with different Pt loading to dramatically change the voltage simulated by the present model not a very productive endeavor. At this point it is useful to look back on Eq. (8), as we can see from the form of the equation the only constant that we can change is i_0. The exchange current density constant varies over a wide range, and thus has a dramatic effect on the performance of fuel cells at low current densities. Hence, it is vital to design fuel cells with high exchange current densities.

4.2. Effect of the temperature on the performance of the PEM fuel cell

The fuel cell's voltage as a function of cell's current density is shown in Fig. 3. In Fig. 4 cell's power density is shown as a function of current density for two different temperatures. We can see from these figures that fuel cell's efficiency is low and that significant part of theoretical output voltage is lost because of different losses inside a cell. We can also notice that increase of fuel cell's operating temperature will cause increase of cell's output voltage and power. If we increase temperature from 298 K to 353 K, fuel cell voltage would increase for 28% (Fig. 3). The reason for this is that higher temperatures improve mass transfer within the fuel
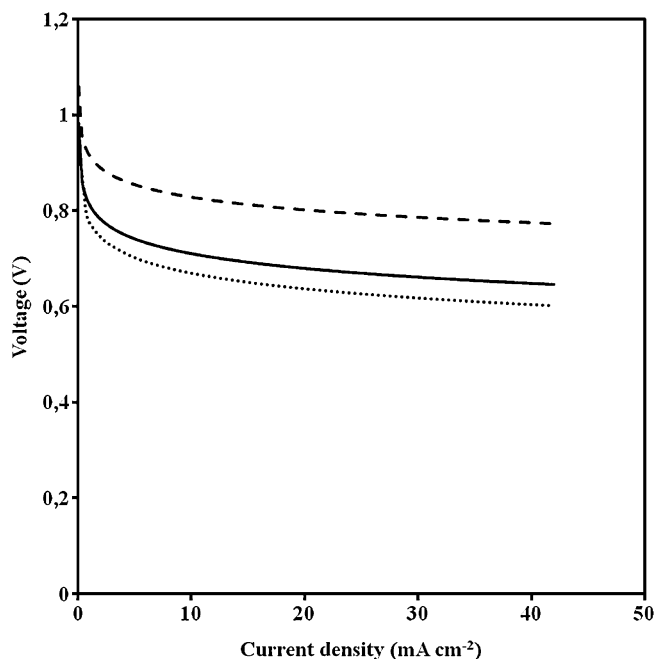
Fig. 3. Fuel cell's voltage as a function of cell's current density for different temperatures at Pt loading = 0.38 mg cm^{-2}; model: (dotted line) 298 K, (solid line) 313 K and (dashed line) 353 K.
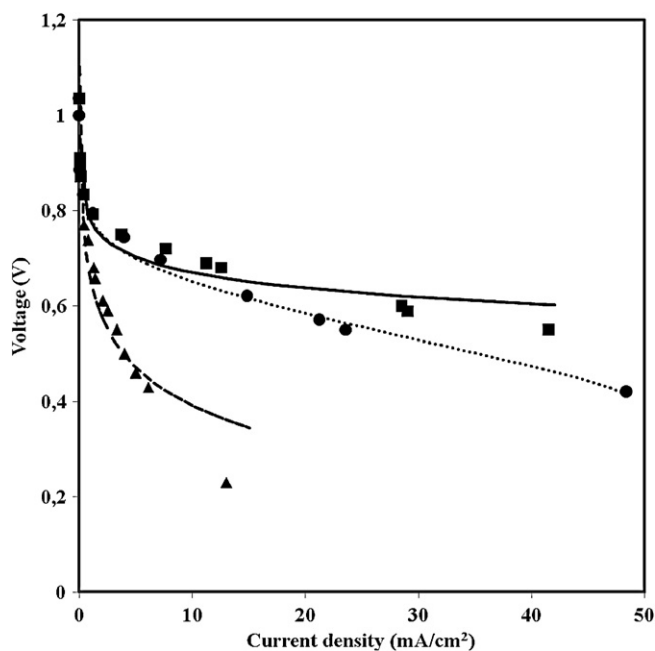
Fig. 2. Fuel cell's voltage as a function of cell's current density at $T = 298$ K, data: (▲) Pt loading = 0.18 mg cm^{-2}, (■) Pt loading = 0.38 mg cm^{-2} and (●) E-TECK electrode with Pt loading = 0.4 mg cm^{-2} [9]; model: (dashed line) Pt loading = 0.38 mg cm^{-2}, (solid line) Pt loading = 0.38 mg cm^{-2} and (dotted line) E-TECK electrode with Pt loading = 0.4 mg cm^{-2}.
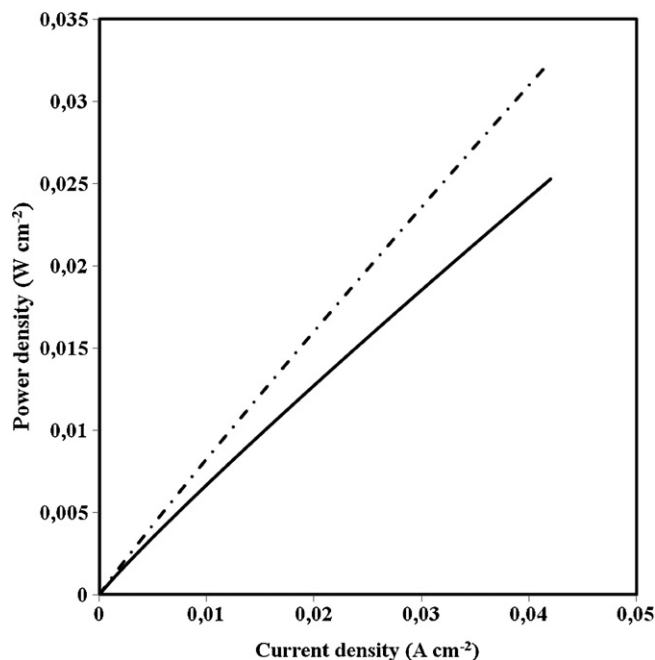
Fig. 4. Fuel cell's power density as a function of cell's current density for different temperatures at Pt loading = 0.38 mg cm^{-2}; model: (solid line) 298 K and (dashed line) 353 K.
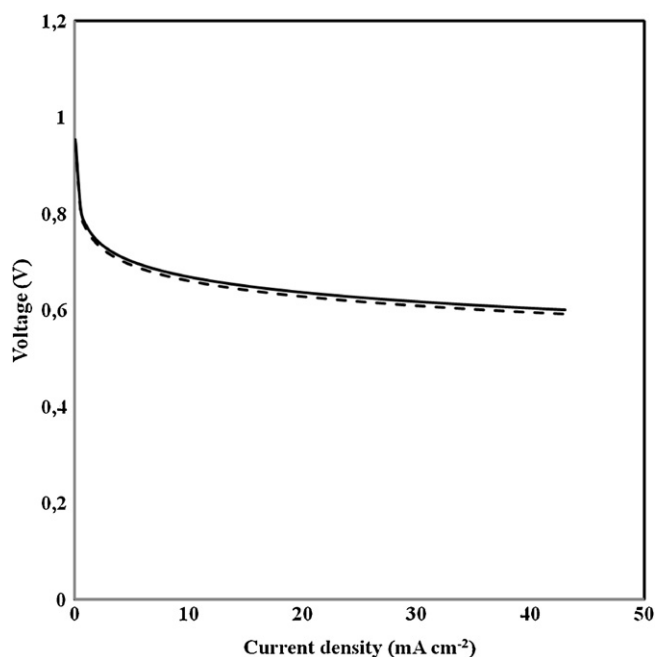
Fig. 5. Fuel cell's voltage as a function of cell's current density for different fuel cell's reactants partial pressure at $T = 298\,K$ and Pt loading $= 0.38\,mg\,cm^{-2}$; model: (dashed line) $P_{H_2} = 0.995 \times 10^5$ Pa and $P_{O_2} = 0.606 \times 10^5$ Pa, (solid line) $P_{H_2} = 1.01 \times 10^5$ Pa and $P_{O_2} = 1.01 \times 10^5$ Pa.
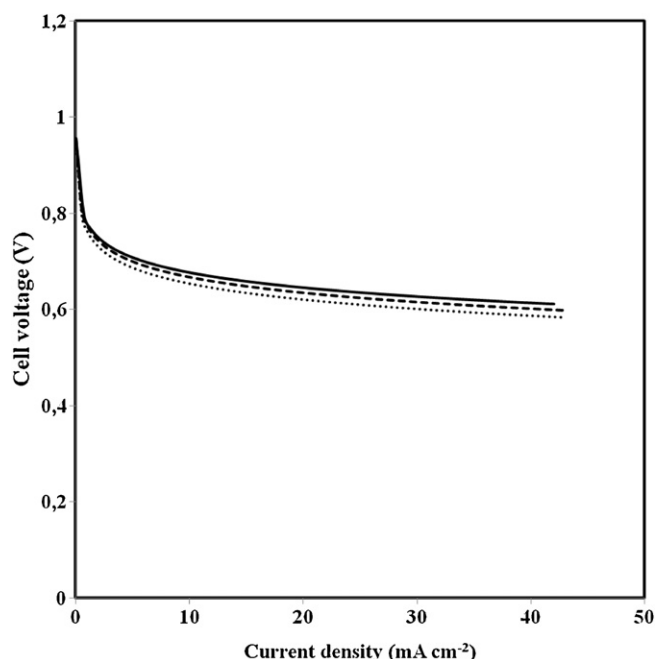

Fig. 6. Fuel cell's voltage as a function of cell's current density for different membrane humidity at $T = 298\,K$ and Pt loading $= 0.38\,mg\,cm^{-2}$; model: (solid line) $\Phi = 100\%$, (dashed line) 50% and (dotted line) $\Phi = 30\%$.

cells and results in a net decrease in cell resistance as a result it improves the reaction rate.

4.3. Effect of the partial pressures and membrane humidity

The change in output power related with increase in partial pressures is shown in Fig. 5. We can see that power increase because of

reactant pressure increase is 1.1% and is smaller than change caused by temperature variations.

Sufficient gas stream humidification is essential to PEM fuel cell operation since water molecules move with the hydrogen ions during the ion exchange reaction. Insufficient humidification water dehydrates the membrane and can lead to cracks or holes in the membrane. If we decrease membrane humidity from 100% to 30%, fuel cell voltage would decrease for 1.8% (Fig. 6). Reducing the membrane humidity can result in slightly slower electrode kinetics, including electrode reaction and mass diffusion rates. We can see from these simulations that we must pay attention on temperature while reactant pressures and membrane humidity are less significant on output voltage and power.

5. Conclusion

Using present PEM fuel cell model, we have analyzed the influence of fuel cell operating parameters (temperature, partial pressures and membrane humidity) on fuel cell's performance. We have found that temperature has significant influence on output voltage and power. However, the influence of partial pressures and membrane humidity is less significant.

Both the electron transfer coefficient and exchange current density are platinum loading dependent. The exchange current density constant varies significantly with platinum loading, and thus has a dramatic effect on the performance of fuel cell at low current densities. This parameter is vital to design the PEM fuel cell.

Acknowledgement

References

[1] R. Cownden, M. Nahon, M.A. Rosen, Int. J. Hydrogen Energy 26 (2001) 615–623.
[2] A. Rowe, X. Li, J. Power Sources 102 (2001) 82–96.
[3] D. Bevers, M. Wöhr, J. Appl. Electrochem. 27 (1997) 1254–1264.
[4] G. Maggio, V. Recupero, L. Pino, J. Power Sources 101 (2001) 275–286.
[5] J.C. Amphlett, R.F. Mann, B.A. Peppley, P.R. Roberge, A. Rodrigues, J. Power Sources 61 (1996) 183–188.
[6] J. Hamelin, K. Agbossou, A. Laperrière, F. Laurencelle, T.K. Bose, Int. J. Hydrogen Energy 26 (2001) 625–629.
[7] H.P.L.H. van Bussel, F.G.H. Koene, R.K.A.M. Mallant, J. Power Sources 71 (1998) 218–222.
[8] Z. Zhang, X. Huang, J. Jiang, B. Wu, J. Power Sources 161 (2006) 1062–1068.
[9] R. Chebbi, A. Beicha, W.R.W. Daud, R. Zaamouche, Appl. Surf. Sci. 255 (2009) 6367–6371.
[10] R.F. Mann, J.C. Amphlett, M.A.I. Hooper, H.M. Jensen, B.A. Peppley, P.R. Roberge, J. Power Sources 86 (2000) 173–180.
[11] M.G. Santarelli, M.F. Torchio, P. Cochis, J. Power Sources 159 (2006) 824–835.
[12] H. Görgün, M. Arcak, F. Barbir, J. Power Sources 157 (2006) 389–394.
[13] J.H. Hirschenhofer, IEEE AES Syst. Mag. (1994) 10–15.
[14] L.R. Jordan, A.K. Shukla, T. Behrsing, N.R. Avery, B.C. Muddle, M. Forsyth, J. Power Sources 86 (2000) 250–254.
[15] J.M. Song, S.Y. Cha, W.M. Lee, J. Power Sources 94 (2001) 78–84.
[16] J.C. Amphlett, R.M. Baurnet, R.F. Mann, J. Electrochem. Soc. 142 (1995) 1–15.
[17] J. Laminie, A. Dicks, Fuel Cell Systems Explained, 2nd ed., Wiley & Sons, England, 2005.