EFFECTS OF OPERATING PARAMETERS ON PERFORMANCE OF A SINGLE DIRECT METHANOL FUEL CELL

by

Ebrahim ALIZADEH, Mousa FARHADI *, Kurosh SEDIGHI, and Mohsen SHAKERI

Faculty of Mechanical Engineering, Babol University of Technology,
Babol, Islamic Republic of Iran

Original scientific paper
UDC: 621.352.6:547.261
DOI: 10.2298/TSCI1002469A

In this study the effect of various operating conditions on 10 cm ×10 cm active area of in-house fabricated direct methanol fuel cell was investigated experimentally. The effect of the cell temperature, methanol concentration, and oxygen flow rate on cell performance was studied. The study reveals that current density is not monotonous function of temperature, but has an optimum operating condition for each cell voltage. The experiments also indicate that the cell performance increases with an increased of oxygen flow rate up to a certain value and then further increase has no significant effect. Furthermore, for methanol concentration greater than 1.5 M, a reduction of cell voltage was indicated which is due to an increase of methanol cross over.

Key word: *polarization curve, fuel cell performance, methanol concentration*

Introduction

Direct methanol fuel cell (DMFC) offer several unique features, such as, their compact and lightweight systems, high power density and energy capacity, easy storage of liquid fuel, ambient temperature operation and without charging [1, 2]. These benefits suggest that this type of fuel cell is a promising power source for portable and other mobile applications [3]. A DMFC is an electrochemical device that converts chemical energy stored in methanol into the electrical energy [4]. The reactions that take place in a DMFC are:

$$CH_3OH(l) \quad H_2O(l) \qquad CO_2(g) \quad 6H\ (l) \quad 6e \tag{1}$$

$$\frac{3}{2}O_2(g) \quad 6H\ (l) \quad 6e \qquad 3H_2O(g) \tag{2}$$

Hence, the overall reaction is:

$$CH_3OH(l) \quad H_2O(l) \quad \frac{3}{2}O_2(g) \qquad CO_2(g) \quad 3H_2O(g) \tag{3}$$

* Corresponding author; e-mail: mfarhadi@nit.ac.ir

John *et al*. [5] reported that cell performance improved with increasing cathode back pressure and decreasing methanol concentration. Sang *et al*. [6] showed that cell performance improved with increasing of the cell temperature, cathode flow rate, and cathode backpressure. Ge *et al.* [7] have been studied the effects of cell operating temperature, methanol concentration, anode flow rate, air flow rate, and cathode humidification and concluded that all the studied operating parameters, except the cathode humidification, have significant effects on the DMFC cell performances, and the cathode humidification has almost negligible effect.

Experimental detail

A single DMFC was designed and fabricated for this study. Graphite plates with thickness of 300 μm have been used as bipolar plates for current collection and flow distribution. A single serpentine channel, 10 mm ×10 mm was machined. The width of the ribs was 1 mm. The membrane electrode assembly (MEA), used in this work had an active area of 10 cm ×10 cm and consist of two carbon cloth diffusion layers, two catalyst layers and the Nafion® membrane 117. Both anode and cathode electrodes used carbon cloth, catalyst was Pt-Ru on the anode side with a loading of 4 mg/cm^2, and the cathode side catalyst was Pt-black with loading of 4 mg/cm^2. The experiments were carried out in the test loop shown in fig. 1.

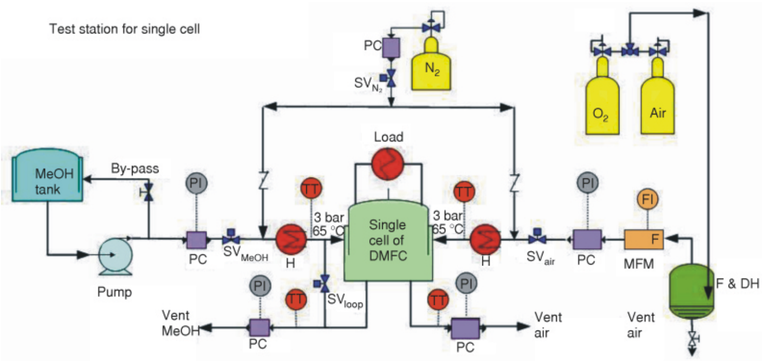

Figure 1. Schematic of the test loop
PC – pressure controller, SV – solenoid valve, PR – pressure release, H – heater, PI – pressure indicator, FI – flow indicator, MFM – mass flow meter, TT – temperature measurement, MeOH – methyl alcohol

Results and discussion

In this study, the effect of the operating parameters on the DMFC performance was investigated. A series of tests were conducted with various parameters including cell temperature, methanol concentration, and oxygen flow rate.

Effect of cell temperature

In general, a higher operating temperature results in higher cell potential; however, for each fuel cell design there is an optimal temperature. Jung *et al*. [8] found that by increasing the operating temperature, the performance of the cell increases when using Nafion® 117 and 2.5 M methanol. They attributed this higher performance to the combined effects of a reduction of ohmic resistance and polarization. In fact, the ionic conductivity of Nafion membranes increases by increasing the temperature [9]. This result agrees with those obtained by Surampudi *et al*. [10] with Nafion® 117 membranes and 2 M methanol fuel cell in the range of 30-90 °C, and also with the results in refs. [11-13]. These results showed that a difference in the operation temperature makes a significant difference in the cell performance. It should be mentioned that the increase of the temperature increases the methanol cross over [9, 14]. The results found in the literatures show that the increase of the temperature improves the cell performance. For this reason, some authors have studied the possibilities of vapor-feed DMFC [15]. Generally the higher cell temperature increases the activity of the catalyst; therefore the rate of electrochemical reaction at the surface of the catalyst is increased. By increasing the temperature, the potential loss ($T\Delta S/nF$) is also increased (eq. 4):

$$E \qquad \frac{\Delta H}{nF} \quad \frac{T\Delta S}{nF} \tag{4}$$

However, by increasing the cell temperature, current density increases and significantly improvement of mass transport properties is observed:

$$i_0 \quad i_0^{\mathrm{ref}} a_\mathrm{c} L_\mathrm{c} \quad \frac{P_\mathrm{r}}{p_\mathrm{r}^{\mathrm{ref}}}^{\gamma} \quad \exp \quad \frac{E_\mathrm{c}}{\mathrm{R}T} \quad 1 \quad \frac{T}{T_\mathrm{ref}} \tag{5}$$

A set of experiments were carried out to study the effect of single cell temperature in the range of 40-65 °C. In this set of experiments oxygen flow rate was set at 2.0 slpm*, methanol flow rate was 10.0 ml per minute, cathode back pressure was 0.5 bar and methanol concentration was 1.0 M. The polarization curves of this experiment are shown in figs. 2, 3, and 4. It can be seen that current density increases with cell temperature. This is as expected, since both methanol oxidation kinetics and cathode kinetics improve as temperature increases. The results presented in fig. 2 demonstrate that the temperature is a key parameter affecting cell performance.

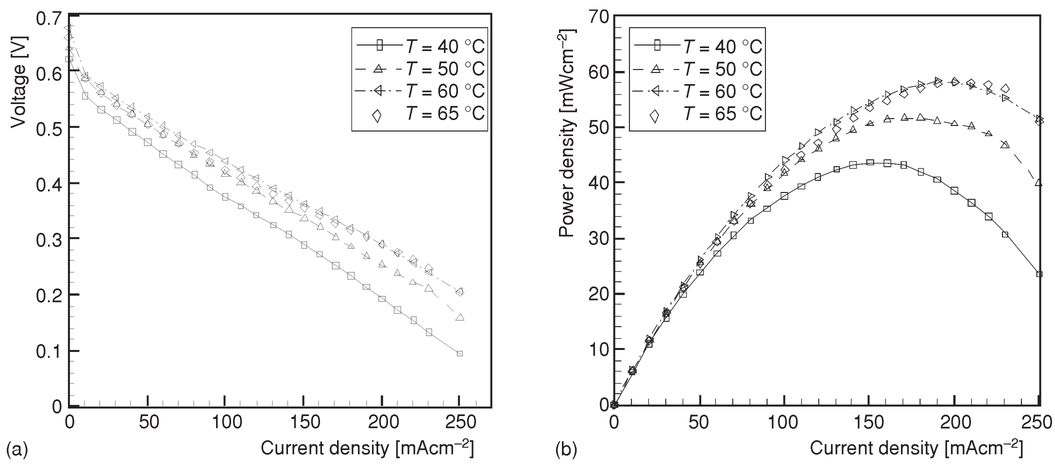

Figure 2. Experimental results at different fuel cell operating temperatures
(a) voltage-current density curves; (b) power density-current density curves at different temperatures

* slpm – standard liter per minute, [Lm^{-1}]

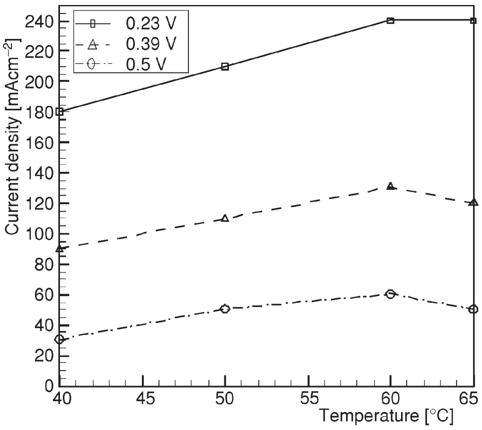

Figure 3. Single cell current density as a function of single cell operating temperature at different cell voltage

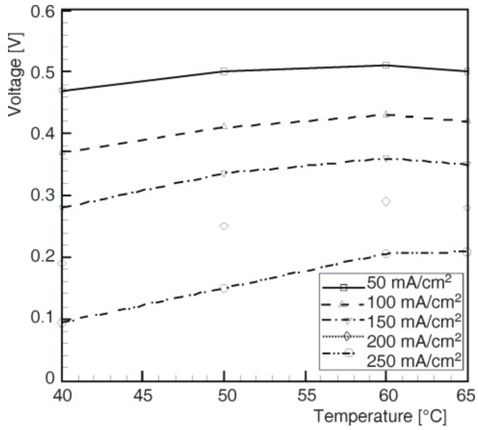

Figure 4. Single cell voltage as a function of single cell operating temperature at different current density

It can be seen that current density increases with cell temperature. This is as expected, since both methanol oxidation kinetics and cathode kinetics improve as temperature increases. The electrochemical kinetics on cathode and anode increase with temperature; then enhance the mass transfer of reactants and can benefit proton transportation through the Nafion membrane [16]. On the other hand, higher cell temperature also has the following negative effects: (a) the oxygen partial pressure decreases with temperature due to the increase of vapor partial pressure, which causes both decreases in open-cell voltage and increases in concentration over potential, (b) the rate of methanol cross over increases with temperature thus decreases the cell performance, and (c) water transfer from anode to cathode through the membrane increases with temperature, and the additional water increases the liquid water fraction in both the cathode catalyst layer and diffusion layer. This phenomenon causes an increase in concentration polarization. Figure 2 shows that increasing temperature from 40-60 °C leads to increase current density and improves performance but further increasing has a negative effect on cell performance. It is due to the increasing of methanol cross over.

The effect of temperature is the resulting effects of both the positive effect on kinetics and the combined negative effects. In order to closely examine the effects of operating temperature, figs. 3 and 4 are produced; fig. 3 shows relationships between current density and temperature at different cell voltages and fig. 4 shows relationships between voltage and temperature at different current density. From fig. 3, it can be seen that the current density is not a monotonous function of temperature, but has a maximum for each cell voltage. It is also clear that the maximum current densities are different at different cell voltages. The maximum current density increases as cell voltage decreases. Figure 4 shows that with increasing cell temperature the cell voltage increased, and with increasing the current density the cell voltage decreased.

The positive slope on the curves of current density *vs*. temperature and voltage *vs*. temperature extends to a higher temperature region, and therefore, the maximum increases with decrease in cell voltage. These results show a good correspondence with the results in refs. [7, 9]. Fuel cell performance usually improves with elevated temperature. Figures 3 and 4 show that increasing cell temperature from 60-65 °C leads to negative slope on the curve of current density and voltage *vs*. temperature.

Effect of methanol concentration

If methanol cross over is a cause of a reduction in cell voltage it would be expected that a higher concentration of methanol in the feed to the anode would decreases the cell voltage as a result of potentially higher rates of transport through the membrane. In fact, it has been observed that the open circuit voltages decrease with increasing methanol concentration [8]. This lower performance of the cell at higher methanol concentrations is attributed to the fuel cross over phenomenon [9-12, 17]. It was found that the cathode electrode performance is significantly lowered at higher methanol concentration [13]. However, at high current densities, it is observed a lower performance of the cell at lower concentration of methanol. This is probably due to the concentration polarization effects. It is necessary, thus, to find the optimal concentration under the operating conditions of the fuel cell. Due to the cross over effect, an increased methanol concentration affects not only the anode side but also more methanol is transported through the membrane at high methanol concentrations, so the potential of the cathode decreases and more water is formed [18].The other reason for decreasing performance of fuel cell is that the catalyst reaction of the anode is restricted to high methanol concentration. Non-reacted methanol decreases the performance due to the methanol cross over phenomenon permeating through the membrane from the anode to the cathode side as the methanol concentration increases [6].

A set of experiments were carried out to study the effect of methanol concentration in the range of 0.5-3.0 M. In this set of experiments oxygen flow rate was set at 2.0 slpm, methanol flow rate was 10.0 ml per minute, cathode back pressure was 0.5 bar, and the cell temperature was 65 °C. The polarization curves of this experiment are shown in figs. 5, 6, and 7. The higher the concentration is, the more severe the problem of methanol cross over becomes. From fig. 5(a) the open circuit voltage decreased with increasing methanol concentration to3 mol/L, because the cross over of methanol formed a mix potential [19].

Figure 6 shows that current density decreases sharply with increasing concentration when the methanol concentration is greater than 1.5 M. It is clear from figs. 6 and 7 that the best

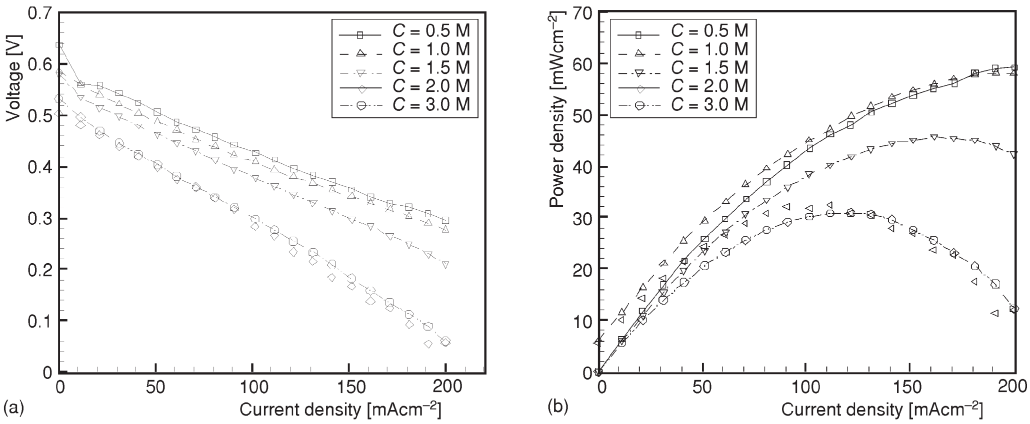

Figure 5. Experimental results for different methanol concentrations at channel depth: 1 mm, cell temperature, 65 °C; methanol flow rate, 10 ml per minute; oxygen flow rate, 2.0 slpm cathode back pressure, 0.5 bar
(a) voltage-current density curves; (b) power density-current density curves at different methanol concentration

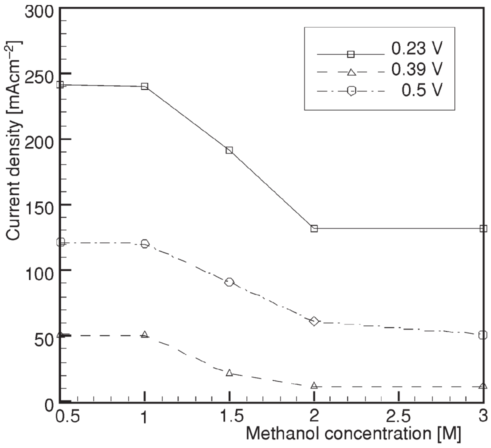

Figure 6. Single cell current density as a function of methanol concentration at different cell voltages

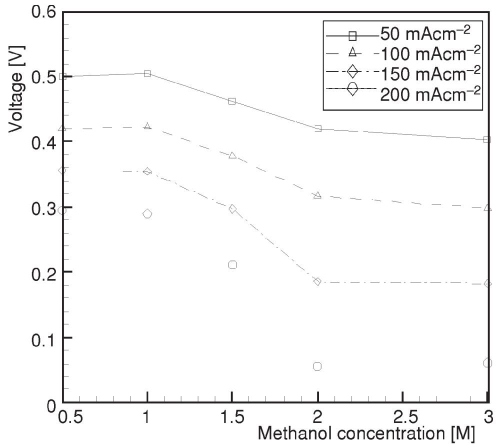

Figure 7. Single cell current density as a function of methanol concentration at different current density

concentration of methanol is between 0.5 to 1.0 M. At higher concentration of methanol, cross over increases so the cell current density reduces.

Effect of oxygen flow rate

The cell performance increases with oxygen flow rate up to a certain value, then the oxygen flow rate has no significant effect (fig. 8). At this experiment the optimum value of the oxygen flow rate is about 2.0 slpm. This result is similar to hydrogen fuel cells and is as expected. With lower air flow rate, oxygen concentration decreases significantly along the flow channels, and results in lower current density. When air flow rate is high enough, any further in-

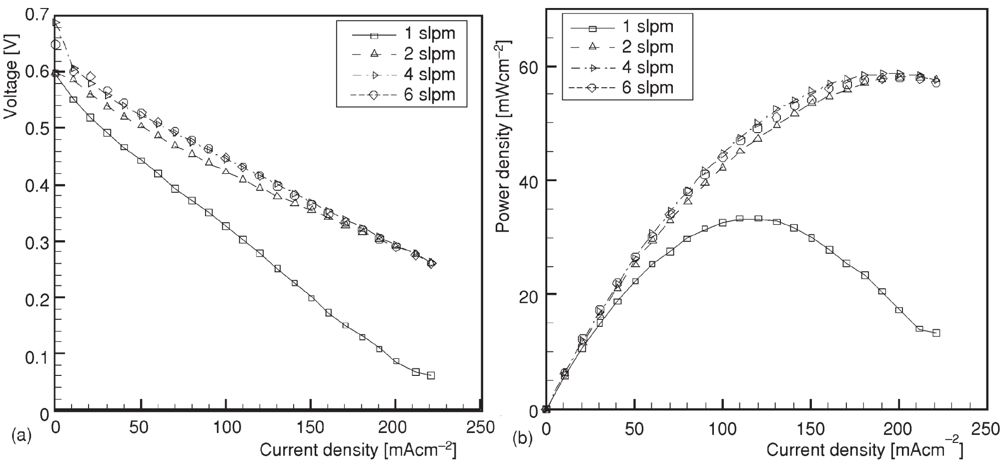

Figure 8. Experimental results for different oxygen flow rate
(*a) voltage-current density curves at different oxygen flow rate; (b) power density-current density curves at different oxygen flow rate*

crease in flow rate will change the oxygen concentration profile only slightly; thus, it has a negligible effect. Additionally, air flow plays a critical role in preventing flooding by removing liquid water from the gas diffusion layer and from the channels [7]. Increasing the oxygen flow rate can enhance the transportation of oxygen to the catalyst layer. This phenomenon causes to improve the ability of oxygen reaction with the catalyst and impedes the reaction of the methanol cross over from the anode side. On the other hand, the speed discharge of water produced is increased on the cathode side. The open circuit voltage of the cell increases with the oxygen flow rate. One of the factors contributing to this phenomenon is that the higher oxygen flow rate reduces the mixed potential caused by the methanol cross over [20].

A set of experiments were carried out to study the effect of oxygen flow rate (1.0, 2.0, 4.0, 6.0 slpm). In this set of experiments methanol flow rate was set at 10.0 ml per minute, methanol concentration was 1 M, cathode back pressure was 0.5 bar, and the cell temperature was 65 °C. The polarization curves of this experiment are shown in fig. 8, 9, and 10.

Figures 9 and 10 show that air flow rate reaches a certain value (2.0 slpm); any further increase has no significant effects over the cell voltage and current.

From figs. 9 and 10 when oxygen flow rate is about 1.0 slpm, oxygen does not exit sufficiently along the channel because of this current density is low. But with increasing the oxygen flow rate, oxygen concentration in the channel increases then current density and voltage increase. Further increasing of oxygen flow rate has no significant effect on the cell performance.

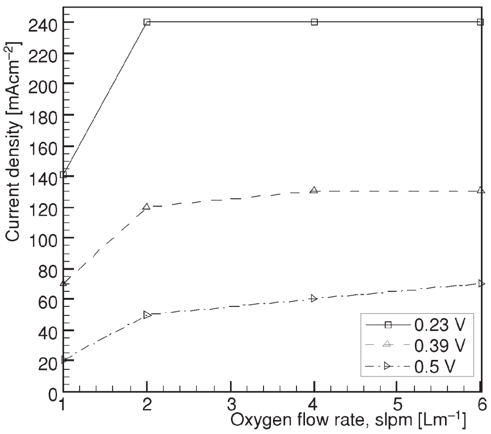

Figure 9. Single cell current density as a function of oxygen flow rate at different cell voltage

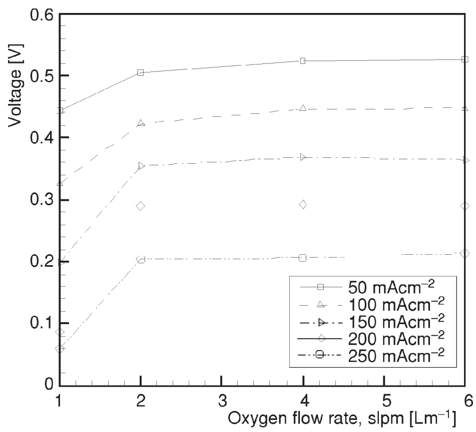

Figure.10 Single cell current density as a function of methanol concentration at different cell voltage

Conclusions

In this study the effect of various operating parameters on DMFC performance was investigated experimentally. A series of tests were conducted with various parameters including cell temperature, methanol concentration, and oxygen flow rate. The membrane electrode assembly (MEA) was used Nafion® 117, by loading a Pt-Ru (4 mg/cm^2) catalyst at the anode side and Pt-black (4 mg/cm^2) catalyst at the cathode side and the active area 10 cm ×10 cm.The main results are summarized as:

In general, a higher operating temperature results in higher cell potential. The results show that the current density is not a monotonous function of temperature, but has a maximum for each cell voltage. It was also observed that the maximum current densities are different at different cell voltages. The maximum current density increases as cell voltage decreases. With increasing cell temperature the cell voltage increases, and with increasing the current density the cell voltage decreases. For each cell design there is optimum cell temperature. In this experiment, many tests were performed and the best temperature was 60 °C reported. Further increasing of cell temperature has the negative effect on cell performance because of methanol cross over is increased and the membrane is dried.

If methanol cross over is a cause of a reduction in cell voltage it would be expected that a higher concentration of methanol in the feed to the anode would decrease the cell voltage as a result of potentially higher rates of transport through the membrane. Results show that the current density decreases sharply with increasing concentration when the methanol concentration is greater than 1.5 M. At this experiment the optimum concentration of methanol is between 0.5 to 1.0 M.

Increasing the oxygen flow rate can enhance the transportation of oxygen to the catalyst layer. This phenomenon causes to improve the ability of oxygen reaction with the catalyst and impedes the reaction of the methanol cross over from the anode side. The cell performance increases with increase oxygen flow rate up to a certain value, then the oxygen flow rate has no significant effect when oxygen flow rate reaches a certain value, any further increase has no significant effect.

For this single direct methanol fuel cell, optimum cell temperature was 60 °C, oxygen flow rate was 2.0 slpm and methanol concentration was 1.0 M.

Acknowledgment

The authors acknowledge the support of Center of Fuel Cell Research in Babol University of Technology for this study.

Nomenclature

a – transfer coefficient, [–]
E – electrical voltage, [V]
F – Faraday constant, [$\mathrm{Cmol^{-1}}$]
H – enthalpy, [J]
I_0 – current density, [$\mathrm{Am^{-3}}$]
L – channel length, [m]
n – number of electron
p – pressure, [Pa]
R – gas constant, [$\mathrm{Jkg^{-1}K^{-1}}$]
S – entropy, [$\mathrm{Jkg^{-1}}$]
T – temperature, [K]

Subscripts and superscripts

c – cathode
r – relative
ref – reference

Reference

[1] Dyer, C. K., Fuel Cells for Portable Applications, *Journal of Power Sources, 106* (2002), 1, pp. 31-34
[2] Larminie, J., Dicks, A., Fuel Cell Systems Explained, 1nd ed., John Wiley & Sons, Inc., Oxford, England, 2003
[3] Li, Y. S, Zhao, T. S., Liang., Z. X., Performance of Alkaline Electrolyte-Membrane Based Direct Ethanol Fuel Cells., *J. Power sources, 187* (2009), 2, pp. 387-392

[4] Faghri, A., Guo., Z., Challenges and Opportunities of Thermal Management Issues, Related to Fuel Cell Technology and Modeling, *International Journal of Heat and Mass Transfer, 48* (2005), 19-20, pp. 3891-3920
[5] Cruickshank, J., Scott., K., The Degree and Effect of Methanol Crossover in the Direct Methanol Fuel Cell. *J. Power Sources, 70* (1998), 1, pp. 40-47
[6] Hern, S., Chang, S., Lee., S., Effect of Operating Parameters on the Direct Methanol Fuel Cell Using Air or Oxygen as an Oxidant Gas, *Energy & Fuels, 22* (2008), 2, pp. 1212-1219
[7] Ge, J., Liu., H., Experimental Studies of a Direct Methanol Fuel Cell, *J. Power Sources, 142* (2005), 1-2, pp. 56-69
[8] Jung, D. H., *et al*., Performance of a Direct Methanol Polymer Electrolyte Fuel Cell, J. Power Sources, 71 (1998), 1-2, pp. 169-173
[9] Narayanan,S. R., *et al*., Recent Advances in PEM Liquid-Feed Direct Methanol Fuel Cells, *Proceedings*, 11th Annu. Battery Conf. Appl. Adv., Long Beach, Cal., USA, 1996, pp. 113-122
[10] Surampudi, S., *et al*., Advances in Direct Oxidation Methanol Fuel Cells., *J. Power Sources, 47* (1994), 3, pp. 377-385
[11] Küver, A., Vielstich., W., Investigation of Methanol Crossover and Single Electrode Performance During PEMDMFC Operation, A Study Using a Solid Polymer Electrolyte Membrane Fuel Cell System., *J. Power Sources, 74* (1998), 2, pp. 211-218
[12] Scott, K., Taama, W., Cruickshank, J., Performance of a Direct Methanol Fuel Cell, *J. Appl. Electrochem, 28* (1998), 3, pp. 289-297
[13] Ravikumar, M. K., Shukla, A. K., Effect of Methanol Crossover in a Liquid-Feed Polymer-Electrolyte Direct Methanol Fuel Cell, *J. Electrochem. Soc, 143* (1996), 8, pp. 2601-2606
[14] Kauranen, P. S., Skou., E., Methanol Permeability in Perfluorosulfonate Proton Exchange Membranes at Elevated Temperatures., *J. Appl. Electrochem, 26* (1996), 9, pp. 909-917
[15] Shukla, A. K., *et al*., A Vapour-Feed Direct-Methanol Fuel Cell with Proton-Exchange Membrane Electrolyte., *J. Power Sources, 55* (1995), 1, 87-91
[16] Mennola, T., *et al*., Measurement of Ohmic Voltage Losses in Individual Cells of a PEMFC Stack, *J. Power Sources, 112* (2002), 1, pp. 261-272
[17] Cruickshank, J., Scott, K., The Degree and Effect of Methanol Cross Over in Direct Methanol Fuel Cell, *J. Power Sources, 70* (1998), 1, pp. 40-47
[18] Oedegaard, A., Development and Characterisation of a Portable Direct Methanol Fuel Cell Stack, Ph. D. thesis, University Duisburg-Essen, Germany, 2005
[19] Okajima,K., *et al*., Performance of Liquid-Feed Direct Methanol Fuel Cell at Room Temperature, 203rd *Meeting of the Electrochemical Society, Paris, MA2003-01, 2003*
[20] Wang, M., Guo, H., Ma., C., Dynamic Characteristics of a Direct Methanol Fuel Cell, *J. Fuel Cell Science and Technolgy, 3* (2006), May, pp. 202-207

Paper submitted: July 25, 2009
Paper revised: November 19, 2009
Paper accepted: December 28, 2009