Direct Methanol Fuel Cells : Methanol Crossover and its Influence on Single DMFC Performance

S.Q. Song[1], **W.J. Zhou**[1], **W.Z. Li**[1], **G. Sun**[1], **Q. Xin**[1,2], **S. Kontou**[3] **and P. Tsiakaras**[3]
[1]Direct Alcohol Fuel Cell Lab, [2]State Key Lab of Catalysis, Dalian Institute of Chemical Physics, CAS P. O. Box 110, Dalian 116023, China
[3]Department of Mechanical and Industrial Engineering, School of Engineering,
University of Thessaly, Pedion Areos, 383 34, Greece
Corresponding authors: xinqin@dicp.ac.cn (Q. Xin); Tel &Fax: +86-411-84379071,
tsiak@mie.uth.gr (P. Tsiakaras); Tel: +30-24210-74065, Fax: +30-24210-74050.

Abstract. In the present investigation, the methanol crossover rate through Nafion®-115 membrane at different temperatures and different concentrations had been investigated in a fuel cell test apparatus by using gas chromatography analysis. The single *direct methanol fuel cell* (DMFC) tests were carried out to investigate the effect of the concentration of methanol aqueous solutions and cell temperature on methanol crossover and consequently, on the open circuit voltage and the cell performance of DMFC. It can be found that the methanol crossover rate through Nafion® membrane increases as methanol concentration and temperature increase. It can also be found that methanol crossover presented a negative effect on the open circuit voltage and the single DMFC performance. Single DMFC test results showed that an improved cell performance was obtained as temperature increased although the methanol crossover rate increased with temperature increment.

1. Introduction

In the recent years, *direct methanol fuel cells* (DMFCs) have been obtained an impressive growth of interest due to their potential applications for portable and stationary power sources because of their easy handling of fuel, small volume and light weight [1-3]. The growth of the corresponding research interest can be estimated from Fig. 1, which represents the number of DMFC refereed publications during the past fifteen years (statistics from www.sciencedirect.com). However, there are still problems related to DMFCs with a sluggish anode kinetics and methanol crossover, which leads to the much worse single DMFC performance than other type such as proton exchange membrane fuel cells fed by H_2. It has been found that PtRu catalysts are the best for methanol electro-oxidation [4-5]. Nevertheless, as methanol crossover is concerned, methanol molecules will reach the cathode, and platinum catalyst is always used as the cathode catalyst, even if it will not oxidize methanol as effectively as the PtRu catalyst, it will do more or less. The oxidation of methanol at the cathode is not only a waste of the fuel, it will also compete the Pt active sites

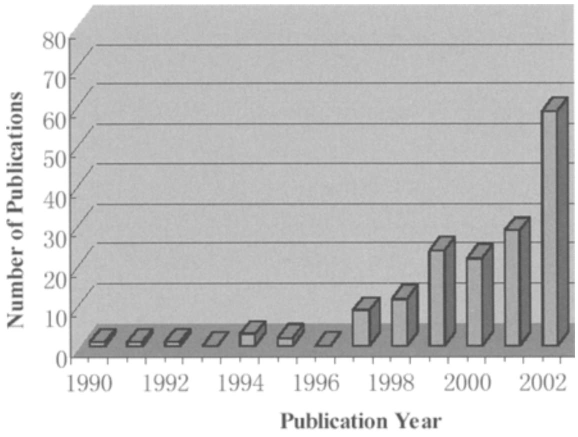

Fig. 1. Escalation of direct methanol fuel cells publications, in the past fifteen years.

for oxygen adsorption and oxidation, at the same time, it will reduce the cell voltage due to the mixed potential formed at the cathode [6]. Much effort has been made to eliminate, or at least to reduce methanol crossover to some degree involving adopting high effective anode catalysts and methanol-tolerant cathode catalysts [7-8], optimizing the feed concentration of methanol aqueous solutions [9-10], developing novel electrolytes or doping Nafion® membranes [11-16].

In the present investigation, the effects of temperature and the concentrations of aqueous methanol solutions on methanol crossover rate through bare Nafion®-115 membrane had been investigated in a fuel cell test apparatus by a TCD gas chromatograph (Varian CP 3800) equipped with a packed Parapak Q column. The single DMFC tests were carried out to evaluate the effect of aqueous methanol concentration and cell temperature on single DMFC's open circuit voltage and performance.

2. Experimental Description

2.1. Methanol Crossover Measurements. Methanol crossover measurements were carried out in a single fuel cell test apparatus, which has been previously described in details [17]. Nafion®-115 membrane was fixed by two polyester frames then clamped between two bipolar plates with silicone rubber gaskets to keep sealed. The effective area of each membrane sample was 3.4x3.4 cm^2. Methanol aqueous solution was pumped through the anode compartment at a flow rate of 1.0 mL/min. High-purity nitrogen at a pressure of 2 atm was fed at a flow rate of 290 mL/min to sweep off the permeated methanol through Nafion® membrane and a cold trap collected the effluent mixture for 45 min. Finally, the amount of the permeated methanol was determined by a TCD gas chromatograph (Varian CP 3800) equipped with a packed Parapak Q column.

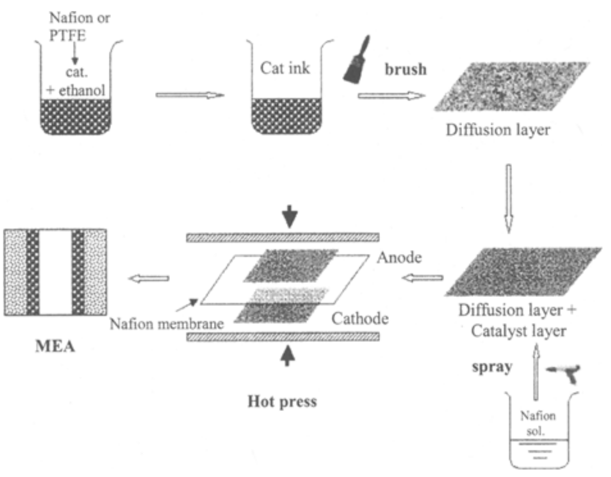

Fig. 2. The schematic presentation of the detailed membrane electrode assembly preparation procedure.

2.2 *Membrane Electrode Assembly (MEA) Preparation.* The detailed preparation process of *membrane electrode assembly* (MEA) is schematically presented in Fig. 2. Catalyst inks were prepared by mechanically and ultrasonically mixing PtRu/C (20Pt~10Ru wt.%, Johnson Matthey Corp.) with 5 % Nafion solution for the anode and Pt/C (20 wt.%, Johnson Matthey Corp.) with 10% PTFE solution for the cathode respectively. The appropriate amounts of anode and cathode inks were uniformly spread by a brush to the as-prepared anode and cathode diffusion layers with a given area to give a respective metal loading of about 2.0 mg/cm^2 for the anode and 1.0 mg/cm^2 for the cathode. MEA was obtained by hot-pressing the catalyst layer onto the each side of Nafion®-115 membrane at about 140°C under 100 mg/cm^2 for 90 s after spraying *ca.* 0.5 mg/cm^2 Nafion solution onto the catalyst layer surfaces of both the anode and the cathode.

2.3. Single DMFC Tests. The fuel cell test apparatus used in the present investigation included a dynamic hydrogen electrode (DHE) as a reference electrode to determine the anode and cathode potentials respectively during the cell performance test process, which has been previously described [17]. During the operation of the single DMFC test, the methanol aqueous solution was supplied to an inlet located at the bottom of the anode at a flow rate of 1.0 mL/min, while the unhumidified oxygen was fed into an inlet located at the top of the cathode from the cylinder at ambient temperature and a backpressure regulator controlled the desired gas pressure. The DHEs were created by supplying 1 atm hydrogen humidified at 85°C at a flow rate of 40 mL/min. The polarization curves of DMFC were obtained using a Fuel Cell Test System (Arbin Instrument Corp.) in a galvanodynamic polarization mode.

3. Results and Discussion

It is well known that methanol crossover has a seriously negative effect on the cell performance. In the present investigation, methanol crossover rate through bare Nafion®-115 membrane at different temperature and different concentration of methanol aqueous solutions were determined by using a gas chromatography analysis and the results are shown in Table 1. It can be found from Table 1 that methanol crossover rate increases as the temperature or the feed concentration of methanol aqueous solutions increase. The increased methanol crossover rate

Table 1. The effect of temperature and the concentration of methanol aqueous solutions at room temperature and the effect of the temperature with 1.0 mol/L methanol aqueous solutions supplied to the system on the methanol crossover rates through bare Nafion®-115 membrane.

		Methanol crossover rate, 10^{-8} (mol/cm^{2}s)
Methanol concentration (mol/L)	0.25	2.0
	0.5	4.7
	1.0	11.6
	2.0	24.7
	4.0	63.9
Temperature (°C)	30	2.0
	45	3.5
	60	7.5
	75	11.6
	90	15.3

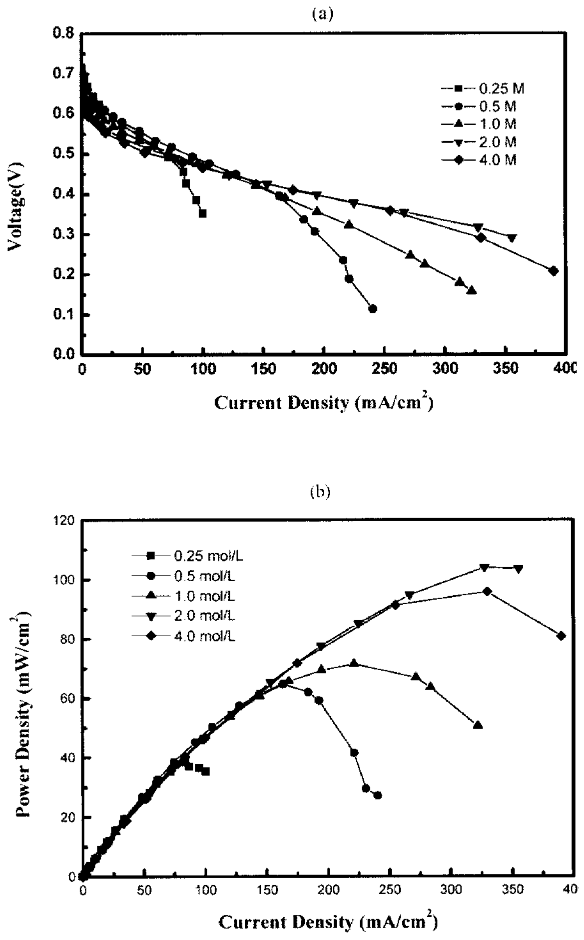

Fig. 3. Effect of methanol concentration on the single DMFC's performance. T_{cell} = 75°C. Anode: PtRu/C (20Pt~10Ru wt.%, Johnson Matthey Corp.), metal loading: 2.0 mg (Pt+Ru) /cm^2, Flow rate of methanol aqueous solutions: 1.0 mL/min. Cathode: Pt/C (20Pt wt.%, Johnson Matthey Corp.), metal loading: 1.0 mg Pt /cm^2, P_{O2} = 2 atm. Electrolyte: Nafion®-115 membrane.

due to the temperature increment could be attributed to the easily transportation of methanol molecules through the Nafion® membrane resulting from their accelerated mobility because of the elevated temperature. Another probably reason for this is due to the fact that at higher temperature the polymer backbone expands due to softening of the fluorinated chain [18]

The permeation of water and methanol through the bare membrane will take place under the driving forces of concentration and pressure gradients. Under the same pressure gradient conditions, the methanol crossover rate is linearly proportional to the feed concentration of methanol aqueous solutions [19] leading to the results in the present investigation and reported in Table 1.

The concentration of methanol aqueous solutions on the single DMFC performance is shown in Fig. 3. It can be clearly seen in Fig. 3 that methanol concentration has an obvious effect on the DMFC's performance. When the concentrations of methanol aqueous solutions are 0.25 mol/L, 0.5 mol/L, 1.0 mol/L, 2.0 mol/L and 4.0 mol/L respectively, the corresponding peak power densities are about 38 mW/cm^2, 66 mW/cm^2, 71 mW/cm^2, 104 mW/cm^{2}and 96 mW/cm^2. Considering from the maximum power density point of view, it seems that the optimum feed concentration of methanol aqueous solution is 2.0 mol/L. However, it can also be seen in Fig.3 that in different discharge range, the methanol concentrations present different effect on the single DMFC performance.

For the sake of clarity, the DMFC's IV curve at low current densities is enlarged and shown in Fig. 4. It can be distinguished from Fig. 4 that at lower current densities, the cell performance increases as the methanol concentration decreases, which could be attributed to the fact that at low current density, methanol crossover markedly affects cell performance [6] and accordingly the higher methanol crossover rate due to the higher methanol feed concentration, as shown in Table 1, will lead to the worse cell performance. Furthermore, the open circuit voltage of the fuel cell at given operation conditions, is calculated according eq. (1), where V_{OCV} is the open circuit voltage of the fuel cell, E is the theoretical value of the open circuit voltage of the fuel cell, i_n and i_0 denote internal current density due to fuel crossover and exchange current density respectively [6]. From eq. (1) it can be deduced that the open circuit voltage of single DMFC

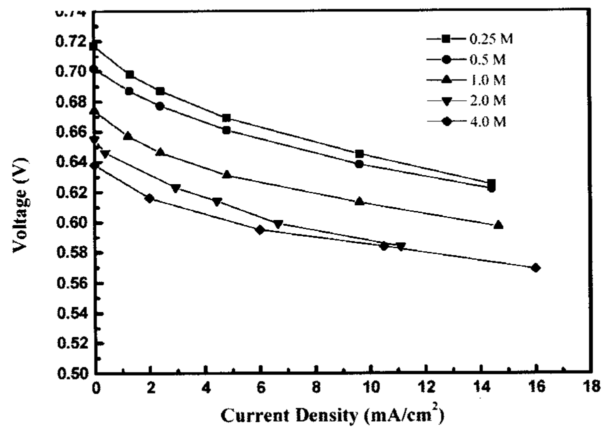

Fig. 4. IV data of single DMFC with different methanol feed concentration at lower current densities. T_{cell} = 75 °C. Anode: PtRu/C (20Pt~10Ru wt.%, Johnson Matthey Corp.), metal loading: 2.0 mg (Pt+Ru) /cm^2, Flow rate of methanol aqueous solutions: 1.0 mL/min. Cathode: Pt/C (20Pt wt.%, Johnson Matthey Corp.), metal loading: 1.0 mg Pt /cm^2, P_{O2} = 2 atm. Electrolyte: Nafion®-115 membrane.

decreases as the internal current density increases. On the other hand, the latter is positively affected by the permeated methanol quantity [6], leading to the behavior observed here in Fig. 4.

$$V_{OCV} = E - A\ln\left(\frac{i_n}{i_o}\right) \qquad (1)$$

The effect of cell temperature on single DMFC performance and anode and cathode polarization is presented in Fig. 5. It can be clearly seen from Fig.5 (a) that the DMFC's performance is significantly improved as the temperature increases. The maximum power density increases from about 40 mW/cm^2 at 45°C to about 75 mW/cm^2 at 75°C. The latter case is almost twice higher than the former, which could be attributed to the reduced activation overpotential due to the increased the cell temperature [6]. Nevertheless, one can distinguish from Fig. 5 (b) that, in the case of anode polarization, the anode potential is increased as the cell temperature increases, while in the cathode polarization case, the cathode potential decreases at lower current density along with the cell temperature increment. At the same time, even if in the higher current density range, there is still no obvious increase in cathode potential. This could be due to the more serious effect of methanol crossover resulting from the increased permeated methanol quantity caused by the incremental temperature. On the other hand, the methanol crossover reduces as the current from the cell increase. As the result, the effect of the methanol crossover on the cathode potential is reduced, consequently leading to a little improvement in the cathode potential due to the higher cell temperature at high current densities. In addition, it is also be worth noting that, as it can be derived from Fig. 5, that the difference between cathode and anode potentials does not correspond exactly to the cell voltage in the V-I curve. The reason is probably that the IR drop in the electrolyte is present in both anode and cathode potentials versus current density curves.

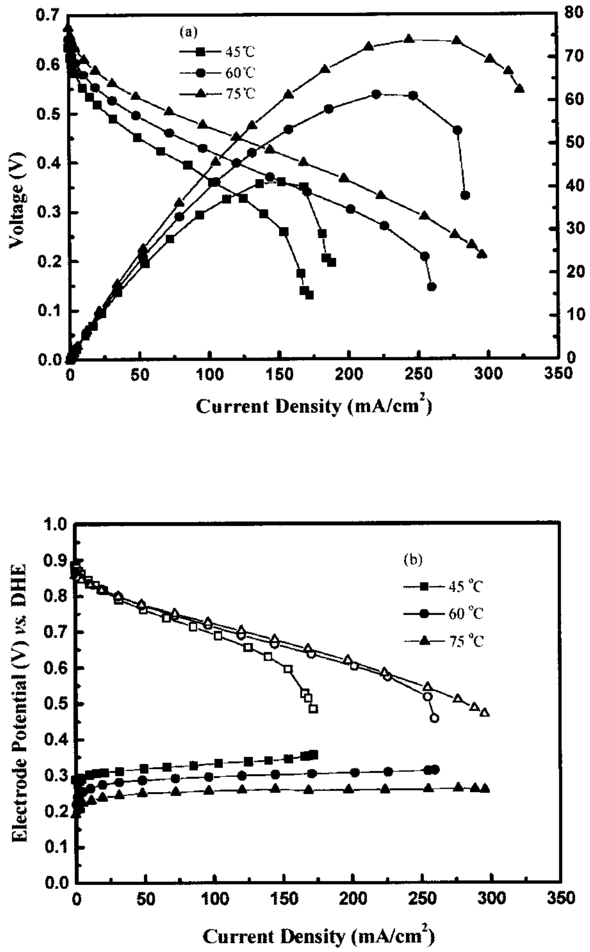

Fig. 5. Galvanostatic polarization data of single DMFC at different temperature. (a) Cell performance. (b) Electrode potential against current density. The solid symbols correspond to anode polarization and open symbols to cathode polarization. Anode: PtRu/C (20Pt~10Ru wt.%, Johnson Matthey Corp.), metal loading: 2.0 mg (Pt+Ru)/cm^2, $C_{methanol}$ = 1.0 mol/L, flow rate: 1.0 mL/min. Cathode: Pt/C (20Pt wt.%, Johnson Matthey Corp.), metal loading: 1.0 mg Pt/cm^2,P_{O2} = 2 atm. Electrolyte: Nafion®-115 membrane. (■ 45 °C, ● 60 °C, ▲ 75 °C).

Based on the experimental results, it can be found that, in order to maximize the single DMFC's performance, it is desired to optimize the operation conditions. In the case of the feed methanol concentration, it is suggested to regulate the concentration of methanol aqueous solutions referring to the discharge current density. In the case of the cell temperature, it is necessary to consider the compromise between the effects of the cell temperature on reducing activation loss and increasing methanol crossover.

4. Conclusions

Methanol crossover from the anode to the cathode through Nafion®-115 membrane increases as the temperature and the feed concentration of methanol in the aqueous solutions increases. Methanol crossover presents an obvious effect on the open circuit voltage and cell performance of single DMFC. There is an optimum feed concentration of methanol aqueous solution for a better single DMFC performance. Single DMFC exhibits an improved whole cell performance even if the increased methanol crossover due to the increased cell temperature counteracts the positive effect of the cell temperature.

5. Acknowledgements

The authors gratefully acknowledge financial support from National Natural Science Foundation of China (Grant No.: 20173060). We would also like to thank the "China-Greece Joint Research and Technology Programme 2003-2005" (cod.2000 ΣE 01330005) for funding.

6. References

[1] R. Dillon, S. Srinisasan, A.S. Aricò, A. Antonucci, J. Power Sources **127**, 112 (2003).

[2] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources **86**, 111 (2000).

[3] C. Lim, C. Y. wang, J. Power Sources **113**, 145 (2003).

[4] M. Watanabe, M. Motoo, J. Electroanal. Chem. **60**, 267 (1975).

[5] D. Chu, S. Gilman, J. Electrochem. Soc. **143**, 1685 (1996).

[6] J. Larminie, A. Dicks, Fuel Cell Systems Explained, Second edition, Wiley, 2001, P149.

[7] L.S. Gojkovi, S. Gupta, R.F. Savinell, J Electroanal. Chem. **462**, 63 (1995).

[8] L. Xiong, A. Manthiram, Electrochim. Acta, (2004), in press.

[9] K. Scott, W.M. Taama, P. Argyroloulos, A. Hamnet, J. Power Sources **83**, 204 (1999).

[10] H. Dohle, H. Schmitz, T. Bewer. K. Merge, D. Stolten, J. Power Sources **106**, 313 (2002).

[11] R. Nolte, K. Ledjeff, M. Bauer, R. Mülhaupt, J Membr. Sci. **83**, 211 (1993).

[12] J. Kerres, W. Cui, R. Disson, W. Neubrand, J Membr. Sci. **139**, 211 (1998).

[13] H. Uchida, Y. Mizuno, M. Watanabe, J Electrochem. Soc. **149**, A682 (2002).

[14] Y.M. Kim, K.W. Park, J.H. Choi, I.S. Park, Y.E. Sung, Electrochem. Comm. **5**, 571 (2003).

[15] E.N. Miyake, J.S. Wainright, R.F.Savinell, J Electrochem. Soc. **148**, A905 (2001).

[16] W.C. Choi, J.D. Kim, S.I. Woo, J. Power Sources **96**, 411 (2001).

[17] S.Q. Song, W.J. Zhou, Z.X. Liang, R. Cai, G. Sun, Q. Xin, V. Stergiopoulos and P. Tsiakaras, Appl. Catal. B **55**, 65 (2004).

[18] V. Gogel, T. Frey, Y. Zhu, K. A. Friedrich, L. Jörissen, J. Garche, J. Power Sources **127**, 172 (2004).

[19] J. Cruickshank, K. Scott, J. Power Sources **70**, 40 (1998).

Paper presented at the Patras Conference on Solid State Ionics - Transport Properties, Patras, Greece, Sept. 14 - 18, 2004.

Manuscript rec. Sept. 6, 2004; rev. Nov. 3, 2004; acc. Nov. 10, 2004.