



Short communication

# Single passive direct methanol fuel cell supplied with pure methanol

Ligang Feng, Jing Zhang, Weiwei Cai, Liangliang, Wei Xing\*, Changpeng Liu

State Key Laboratory of Electro-analytical Chemistry, Changchun Institute of Applied Chemistry, Jilin Province Key Laboratory of Low Carbon Chemical Power, Graduate School of the Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, PR China

## ARTICLE INFO

### Article history:

Received 26 October 2010

Received in revised form

22 November 2010

Accepted 22 November 2010

Available online 27 November 2010

### Keywords:

Passive direct methanol fuel cell

Pervaporation membrane

Pure methanol

Power density

## ABSTRACT

A new single passive direct methanol fuel cell (DMFC) supplied with pure methanol is designed, assembled and tested using a pervaporation membrane (PM) to control the methanol transport. The effect of the PM size on the fuel cell performances and the constant current discharge of the fuel cell with one-fueling are studied. The results show that the fuel cell with PM 9 cm<sup>2</sup> can yield a maximum power density of about 21 mW cm<sup>-2</sup>, and a stable performances at a discharge current of 100 mA can last about 45 h. Compared with DMFC supplied with 3 M methanol solution, the energy density provided by this new DMFC has increased about 6 times.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

The DMFC is a promising power source for portable applications due to its high energy density, long life and so on [1–4]. The theoretical specific energy and energy density of pure methanol are about 6100 Wh kg<sup>-1</sup> and 4800 Wh L<sup>-1</sup>. In practice, the fuel supplied at the anode of passive DMFC must be a low methanol concentration (less than 5 M). Therefore, this will lead to a short runtime of the fuel cell, and the specific energy and energy density will be largely decreased. In order to increase the operation time, several efforts [5–8] have been carried out to develop advanced DMFC technology. Abdelkareem et al. [5,9,10] employed a porous carbon plate to increase the mass transport resistance on the anode and realized to supply the fuel cell with high methanol concentration over 20 M. Kim et al. [11,12] used the hydrogels to control the methanol transport from the fuel reservoir to the anode even at high fuel concentration.

Pervaporation membrane (PM) was employed for the separation of mixture of liquids and several new membranes were reported to separate the small molecular substances such as methanol, ethanol, and water and so on [13–15]. Based on the properties of PM, in our experiment, the work was tentatively to introduce the PM into a single passive DMFC and to check if it can be used to control the methanol transport on the anode. Therefore, in this communication, a new fuel cell structure was proposed with PM to control the methanol transport when the fuel was supplied with pure

methanol. The experiment results demonstrated that the passive DMFC with the proposed new structure can successfully operate with pure methanol. Under the same condition, the discharge time of the proposed DMFC supplied with pure methanol at a constant current was much longer than that of the conventional fuel cell supplied with methanol solution.

## 2. Experimental

### 2.1. Membrane electrode assembly

Pt–Ru and Pt black catalysts (Johnson Matthey) were used as anodic and cathodic electrocatalysts, respectively. The carbon papers (TGP-H-60, Toray) with 20% and 40% polytetrafluoroethylene (PTFE) content were used as anodic and cathodic backing layers, on which carbon black (Vulcan-XC 72) with PTFE content of about 20% and 40% as the micro-porous layer had been pre-coated with a loading of 2 mg cm<sup>-2</sup> respectively. Nafion®-117 membrane (DuPont Co., USA) was pretreated before use [16,17]. The catalyst ink consisted of the catalyst, deionized water, isopropyl alcohol and Nafion solution (5 wt.%, DuPont Co., USA) was coated on the carbon backing layer to fabricate the electrodes. The catalyst loading as high as 8 mg cm<sup>-2</sup> is used on each electrode to achieve high performance. The Nafion ionomer loading in the catalyst was 10 wt.% for the cathode and 15 wt.% for the anode, defining by the ratio that dry ionomer takes up in the catalyst layer. The MEA, area of 9 cm<sup>2</sup>, was fabricated by sandwiching the membrane between the anode and the cathode, and then it was hot-pressed at 408 K and 5 MPa for 3 min.

\* Corresponding author. Tel.: +86 431 85262223; fax: +86 431 85685653.  
E-mail address: [xingwei@ciac.jl.cn](mailto:xingwei@ciac.jl.cn) (W. Xing).

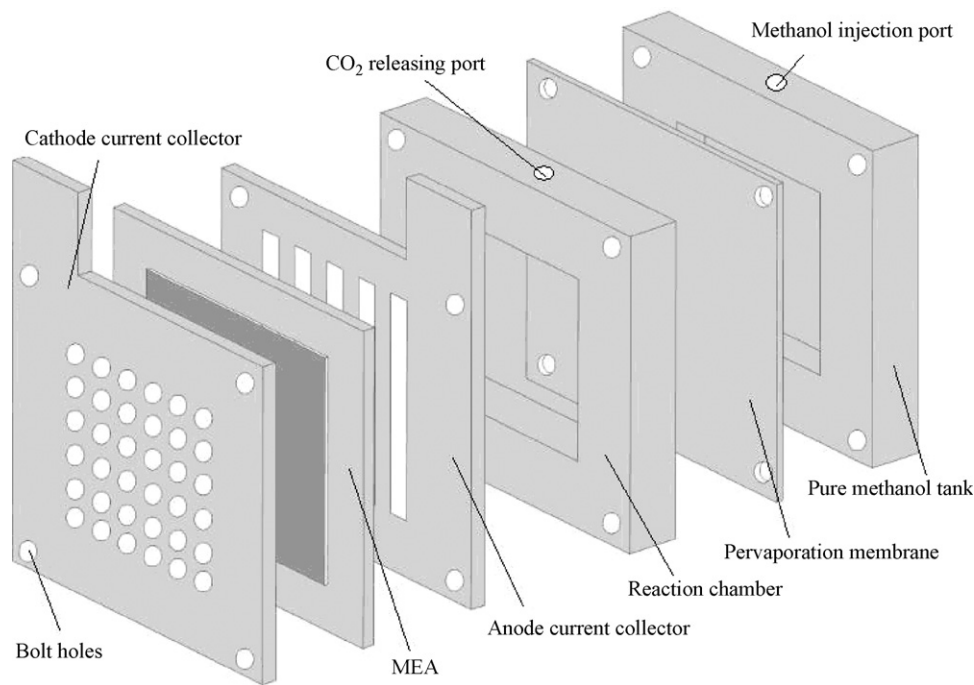


Fig. 1. Schematic diagram of the structure for the DMFC-P.

## 2.2. Fuel cell design and test

The single fuel cell structure is shown in Fig. 1, which is a modification for the conventional fuel cell structure [18]. The fuel tank is divided into two tanks: a pure methanol tank and a low methanol concentration tank (reaction chamber). The PM of 0.17 mm thick was bought from Beijing Hongzhi Jiahe Technology Co., China and used as-received. The PM was fixed between the two tanks to control the methanol transport. The fixing of the PM was not clear in Fig. 1, here, it was further explained. In order to easily change the effective PM size, the PM was sandwiched between two polycarbonate sheets (0.5 mm thick). The apparent PM size was close to that of the polycarbonate sheet and an open size of the desired effective PM area was machined on the polycarbonate sheet. The fringe of the open size was covered by adhesive-sealant silicone and then the PM was sandwiched between the two polycarbonate sheets. The PM sandwiched between the polycarbonate sheets was fixed between the pure methanol tank and reaction chamber at the anode. The low methanol concentration tank was the reaction chamber for the anodic oxidation of methanol and it was about 3 mm in thickness. The volumes of the reaction chamber and the pure methanol tank were about 2.7 mL and 5 mL, respectively. Other components such as current collectors, fuel cell body were the conventional parts used in fuel cell [19,20].

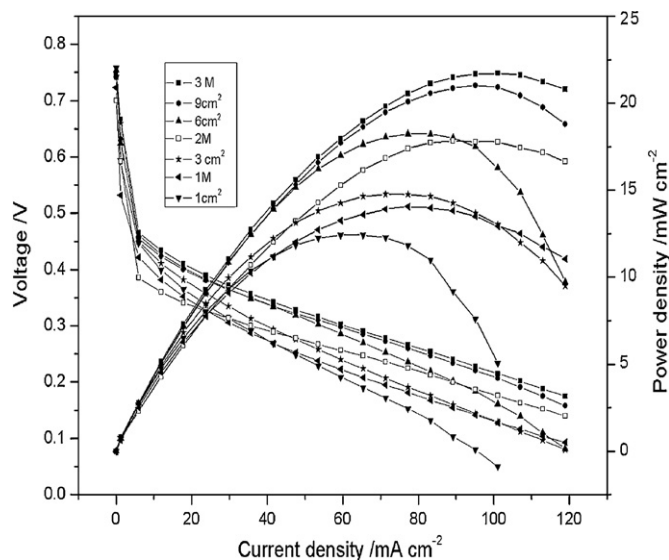
The polarization curves of the single fuel cell were measured during discharge process with a Fuel Cell Test System (Arbin Instruments Co.). The discharge curves of voltage vs. time were also tested at a constant current to record the voltage. For comparison, the MEA prepared in the same patch was also tested in a conventional single fuel cell with a dilute methanol solution. The designed fuel cell supplied with pure methanol was denoted as DMFC-P, and the conventional fuel cell supplied with a dilute methanol solution was denoted as DMFC-S. For the DMFC-S, the volume of the fuel tank was about 7.7 mL, which equaled to the sum of the volume of the reaction chamber and the pure methanol tank of the DMFC-P. The fuel cell was tested at ambient conditions (20–25 °C).

## 3. Results and discussion

Prior to testing the DMFC-P, a small amount of water of about 2 mL was syringed into the reaction chamber to wet the anode of the fuel cell. According to the anodic oxidation of methanol, the water is necessary for the reaction. Therefore, the syringed water can be used to dilute the penetrated methanol for the initial anodic methanol oxidation. The water needed for the reaction during the fuel cell operation was obtained from the water created on the cathode [20–22]. According to our experiment, if the MEA has been soaked in the water, the foregoing step could be omitted. The pure methanol was injected and the injection port was sealed completely during the operation. Before testing, the voltage of open circuit was recorded until the stable high voltage was reached; the process lasted for several minutes. For the purpose of comparison, the DMFC-S fed with a dilute methanol solution was tested in the same conditions.

### 3.1. Effect of pervaporation membrane size

In order to know the effect of the PM size on the performances of the DMFC-P and to find an optimal PM size, the PM with apparent area of about 9, 6, 3 and 1 cm<sup>2</sup> was employed. Because of the difficulty to measure the methanol concentration in the anodic catalyst layer, the polarization curves of the DMFC-S supplied with different methanol solution were tested and according to the similar curves, the methanol concentration of the DMFC-P was obtained by a rough estimate. The polarization curves and power density curves are shown in Fig. 2. The features of the curve for the DMFC-S were consistent with the results published elsewhere [23,24]. When the methanol concentration was increased, the performance became much better and the maximum power density was about 22 mW cm<sup>-2</sup> for the DMFC-S with 3 M methanol solution. For the DMFC-P, the performance of PM with 9 cm<sup>2</sup> was about 21 mW cm<sup>-2</sup>, which was close to the performance of the DMFC-S with 3 M methanol solution. When the PM size was decreased, it was evident from Fig. 2 that the maximum power density was also decreased. The cell performance of PM with 6 cm<sup>2</sup> was between

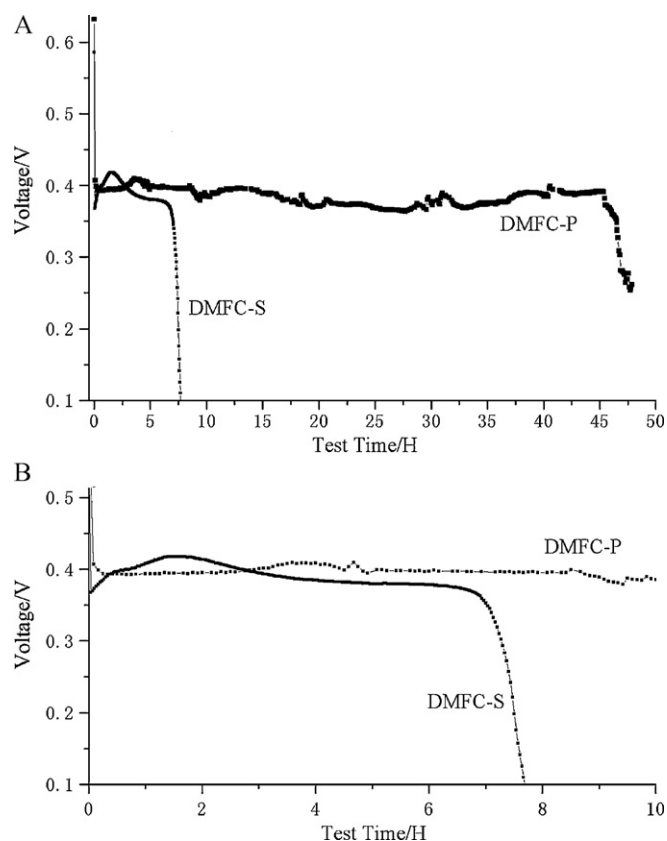


**Fig. 2.** Polarization and power density curves for the DMFC-P with different PM size and for the DMFC-S with different methanol concentrations.

the performance of 3 M and 2 M methanol solution for the DMFC-S. For PM with 3 and 1 cm<sup>2</sup>, the corresponding performances were higher and lower than those of 1 M methanol solution for the DMFC-S, respectively. Therefore, the concentration of methanol on the anodic side of DMFC-P can be approximately estimated according to the polarization curves in Fig. 2. For the DMFC-P, the best power density was obtained by using PM with 9 cm<sup>2</sup>. It was interesting that the polarization curves with different PM sizes for the DMFC-P have similar features. For instance, when the current density was below 50 mA cm<sup>-2</sup>, the performance was close to that of the DMFC-S supplied with methanol solution. However, when the current density was above 60 mA cm<sup>-2</sup>, the polarization curve decreased much faster than that of DMFC-S supplied with methanol solution. This reason can be explained by the transport limitation of the methanol. At high current density, the performance is controlled by the transport rate of methanol. For the DMFC-P, at high current density, the methanol penetrated through the PM cannot meet the demand of methanol consumed during the fuel cell operation. Therefore, the polarization curves appeared the limitation of the mass transport.

### 3.2. Discharge time of the fuel cell with one-fueling

For the passive DMFC, from a practical aspect, it is much better if the cell can operate for a longer time with one-fueling. The following experiment was conducted on the DMFC-P supplied with 5 mL pure methanol and 2 mL water using PM with 9 cm<sup>2</sup>. For the purpose of comparison, the DMFC-S supplied with the same volume of 3 M methanol solution was evaluated. The two kinds of DMFC were operated at 100 mA at ambient conditions. The curves of the output voltage vs. runtime are shown in Fig. 3A and the curves of the initial 10 h are also shown in Fig. 3B. The fluctuation of voltage was very small for the DMFC-P, but the reasons were complicated. There were several parameters that may lead to the fluctuation of voltage such as the temperature fluctuation in the fuel cell, the change of methanol transport rate, the change of water amount from cathode and the evolution of CO<sub>2</sub> gas product at anode. It was evident that the operation time of the DMFC-P was much longer than that of the DMFC-S; meanwhile, the output voltage of the DMFC-S was stable, which was close to that of the DMFC-S with 3 M methanol solution. Because of using the pure methanol, it was no doubt that the DMFC-P had a long runtime. Above the acceptable voltage of 0.35 V, the runtime of DMFC-P and DMFC-S was 45 and 7 h, respec-



**Fig. 3.** (A) Curves of the output voltage vs. runtime for the DMFC-P and DMFC-S at 100 mA. (B) Curves of the (A) in the initial 10 h for DMFC-P and DMFC-S.

tively. The corresponding energy density (defining as energy vs. fuel volume) was about 260.57 and 41.4 Wh L<sup>-1</sup> for the DMFC-P and DMFC-S, respectively, which indicated that the energy density increased about 6 times. In fact, the Faradic efficiency and energy efficiency of the DMFC-P were still low. Specifically, the energy efficiency was 8% and 7% for the DMFC-P and DMFC-S, respectively. Compared to the DMFC-S, the energy efficiency of the DMFC-P was not greatly increased. It can be mainly attributed to the evaporation and crossover of the pure methanol. However, it was evident that the discharge time of the DMFC-P was greatly increased with the same fuel cell system volume as compared with that of the DMFC-S. Based on this point, the DMFC-P has advantage than the conventional passive DMFC supplied with dilute methanol solution. From the above discussion, PM can be successfully used to control the methanol transport, and the DMFC-P can yield a stable and good performance for a long runtime with one-fueling. Though there are some difficulties in practical application, it gives us a hope or an idea to increase the operation time for passive DMFC.

## 4. Conclusions

A new single passive DMFC supplied with pure methanol using a PM to control the methanol transport was designed and tested. The maximum power density of approximately 21 mW cm<sup>-2</sup> was obtained with the PM size of 9 cm<sup>2</sup>. When the fuel cell was discharged at 100 mA, the operation time of the DMFC-P was increased about 6 times as compared with that of the DMFC-S.

## Acknowledgements

This work was supported by the High Technology Research Program (863 program 2007AA05Z159, 2007AA05Z143) of the Science

and Technology Ministry of China, the National Natural Science Foundation of China (20933004, 21011130027 and 21073180).

## References

- [1] C.Y. Chen, P. Yang, *J. Power Sources* 123 (2003) 37.
- [2] Z. Guo, A. Faghri, *J. Power Sources* 160 (2006) 1183.
- [3] A.A. Kulikovskiy, H. Schmitz, K. Wippermann, J. Mergel, B. Fricke, T. Sanders, D.U. Sauer, *Electrochem. Commun.* 8 (2006) 754.
- [4] R. Rashidi, I. Dincer, G.F. Naterer, P. Berg, *J. Power Sources* 187 (2009) 509.
- [5] Y.H. Chan, T.S. Zhao, R. Chen, C. Xu, *J. Power Sources* 176 (2008) 183.
- [6] A. Faghri, Z. Guo, *Appl. Therm. Eng.* 28 (2008) 1614.
- [7] M.Y. Lo, I.H. Liao, C.C. Huang, *Int. J. Hydrogen Energy* 32 (2007) 731.
- [8] Z. Guo, A. Faghri, *J. Power Sources* 167 (2007) 378.
- [9] M.A. Abdelkareem, N. Morohashi, N. Nakagawa, *J. Power Sources* 172 (2007) 659.
- [10] M.A. Abdelkareem, N. Nakagawa, *J. Power Sources* 162 (2006) 114.
- [11] W.J. Kim, H.G. Choi, Y.K. Lee, J.D. Nam, S.M. Cho, C.H. Chung, *J. Power Sources* 163 (2006) 98.
- [12] W.J. Kim, H.G. Choi, Y.K. Lee, J.D. Nam, S.M. Cho, C.H. Chung, *J. Power Sources* 157 (2006) 193.
- [13] X.H. Liu, Y.A. Sun, X.H. Deng, *J. Membr. Sci.* 325 (2008) 192.
- [14] S. Zereszki, A. Figoli, S.S. Madaeni, S. Simone, E. Drioli, *J. Appl. Polym. Sci.* 118 (2010) 1364.
- [15] Y.J. Wang, L.R. Yang, G.S. Luo, Y.Y. Dai, *Chem. Eng. J.* 146 (2009) 6.
- [16] J. Zhang, G.P. Yin, Z.B. Wang, Y.Y. Shao, *J. Power Sources* 160 (2006) 1035.
- [17] R. Chen, T.S. Zhao, *Electrochim. Acta* 52 (2007) 4317.
- [18] J.G. Liu, T.S. Zhao, Z.X. Liang, R. Chen, *J. Power Sources* 153 (2006) 61.
- [19] T. Shimizu, T. Momma, M. Mohamedi, T. Osaka, S. Sarangapani, *J. Power Sources* 137 (2004) 277.
- [20] Z. Guo, A. Faghri, *Commun. Heat Mass* 35 (2008) 225.
- [21] G.Q. Lu, F.Q. Liu, C.-Y. Wang, *Electrochem. Solid-State Lett.* 8 (2005) A1.
- [22] G. Jewett, Z. Guo, A. Faghri, *J. Power Sources* 168 (2007) 434.
- [23] B. Bae, B.K. Kho, T.-H. Lim, I.-H. Oh, S.A. Hong, H.Y. Ha, *J. Power Sources* 158 (2006) 1256.
- [24] C. Coutanceau, R.K. Koffi, J.M. Léger, K. Marestin, R. Mercier, C. Nayoze, P. Capron, *J. Power Sources* 160 (2006) 334.