Short communication

Effect of current-collector structure on performance of passive micro direct methanol fuel cell

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Abstract

The effect of current-collector structure on the performance of a passive micro direct methanol fuel cell (DMFC) is reported. The system consists mainly of a membrane electrode assembly, two current-collectors, two gaskets and two end-plates. It does not include any pump and the delivery of fuel and air is realized completely by natural convection and diffusion, which significantly decreases the complexity and lowers the cost of the micro DMFC. The performance of the micro DMFC with different current-collectors is tested and compared. The results indicate that the exposure ratio of the anode current-collector should be higher than that of the cathode counterpart to ensure good fuel delivery at the anode and to minimize the contact resistance at the cathode.
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1. Introduction

The world-wide proliferation of portable electronic devices – including laptop computers, personal data assistants, mobile phones and other power hungry products – has created a large and growing demand for energy sources that are compact, lightweight and powerful. Existing rechargeable battery technology, which has greatly matured, simply does not meet the needs of users. The gap is expected to widen in the next few years as devices become more powerful and more sophisticated. This scenario presents an enormous opportunity for new power technologies and products.

To address the growing demand for compact energy sources, many types of alternative power generators are being developed. Generally, they can be grouped into four categories, namely, rockets [1,2], indirect energy conversion devices [3,4], direct energy conversion devices [5,6], and fuel cells [7,8]. It should be noted that the first three categories of micro power generators,

all include a micro combustion chamber, and the system should work under high temperature, which places high demands on the properties of the component materials. The direct methanol fuel cell (DMFC) can work at close to room temperature, has a much high energy-conversion efficiency and its construction is simple. Thereby, it is a good candidate for use in commercial electronics and micro devices. Having a theoretical energy density of about 6080 Wh kg^{-1}, methanol stores about 10 times more energy than the best lithium-ion batteries. This advantage translates into longer usage time between replacement of fuel cartridges and also more energy available to support consumer demand. Another significant advantage of the DMFC over the rechargeable battery is its potential for instantaneous refuelling. Unlike rechargeable batteries that require hours for recharging, a DMFC can have its fuel replaced in minutes. Furthermore, the by-products of a micro DMFC, namely, carbon dioxide and water, are ecologically benign. These significant advantages make DMFC a promising power source for the portable electronic devices market.

To improve the performance of DMFCs, significant efforts are being made to develop new membranes [9–12], to optimize the flow-field [13–15], and to improve the chemical kinetics of electrodes [16–18]. There are a few reports of studies on prototype micro passive-feeding DMFCs [19,20]. Relatively, few

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papers have discussed that the structure of the current-collector should be different for the anode and the cathode. In this paper, a passive prototype DMFC is introduced, and the effect of current-collector structure both at the anode and the cathode on the performance of DFMC is compared.

2. Design of micro direct methanol fuel cell

A prototype micro DMFC was assembled, see Fig. 1. The system is mainly composed of two end-plates, two current-collectors, two gaskets, and one membrane electrode assemblies (MEA). A fuel chamber was cut in the anode end-plate. The system, which used liquid methanol without a reformer, could be operated at ambient conditions, which significantly reduced the thermal management challenges for small systems. The system did not have any pump, and the delivery of fuel and air was realized completely by natural convection. This set-up simplifies the structure and significantly decreases the cost of the micro DMFC. Liquid methanol is to a great extent easier to store and transport without auxiliary devices for intermediate fuel processing that are required by hydrogen–oxygen fuel cells.

The membrane electrode assembly is an important component of the micro DMFC. It is usually composed of five layers, namely, a gas diffusion layer (GDL), a catalyst layer (CL), a proton-exchange membrane (PEM), a second CL, and a second GDL. Between the GDL and the PEM, there is a layer of catalyst particles. These catalyst particles can either be supported on carbon or unsupported. The catalyst on the anode of the DMFC is usually binary platinum/ruthenium metal and that on the cathode is platinum. This is the layer where the electrochemical reactions take place and is about 10 μm thick. The PEM is covered with the catalyst layer and then squeezed between two porous, electrically conductive GDLs. The DGL is typically made from carbon cloths or carbon-fiber paper and often a hydrophobic agent such as polytetrafluorethylene (PTFE); it has a porosity of 0.3–0.8 and thickness of 100 μm. The GDL serves three functions: (i) it provides a porous path which ensures good reactant access to all parts of the electro-catalytic layer; (ii) it provides good electrical contact for the transport of electrons to and from
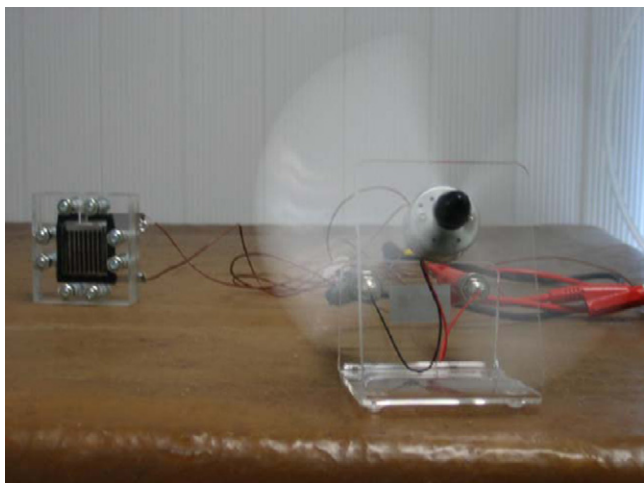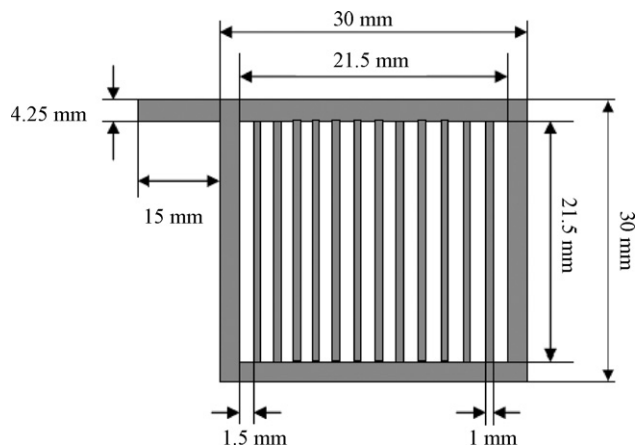

Fig. 2. Dimensions of current-collector with parallel flow-field.

the current-collector plate to the reaction site; (iii) acts as the electrode of the fuel cell.

In our micro DMFC, the most common Nafion™ membrane (N-117) made by Dupont is employed as the PEM and has a thickness of 178 μm. The unsupported catalyst loading on the anode side is 4.0 mg cm^{-2} of Pt/Ru (proportion 1:1), while the catalyst loading on the cathode side is 2.0 mg cm^{-2} of Pt. The MEA has an active area of 5.0 cm^2.

Stainless steel (s316) is employed as the current-collector instead of traditional silicon or graphite in our micro DMFC. This is because stainless steel has much better conductivity and mechanical properties, which are very important for the miniaturization of fuel cells, and can also reduce electrical resistance. Two current-collectors, as shown in Figs. 2 and 3, with different flow-fields are designed for the purpose of comparison. The first design has parallel channels (the exposure ratio is 58%) while the second has an array of holes that serves as passages for fuel and oxidant (the exposure ratio is 36.8%). The first design is expected to improve the flow of fuel in the anode and decrease water flooding in the cathode, while the second design is expected to decrease the contact resistance between the MEA and the collectors due to both the lower exposure ratio and the more rigid structure. Two gaskets made of rubber, each with a thickness of 0.5 mm, are employed to prevent any leakage of methanol from the fuel reservoir.

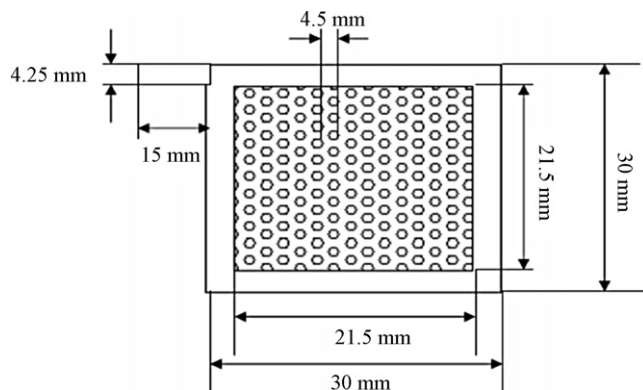Fig. 1. A prototype micro DMFC (overall size: 5 cm × 5 cm × 1.6 cm).

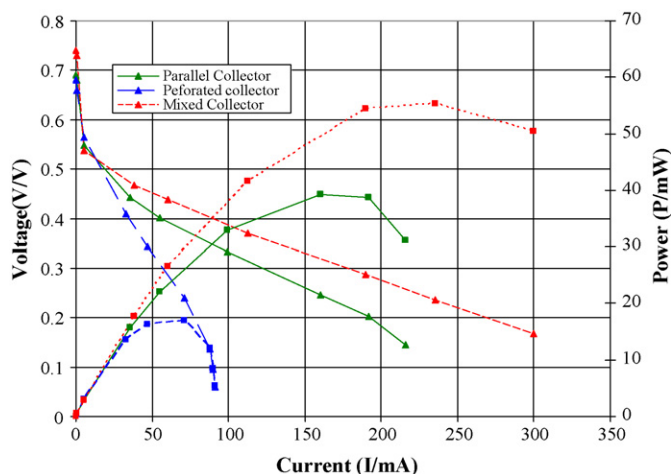Fig. 3. Dimensions of current-collector with perforated flow-field (pore size: 3 mm).

Fig. 4. Performance of micro DMFC with different current-collectors (methanol concentration: 3 wt.%).

Transparent acrylate is used to fabricate the end-plate so that the formation of CO_2 bubbles at the anode and water flooding at the cathode can be observed. A reservoir of about 4.5 cm^3 is built into the anode end-plate to allow direct contact between the anode and the methanol fuel. A window is cut in the cathode end-plate to expose the cathode to the surrounding air. Methanol diffuses into the catalyst layer from the built-in reservoir, while oxygen from the surrounding air diffuses into the cathode catalyst layer through the opening in the cathode fixture.

3. Results and discussion

The performance of the micro DMFC under different operating parameters is measured by a simple set-up. The cell is connected to a variable resistor (load) to draw current. An ammeter is connected in series to the circuit to measure the current drawn and a voltmeter is connected in parallel to the resistor to measure the operating voltage. The current and voltage readings produced by the DMFC for different resistors value ranging from 0.1 to 1000 Ω were recorded. For each set of readings taken, a waiting period of more than 60 s was used to obtain stable voltage and current readings. The operating temperature of the micro

DMFC was measured by a K-type thermocouple used together with an Agilent® Data Acquisition/switch unit.

Prior to experimental testing, the MEA was pre-treated by filling the fuel reservoir with 3 wt.% methanol solution and allowing the cell to stand for 5 h. Such pre-treatment allowed the MEA to be completely hydrated to improve the proton conductivities of both the PEM and the electrode. All experiments were conducted under ambient conditions (21 °C, 1 atm). In the following sections, the performance of the micro DMFC under different parameters is reported.

3.1. Performance of micro DMFCs with different current-collectors

The performance of the micro DMFC with following designs of current-collector combinations is measured.

(i) Both the anode and the cathode are current-collectors with parallel flow-fields (parallel collector).
(ii) Both the anode and the cathode are current-collectors with perforated flow-fields (perforated collector).
(iii) The anode current-collector has parallel flow-field, while the cathode current collector has perforated flow-field (mixed collector).

All the other conditions are the same.

For each cell, the performance with different methanol concentrations is tested. The results for a 3 wt.% methanol solution are shown in Fig. 4. The cell with a parallel collector performs much better than that with a perforated collector. This can be due to the fact that the exposure ratio of the perforated collector is much lower than that of the parallel collector, and thereby decreases the delivery of fuel/oxidant. Furthermore, because the perforated collector is poor at removing the carbon dioxide produced at the anode and the water produced at the cathode, this blocks the access of fuel and air to the active sites and thus degrades system performance. On the other hand, the parallel collector allows easy removal of carbon dioxide gas from the anode and easy flow of water down the cathode along the flow-field channels. Hence, the cell with a parallel collector exhibits better performance. This effect can be observed from the photographs taken by a digital camera (see Figs. 5 and 6).
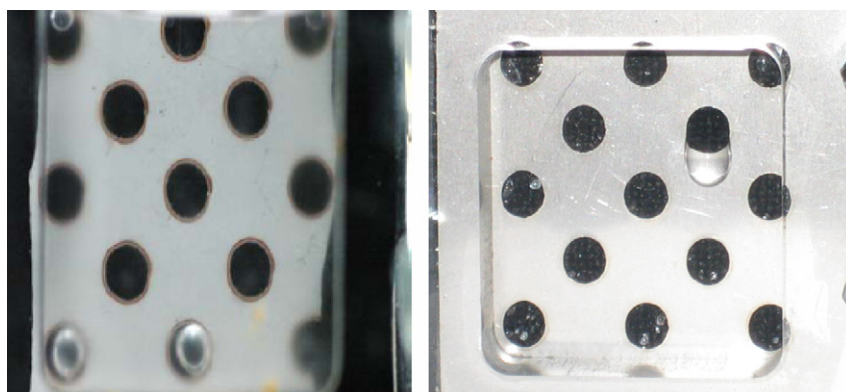

Fig. 5. Photographs of anode CO_2 gas blocking (left) and cathode water flooding (right) at perforated collectors.
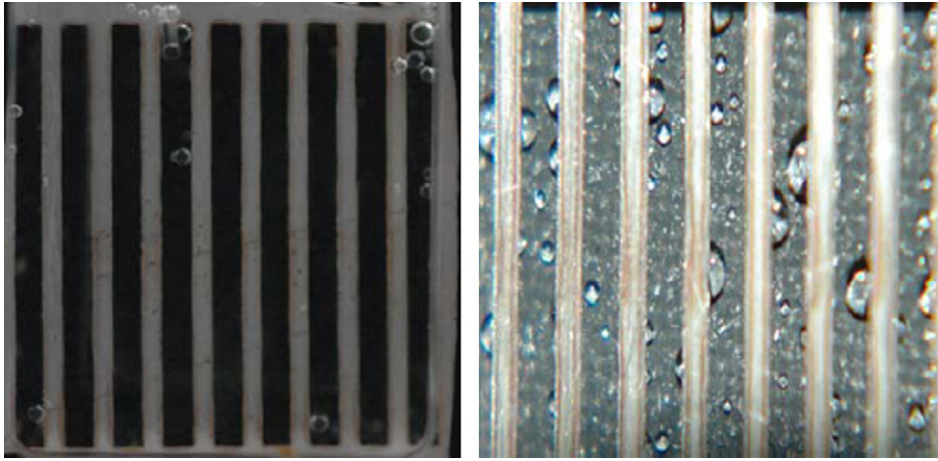
Fig. 6. Photographs showing anode CO_2 gas formation (left) and cathode water formation (right) at parallel collectors.

Contrary to intuition where the mixed collector should have intermediate performance, the mixed collector cell shows the best performance among the three different combinations. This can be explained by the fact that porous media in MEA is more favorable for the delivery of gas oxygen than that of liquid methanol. Furthermore, cathode kinetics is faster than that of the anode, thereby, even if some of the cathode pores is being blocked due to the flooding of water, the supply of air to the cathode is still sufficient for the cathode kinetics to keep up with anode kinetics. Since the perforated current collector, due to its rigid structure, has a better contact with the MEA and reduces contact resistant, its performance is hence better than the parallel collector cell. Similar trends are observed for higher methanol concentration solution (see Fig. 7).

From the above results, it is evident that further studies on the design of the cathode and the anode current collectors have to be done to optimize the performance of the DMFC. Particularly, the focus of the research on the design of the anode current collector should be on improving fuel delivery and CO_2 removal while that of the cathode current collector should be on decreasing Ohmic resistance.
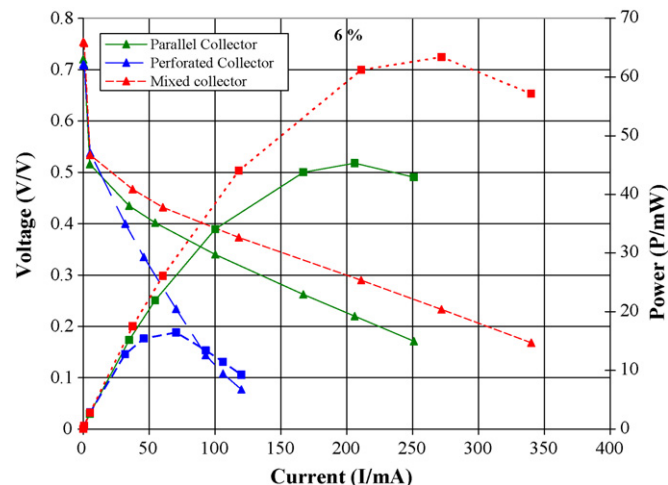
3.2. Performance of the micro DMFC under different methanol concentration

The experiments were conducted for different methanol concentration of 3, 6 and 9 wt.%. The current-collector at the anode has a parallel flow-field, while the current-collector at the cathode has a perforated flow-field, since this kind of current collector-combination produces the best performance, as shown above. The polarization curves obtained for different methanol concentrations are given in Fig. 8. Under ambient conditions, the maximum power output of the micro DMFC is 56, 65 and 52 mW when the concentration of the methanol solution is 3, 6 and 9 wt.%, respectively. These data correspond to an output power density of 11.2, 13 and 10.4 mW cm^{-2}.

From Fig. 8, it is observed that the micro DMFC performs better when the concentration of methanol fuel is increased from 3 to 6 wt.%. This is attributed to the fact that an increase in methanol concentration improves reaction kinetics at the anode and enhances mass transport from the fuel reservoir to the anode catalyst layer. The increase in performance can also be partly due to an increase in the methanol crossover rate at the higher methanol concentration of 6 wt.%. The increase in this rate increases the amount of permeated methanol and thus raises

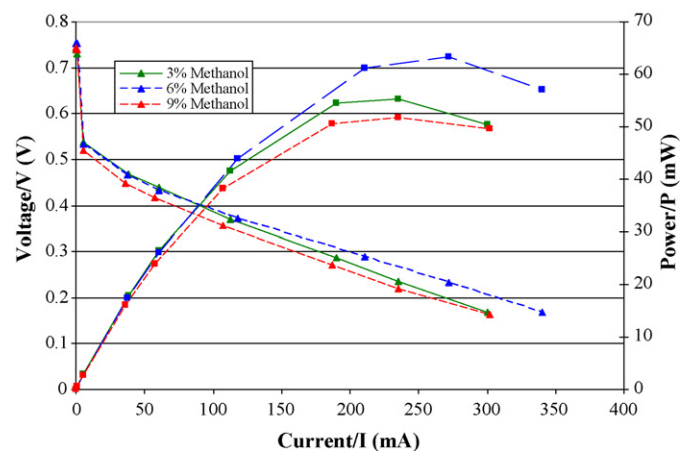Fig. 7. Performance of micro DMFCs with different current-collectors (methanol concentration: 6 wt.%).

Fig. 8. Performance of micro DMFCs with different methanol concentrations.

the cell temperature since the permeated methanol undergoes exothermic oxidation at the cathode. This rise in temperature in turn improves the reaction kinetics at both the anode and the cathode and consequently enhances the performance of the cell.

When the concentration of methanol fuel is further increased from 6 to 9 wt.%, the performance of the micro DMFC decreases. This is because the permeated methanol undergoes oxidation simultaneously with oxygen reduction at the cathode. This generates a mixed potential at the cathode which lowers the potential and thereby the cell performance. In addition, methanol oxidation at the cathode poisons the Pt catalyst which also contributes to the reduction in cell performance. With increase in methanol concentration, this second effect will be more dominant. It is expected that the performance of the cell will be best at an optimum fuel concentration which results from a balance of the two effects.

3.3. Performance of micro DMFC at different operating temperatures

Experiments were conducted at 21, 31 and 41 °C, respectively. The same fuel cell as mentioned above was employed for testing. 3 wt.% methanol was used as the fuel, and the resulting polarization curve is presented in Fig. 9. The system is able to deliver 92.5 mW of electrical power at 41 °C. This corresponds to a voltage of 0.22 V and a current of 370 mA.

Consistent with the discussion for methanol concentration, the data in Fig. 9 demonstrate that an increase in temperature enhances the performance of the DMFC. This can be attributed to improved electrokinetics at both the anode and the cathode at the higher temperature. At the same time, an increase in operating temperature can also improve natural convection due to a higher temperature difference between the MEA and the fuel/environmental gas. It must also be noted, however, that too high temperature will shorten the working life of the fuel cell, and will decrease the efficiency of the micro DMFC due to higher methanol crossover.
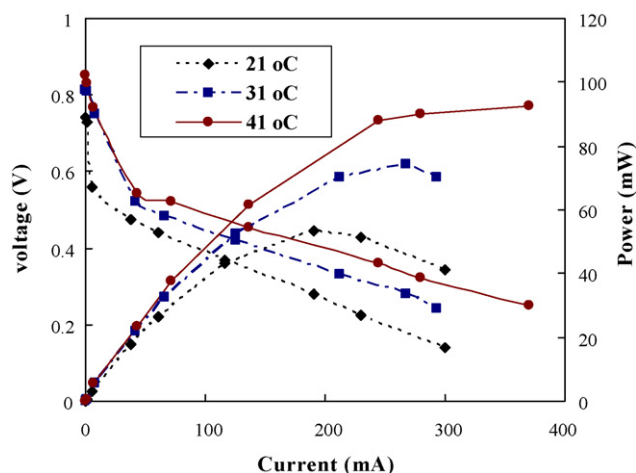

Fig. 9. Performance of micro DMFCs at different operating temperatures (methanol concentration: 3 wt.%).

4. Conclusions

A prototype micro DMFC with an active area of 5 cm^2 has been developed. The system does not have any pump, and the delivery of fuel and air is realized completely by natural convection/diffusion, which significantly simplifies the structure of the micro DMFC and minimizes the cost. The system is able to deliver 92.5 mW at 41 °C, which corresponds to a voltage of 0.22 V and a current of 370 mA. The maximum output power density under ambient conditions is 13 mW cm^{-2}, with a voltage of 0.235 V and a current density of 54.4 mA cm^{-2}, when the concentration of the methanol solution is 6 wt.%.

The performance of the micro DMFC under different operating parameters has been experimentally studied and the following conclusions can be drawn.

(i) A micro DMFC with a parallel flow-field at the anode and a perforated flow-field at the cathode performs best.
(ii) The power output of the micro DMFC varies with methanol concentration and there exists an optimum concentration of 6 wt.% for maximum power output at ambient operating temperature.
(iii) The performance of the micro DMFC increases with temperature.

Although great progress has been achieved, commercialization of the micro DMFC requires much further work such as reducing the methanol crossover, improving the chemical kinetics, and recycling the water generated at the cathode.

Acknowledgement

References

[1] S. Orieux, C. Rossi, D. Esteve, Sens. Acturators A 101 (2002) 383–391.
[2] A.P. London, A.A. Ayon, A.H. Epstein, S.M. Spearing, T. Harrison, Y. Peles, J.L. Kerrebrock, Sens. Acturators A 92 (2001) 351–357.
[3] I.A. Waitz, G. Gauba, S.T. Yang, J. Fluids Eng. 120 (1998) 109–117.
[4] S. Whalen, M. Thompson, D. Bahr, C. Richards, R. Richards, Sens. Acturators A 104 (2003) 290–298.
[5] L. Sitzki, K. Borer, E. Schuster, P.D. Ronney, S. Wussow, The Third Asia-Pacific Conference on Combustion, Seoul, 24–27 June, 2001, pp. 1–4.
[6] W.M. Yang, S.K. Chou, C. Shu, Z.W. Li, H. Xue, Appl. Phys. Lett. 84 (2004) 3864–3866.
[7] G.Q. Lu, C.Y. Wang, T.J. Yen, X. Zhang, Electrochimica 49 (2004) 821–828.
[8] J.R. Yu, P. Cheng, Z.Q. Ma, B.L. Yi, J. Power Sources 124 (2003) 40–46.
[9] Y.M. Kim, K.W. Park, J.H. Choi, I.S. Park, Y.E. Sung, Electrochem. Commun. 5 (2003) 571–574.
[10] P. Dimitrova, K.A. Fredrich, B. Vogt, U. Stimming, J. Electroanal. Chem. 532 (2002) 75–83.
[11] G.W. Zhang, Z.T. Zhou, J. Membr. Sci. 261 (2005) 107–113.
[12] T. Yamaguchi, F. Miyata, S.I. Nakao, J. Membr. Sci. 214 (2003) 283–292.
[13] A.S. Arico, P. Creti, V. Baglio, E. Modica, V. Antonucci, J. Power Sources 91 (2000) 202–209.

[14] J.C. Amphlett, B.A. Peppley, E. Halliop, A. Sadip, J. Power Sources 96 (2001) 204–213.

[15] H. Yang, T.S. Zhao, Electrochim. Acta 50 (2005) 3243–3252.

[16] Y. Takasu, T. Kawaguchi, W. Sugimoto, Y. Murakami, Electrochim. Acta 48 (2003) 3861–3868.

[17] R.G. Allen, C. Lim, L.X. Yang, K. Scott, S. Roy, J. Power Sources 143 (2005) 142–149.

[18] S.Q. Sun, Z.X. Liang, W.J. Zhou, G.Q. Sun, Q. Xin, V. Stergiopoulos, P. Tsiakaras, J. Power Sources 145 (2005) 495–501.

[19] K. Wozniak, D. Johansson, M. Bring, A.S. Velasco, P. Enoksson, J. Micromech. Microeng. 14 (2004) s59–s63.

[20] T. Shimizu, T. Momma, M. Mohamedi, T. Osaka, S. Sarangapani, J. Power Sources 137 (2004) 277–283.