

Stable operation of air-blowing direct methanol fuel cells with high performance

Jun-Young Park^{a,*}, Jin-Hwa Lee^a, Jirae Kim^b, Sangil Han^a, Inseob Song^a

^a Samsung SDI Co. Ltd., 575 Shin-dong, Yeongtong-gu, Suwon-si, Gyeonggi-Do 443-391, Republic of Korea

^b Samsung Advanced Institute of Technology, San 14-1, Nongseo-Dong, Giheung-Gu, Yongin-Si, Gyeonggi-Do 449-712, Republic of Korea

Received 23 August 2007; received in revised form 24 October 2007; accepted 10 December 2007

Available online 17 January 2008

Abstract

A membrane electrode assembly (MEA) that is a combination of a catalyst-coated membrane (CCM) for the anode and a catalyst-coated substrate (CCS) for the cathode is studied under air-blower conditions for direct methanol fuel cells (DMFCs). Compared with MEAs prepared by only the CCS method, the performance of DMFC MEAs employing the combination method is significantly improved by 30% with less methanol crossover. This feature can be attributed to an enhanced electrode|membrane interface in the anode side and significantly higher catalyst efficiency. Furthermore, DMFC MEAs designed by the combination method retain high power density without any degradation, while the CCM-type cell shows a downward tendency in electrochemical performance under air-blower conditions. This may be due to MEAs with CCM have a much more difficult structure of catalytic active sites in the cathode to eliminate the water produced by electrochemical reaction. In addition, DMFCs produced via combination methods exhibit a lower water crossover flux than CCS alternatives, due to the comparatively dense structure of the CCM anode. Hence, DMFCs with a combination MEA structure demonstrate the feasibility of a small fuel cell system employing the low noise of a fan, instead of a noisy and large capacity air pump, for portable electronic devices.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Direct methanol fuel cell; Air-blower system; Catalyst-coated membrane; Catalyst-coated substrate; Water transport; Methanol crossover

1. Introduction

Direct methanol fuel cells (DMFCs) have recently received increased recognition as notable alternatives to present Li-ion batteries for portable electronic devices, such as notebook personal computers, mobile phones and personal digital assistants (PDAs), because of the easy handling of fuel and small system volume capability [1–3]. Since DMFCs use mainly methanol diluted by water to decrease methanol crossover, water tends to diffuse from the anode to the cathode through the membrane under a concentration gradient and the hydraulic pressure of water [4,5]. In addition, oxygen reduces on the cathode side, producing water. Furthermore, protons formed by methanol oxidation in the anode are transported to the cathode together with electro-osmotically dragged water molecules [6]. Accordingly, the cathode side is readily flooded which results in a high back-

pressure in the bipolar plate [7]. Thus water management is one of the main issues with DMFCs that must be overcome for their application in portable electronic devices [8].

In general, a large excess of stoichiometric air is necessary to avoid cathode flooding during DMFC operation. Most of the water will be carried away by high air flow rates at normal DMFC operating conditions. On the other hand, such flow rates make it difficult to design small fuel cell systems that require a large capacity air pump with substantial parasitic power loss [9]. There would also be a high level of noise due to operating an air pump with high back pressure. This would not be agreeable to users of portable electronic devices. Hence, the development of DMFCs that operate satisfactorily under air-blower conditions becomes necessary.

The fabrication method and process conditions of the membrane electrode assembly (MEA) influence DMFC performance, which depends significantly on the electrocatalytic activity and efficiency of each electrode. To operate DMFCs under air-blower conditions, cathode electrodes in the MEA should be designed with consideration to two factors. One is elimination of the water

* Corresponding author. Tel.: +82 31 210 7806; fax: +82 31 210 7374.
E-mail address: jy3000.park@samsung.com (J.-Y. Park).

produced by electrochemical reaction with stable operation; the other is supplying air to catalytic active sites to produce the required amount of power [10]. In this study, the new concept of MEA structure is developed for air-blowing DMFCs. A comparative study of the effect of the MEA preparation method on the DMFC performance is undertaken for an air-blower system. The influence of the microstructure of the electrodes on their electrochemical performance is investigated at various operation conditions. The investigation also includes short-term stability tests for assessing the effect of air blowing on the performance of DMFCs.

Additionally, in order to examine the phenomena occurring at the cathode, mass balance research is performed through an understanding of the mass-transport phenomena of MEAs, such as methanol crossover and water transport through the membrane [11,12].

2. Experimental

2.1. Preparation of diffusion and catalyst layers

A mixed suspension of carbon powder (Vulcan XC-72, Cabot), polytetrafluoroethylene (PTFE, 60 wt.% emulsion, E-TEK), and isopropyl alcohol (IPA) was sprayed on to 400- μm thick carbon paper (GDL 10 series, SGL carbon group) from the gas-diffusion layer (GDL) of both electrodes. The prepared GDLs were then sintered at 350 °C for 1 h. The catalyst inks were made from the PtRu black (HiSPEC 6000, Johnson Matthey) for the anode and Pt black (HiSPEC 1000, Johnson Matthey) for the cathode and mixed with distilled water, Nafion solution (20 wt.%, Dupont), and IPA. The Pt loading on both electrodes was 6 mg cm⁻² and controlled by weight. The Nafion ionomer content in all anode catalyst layers was controlled at 12.5 wt.%. To find the cathode electrode appropriate for air-blower-type

DMFCs, the Nafion content for the cathode catalyst layers was systemically varied from 0 to 40 wt.% in the catalyst-coated substrate (CCS) type MEAs. The optimized Nafion content for CCS-type MEAs was then applied to fabricate the catalyst-coated membrane (CCM) type MEA and the combination MEA was prepared using the CCM for the anode and the CCS for the cathode.

2.2. Preparation of CCS-type MEAs

The prepared catalyst inks were directly coated on the GDLs for the anode and cathode, and then dried at an oven temperature of 110 °C. In order to form an MEA, two catalyst-coated GDLs were then pressed on to a membrane (Nafion 115, Dupont) at 130 °C and 0.2 tonnes cm⁻². The microstructures and morphologies of cross-sectioned MEAs were examined by means of scanning electron microscopy (SEM, Hitachi S-4500).

2.3. Preparation of CCM-type MEAs

For the preparation of the CCM, the prepared catalyst ink was sprayed on to a PTFE transfer film. The mixtures on the PTFE film were transferred on to a Nafion membrane by hot pressing at 130 °C under a pressure of 0.5 tonnes cm⁻². Formation of the MEA was undertaken by hot-pressing each of the prepared GDLs on to the catalyst-coated membranes at 130 °C and 0.2 tonnes cm⁻².

2.4. Preparation of combination MEAs from anode CCM and cathode CCS

The combined MEAs were prepared by hot-pressing the anode CCM and the cathode CCS together, as described in

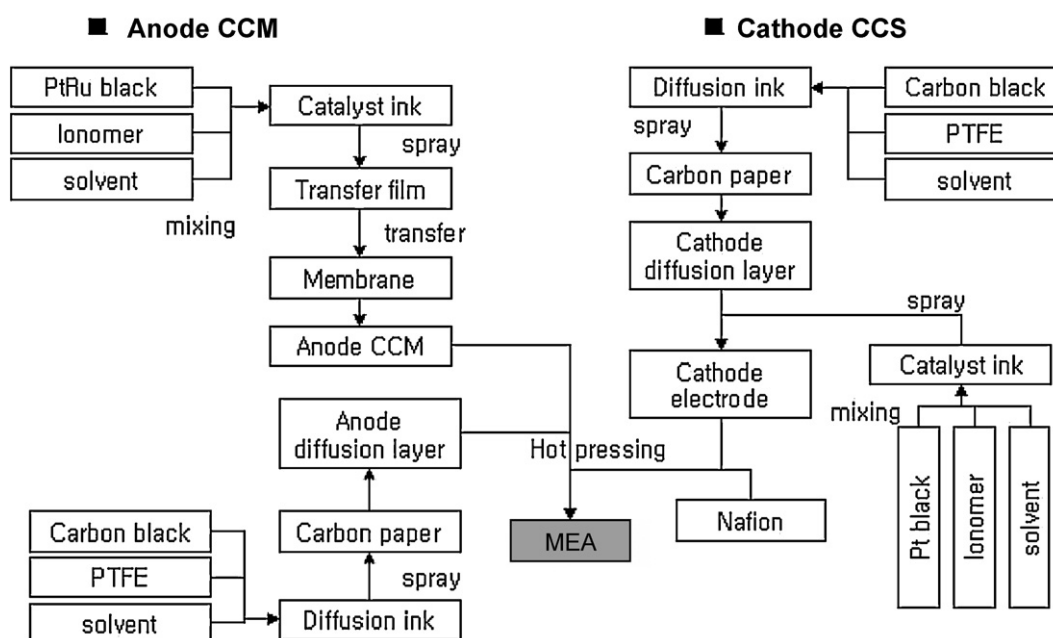


Fig. 1. Schematic diagram for preparation of a combination MEA prepared using an anode CCM and a cathode CCS.

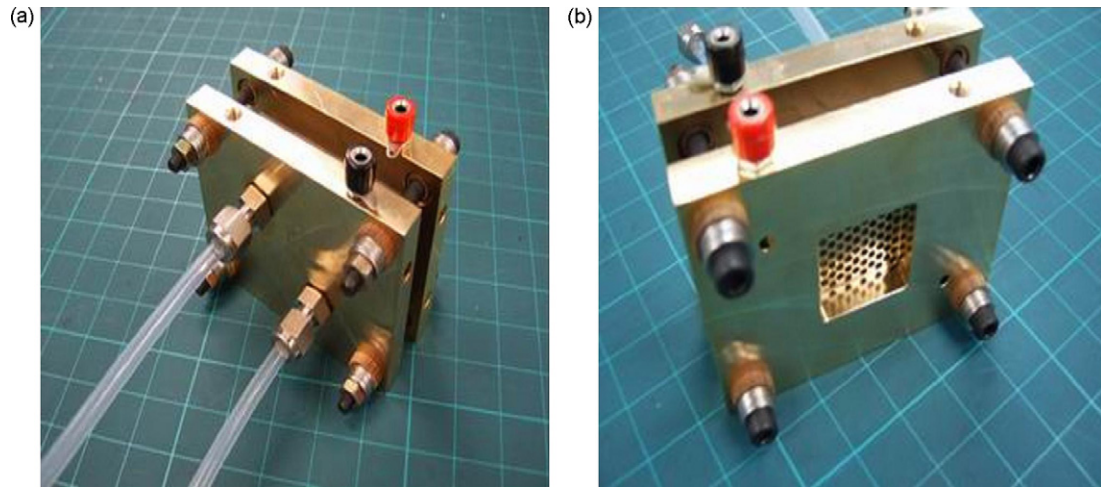


Fig. 2. Experimental single-cell hardware assembly for cathode: (a) an active, closed air supply path used in this work and (b) a conventional passive, air-breathing path.

Sections 2.2 and 2.3, respectively. A schematic diagram of the process is given in Fig. 1.

2.5. Fuel cell performance

All measurements of the electrochemical performance of DMFCs were undertaken with an Arbin (USA) fuel cell test station. The active area of the cell was 10 cm^2 ; the single-cell hardware assembly is shown in Fig. 2. A closed, active-type cell hardware (Fig. 2(a)) for the cathode was employed to investigate the electrochemical performance of the cell with respect to the air flow rate, since a conventional passive, air-breathing version (Fig. 2(b)) was too complicated to quantify the amount of dry air in a real system. In order to simulate the air-blower DMFC condition, however, a bipolar-plate design consisting of parallel grooves on a graphite block was used to eliminate the effect of backpressure in the cathode, as shown in Fig. 3. The bipolar plate for the anode had a serpentine-type flow-

field design. The cathode channels were 1 mm wide and 2 mm deep, and the anode channels were 0.7 mm wide and 0.8 mm deep.

For the DMFC measurements, the anode and cathode were fed with 1.0 M methanol solution and dry air, respectively, at a flow rate with a stoichiometry of three without backpressure. The cell was raised to the desired temperature by an electrical heater placed in the current-collector plate. The electrochemical performance of DMFCs was measured at 50, 60, and $70\text{ }^\circ\text{C}$. The power density was determined from current–voltage curves. To investigate of the short-term stability of cells, the current–voltage characteristics of the DMFCs were investigated over 2 weeks (1–2 tests per day). In addition, to examine the effect of the fabrication methods on the mass-transport properties of DMFC MEAs, mass balance research were conducted at 100 mA cm^{-2} and $50\text{ }^\circ\text{C}$ for 6 h. Details on equipment fabrication and measurements may be found in a previous study [13].

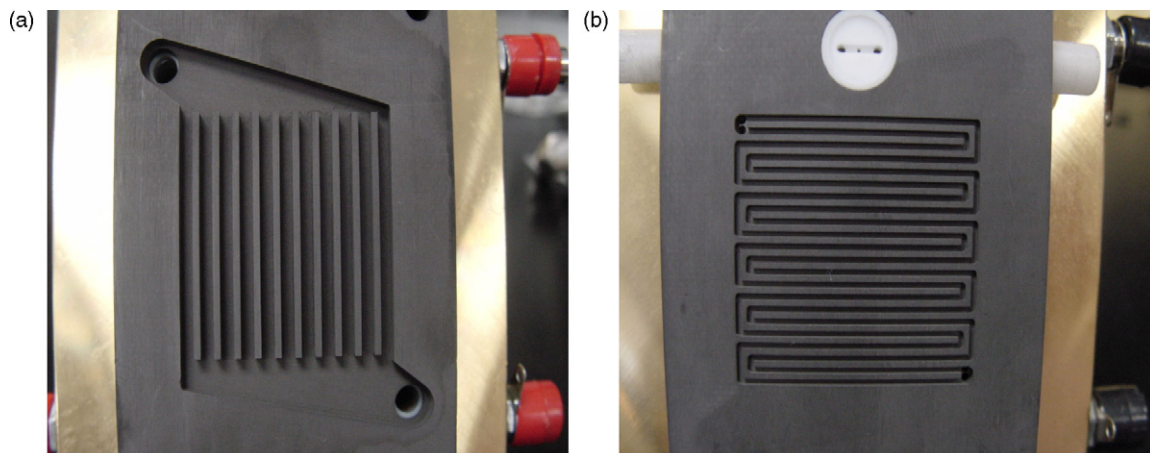


Fig. 3. Design of bipolar plates for: (a) cathode, parallel-type flow field and (b) anode, serpentine-type flow field.

3. Results and discussion

3.1. Electrochemical performances of CCS-type MEAs

In order to increase the interfacial bonding and thereby from a strong proton-conducting ionomer network between the catalyst layer and the membrane, Nafion ionomer was spread on to the cathode catalyst layer. Optimization of the ionomer amount is essential to eliminate the water produced by the electrochemical reaction without the adverse effect of water flooding of the cathode [10]. The effect of the Nafion ionomer in the catalyst layers on the electrochemical performance of DMFCs is shown in Fig. 4. Notably, an increase in ionomer content until around 16 wt.% resulted in significantly improved cell performance, with power densities up to 87 mW cm^{-2} at 0.4 V and 70°C . Zero ionomer content in the catalyst layers gave the poorest performance for all MEAs. This may be explained by the enhanced mobility of protons in the catalyst layer since the ionomer is an ionic conductor. Further increase in the Nafion ionomer content resulted in decreased performance of DMFCs due to the increase in interfacial resistance between the catalyst layer and the membrane caused by the excessive ionomer content. Current density–voltage curves at 70°C are displayed in Fig. 5 in terms of ionomer content. The results indicated that the ionomer content exerts a marked effect on the electrochemical performance of MEAs, particularly in the mass-transport region.

Scanning electron micrographs of cross-sections of the CCS-type MEA are presented in Fig. 6. The overall thickness of the catalyst layer was not discernible by SEM cross-sectional analysis. Also, the interfacial boundary of the catalyst layer and the porous diffusion layer was non-uniform and non-distinctive. The loss of catalytic active sites was significant by incorporation of particles into the porous diffusion layer. Thus, there is still room for increasing the power density of DMFCs by improving the degree of utilization of catalytic materials using alternative MEA structures.

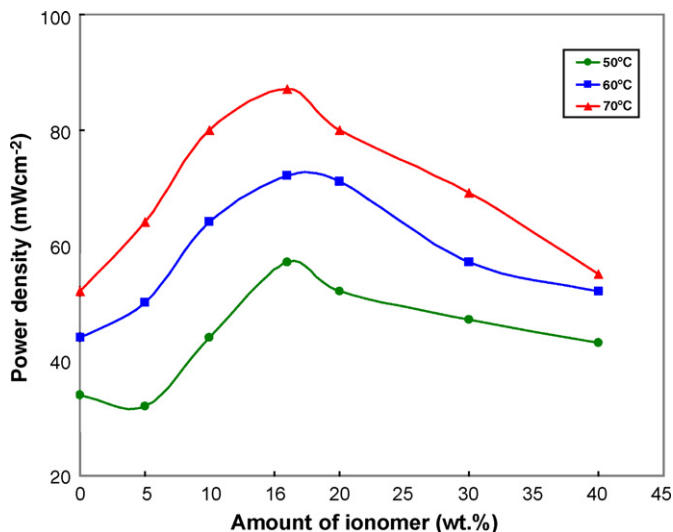


Fig. 4. Influence of Nafion ionomer in catalyst layers on power densities at a cell voltage of 0.4 V and a temperature of 50, 60, and 70°C .

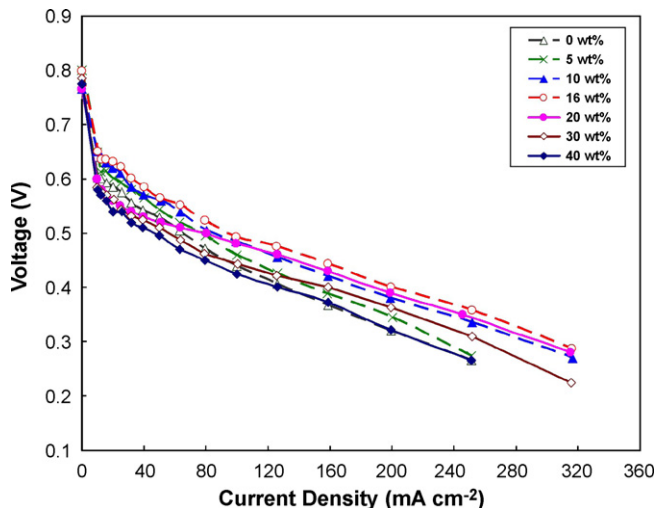


Fig. 5. Current density–voltage polarization curves at cell temperature of 70°C in terms of amount of ionomer in cathode catalyst layer.

3.2. Electrochemical performance of CCM-type MEAs

In order to fabricate high-power MEAs through maximizing catalyst utilization at a low loading of precious metal, MEAs were prepared by the decal method after catalyst slurries were coated on the thin PTFE film. Scanning electron micrographs of the MEA with CCM showed a more continuous and uniform electrode surface than that of MEAs prepared by the CCS method, see Fig. 7. At the anode side, the overall thickness of the catalyst layer was $30\text{--}40 \mu\text{m}$, as determined by SEM cross-sectional analysis and equally fine surfaces were seen. For the cathode side, the catalyst layer thickness was almost $10\text{--}25 \mu\text{m}$ and it had a curved surface shape.

The current–voltage polarization characteristics of CCM-type MEAs investigated on a daily basis are given in Fig. 8. The MEAs exhibited gradually decreasing behaviour in performance each day. The performance was apparently characterized by steadily distinct potential losses at high current density regions due to mass-transport limitations. This decline, which occurred

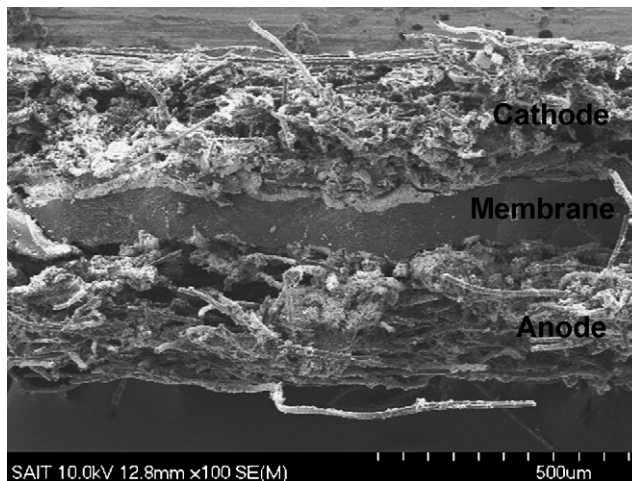


Fig. 6. Scanning electron micrograph of a cross-sectioned MEA prepared by catalyst-coated substrate (CCS) method.

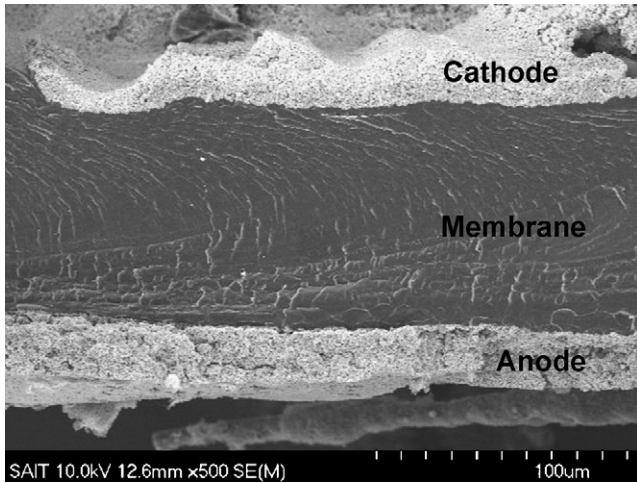


Fig. 7. Scanning electron micrograph of a cross-sectioned MEA prepared by catalyst-coated membrane (CCM) method.

within several days might be due to a gradual build-up of water by methanol crossover, water crossover, and the oxygen reduction reaction at the cathode side. That is, these phenomena could be attributed to the morphologically and structurally limited accessibility of the air supply toward the embedded cathode electrode to remove water molecules in air-blow type systems. This observation was somewhat affirmed by investigations of performance recovery using nitrogen purging for the cathode in degraded CCM-type MEAs. As seen in Fig. 9, a degraded MEA with CCM had a power density of 80 mA cm^{-2} at 0.4 V and 50°C after nitrogen purging of the cathode for 5 h. Rather, this MEA displayed better DMFC performance than that of the initial state after nitrogen purging. The performance decreased within several days, however, and exhibited severe mass-transport limitation at high current densities.

To monitor the short-term operational stability of the CCM-type DMFC MEA, changes in the current density were measured in the potentiostatic mode (at 0.4 V). As shown in Fig. 10,

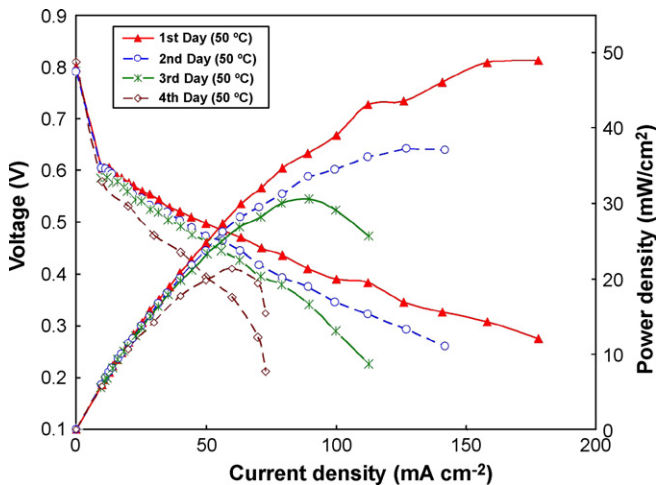


Fig. 8. Downward tendency of power density in polarization curves of CCM-type MEAs investigated on a daily basis.

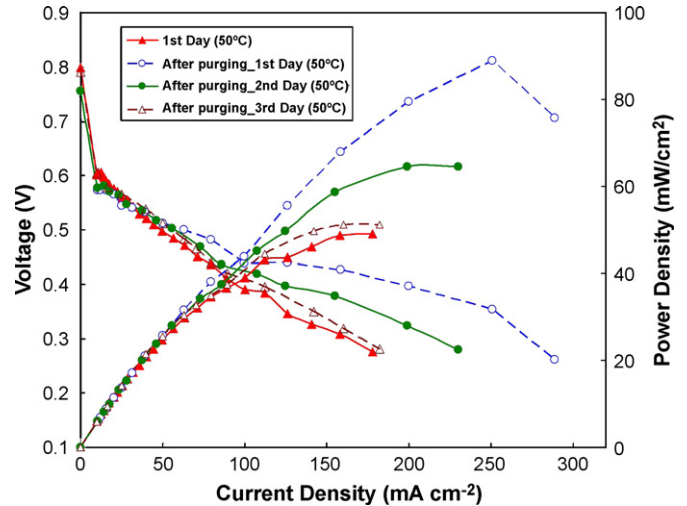


Fig. 9. Recovery of cell performance as maximum power density in polarization curves after overnight purging of cathode nitrogen.

the current density of the DMFC at 0.4 V was maintained at 160 mA cm^{-2} with fluctuations of 11% for 4 h of operation. It rapidly decreased, however, due to cathode water flooding under an air-blowing condition after an applied potential of 0.4 V for 4 h. Some variability in the individual performance of the cells notwithstanding, the current density declined dramatically to 100 mA cm^{-2} during continuous operation for 6 h. The fluctuation in current density of 20 mA cm^{-2} might be caused by the sporadic production of water molecules, which disturbed the supply of the air at the cathode side. These results indicated that the water molecules produced in the cathode almost blocked the electrode path from supplying air under an air-blowing condition. The optimization of the CCM-type MEA for blower-type fuel cell systems still requires the resolution of water management issues through additional systematic research and development.

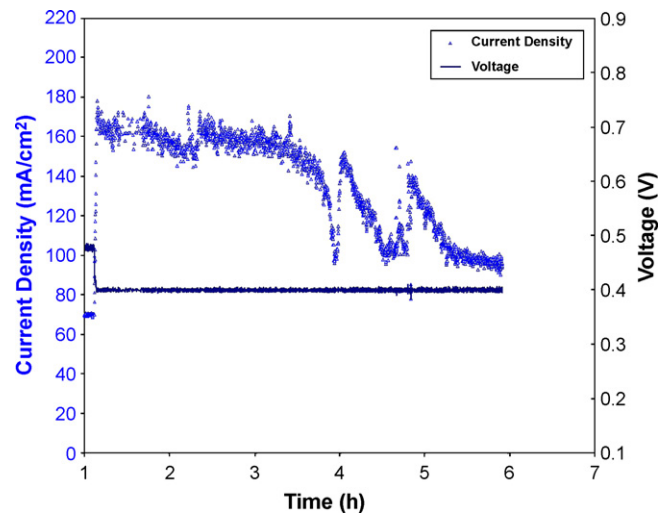


Fig. 10. Operational stability of CCM-type MEA, measured for 6 h at 50°C in constant voltage (0.4 V) operations.

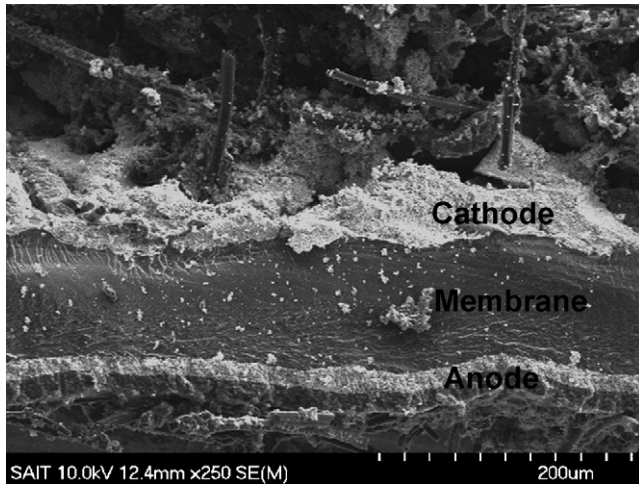


Fig. 11. Scanning electron micrograph of a cross-sectioned combination MEA prepared by anode CCM and cathode CCS.

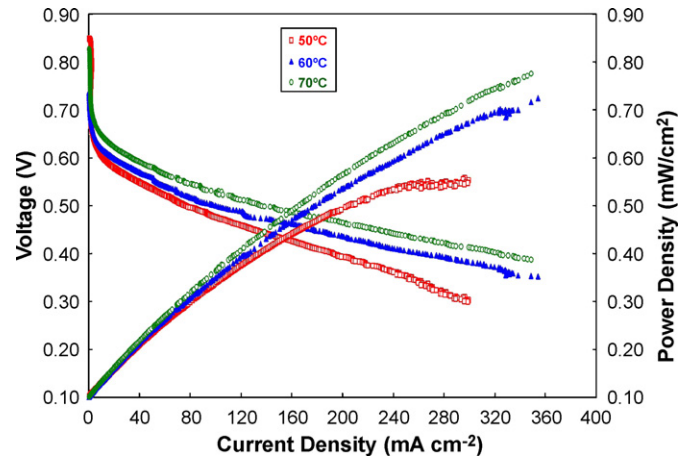


Fig. 12. Electrochemical performance of DMFCs prepared using combination structures of anode CCM and cathode CCS.

3.3. Electrochemical performance of combination MEAs fabricated by anode CCM and cathode CCS

MEAs were made by combination of a CCM for the anode and a CCS for the cathode, since a thin dense cathode layer prepared by CCM might make difficult the accessibility of air, the removal of water produced by methanol oxidation and the oxygen reduction reaction, as confirmed in the previous Section. On the other hand, the anode was fabricated by the CCM method to obtain high power density through maximizing catalyst utilization. A SEM image of the cross-section of the combination MEA is shown in Fig. 11. The anode side seemed to be rela-

tively uniform over the entire surface. On the other hand, the carbon paper in the cathode side mostly contained macropores with loosely populated carbon particles. This morphological structure might have a beneficial influence on removing the water produced by supplying adequate air to catalyst active sites.

The electrochemical performance of DMFC MEAs prepared using the combined structure are given in Fig. 12. Cells with the combined structure achieved a power density of 130 mW cm^{-2} at 0.4 V and 70°C , which was much higher than the 43 mW cm^{-2} of cells with CCS. The improvement of the DMFCs by using the combined structure might be due to the enhanced anode-electrode|membrane interface and highly effec-

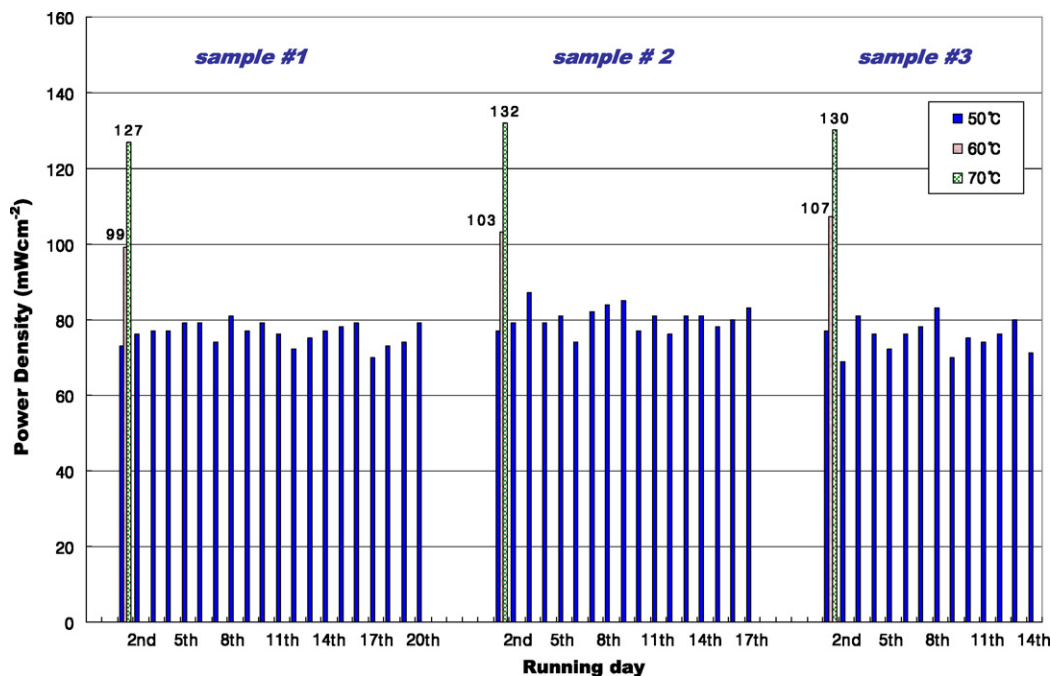


Fig. 13. Changes in power density of DMFCs prepared using combination methods measured at 0.4 V and $50, 60$ and 70°C on a daily basis (samples #1, #2, and #3 made by same procedure to obtain reproducible results).

tive electrochemical reaction sites in the gas-diffusion layers [10,14]. Additionally, DMFCs retain high power density without any degradation in the daily investigation for 2 weeks, as shown in Fig. 13.

3.4. Comparison of methanol and water crossover for MEAs prepared by CCS methods and by combination methods

In general, accurate water exhaust control is crucial in developing air-blown type DMFCs with high specific energy [13]. In order to understand the phenomena that occur at the cathode, mass balance research is a practical way of characterizing the mass-transport phenomena of MEAs, such as methanol crossover, water crossover and methanol utilization efficiency. The flux of methanol that undergoes electro-oxidation in DMFC MEAs can be predicted by Faraday's law [15]:

$$J_{\text{CH}_3\text{OH}} = \frac{i_{\text{cell}}}{6F} \quad (1)$$

where $J_{\text{CH}_3\text{OH}}$ is the molar flux of methanol; i_{applied} is the current density; F is 96 500 (Cmol^{-1}). The fuel utilization efficiency defines the ratio of the amount of reacted methanol for producing current to the total methanol supplied.

The cells prepared using the combination method gave a higher methanol utilization efficiency of 66% while CCS-type DMFC MEAs showed a methanol utilization of around 58% at 50 °C and 100 mA cm^{-2} . Also, water is transported from the anode to the cathode by electro-osmotic drag of protons during the operation of the fuel cell [4,5]. If the water transport coefficient is defined as the water flux through the membrane normalized by the protonic flux [5], the resulting values are 3.15 and 0.81 for MEAs prepared by CCS and combination methods, respectively. The increase in water flux would eventually cause more severe problems with water management in air-blown DMFCs.

Additionally, the fuel-to-electricity conversion rate (FECR) of the DMFC is defined by

$$\text{FECR}(\text{Wh cm}^{-3}, \text{Wh g}^{-1}) = \frac{V i t}{q_{\text{CH}_3\text{OH}}} \quad (2)$$

where V , i , t , and $q_{\text{CH}_3\text{OH}}$ are voltage, current, time and the amount of consumed methanol, respectively. The measured energy conversion rates at 50 °C and 100 mA cm^{-2} are around 1.19 and 1.16 Wh cm^{-3} for DMFCs prepared using the combined structure and CCS, respectively. The higher FECR of the combination MEAs might be due to higher power density with less methanol crossover, in comparison with that for CCS MEAs.

The relative values of methanol crossover, water crossover, and FECR for the DMFCs with CCS and combination methods are given in Fig. 14. It is interesting to note that the two types of MEA showed a large difference in the relative values of water crossover, while the differences in methanol crossover and FECR were relatively small. This means that DMFCs with combination methods experience lower water crossover, due to the comparatively dense structure of the anode catalyst layer,

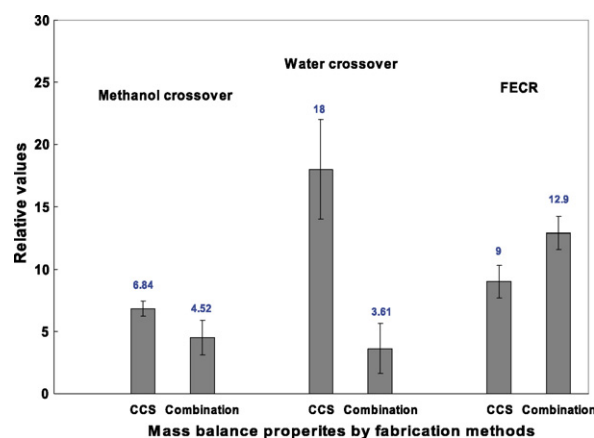


Fig. 14. The relative values of methanol crossover, water crossover, and FECR for the DMFCs with CCS and combination methods.

and that this feature resulted in stable operation of DMFCs with high power density.

4. Conclusions

With optimization of the MEA structure through various fabrication methods, stable operation of DMFCs with high power density were possible under air-blown conditions. As a design parameter of MEA fabrication, the amount of Nafion ionomer had a significant effect on the power density of DMFCs. The ionomer loading that gave the overall best cell performance in a DMFC prepared by CCS is around 16 wt.%.

While CCM-type MEAs showed gradually decreasing behaviours in performance investigated on a daily basis, MEAs prepared using both anode CCM and cathode CCS maintained a high power density without any performance degradation for 2 weeks. This might be due to the enhanced electrode|membrane interface at the anode and improved accessibility of air supply toward the embedded electrode to remove water molecules at the cathode. This explanation was also confirmed by the study of the performance recovery of the degraded CCM-type MEA by nitrogen purging of the cathode. Furthermore, DMFCs prepared with combination methods displayed a lower water crossover flux than CCS due to the comparatively dense structure of the CCM anode, which resulted in stable operation with high power density.

Acknowledgments

This work was supported by both the Energy Laboratory of Samsung SDI and the Energy and Materials Research Laboratory of Samsung Advanced Institute of Technology (SAIT) for development of a mobile fuel cell system. The authors thank all members involved in the fuel cell project in Samsung SDI and SAIT.

References

- [1] X. Ren, M.S. Wilson, S. Gottesfel, J. Electrochem. Soc. 143 (1996) L12–L15.

- [2] H. Chang, J.R. Kim, J.H. Cho, H.K. Kim, K.H. Choi, *Solid State Ionics* 148 (2002) 601–606.
- [3] K. Scott, W.M. Taama, P. Argyropoulos, *J. Power Sources* 79 (1999) 43–59.
- [4] T. Schaffer, T. Tshinder, V. Hacker, J. Basenhard, *J. Power Sources* 153 (2006) 210–216.
- [5] F. Liu, G. Lu, C.-Y. Wang, *J. Electrochem. Soc.* 153 (2006) A543–A553.
- [6] X. Ren, W. Henderson, S. Gottesfeld, *J. Electrochem. Soc.* 144 (1997) L267–L270.
- [7] B.S. Pivovar, W.H. Smyrl, E.L. Cussler, *J. Electrochem. Soc.* 152 (2005) A53–A60.
- [8] M. Baldauf, W. Preidel, *J. Power Sources* 84 (1999) 161–166.
- [9] D. Kim, E. Cho, S.-A. Hong, I.-H. Oh, H. Ha, *J. Power Sources* 130 (2004) 172–177.
- [10] J. Xie, K.L. More, T.A. Zawodzinski, W.H. Smith, *J. Electrochem. Soc.* 151 (2004) A1841–A1846.
- [11] X. Ren, S. Gottesfeld, *J. Electrochem. Soc.* 148 (2001) A87–A93.
- [12] K. Scott, W.M. Taama, P. Argyropoulos, K. Sundmacher, *J. Power Sources* 83 (1999) 204–216.
- [13] S. Kang, S.J. Lee, H. Chang, *J. Electrochem. Soc.* 154 (2007) B1179–B1185.
- [14] H. Tang, S. Wang, M. Pan, S.P. Jiang, Y. Ruan, *Electrochim. Acta* 52 (2007) 3714–3718.
- [15] M. Faraday, *Experimental Researches in Electricity*, Series IV, Royal Institution, London, 1833, pp. 119.