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On mass transport in an air-breathing DMFC stack

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SUMMARY

An 8-cell air-breathing direct methanol fuel cell (DMFC) stack with the active area of 5 cm^2 of each cell has been developed. Stainless steel plates of 500 μm thickness with flow channels were fabricated using photochemical etching method as the current collectors. Different conditioning methods for membrane electrode assembly (MEA) activation were discussed. With proper control of water crossover to the cathode, cathode flooding was avoided in the DMFC stack. Methanol crossover at open circuit voltage (OCV) in the air-breathing DMFC was measured. Further, it was found that flow maldistribution might occur in the parallel flow field of the stack, making carbon dioxide gas management at the anode necessary. Using humidified hydrogen in the anode with a high flow rate, the oxygen transport limiting current density was characterized and found to be sufficient in the air-breathing cathode. The stack produced a maximum output power of 1.33 W at 2.21 V at room temperature, corresponding to a power density of 33.3 mW cm^{-2}. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS: DMFC; air breathing; cathode flooding; water management; methanol crossover; mass transport limitation

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) are promising power sources for portable applications with power requirements ranging from micro Watts to several hundred Watts (Narayanan and Valdez, 2003; Ren *et al*., 2000; Weber *et al*., 2003; Arico *et al*., 2001; Lu *et al*., 2004; Yang and Manthiram, 2004). Compared to hydrogen proton exchange membrane fuel cells, DMFCs are much simpler in construction without the need for bulky auxiliary components, such as a fuel

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processor and a humidifier in the system. Further simplification in the auxiliary parts of a DMFC system to minimize the power consumption includes air-breathing operation of the cathode (Shimizu *et al.*, 2004; Liu *et al.*, 2004; Kim *et al.*, 2004; Chen and Yang, 2003).

Excessive water is present in the DMFC cathode due to water production at the cathode and water transport from the anode to the cathode by electro-osmotic drag and forward diffusion from the anode to the cathode. As reported in the literature on air-breathing DMFCs (Liu *et al.*, 2004; Chen and Yang, 2003), cathode flooding is a serious issue that significantly degrades cell performance. The traditional method using high air flow rate to prevent cathode flooding in air-circulating DMFCs is not possible in air-breathing DMFCs, making research on MEAs with low water crossover especially important. In addition, since air is passively delivered from the ambient in air-breathing cells, it is critical to verify if the oxygen transport is adequate to avoid a premature mass transport limitation.

In this paper, an 8-cell air-breathing DMFC stack was developed. By utilizing the water backflow from the cathode to the anode through the membrane, cathode flooding was avoided. Methanol mass transport including methanol crossover was studied. Oxygen transport phenomenon in the air-breathing cathode was characterized electrochemically.

2. EXPERIMENTAL

Cell design: Stainless steel plates with a thickness of 500 μm were used as bipolar plates to collect current. Flow channels were fabricated in the plates by photochemical etching method. The effective area of each cell was 5 cm^2 and total gross area was 33 mm × 33 mm. In order to minimize contact resistance and prevent corrosion, a gold layer of 300 nm in thickness was deposited on the interior side of each stainless steel plate. A rectangular polycarbonate plate (145 mm × 33 mm × 5.6 mm) was fabricated with liquid feeding channels to support 8 individual cells (4 cells on each side). The gross volume of this 8-cell stack is about 34 cm^3. Figure 1 shows the flow path arrangement for the 8-cell stack. The flow paths are parallel with the length of each flow channel being equal to ensure uniform flow distribution to each cell.

MEA preparation: Catalyst-coated membrane (CCM) was prepared by the decal method. Unsupported Pt/Ru black (HiSPEC 6000, Pt:Ru = 1:1 atomic ratio, Alfa Aesar) and

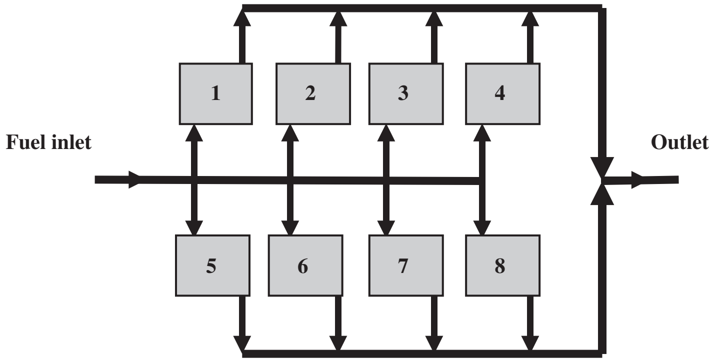

Figure 1. Parallel flow paths for eight cells in a stack.

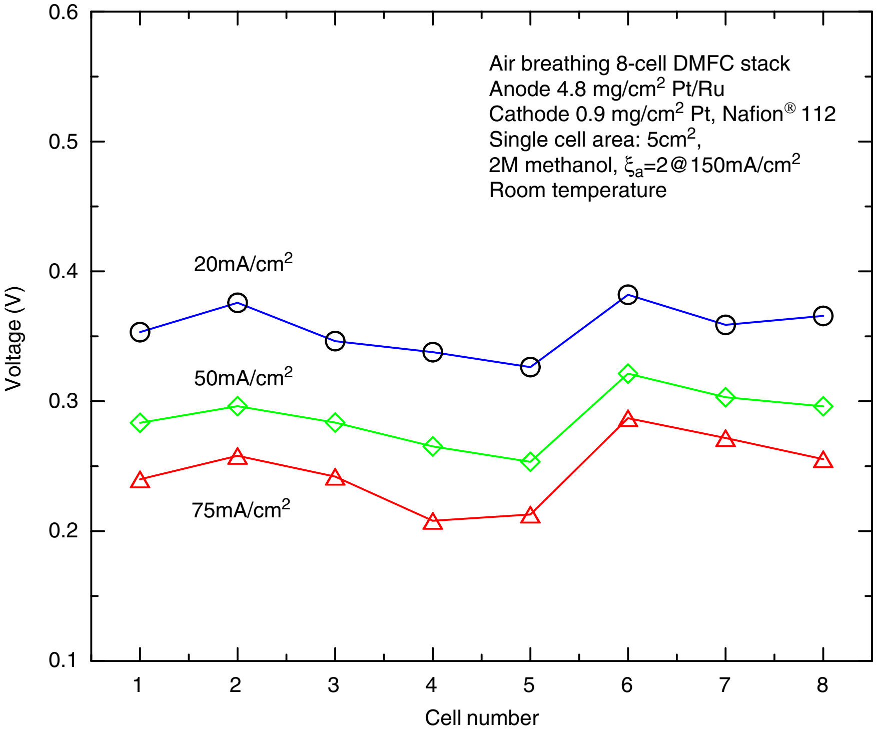

Figure 2. Voltage distribution after humidified hydrogen conditioning.

carbon-supported Pt catalyst (40% Pt/Vulcan XC72; E-TEK) were used as catalysts for the anode and cathode, respectively. The catalysts were first wetted by a small amount of de-ionized (DI) water, following by adding iso-propanol (IPA), ionomer solution (5 wt% Nafion solution, 1100 EW, Dupont) and ethylene glycol. After sufficient magnetic stirring, the mixture ink was treated ultrasonically for 1–2 min and then coated on a Teflon substrate. The coated Teflon film was dried for several hours in an oven at 80°C before hot-pressed to a pretreated Nafion 112 membrane at 125°C and 100 atm for 3 min. The loadings of Pt/Ru and Pt/C in the catalyst layer of anode and cathode were 4.8 and 0.9 mg cm^{-2}, respectively.

Twenty weight per cent wet-proofed carbon paper (Toray 090) of 0.26 mm thickness was used as the backing layer for the anode. A mixture solution containing Vulcan XC72R carbon black and 40 wt% of Teflon (TFE 30, Dupont) was coated on the carbon paper to form a microporous layer (MPL) of approximately 30 μm in thickness. The gas diffusion layer (GDL) for the cathode is a carbon cloth, on which a micro porous layer containing carbon black and Teflon are coated.

Test apparatus: A digital pump (Series I digital pump, Laballiance) with controllable flow rate ranging from 0.01 to 10 ml min^{-1} was used to deliver aqueous methanol solution. In this work, 2 M methanol solution was used to test cell performance. The 8-cell DMFC was tested at room temperature without active heat management. A multi-channel electronic load system (Arbin) in the galvanodynamic polarization mode was used to measure polarization curves.

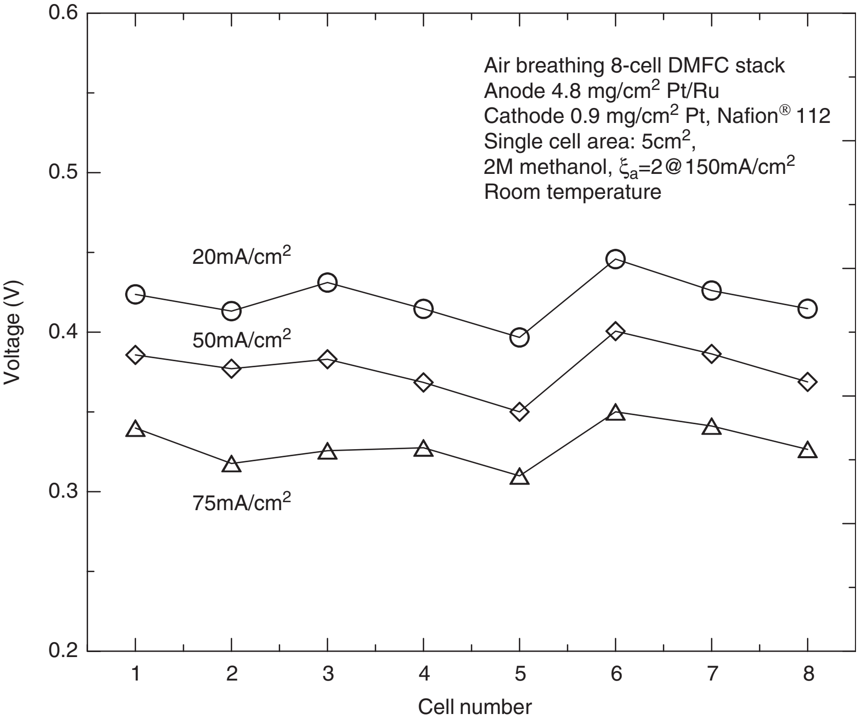

Figure 3. Voltage distribution after conditioning with the shielded cathode.

3. RESULTS AND DISCUSSIONS

MEA conditioning methods: Several methods were used to activate the catalysts in this 8-cell air breathing DMFC stack. Polarization curves were scanned from open circuit voltage to 0.1 V repeatedly for 2 h to condition the MEAs at room temperature. Following the voltage scan conditioning, cell performance was found to increase slightly. In another method, humidified hydrogen was used to condition the MEA for 2 h. After the conditioning, 2 M methanol solution was supplied to the cells to remove residual hydrogen in the channel for an additional 10 min. The cells were then tested, and the performance was found to improve somewhat. Figure 2 shows the voltage distribution for 8 individual cells at different current density after conditioning using humidified hydrogen. At $50\,\mathrm{mA\,cm^{-2}}$, the averaged voltage is only 289 mV. To further improve performance, a third conditioning method was used, in which the outer surfaces of all cathodes were sealed by a film. Thus, air was not supplied to the shielded cathode. A voltage of 1 V (having the same polarity as an operating DMFC) was then applied to each individual cell from an external power supply for about 1 h. In this process, surface oxides on the anode catalyst are reduced by electrochemically generated hydrogen. After this conditioning, the cells were maintained at constant current discharge for 10 min to remove residual hydrogen in the anode. Figure 3 depicts the voltage distribution for the 8 individual cells at three different current densities at steady state by fixing the current density. The little difference between the performance of cells 1 and 5, as well as between the performance of cells 2

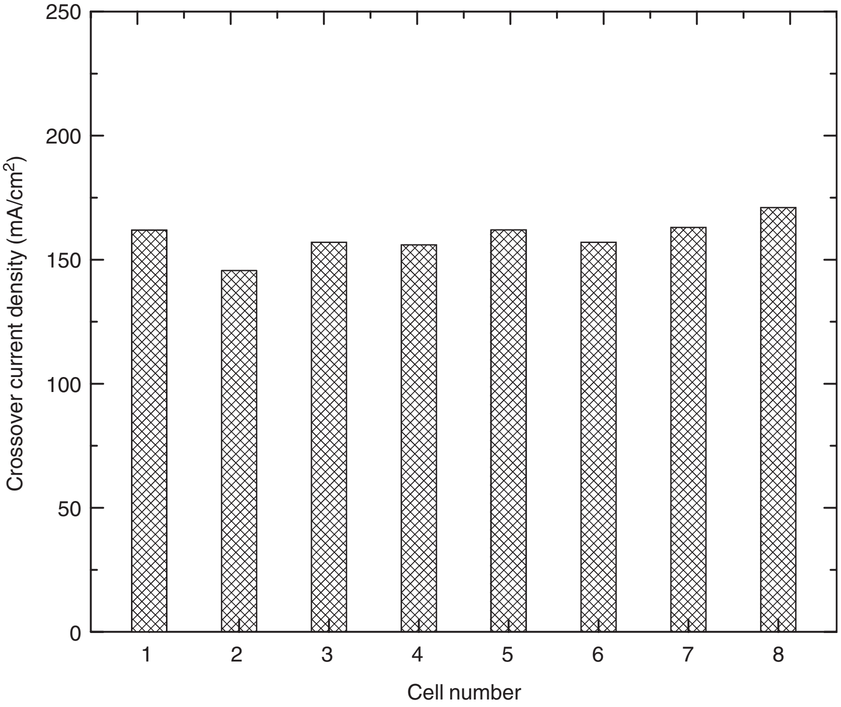

Figure 4. Distribution of methanol crossover rate at OCV.

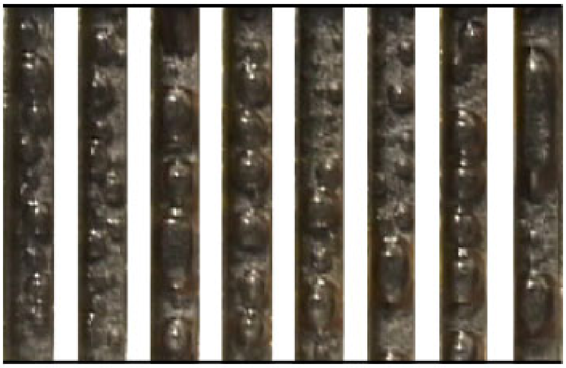

Figure 5. Non-uniform distribution of carbon dioxide gas bubbles in the anode in the transparent DMFC.

and 6, might be due to flow maldistribution which will be further discussed later in this paper. It is seen from Figure 3 that the average voltage at steady state by fixing the current density reached 0.42 V at 25 mA cm^{-2}, 0.38 V at 50 mA cm^{-2}, and 0.33 V at 75 mA cm^{-2}, respectively.

Water transport through membrane: One mole of water reacts with 1 mol of methanol at the anode, and 3 mol of water is produced at the cathode. Water is also transported from the anode

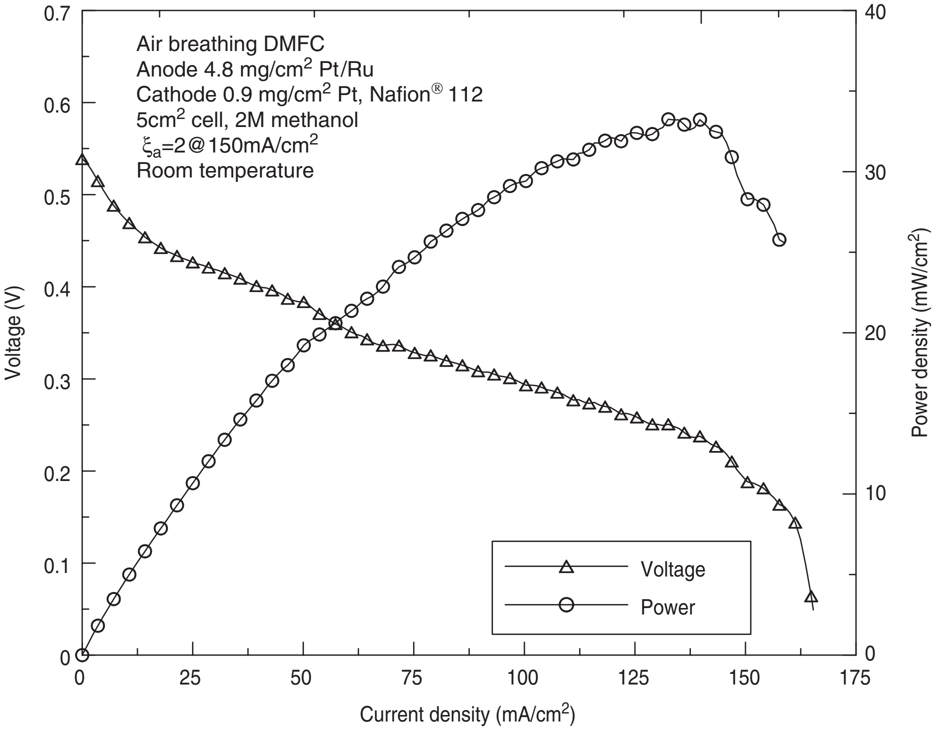

Figure 6. Polarization and power curves of cell #1 with 2 M methanol feed.

to cathode by electro-osmotic drag through the membrane, which is about 2.5 × 6 mols per mol of methanol assuming the electro-osmotic coefficient to be 2.5 per proton for thick membranes, such as Nafion 117 (Ren and Gottesfeld, 2001). Therefore, a total of 18 mol of water per mol of reacted methanol accumulates at the cathode if there is no water back diffusion effect. This excessive amount of water results in severe electrode flooding (Lu and Wang, 2005).

An innovative water management technique was implemented in this DMFC stack by applying a highly hydrophobic microporous layer in the cathode to create hydraulic pressure buildup, and by using a thin membrane (e.g. Nafion 112) to facilitate water backflow via hydraulic permeation (Lu *et al.*, 2005). By properly tailoring the contact angle and the micro pore size of the microporous layer, net water crossover through the MEA can be reduced dramatically. The total rate of water arrived and produced at the cathode can be written as follows:

$$j_{\mathrm{H_2O}} = \left(\alpha + \frac{1}{2}\right)\frac{I}{F} \tag{1}$$

where I is the total current, F is Faraday's constant, and α is the net water transport coefficient, a combined result of electro-osmotic drag, diffusion, and hydraulic permeation through the membrane. At 30°C, the net water transport coefficient, α, for this newly developed MEA is only 0.12 at an air stoichiometry, ξ_c, being 4 at $150\,\mathrm{mA\,cm^{-2}}$ (Lu *et al.*, 2005), as compared to the

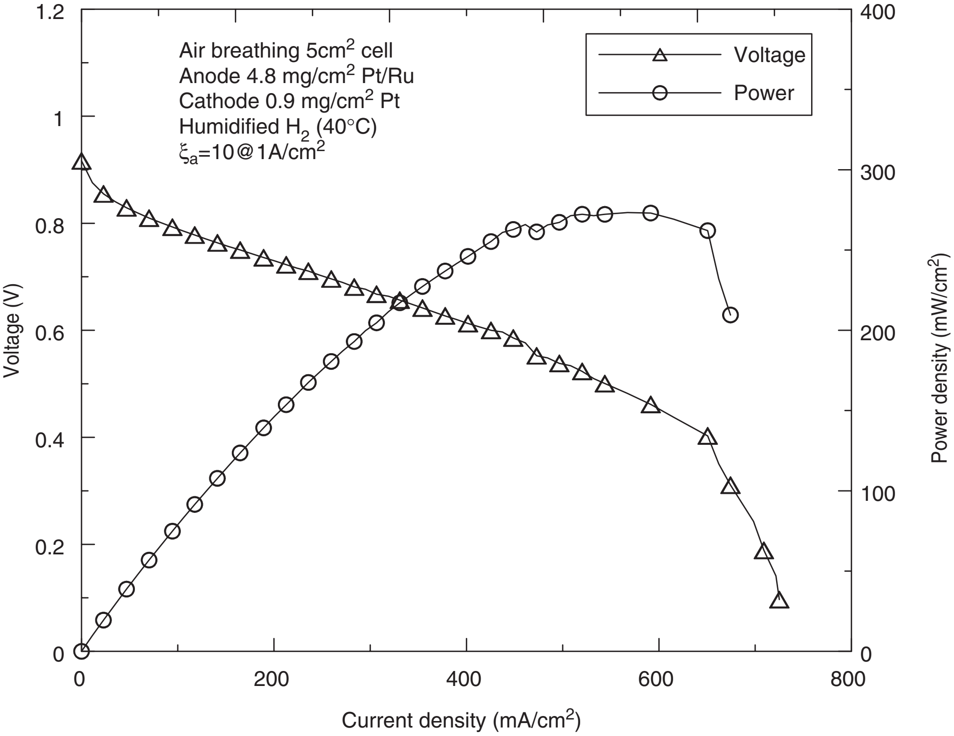

Figure 7. Polarization and power curves of cell #1 fed with humidified hydrogen.

electro-osmotic drag coefficient of about 2.25 at the same temperature (Ren and Gottesfeld, 2001). Thus the total water flux at the cathode is $j_{\mathrm{H_2O}} = 0.62I/F$ for our new MEA, which is only 22.5% of the water flux $j_{\mathrm{H_2O}} = 2.75I/F$ in a traditional MEA when the net water transport coefficient is approximately equal to the electro-osmotic drag coefficient. It is anticipated that the net water transport coefficient of this MEA could be lower, and may even be negative, in air-breathing DMFCs, since a smaller air supply rate will commonly decrease the net water transport coefficient (Liu *et al.*, 2005). Using this advanced MEA, less water accumulated at the cathode and flooding was thus not observed in the present 8-cell stack.

Methanol transport: Instead of using humidified nitrogen at the cathode for an air-circulating DMFC (Ren *et al.*, 2000), methanol crossover at open circuit voltage (OCV) in air-breathing cells was measured using shielded cathodes by a film or by immersing the air-breathing stack in a pool of DI water. Transient voltage scanning from 0 to 1.2 V was applied to each individual cell from an external power source (Multi-channel fuel cell test system, Arbin). Figure 4 depicts the distribution of crossover current densities for the 8 individual cells at OCV. The average crossover current density is about 159 mA cm^{-2} at OCV.

Methanol transport at the anode is also a concern for the 8-cell stack. In the experiments, we found that the flow distribution at the anode in the 8-cell stack was not uniform. For example, the limiting current density for one of the cells was only 25 mA cm^{-2}, while the highest limiting current density was 232 mA cm^{-2}. The anode channels were purged for 3 min with nitrogen and then refilled with the methanol solution afterwards. Subsequently it was found that the limiting

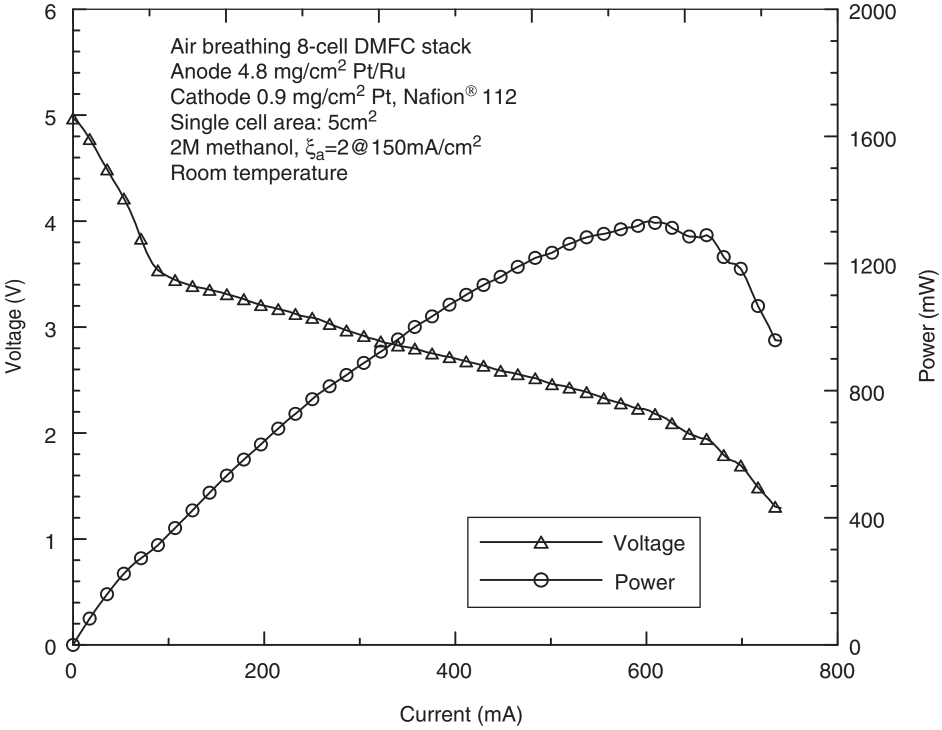

Figure 8. Polarization and power curves of the 8-cell air-breathing DMFC stack.

current densities for different cells reached a reasonably narrow range. Theoretically, the methanol solution should flow through the 8 individual cells uniformly, according to the uniform flow path design shown in Figure 1. However, pressure loss for the flow through each cell might fluctuate dynamically because of non-uniform distribution of the carbon dioxide gas bubbles produced in the anodes, causing the flow rate through each cell to vary. Figure 5 shows the non-uniform distribution of CO_2 bubbles in the anode using the transparent DMFC (Lu and Wang, 2004). In the worst case, large gas bubbles might block an entire flow channel, particularly a narrow one. Therefore, proper gas management in the anode is critical for uniform methanol transport in DMFC stacks with parallel flow field.

Oxygen transport limitation: To evaluate whether the air breathing DMFC suffers from the mass transport limitation, we measured the limiting current density. Figure 6 shows the polarization curve of cell #1 supplied with 2 M methanol solution. Figure 7 shows the polarization curve of cell #1 using fully humidified hydrogen under a very large flow rate. The cell temperature was around 30°C due to natural cooling for both cases given in Figures 6 and 7. The average limiting current density for 8 individual cells using 2 M methanol is $167\,\mathrm{mA\,cm^{-2}}$, while that using humidified hydrogen is $773\,\mathrm{mA\,cm^{-2}}$. Since hydrogen is much more reactive than methanol with minimum activation loss at the anode, and since the large hydrogen flow rate used in these experiments guarantees no mass transport loss at the anode, the limiting current density obtained with supply of humidified hydrogen comes primarily from the mass transport limitation at the air-breathing cathode.

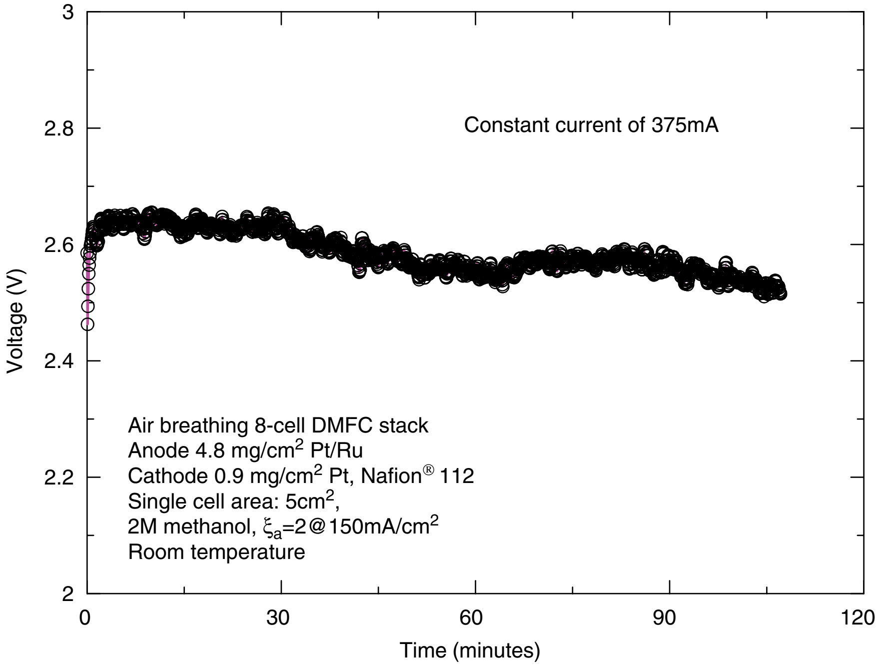

Figure 9. Discharge curve of the DMFC stack at constant current of 375 mA.

The large limiting current density using hydrogen at the anode indicates that the air-breathing cathode inherently has sufficient oxygen-transport limit. When the methanol solution is used at the anode in a DMFC, the cathode may be more flooded than in a hydrogen cell. The increased liquid saturation in the air-breathing cathode of the DMFC could reduce the oxygen-transport limitation moderately. Nonetheless, the low limiting current density in the air-breathing DMFC stack likely comes from the methanol anode.

Stack performance: Figure 8 shows the polarization curve for the 8-cell stack. The cells were connected in series. The stack produced 1.28 W at 2.4 V and the maximum output power was 1.33 W at 2.21 V, corresponding to a power density of 33.3 mW cm^{-2}. Figure 9 displays the stack voltage curve discharged at a current of 375 mA. The stack voltage was found to be higher than 2.54 V (an average of 0.3175 V for each cell) which produced a steady-state power output of 23.8 mW cm^{-2} for more than 100 min without significant degradation.

4. CONCLUSIONS

An 8-cell air-breathing DMFC stack was developed and characterized electrochemically. By using the water backflow from the cathode through a thin membrane under hydraulic pressure difference developed by the hydrophobic microporous layer in the cathode, flooding in the air-breathing cathode was avoided. Methanol crossover at OCV was measured using different methods. Maldistribution of the methanol solution in the anode may happen in the DMFC stack with parallel flowfield because of non-uniform distribution of carbon dioxide bubble in individual cells. It was found that oxygen transport in the air-breathing cathode is sufficient. The 8-cell DMFC stack produced a maximum output power of 1.33 W at 2.21 V, corresponding to a power density of 33.3 $\mathrm{mW\,cm^{-2}}$.

ACKNOWLEDGEMENTS

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