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Study of sintered stainless steel fiber felt as gas diffusion backing in air-breathing DMFC

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Abstract

Adoption of a sintered stainless steel fiber felt was evaluated as gas diffusion backing in air-breathing direct methanol fuel cell (DMFC). By using a sintered stainless steel fiber felt as an anodic gas diffusion backing, the peak power density of an air-breathing DMFC is 24 mW cm^{-2}, which is better than that of common carbon paper. A 30-h-life test indicates that the degraded performance of the air-breathing DMFC is primarily due to the water flooding of the cathode. Twelve unit cells with each has 6 cm^2 of active area are connected in series to supply the power to a mobile phone assisted by a constant voltage diode. The maximum power density of 26 mW cm^{-2} was achieved in the stack, which is higher than that in single cell. The results show that the sintered stainless steel felt is a promising solution to gas diffusion backing in the air-breathing DMFC, especially in the anodic side because of its high electronical conductivity and hydrophilicity.

Keywords: Direct methanol fuel cell; Air-breathing; Gas diffusion backing; Sintered stainless steel fiber felt

1. Introduction

Direct methanol fuel cell (DMFC) that uses liquid methanol directly without reformer is considered as a competitive candidate for portable power sources because methanol has a high energy density (about 6 kWh kg^{-1}). This advantage is important for portable electronic applications such as mobile phones, notebook, and other advanced mobile electronic devices, whose power requirement is increasing for its multifunctional purpose. In order to compete with conventional battery technology, it is very important to eliminate the need of some auxiliary devices such as gas compressors or fans, and reduce the weight and size of fuel cells. One solution to this may be the air-breathing fuel cells in which the cathode gas channels are open to ambient air. Table 1 summarizes the air-breathing direct methanol fuel cells developed recently around the world. It can be seen from Table 1 that the maximum power density achieved is about 20 mW cm^{-2} in single cell, even lower power density in the stack. The performance of the fuel cells, especially in terms of power density, has to be improved before its commercialization.

Among many properties that influence the performance of the fuel cells, the gas diffusion media plays an important role in the performance of membrane electrode assembly (MEA) [9–11]. Gas diffusion media in MEA has several functions in the electrode such as permeation of reactants and products, conductivity of heat and electronic and substrate for electrocatalysts. The most common gas diffusion media used in DMFC is carbon-based fiber products, such as non-woven carbon papers and woven fabrics (or cloth) because of their high porosity (>70%) and good electrical conductivity [12]. Besides the carbon, sintered porous titanium as gas diffusion backing in proton exchange fuel cell had been reported [13]. Sintered metal exhibits a number of advantages, such as high mechanical strength, ductility, and good electrical conductivity. Although sintered stainless steel fiber felt using in gas diffusion media has not been reported, the stainless steel of 316L, 317L, has been used in bipolar plate [14] and current distributor [15]. This indicates that stainless steel has enough corrosion resistance and can be used as gas diffusion media. In this paper, a 316L stainless steel sintered felt as gas diffusion backing was evaluated in air-breathing DMFC. The performance of the single cell using sintered stainless steel felt as anodic gas diffu-

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Table 1
Performance of the air-breathing DMFC around the world

	Concentration of methanol (M)	Peak power density in single cell ($mW\,cm^{-2}$)	Peak power density in the stack ($mW\,cm^{-2}$)	Loading of PtRu in the anode ($mg\,cm^{-2}$)	Loading of Pt in the cathode ($mg\,cm^{-2}$)	Membrane	Temperature (°C)
KIER [1], South Korea	2.5	18		4.5	8	Nafion 115	23–25
SK Corp. [2], South Korea	2	8.5	2–3	8	8	Nafion 115	25–28
INER [3], Taiwan, China	1	21.3	10.7	6.2	6.2	Nafion117	23
Tel-Aviv Univ. [4], Israel	1–6	12.5		5–7	4–7	2 M H_2SO_4 in NP-PCM	20–25
Samsung [5], South Korea	5	10	23	3–8	3–8	Hybrid membrane	
LANL [6], USA	1–2	23	25			Nafion 117	22
NEC [7], Japan	2.5	20–35	10	1–2	1–2	Nafion 115	
Motorola [8], USA	1	30–35	22	4	4		

sion backing is better than that of common carbon paper. A 12-cell air-breathing DMFC stack was fabricated and tested for mobile phones.

2. Experimental

A common carbon paper was used for reference in this paper. Some properties of the carbon papers and sintered stainless steel fiber felt were presented in Table 2. Electrical resistance was determined by two-point measurement through circular (40 mm diameter) gold plated copper contact under pressure of 0.15 bar. Other properties of these materials were from the website of the company or personal communication.

A thin layer of uncatalyzed carbon (Vulcan, XC-72) bounded with 20 wt.% Nafion was applied to carbon paper or sintered stainless steel fiber felt, which was used as anodic gas diffusion backing. Carbon paper combined with a layer of carbon (Vulcan, XC-72) bounded with 20 wt.% PTFE was used as cathodal gas diffusion media in all tests. The loading of XC-72 carbon in all layers is about 1–3 $mg\,cm^{-2}$.

The preparation of catalyst-coated membrane (CCM) was slightly different from the thin-film decal method developed by Wilson and Gottesfeld [16]. The inks containing catalyst and 5 wt.% Nafion solution (Aldrich) were firstly applied to Teflon blanks by spraying. The anode ink composition was 85 wt.% catalyst (90 wt.% PtRu/C, Pt:Ru = 1:1 in atomic ratio, Johnson Matthey Corp.) and 15 wt.% Nafion. The cathode ink composition was 90 wt.% Pt black (Johnson Matthey Corp.) and 10 wt.% Nafion. Nafion 115 was pretreated before the preparation of the (CCM) by boiling for >1 h in each step in 3% H_2O_2, deionized water, 0.5 M H_2SO_4, and again in deionized water. Then, the anode and cathode catalyst layers were transferred from the Teflon blanks to the two sides of a piece of pretreated Nafion 115 to form CCM by hot press at 135 °C and 50 atm for 90 s. The loadings of noble metal in the anode and cathode were 2.5 and 3.0 $mg\,cm^{-2}$, respectively. Finally, MEA was obtained by pressing anode diffusion layer and cathode diffusion layer on each side of the CCM at 135 °C and 100 atm for 150 s.

In single cell test, MEA with 4 cm^2 active area was sandwiched between two 1.0 mm stainless steel plates, which had a series of 3 mm diameter holes for the passage of fuel or ambient air. The cell was held together between acrylic plates by means of several retaining bolts positioned at the periphery of the cell. The volume of the reservoir for the methanol solution in the single cell is about 6.5 cm^3. In order to eliminate the change and inhomogeneity of the concentration of the methanol solution in the stability test of the cell, a metric pump with the flow rate of 1.0 $ml\,min^{-1}$ was employed to supply 1.0 M methanol solution.

The polarization curves were obtained using Fuel Cell Test System (Arbin Instrument Corporation) in a galvanostatic polarization mode.

The micrograph of fiber of carbon paper and sintered stainless steel fiber felt was obtained by Keyence VK-8550 super depth surface profile measurement microscope.

3. Results and discussion

3.1. Comparison of structure and performance of sintered stainless steel fiber felt and carbon paper

Fig. 1 shows the typical *I–V* curves of the air-breathing DMFC using sintered stainless steel fiber felt as anodic gas diffusion backing with different methanol concentration at room temperature (23–25 °C). The performance of the cell was measured after it was kept in deionized water

Table 2
Comparison of properties of carbon paper and sintered stainless steel fiber felt

	Thickness (mm)	Bulk density ($g\,cm^{-3}$)	Porosity (%)	Electrical resistance (through-plane) ($\Omega\,cm^{-2}$)
Carbon paper	0.19	0.3	83	0.83
Sintered stainless steel fiber felt	0.19	1.1	85	0.62

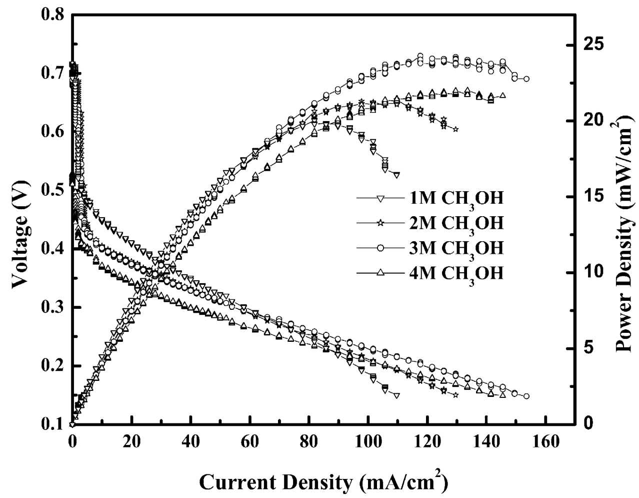

Fig. 1. Performance of the air-breathing DMFC using sintered stainless steel fiber felt with various concentration of methanol.

for overnight to activate prior to the test. It can be found from Fig. 1 that the DMFC performance was improved in the low current density region as the methanol concentration reduced because of the low amount of methanol crossover, whereas the performance was reduced in the high current density region because of polarization of mass transfer. Methanol yields (3 M) the best compromise between methanol crossover and mass transfer and the peak power density is 24 mW cm^{-2}.

Fig. 2 shows performance of air-breathing DMFC with 1.0 M methanol solution at various anodic gas diffusion backings. The cell using sintered stainless steel fiber felt showed better performance than that of carbon paper. It can be seen from Table 2 that the thickness and porosity of two kind of gas diffusion backing are similar, yet sintered stainless steel fiber felt showed higher electrical conductance.

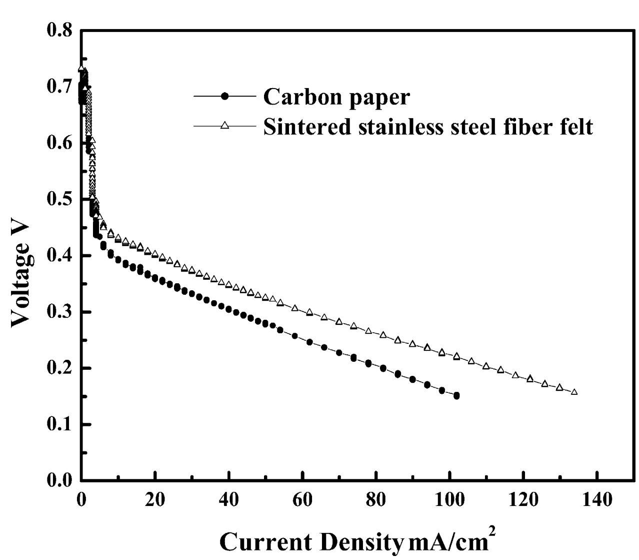

Fig. 2. The polarization curves of air-breathing DMFC using various anodic diffusion backing.

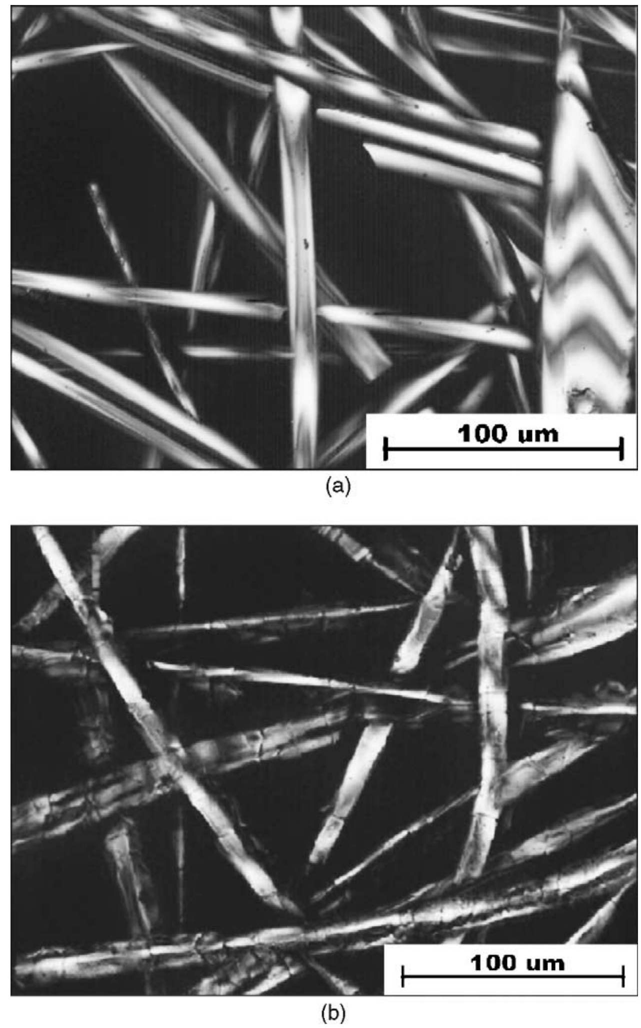

Fig. 3. Micrographs of various gas diffusion backing (a) carbon paper; (b) sintered stainless steel fiber felt.

This would explain why the internal impedance of the MEA with sintered stainless steel fiber felt is smaller than that with carbon paper and shows a slower fall in performance in ohmic polarization region. The electrical conductance of metal is greater than that of carbon materials in nature. Furthermore, in the process of preparation, stainless steel fiber became fused at 1200–1400 °C under the atmosphere of argon. The melt metal among fibers not only make sintered stainless steel fiber felt better strength but also the wonderful electric conductance. Fig. 3 shows the super depth surface profile of carbon paper and sintered stainless steel fiber felt. It can be observed that the diameter of the fiber of both backing materials is about 10–12 μm. The surface of carbon fiber is smooth in carbon papers, yet metal fiber showed a coarse surface. So metal fiber might be more hydrophilic compared with that of carbon fiber in the carbon paper, which made methanol supply easier in high current density. This might be another reason that MEA using sintered stainless steel fiber felt as diffusion media showed a better performance.

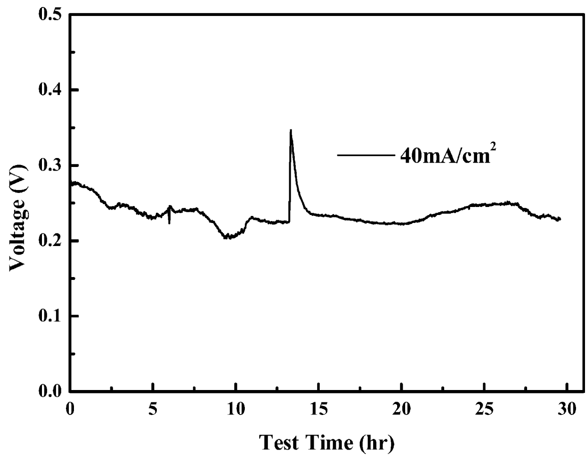

Fig. 4. Thirty-hour stability test under 40 mA cm^{-2} of air-breathing DMFC at room temperature.

Fig. 4 depicts a 30 h stability test of air-breathing DMFC using sintered stainless steel fiber felt as anodic gas diffusion backing under 40 mA cm^{-2}. Liquid water yielded in the cathode expelled from gas diffusion media only when the droplet was big enough. The continuous discharge was interrupted at 13th hour to remove the water at the cathode by a blower. The cell performance decayed quickly during the first few hours in every continuous discharge probably because air diffusion was blocked by excessive water. Therefore, water management appears to be one of the major aspects of air-breathing DMFCs, which must be solved in the long-term application. Chen [3] found the stability of performance could be improved by blowing air to the cathode. But auxiliary blower or fans would increase cost, volume and weight, which restrict commercial viability. In addition, good performance obtained from 20th to 27th hour corresponding to daytime, which has a high average ambient temperature. High temperature surrounding at daytime relative to night may be the reason of abnormal increase of cell performance, which is very sensitive to temperature [2,3].

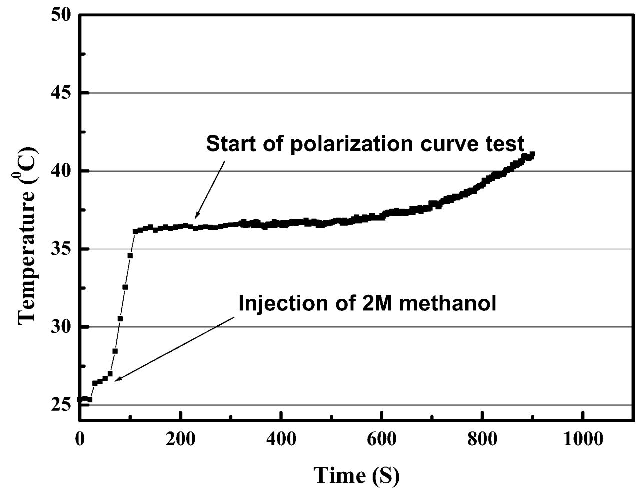

Fig. 6. Variation of temperature of the 12-cell stack during the injection of 2 M methanol and *I–V* test.

3.2. Air-breathing DMFCs stack for mobile phone

The power performance of 12-cell air-breathing DMFCs stack with different concentration of methanol is shown in Fig. 5. The peak power output with 3 M methanol is 1.88 W at 2.2 V and the power density is 26.1 mW cm^{-2}, which is higher than the single-cell test result of 24 mW cm^{-2} obtained with the same MEA structure. Many researchers [3,7] had reported the power density of the stack is lower than that of unit cell because of component assembly problems such as contact ohmic loss. To find out the reason of improvement of performance in the stack, a thermocouple was put in the cell to monitor the temperature in the test. Fig. 6 shows the variation of the temperature of the cell with 2 M

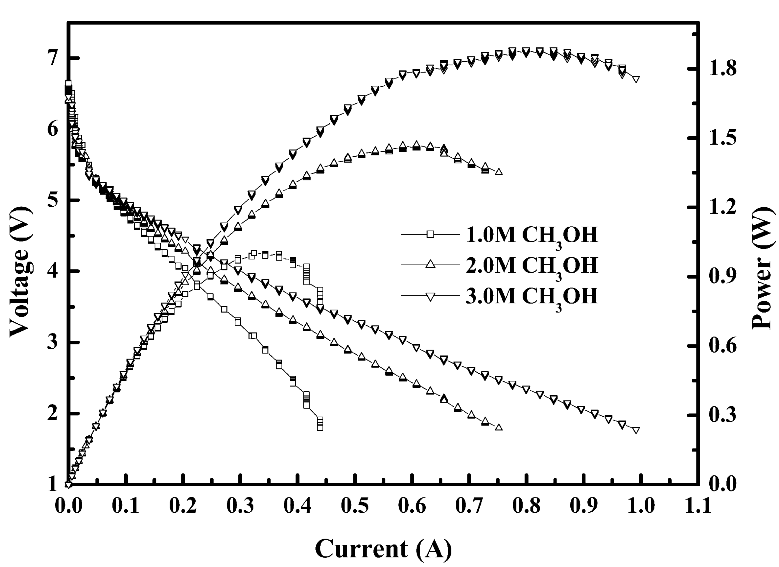

Fig. 5. Performance of the 12-cell air-breathing DMFC stack with various concentration of methanol.

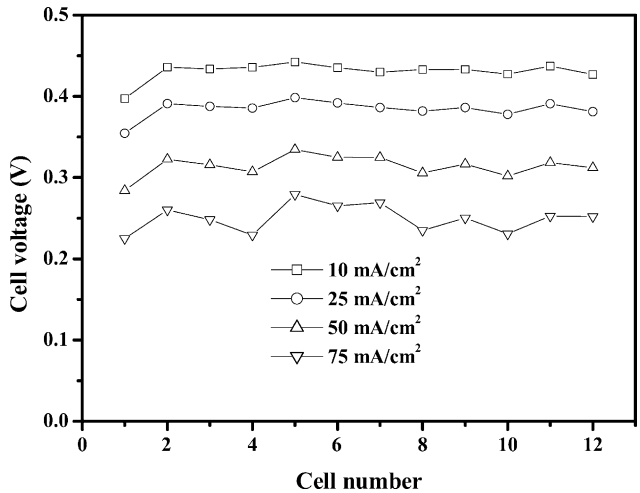

Fig. 7. Distribution of cell voltage in the 12-cell stack.

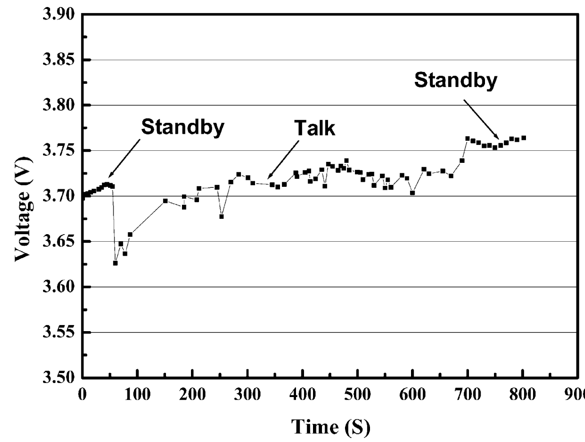

Fig. 9. Voltage variation of the 12-cell stack during talk and standby modes of mobile phone.

methanol during the injection of methanol to the stack and polarization curve test. It can be seen the temperature of the cell rise from 25 to 36 °C when 2 M methanol was injected to the stack. This indicates the methanol crossover react with oxygen in air in the cathode. Moreover, the temperature of the stack rises to 41 °C when the *I–V* test finished due to polarization. However, the temperature of single cell during the injection and *I–V* test did not change because of good dispersion of heat. The higher temperature improved the performance of the cells in the stack.

The voltage distribution of unit cells in the stack is presented in Fig. 7. The distribution of the voltage at low current density is uniform but the voltage variation increased as the load increased. Particularly, the first and fourth cell at the load of 75 mA cm^{-2} was lower than other cells. It seems that the electrode polarization of those cells might be influenced by some problems occurred during electrode preparation, stacking, or operation.

The air-breathing stack coupled with mobile phone is shown in Fig. 8. The outer dimension of the stack is only 160 mm × 40 mm × 10 mm. The reservoir of methanol in the stack is 15 cm^3. The constant voltage diode was connected in series to maintain the output of the stack for the application of mobile phone. The voltage change during the actual operation of mobile phone is shown in Fig. 9. During the 10 min talk time, the voltage increased gradually, and the voltage of the stack rise to 3.75 V when change the talk mode to standby, which is higher than the initial standby voltage. This also can be attributed to the temperature increase during the discharge.

4. Conclusions

The applicability of sintered stainless steel fiber felt as gas diffusion backing in air-breathing direct methanol fuel cell was investigated. The results indicated that the power density of the cell using sintered stainless steel fiber felt as anodic diffusion backing was improved due to its high electric conductance and hydrophilicity. The flooding problem of the cathode by water must be solved before its commercialization. This work also focused on a 12-cell stack fabrication for mobile phone. The temperatures of the stack

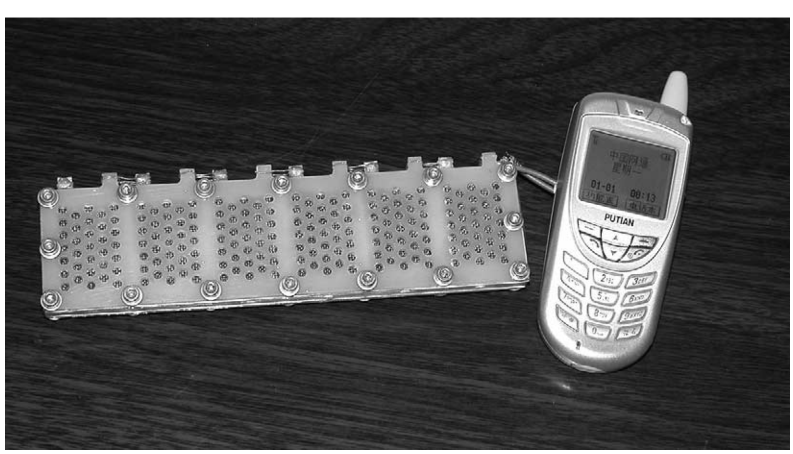

Fig. 8. Photograph of 12-cell air-breathing DMFC coupled with mobile phone.

increase in the process of methanol injection and *I*–*V* tests which make the maximum power density of the stack higher than that of the single cell. The actual operation of mobile phone powered by the stack reveals that air-breathing direct methanol fuel cell is a promising candidate for powering of portable electronic devices.

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