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Design, Fabrication and Characterization of Miniature Direct Methanol Fuel Cell Using Platinum-Sputtered Microcolumn Electrodes with Limited Fuel Source

Young Ho Seo and Young-Ho Cho*

Digital Nanolocomotion Center, Korea Advanced Institute of Science and Technology
373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

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Key words: micro-fuel cell, microcolumn electrode, limited methanol fuel

We present a miniature direct methanol fuel cell (micro-DMFC) using platinum-sputtered microcolumn electrodes with a built-in fuel chamber to improve power density. We designed and fabricated both microcolumn and planar electrodes with an identical projective area of 4.5 mm×4.5 mm. In an experimental study, we performed a single-cell test to compare the microcolumn electrode with the planar electrode. In the single-cell test, the micro-DMFC with microcolumn electrodes showed a maximum power of 24.8 μW (122.4 μW/cm^2) at 0.65 V, while the micro-DMFC with planar electrodes showed a maximum power of 1.1 μW (5.6 μW/cm^2) at a voltage of 0.08 V. The micro-DMFC with microcolumn electrodes showed a constant maximum power of 122.4 μW/cm^2 over 40 min. The micro-DMFC with microcolumn electrodes had a maximum power density 22 times higher than that of the micro-DMFC with planar electrodes in a single-cell test.

1. Introduction

Recently, MEMS has been applied to portable health care and communication systems such as implantable medical devices and distributed systems for diagnosis and monitoring. For these applications, stand-alone microsystems require their own power supply with environmentally friendly materials, room-temperature operation and short charging time.

Because thermoelectric,[1] electromagnetic,[2] micro-turbine,[3] and piezoelectric[4] generators require high temperature, moving parts and secondary energy converters, these

*Corresponding author, e-mail address: dnc@kaist.ac.kr

generators are rarely applied to portable power sources as shown in Table 1. Most of all, these generators require additional energy storage units such as rechargeable batteries, because the generators input energies such as thermal energy and mechanical vibration are difficult to store. Alkaline microbatteries[5] and fuel cells have advantages as portable power sources, because their input energy is chemical energy, which is easily stored in a container. Moreover, these electrochemical energy converters bring about the direct energy conversion of stored chemical energy to electrical energy without the intermediate generation of thermal energy; thus they are not limited by the Carnot cycle, unlike heat engines.[6] Their energy conversion efficiencies (45–65%) are generally 2 times higher than those of heat engines, *e.g.*, diesel generators.[7] Most of all, fuel cells use the environmentally friendly fuel methanol, while batteries require hazardous chemicals like sulfuric acid and potassium hydroxides as electrolyte. The maximum energy available from batteries is determined by the quantity of chemical reactants stored within the battery itself. The battery ceases to produce electrical energy when the chemical reactants are consumed, i.e., discharged. On the other hand, a fuel cell theoretically has the capability of producing electrical energy as long as the fuel and oxidant are supplied to the electrodes. Only, degradation, corrosion, or malfunction of components limits the practical operating life of fuel cells. However, the energy-to-weight ratio of hydrocarbon fuels is at least 10 times larger than that of batteries.[6]

Recently, DMFCs have been actively studied as power sources for portable systems because they can be operated at room temperature, use the cheap and environmentally friendly fuel methanol, and make only H_2O and CO_2 as by-products.[6] Moreover, a DMFC has a simple configuration without moving parts; thus the size of DMFC is easily reduced. However, two major problems occur when the size of a DMFC is reduced. First, the power decreases due to the reduction in cell size. Second, a fuel pump must be removed from the fuel cell system for application in portable power sources. Thus, a fuel chamber is required for limited fuel usage. Previous work on micro-DMFCs[8–12] did not consider the power reduction problem and still used a fuel pump. In addition, they used carbon-based porous electrodes which provide a surface area a thousand times wider than that of planar electrodes. However, carbon-based porous materials are not compatible with MEMS fabrication technologies. In this paper, we suggest a platinum-sputtered microcolumn

Table 1
Characteristics of energy converters for applications in portable power sources.

Converter type	Characteristics
Battery	-Requires recharging, bulky, hazardous chemicals
DMFC	-Light, expensive, low power density
Electromagnetic	-Needs moving parts and magnet, poor MEMS compatibility
Microturbine	-Needs moving parts, requires power generator, high power density
Thermoelectric	-High temperature, low efficiency
Photovoltaic	-Solar energy, low efficiency
Piezoelectric	-Many moving parts, low efficiency

electrode fabricated by MEMS to improve the power density of the micro-DMFC and a built-in fuel chamber in the anode instead of a fuel pump for application to portable microsystems.

2. Working Principle

A micro-DMFC is composed of a fuel electrode(anode), an air electrode(cathode) and a polymer electrolyte. Figures 1 and 2 show schematic and cross-sectional views of a micro-DMFC with microcolumn electrodes, respectively. Figure 3 shows the working principle of a DMFC. In the anode, a mixture of 1 mole of methanol (CH_3OH) and 1 mole of water (H_2O) is changed into 1 mole of carbon dioxide (CO_2), six hydrogen ions (H^+), and six electrons (e^-) via the platinum anode catalyst as shown in eq. (1). After generating electrical work in the load, six electrons flow to the cathode through the electric wire. Six hydrogen ions flow to the cathode through the polymer electrolyte that has good ion conductivity and poor electron conductivity. In the cathode, oxygen in air, six electrons from the electric wire, and six hydrogen ions from the polymer electrolyte are converted into 2 moles of water via the platinum cathode catalyst[6,7] as shown in eq. (2) and Fig. 3. The overall electrochemical reaction in the DMFC is expressed as eq. (3).

$$CH_3OH + H_2O \rightarrow 2CO_2 + 6H^+ + 6e^-, E^{\circ}_{anode} = 0.046\ \text{V} \tag{1}$$

$$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O, E^{\circ}_{cathode} = 1.23\ \text{V} \tag{2}$$

$$CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2, E_{cell} = 1.18\ \text{V} \tag{3}$$

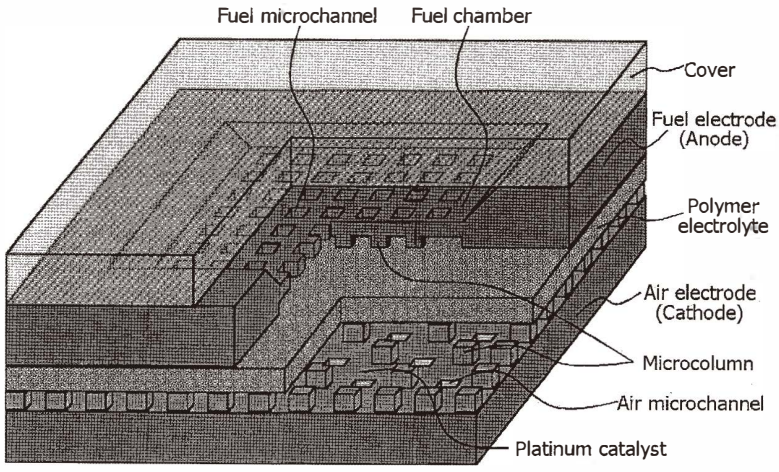


Fig. 1. Perspective view of a micro-DMFC.

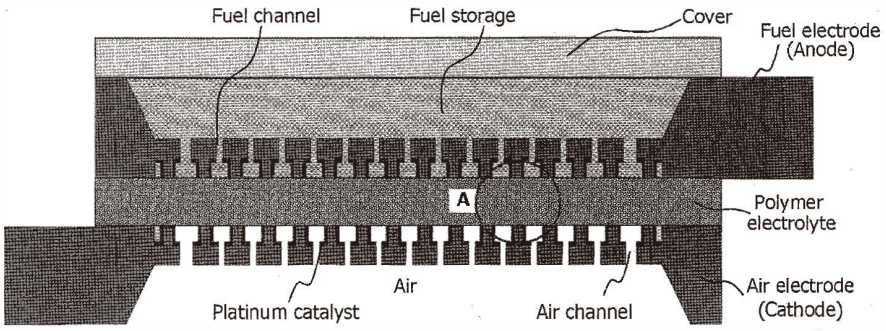


Fig. 2. Cross-sectional view of a micro-DMFC.

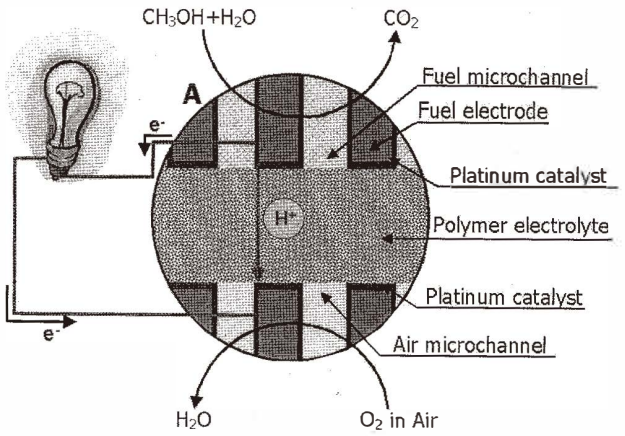


Fig. 3. Working principle of portion A in Fig. 2 of a micro-DMFC.

Because the energy of an electrochemical reaction is determined by the reactants, we theoretically get a voltage of 1.18 V in the DMFC in accordance with eq. (3). Practically, poor electrode kinetics (kinetics losses) causes the electrode reactions to deviate from their ideal thermodynamic values and to incur a practical reduction in the highest theoretical efficiency possible of the cell. Besides kinetic losses, ohmic losses originate from the internal resistance of the fuel cell. Hence, the output voltage of a practical DMFC is substantially lower than that of the ideal cell, which provides 1.18 V at any current. All electrochemical reactions are generated by the adsorption of methanol molecules to the platinum anode and cathode catalysts. Thus, we must increase the surface area of the catalyst to increase current density.

Generally, we obtain the operating voltage equation of a fuel cell at a current density i.[13]

$$V_c = E_{th} - (i + i_n)r - A\log\left(\frac{i + i_n}{i_o}\right) + B\log\left(1 - \frac{i}{i_l}\right) \quad (4)$$

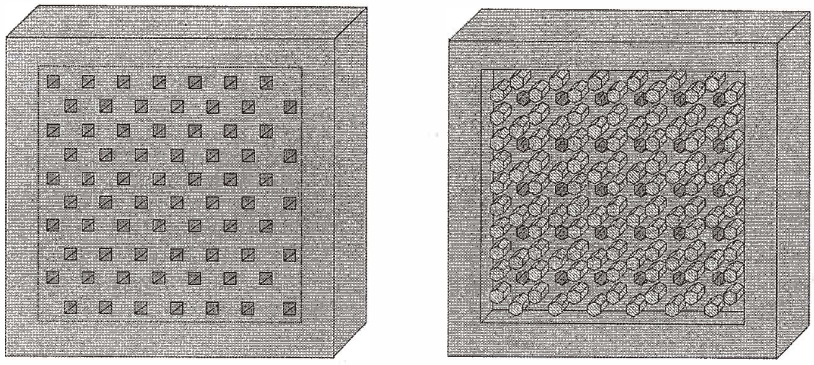
Here, E_{th}, i_n, A, i_o, B, i_l, and r are the reversible open circuit voltage, the internal current density, the slope of the Tafel equation, the exchange current density at the cathode, the constant in the mass transfer overvoltage equation, the limiting current density at the electrode, and the area specific resistance, respectively. However, it is difficult to estimate theoretically the actual operating voltage and current, because eq. (4) has many unknown variables that are irreversibilities of the single cell of the DMFC, such as ohmic losses derived from the contact resistance between the electrode and polymer electrolyte, kinetics losses, and losses from the mass transfer of fuel. In a single-cell test, the current-voltage characteristics are affected by the electrode shape and material, polymer electrolyte shape and material, the fuel channel shape and dimensions, other geometries and fuel type.[7,13] We have experimentally compared open-circuit voltage and current-to-voltage characteristics between the planar electrodes and microcolumn electrodes.

3. Prototype Design and Fabrication

3.1 *Prototype Design*

We designed the microcolumns on the electrodes to increase the surface area of the platinum catalyst to increase power density. The micro-DMFC with microcolumn electrodes is composed of a fuel electrode (anode), an air electrode (cathode) and a polymer electrolyte as shown in Fig. 1. We used platinum and a Nafion™ membrane as a catalyst to assist fuel oxidation and reduction and as a polymer electrolyte, respectively. Actually, the Pt catalyst is easily poisoned by CO, thus generally Pt is used with an additional material such as Ru or Mo. In this paper, we compare the effect of the geometry of the microcolumn electrode with that of the planar electrode, not that of the catalyst material. We used a Pt catalyst, which is an easily deposited material in MEMS. To compare the microcolumn electrode with the planar electrode, we designed and fabricated both microcolumn and planar electrodes with an identical projection area of 4.5 mm×4.5 mm as shown in Fig. 4 and Table 2.

We designed the length of the vertical microchannels and the height of the microcolumns to be 50 μm, due to the limitations of fabricating a PR mask layer for silicon deep etching. The width of the microchannels was 50 μm, which is a lower limitation for smooth liquid flow.[14] In the case of the microcolumn electrode, the cross-sectional shape of the microcolumns was hexagonal, because the honeycomb structure provides a wider surface area than rectangular or circular columns in the same projective area. The microcolumn electrode had 2706 hexagonal microcolumns and 891 hexagonal microchannels, while the planar electrode had 1250 rectangular microchannels. Using hexagonal microcolumns, the surface area of the microcolumn electrode was increased 3.56-fold that of the planar electrode with the same projected area of 4.5 mm×4.5 mm.



(a) (b)

Fig. 4. Electrode configuration: (a) planar electrode with vertical microchannels; (b) microcolumn electrode with microcolumns and vertical microchannels.

Table 2
Dimensions of the fabricated micro-DMFC.

Electrode type	Microcolumn Electrode	Planar Electrode
Total DMFC size	6 mm×6 mm×1.2 mm	
Electrode area(projected)	4.5 mm×4.5 mm	
Fuel chamber size(volume)	5 mm×5 mm×0.42 mm (10.5 μl)	
Intercolumn spacing	100±1.0 μm	N/A
Height of microcolumn	52±0.5 μm	N/A
Depth of microchannel	50±0.5 μm	
Thickness of Nafion™	0.007 inch (178 μm)	

We also designed a built-in fuel chamber on one side of the electrode as shown in Figs. 1 and 2. The methanol fuel was supplied to the platinum catalyst on the microcolumn electrode through vertical microchannels that connect the fuel chamber and the platinum-deposited microcolumn array. The built-in fuel chamber was closed by an acrylic cover to prevent fuel leaks, while the air chamber in the air electrode was exposed to the atmospheric environment as shown in Fig. 2. To fabricate the barrier of the built-in fuel chamber in the electrode, the total size of the electrode was set at 6 mm×6 mm. The built-in fuel chamber was approximately 5 mm×5 mm×0.42 mm (10.5 μl).

3.2 *Fabrication process*

The micro-DMFCs were fabricated using a 3-mask microfabrication process shown in Fig. 5. We used 525±25-μm-thick p-type silicon wafers as electrode structures. To fabricate microcolumns and microchannels on the same side of a silicon wafer, we used a 2-step deep silicon etching process. During this 2-step process, 52±0.5-μm-high hexago-

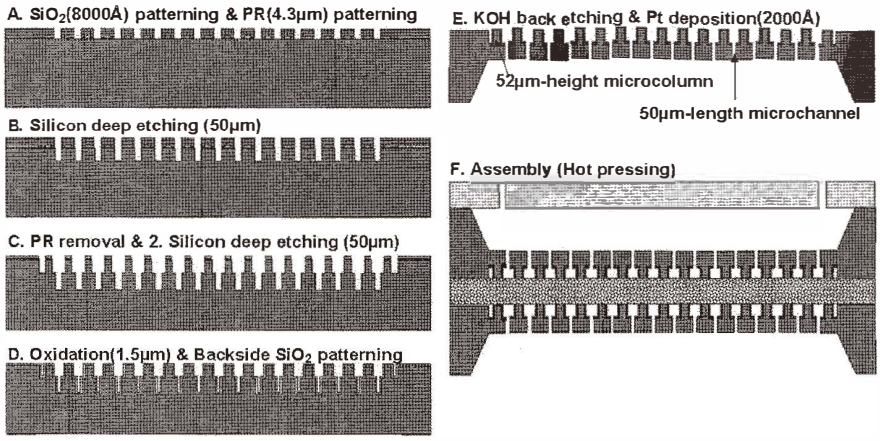


Fig. 5. Fabrication process of the micro-DMFC with microcolumn electrodes.

nal and 50±0.5-μm-deep microchannels were fabricated as shown in Fig. 5(C). Because the microchannels were exposed to the deep silicon etching process twice, the width of the microchannels was defined as 56±0.5 μm, which was wider than the design value of 50 μm. To connect microchannels to the built-in fuel storage, the silicon substrate was etched by KOH using a 1.5 μm-thick silicon dioxide mask. Then a 200 Å/2000-Å-thick Cr/Pt layer was deposited by sputtering as the catalyst layer (Fig. 5(E)).

To assemble the micro-DMFC, we put the polymer electrolyte (Nafion™-117, Sigma-Aldrich Co.) between the two fabricated electrodes and then pressed them at 150°C and 7 bar for 10 min as shown in Fig. 6. Figures 7(a) and 7(b) show the fabricated microcolumn electrode and the assembled micro-DMFC, respectively. The built-in fuel chamber was filled with methanol using a syringe pump and a vacuum pump. Figure 8 shows enlarged SEM photographs of the fabricated microcolumn electrode with hexagonal microcolumns and vertical microchannels and the planar electrode with vertical rectangular microchannels, respectively.

4. Experimental Results

In the experiments for the single-cell test, we used methanol as the fuel and as the air oxidant under ambient pressure. The concentration of methanol was the dominant factor in the power density. The higher the concentration of methanol, the higher the power density. When the concentration of methanol increased to a certain critical value, power density decreased due to fuel crossover, which means the methanol passed through the polymer electrolyte. Therefore, we must select the concentration of methanol considering the occurrence of fuel crossover. Based on a previous study,[15] we select 2M as the concentration of methanol, which provides maximum power density with minimum fuel crossover.

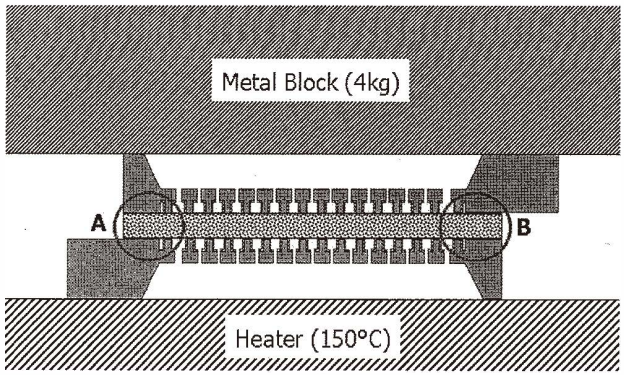


Fig. 6. Nonuniform bonding pressure distribution in hot pressing process.

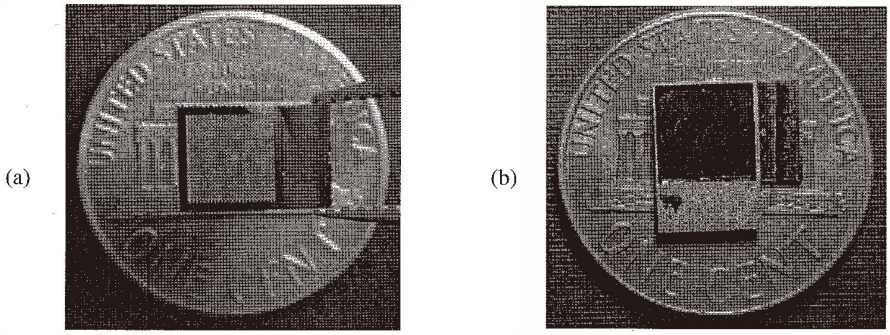
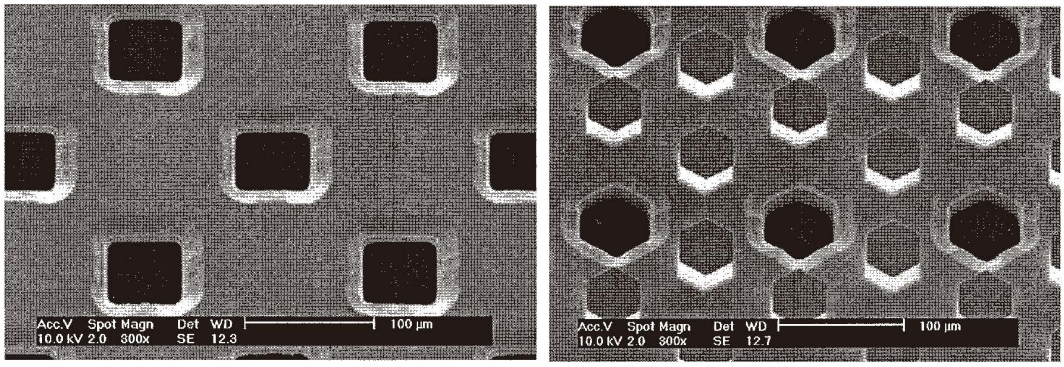


Fig. 7. Top view of fabricated device compared with size of penny: (a) the microcolumn electrode; (b) the micro-DMFC with microcolumn electrodes.



(a) (b)

Fig. 8. Enlarged view of fabricated electrode: (a) planar electrode: (b) microcolumn electrode.

In addition, the Pt catalyst is poisoned by CO, but the avarage lifetime of Pt catalyst is 1 year.[16] Therefore, degradation of the Pt catalyst can be ignored in the experimental study which is carried out within 24 h.

First, we measured the open circuit voltage, which is the terminal voltage without any current. Figure 9 shows the experimental apparatus for the single-cell test. Figure 10(a) shows the open-circuit voltage of micro-DMFCs with microcolumn and planar electrodes. From Fig.10(a), open circuit voltages of the micro-DMFCs with microcolumn and planar electrodes are 864 mV and 325 mV at the projective area of 4.5 mm×4.5 mm, respectively. The open circuit voltage of the micro-DMFC with the planar electrodes is lower than that of the micro-DMFC with the microcolumn electrodes. This maybe due to the difference in active electrode area. As eq. (4) indicates, the theoretical open circuit voltage (OCV) is dropped by an activation overvoltage.[12] Even if the single cell is an open circuit, the current density of the single cell is not zero due to the internal current density, i_n, which comes from fuel crossover. The surface area where the exchange current density, i_o, exists is the active electrode area. From eq. (4), the activation overvoltage of $A\ln\left(\frac{i+i_n}{i_o}\right)$ can differ even if experimental conditions are identical. The active electrode area of the micro-DMFC with microcolumn electrodes is larger than that of the micro-DMFC with planar electrodes. Consequently, the microcolumn electrode has a higher exchange current density, i_o than the planar electrode. Therefore, the micro-DMFC with microcolumn electrodes has a lower activation overvoltage than the micro-DMFC with planar electrodes. The open circuit voltage of the micro-DMFC with microcolumn electrodes is higher than that of the micro-DMFC with planar electrodes.

Figure 10(b) shows the current-voltage curve of three micro-DMFCs with microcolumn electrodes and two micro-DMFCs with planar electrodes. In the current-voltage curve, the micro-DMFCs with the microcolumn and planar electrodes show a maximum power of 24.8 μW(122.4 μW/cm^2) at 0.65 V and 1.1 μW(5.6 μW/cm^2) at 0.08 V, respectively. The power density obtained by the micro-DMFCs with microcolumn electrodes is one thou-

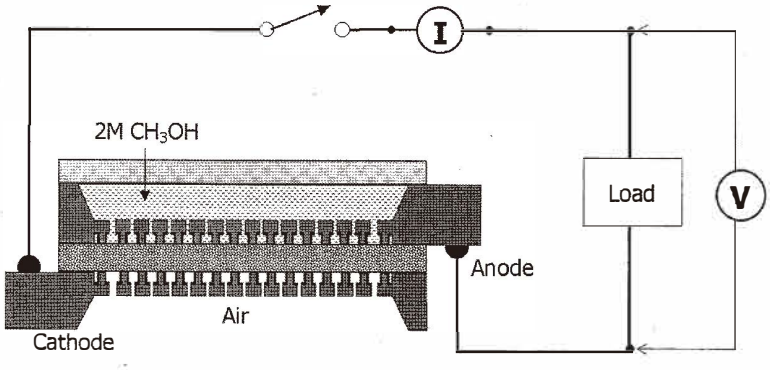


Fig. 9. Experimental apparatus for single-cell test.

(a)

(b)

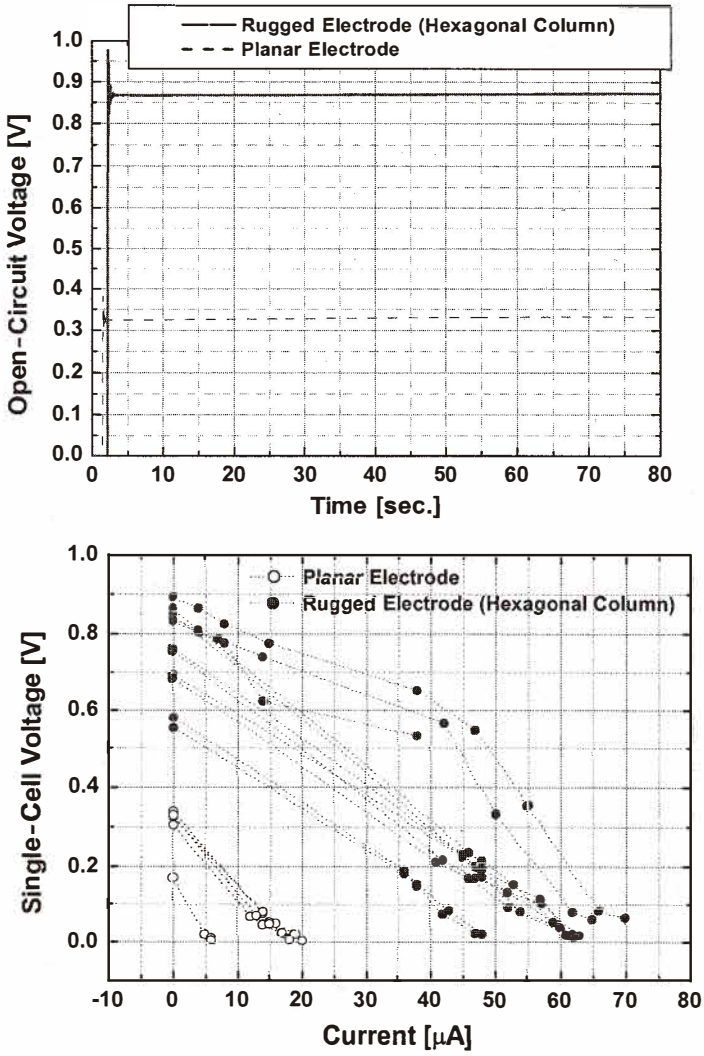


Fig. 10. Measured characteristics of micro-DMFC with microcolumn and planar electrodes using 2M CH_3OH and air: (a) open circuit voltage; (b) voltage vs current.

sand times lower than that obtained by the traditional DMFCs[11,12] with carbon-based porous electrodes. However, the micro-DMFC fabricated using only MEMS technology is the first attempt to produce micro-DMFCs using a built-in fuel chamber with diffusive reactants.

As shown in Fig. 10(b), voltage-current characteristics indicate a high cell-to-cell power deviation. Because all electrodes were fabricated by a batch process and we measured electric power under the same experimental conditions, cell-to-cell power

deviations may results from the instability of the assembly of the upper electrode, Nafion™, and the lower electrode due to nonuniform bonding pressure distribution and misalignment in the hot processing. As shown in Fig. 6, the applied pressure is concentrated in the A and B regions, thus resulting in a nonuniform bonding interface between the electrodes and Nafion™. However, in spite of the nonuniform bonding interface, the micro-DMFC with microcolumn electrodes shows a 22-fold higher power density than the micro-DMFC with planar electrodes. The micro-DMFC with microcolumn electrodes shows a constant maximum power of 122.4 μW/cm^2 for 40 min as shown in Fig. 11.

6. Conclusions

To improve power density in micro-DMFCs, a microcolumn electrode is proposed. We designed and fabricated both microcolumn and planar electrodes with an identical projective area of 4.5 mm×4.5 mm to compare the characteristics of the microcolumn electrode with those of planar electrodes and to compare a DMFC based on microcolumn electrodes with one based on planar electrodes. In the single-cell test, the micro-DMFC with microcolumn electrodes demonstrated a maximum power of 24.8 μW(122.4 μW/cm^2) at 0.65V and a projective area of 4.5 mm×4.5 mm, while the micro-DMFC with planar electrodes showed a maximum power of 1.1 μW(5.6 μW/cm^2) at a voltage of 0.08 V and the same projective area. Cell-to-cell power deviation may result from the instability of the assembly of the upper electrode, Nafion™, and the lower electrode due to nonuniform bonding pressure distribution and misalignment in hot processing. Low electric power may be caused by the poor contact between the electrodes and Nafion™. The micro-

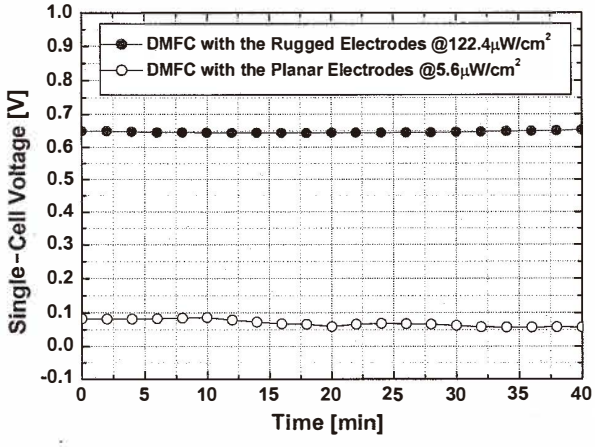


Fig. 11. Measured lifetime of the micro-DMFC with microcolumn and planar electrodes using 2M CH_3OH and air.

DMFC with microcolumn electrodes showed a constant maximum power of 122.4 μW/cm^2 for 40 min. From experimental studies, the micro-DMFC with microcolumn electrodes showed a maximum power density 22 times higher than the micro-DMFC with planar electrodes in the single-cell test. Consequently, we verified that this prototype of the micro-DMFC with microcolumn electrodes has potential application in portable power sources for portable health care and communication systems such as low-power digital signal processors and glucose sensors.

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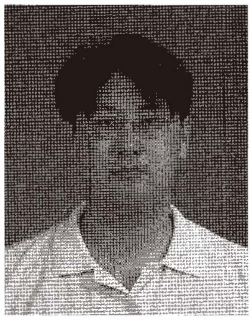
About the Author



Young Ho Seo was born in Pusan, Korea, in 1975, He received his B.S. degree from Pusan National University, Pusan, Korea, in 1998, his M.S. degree from Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea, in 2000, and his Ph.D. degree from the Korea Advanced Institute of Science and Technology (KAIST), for his MEMS-based fuel cell development completed in August, 2003. In September 2003, Dr. Seo moved to the Korea Institute of Machinery and Materials (KIMM), where he is currently a Senior Researcher in the Department of Intelligence and Precision Machine.

Dr. Seo's research interests are focused on the development of milli-to-micro and micro-to-nano interface technologies and mass-production technologies of Bio-MEMS and Optical MEMS components using injection molding processes.

Young-Ho Cho received his B.S. degree *summa cum laude* from Yeungnam University, Daegu, Korea, in 1980; his M.S. degree from the Korea Advanced Institute of Science and Technology (KAIST), Seoul, Korea, in 1982; and his Ph.D. degree from the University of California at Berkeley for his electrostatic actuator and crab-leg microflexure research completed in December, 1990.

From 1982 to 1986 he was a Research Scientist at CAD/CAM Research Laboratory, Korea Institute of Science and Technology (KIST), Seoul, Korea. During 1987-1991, he worked as a Postgraduate Researcher (1987-1990) and a Postdoctoral Research Associate (1991) of the Berkeley Sensor and Actuator Center (BSAC) at the University of California at Berkeley. In August 1991, Dr. Cho moved to KAIST, where he is currently an Associate Professor in the Departments of BioSystems & Mechanical Engineering as well as the Director of the Digital Nanolocomotion Center.

Dr. Cho's research interests are focused on optomechanical and biofluidic MEMS with micro-/nano-scaled actuators and detectors for photon manipulation and biomedia processing. In Korea, he has served as the Chair of the MEMS Division in the Korean Society of Mechanical Engineers, the Chair of the Steering Committee in Korea National MEMS Programs, the Chair of the Steering Committee in Korean Next Generation Technology Development Program, the Leader of the Nanobio-Group in National NanoForum and the Committee of National Nanotechnology Planning Board. Dr. Cho has also served for the international technical society as the General Co-Chair of IEEE MEMS Conference 2003, the Program Committee of IEEE Optical MEMS Conference, the Chief Delegate of the Republic of Korea in World Micromachine Summit. Dr. Cho is a member of IEEE and ASME.