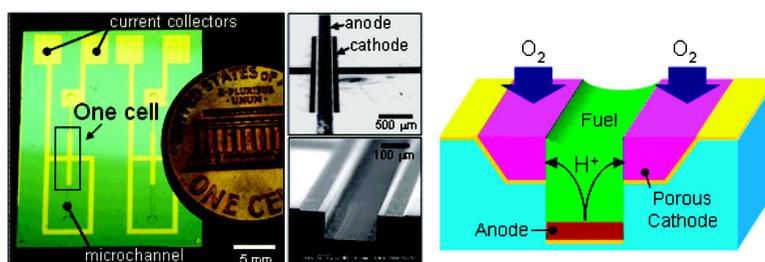Communication

On-Chip Fuel Cell: Micro Direct Methanol Fuel Cell of an Air-Breathing, Membraneless, and Monolithic Design

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On-Chip Fuel Cell: Micro Direct Methanol Fuel Cell of an Air-Breathing, Membraneless, and Monolithic Design

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This paper proposes a novel design for a microfuel cell as an on-chip power source and demonstrates its fabrication and operation to prove the concept. The design of the on-chip cell concurrently realizes air-breathing, membraneless, and monolithic structures. Its simple design is important from the viewpoints of fabrication (e.g., replication), integration, and compatibility with other microdevices.

The rapid development of miniature devices (e.g., microsensors[1]) has resulted in an increasing demand for miniature power sources. For example, microfuel cells,[2,3] microbatteries,[4] and microsolar cells[5] have been considered as possible on-chip power sources. Fuel cells operating on liquid fuel (e.g., methanol aq. and glucose aq.) have several desirable properties, including high energy density, a simple system, and low-temperature operation (<60 °C). Thus, we used microelectromechanical systems (MEMS) technology to fabricate a microdirect methanol fuel cell (μ-DMFC) with a "monolithic" structure, in which two electrodes are formed on a single substrate.[2] This structure is suitable for microfuel cells in terms of (i) the monolithic structure eliminates the troublesome alignment of the microelectrodes and (ii) the device can be replicated on polymer substrates, due to the simple microchannel-based structure.[6] However, performance was limited by the lack of an oxidant supply, resulting from the utilization of dissolved oxygen,[7] which is dilute (1–2 mM at 25 °C) and has a low diffusion coefficient (2×10^{-5} cm²/s) compared to the general oxidant for fuel cells, i.e., gaseous oxygen (0.2 cm²/s).[8,9] To improve design for on-chip fuel cells, we designed a novel monolithic μ-DMFC with an "air-breathing" structure for utilizing oxygen in the air (passive supply).

Here we propose an on-chip μ-DMFC of an air-breathing, membraneless, and monolithic design. To concurrently realize a structure that is both monolithic and air-breathing, it was necessary to omit the electrolyte membrane separating the anodic and cathodic compartments, since an air-breathing structure requires that the cathode is exposed to air. Since the omission of a membrane not only reduces the volume but also enhances flexibility in cell design, membraneless structures are extremely useful in the miniaturization of fuel cells. The membraneless fuel cells reported so far can be classified into two types: laminar flow-based fuel cells (LFFCs)[9,10] and fuel cells with selective catalysts (e.g., biofuel cells).[11] Though LFFCs are of great interest in terms of their concept based on a virtual membrane, capillary force limits their size to millimeter scale.[3] For this reason, we applied a selective catalyst for oxygen reduction, Pd–Co,[12,13] as a possible sample catalyst to introduce a membraneless structure.

Figure 1 illustrates the proposed design. The microchannel-based structure supplies liquid fuel by capillary force to the anode formed on the bottom of the channel. Through the liquid fuel containing electrolytes, protons generated from the methanol oxidation on the anode transfer to the porous cathode exposed to air and then react with oxygen to produce H_2O.
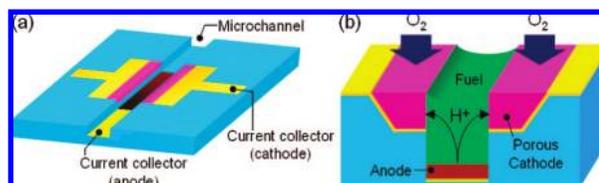

Figure 1. Schematic diagrams of the air-breathing, membraneless, and monolithic design of an on-chip fuel cell: (a) Layout of current collectors and a microchannel. The cell consists of two cathodes at the top of the channel and an anode on the bottom. (b) Cross-sectional view of the electrodes and the microchannel filled with a fuel solution.

Scheme 1. Fabrication Procedure for the On-Chip Fuel Cells (before Catalyst Deposition)
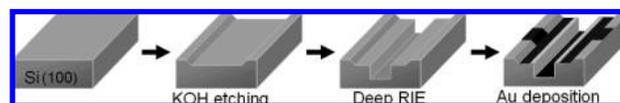
The proposed design was fabricated on a Si substrate through a series of microfabrication processes (Scheme 1), including etching of a microchannel, deposition of Au current collectors, and electrodeposition of catalysts. First, a shallow trapezoidal channel (depth, 5 μm; top width, 400 μm; bottom width, 390 μm; length, 6 mm) was etched by KOH on a Si(100) substrate, after lithographic patterning of a photoresist. Second, along the bottom of the shallow channel, a deeper rectangular channel (depth, 100 μm; width, 200 μm) was etched by deep reactive ion etching (RIE), after lithographic patterning of a photoresist. Third, a Au layer (thickness, 200 nm) was electron-beam deposited to create current collectors, using a 3-D lithography technique after patterning of a photoresist.[14] Finally, the current collectors were catalyzed by electrodeposition of a Pt–Ru alloy for the anode and of a Pd–Co alloy for the cathode, as described in our previous reports.[12]

As shown in Figure 2, the fabricated cell is composed of a small power-generating area (width, 400 μm; length, 6 mm), a microchannel for the fuel supply, and current collectors for evaluation. Though this proof-of-concept prototype cell has large current collectors, only small interconnections are required for real on-chip applications. In addition, the integration of multiple cells was demonstrated as shown in Figure 2a (two cells).

Cell performance was evaluated in terms of the current–voltage (I–V) characteristics and the endurance under ambient conditions, simply by dropping a 2 M methanol solution containing a supporting electrolyte onto the end of the microchannel. As shown in Figure 3a, it is of great importance that reasonable voltage was obtained without a separate membrane and liquid flow mechanism (pumps). In the case of H_2SO_4 (electrolyte), the maximum power was ca. 1.4 μW, and the open circuit voltage was ca. 0.50 V. Na_2SO_4 was also tested as a supporting electrolyte, since operation of fuel cells under neutral conditions is attractive from the viewpoint of its high
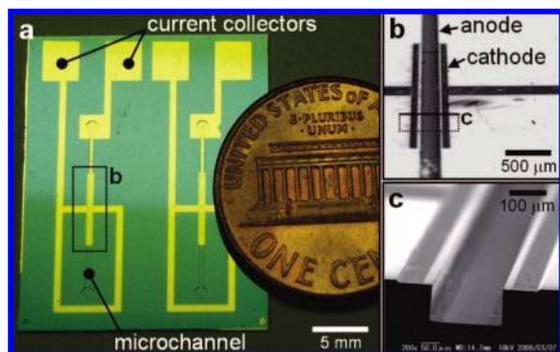
Figure 2. Observation of the on-chip fuel cell fabricated on a Si substrate (without catalysts). (a) Photograph (top view) of two cells integrated on a silicon substrate. SEM images: (b) Birds-eye view of the power generating area composed of one anode and two cathodes; (c) cross-sectional view of the microchannel.
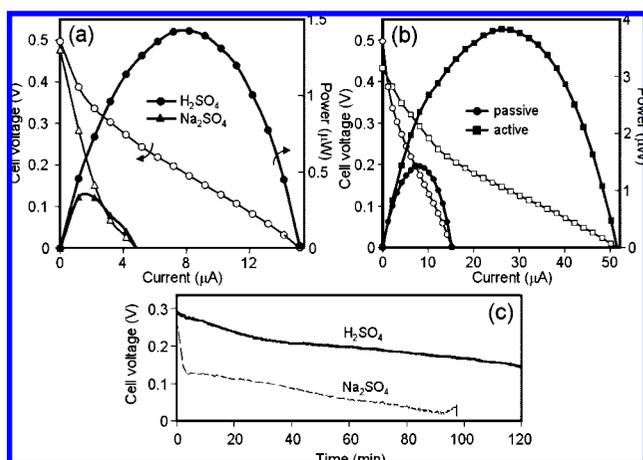

Figure 3. Cell performance of the on-chip μ-DMFC operated on 2 M methanol under ambient conditions ($\sim$25 °C). I–V curves ($\bigcirc$) and I–P curves ($\bullet$) (1 min/point): (a) Comparison between 0.5 M H_2SO_4 and 0.5 M Na_2SO_4 used as supporting electrolytes; (b) comparison with our previous cell (active type). Catalysts and electrolyte (H_2SO_4) are the same in both cells. (c) Endurance test: at 4.2 μA for H_2SO_4 and at 1.1 μA for Na_2SO_4.

biocompatibility and low causticity. The maximum power was ca. 0.2 μW, less than that obtained using H_2SO_4, while the open circuit voltage was ca. 0.48 V, comparable to that using H_2SO_4. The difference in performance can be attributed to the pH dependence of the catalytic activity[15] and also to the difference in oxygen solubility.[8]

Compared to our previous cell with pumps, the I–V characteristic of the new cell is still lower (see Figure 3b). In the case of H_2SO_4, since the catalysts and the fuel supply could possibly be the same, the lower performance is mainly attributable to the oxygen supply, i.e., the air-breathing supply. However, the I–V characteristic does not include energy loss caused by pumps, which became as high as >100 μW in our previous cell due to the large capillary force in the microchannels.[3] Therefore, the net power of the new cell is higher than that produced by the previous cell. Moreover, compared with an on-chip fuel cell that used hydrogen as fuel (power, 0.5 μW at 0.54 V; size, 4 mm²),[16] the power of our on-chip cell is superior though smaller.

In the endurance test (Figure 3c), the cell continued to generate electric power for more than 1 h, even though it does not have a cover for preventing fuel evaporation. The gradual decrease in

voltage can be mainly attributed to the consumption of fuel, though some concern remains about the fuel loss caused by evaporation. In the case of Na_2SO_4, voltage was dramatically degraded in the first 5 min, and these behaviors on voltage reduction were reproduced after a rinse with H_2O. Thus, the sharp decrease was not attributable to degradation in the catalysts but probably to local acidification around the anode,[15,17] caused by carbonate ions originating from the methanol oxidation. However, detailed studies are needed to determine the mechanism.

In sum, we have proposed a novel μ-DMFC suitable as an on-chip power source. The prototype cell proved that the concept, i.e., to generate electric power without pumps, was valid. Though the net performance was higher than that of other on-chip fuel cells, we believe that optimizing the loading of catalysts and/or the microstructures of electrodes (for example, by adding an ionomer to the cathode in a technique similar to that for conventional fuel cells) will result in further improvements in the performance.

Supporting Information Available: Materials and detailed fabrication procedures; scheme of the preparation procedure; schematic illustration of Figure 2a; additional SEM images and a photograph; I–V curves obtained at a fast scan (1 s/point).This material is available free of charge via the Internet at http://pubs.acs.org.

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