A Flexible Ascorbic Acid Fuel Cell with a Microchannel Fabricated using MEMS Techniques

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Abstract. We fabricated a miniature ascorbic acid fuel cells equipped with a microchannel for the circulation of ascorbic acid (AA) solution using micro electronic mechanical system techniques. The fuel cell was fabricated on a flexible polyimide substrate, and its porous carbon-coated aluminium (Al) electrodes of 2.8 mm in width and 11 mm in length were formed using photolithography and screen-printing techniques. The porous carbon was deposited by screen-printing of carbon-black ink on the Al electrode surfaces in order to increase the effective electrode surface area and to absorb more enzymes on the cathode surface. The microchannel with a depth of 200 μm was fabricated using a hot-embossing technique. A maximum power of 0.60 μW at 0.58 V that corresponds to a power density of 1.83 μW/cm² was realized by introducing a 200 mM concentrated AA solution at room temperature.

1. Introduction

Recently, great attention has been paid to the appearance of power sources, especially for human wearable or portable electronic equipment. These power sources have to correspond to ubiquitousness for the next generation, and it is necessary to develop highly convenient and miniaturized devices using safe materials for a human body. An ascorbic acid (AA), also known as vitamin C, is an environmentally and biologically friendly compound. Furthermore, it has been well known that the AA oxidation advanced on the carbon electrodes without metal catalysts [1,2]. Fujiwara et al. have reported a fuel cell adopting AA and without catalysts on the anode [3-6]. This device does not require a precious metal catalyst on the anode, and does not release any toxic product. Moreover, Fukushi et al. have reported a miniature glucose fuel cell with a microchannel fabricated on polyimide (PI) substrates using micro electronic mechanical system (MEMS) technologies [7]. This paper reported on relatively low cost and miniaturized fuel cells adopting enzymes instead of precious catalysts and MEMS fabrication processes. The fuel cells were superior in flexibility and disposability. We also report the fabrication and characterization of miniaturized ascorbic acid fuel cells (AAFCs) with microchannels fabricated on PI substrates using thermal nanoimprinting techniques [8-10] and MEMS technologies.
2. Experimental

2.1. The power generation mechanism and the schematic of the AAFCs

Figure 1 describes the possible power generation mechanism of the AAFCs. The AAFCs was composed of an anode with no catalysts and a bilirubin oxidase (BOD)-adsorbed cathode [11-14]. On the anode, the AA was oxidized on the electrodes surface, and dehydro ascorbic acid (DHAA) was generated. As a result, the electrons and protons were produced on the anode. The electrons were transferred from the anode to the cathode via an external circuit to extract electricity. Oxygen (O$_2$) in the fuel solution was reduced by BOD immobilized on the cathode to water (H$_2$O) on reaction with electrons and protons. Figure 2 shows the layout of the electrodes and the schematic of the AAFCs with the microchannel and the photography of the fabricated AAFCs. The cathode has a width of 2.8 mm (W) and length of 10 mm (L$_1$), and the anode has a width of 2.8 mm (W) and a length of 1 mm (L$_3$). These electrodes were fabricated by photolithography on a PI film (Kapton, DuPont), coated with aluminium (Al) and then modified by carbon black. The gap between the cathode and anode was 0.5 mm (L$_2$). The microchannel was fabricated on another PI film (Kapton, DuPont), and it was designed to have a width of 3 mm, a depth of 200 μm, and a length of 11.5 mm. These two patterned PI substrates were adhered to form a fuel cell by double-sided Kapton tapes (Sumitomo 3M). The cathode was designed to be larger than the anode to account for the lower concentration of oxygen in comparison to that of AA; to reduce the flux of oxygen in the upstream to the anode and consequently to improve the AA oxidation performance [15]. In order to investigate the characteristics of the anode and cathode independently using cyclic voltammetry, one of the electrode areas was fabricated to be a silver-silver chloride (Ag|AgCl) reference electrode by coating the Al surface with an ink of Ag|AgCl (BAS Inc.).

![Figure 1](image1.png)  \textbf{Figure 1.} The possible power generation Mechanism.

![Figure 2](image2.png)  \textbf{Figure 2.} The layout of the electrodes and the schematic of the AAFCs with the microchannel and the photography of the fabricated AAFCs.

2.2. Fabrication processes of the carbon-modified electrodes and microchannel

The carbon-modified electrodes were fabricated on a PI sheet using conventional MEMS fabrication processes [7]. In order to increase the effective electrode surface area and the amount of enzymes on the electrode surfaces, we coated the fabricated Al electrode surfaces with the carbon-black ink [15-18]. Porous structures were clearly observed by a scanning electron microscopy, which suggested an increase in the electrode surface area. The microfluidic channel was also fabricated on the PI substrate using photolithography and hot-embossing as previously reported [7].
2.3. Fabrication processes of the enzyme-modified cathode

0.03 mg of BOD was mixed with 20 μl of phosphate buffer solution (50 mM, pH 7.0). 20 μl of the BOD solution was dropped on the cathode (surface area of 28 mm²). Then the cathode was subjected to UV-ozone treatment for 15 min and left to dry for 40 min. According to a previous report, BOD was stable in circumneutral pH and didn’t generate reaction intermediates during oxygen reduction process [19].

2.4. Measurements

Electrochemical measurements were performed in 200 mM ascorbic acid solution (AAS) and 50 mM pH 7.0 phosphate buffer solution (PBS) at room temperature. The electrochemical properties of the electrodes were characterized using a potentiostat (Electrochemical Analyser, HA-1518, HokutoDenko) having a three electrodes system, wherein the enzyme-modified electrode was the working electrode, the Ag/AgCl modified electrode was the reference and platinum was the counter electrode. The power measurement systems were performed introducing the AAS into the reaction chamber through the microchannel by pulling a syringe pump. The power generated was evaluated by measuring the cell voltage while varying the external load resistance between 0 and 3 MΩ. The following equation was used:

$$W = \frac{V^2}{R}$$

where $R$ is the load resistance, and $V$ is the generated voltage measured between the terminals of the fuel cell. The power density was calculated by dividing $W$ with the total area of the anode and cathode, which was 30.8 mm².

3. Results and discussion

Figure 3 shows the cyclic voltammograms of the anode. The potential was scanned toward positive potential direction from -0.6 V to 0.8 V. The electrochemical measurements were performed on (a) porous carbon modified electrodes (PCE) in AAS, (b) glassy carbon electrodes (GCE) in AAS, and (c) PCE in PBS, respectively. The maximum current density on the PCE was 24 mA/cm² at 0.80 V, and it was approximately 2.5 times higher than that of the GCE. The potential at the AA oxidation reaction on the PCE was 0.13 V, and that on the GCE was 0.31 V. The potential at the oxidation reaction of the AA on the PCE was 0.18 V lower than that on the GCE. It was considered that these results were due to the increase of the active surface areas of the porous carbon. The current density in the PBS was very small compared to others. In contrast, the increasing of the current density associated with the oxidation reaction appeared clearly in the AAS. The current was assumed to be generated by oxidation of AA, because phosphoric acid did not contribute to the oxidation reaction.

Figure 4 shows the cyclic voltammograms of the cathode. The potential was scanned toward negative potential direction from 0.8 V to -0.6 V. The electrochemical measurements were performed on PCE in (A) AAS and (B) PBS, respectively. The maximum current density was -1.2 mA/cm² at -0.59 V. The current density of the cathode was 20 times lower than that of the anode. According to the previous reports, the higher current density of the cathode was obtained by stirring or bubbling the fuel [2,19-22]. Based on these results, it was assumed that the oxygen supply to the cathode was not enough because the cathode of this device in the microchannel was not exposed to the air. The lack of the oxygen supply caused the decrease of the current density. In order to solve this problem, it may be possible to adopt hydrofuge processes to the cathode or supply oxygen near the cathode. The reduction potential measured in the AAS was 0.36 V lower than that of the PBS. The possible reason for this may be due to the fact that AA oxidation occurred instead of the reduction of $O_2$ on the cathode. Fujiwara et al. reported that this unfavorable oxidation reaction at the cathode can be avoided by the use of an ion-exchange film (Nafion, DuPont) that repels AA by the electrostatic repulsion [3].
Therefore, we assume that the current density on the cathode of the cell investigated here can be further increased by the use of the electrolyte films by suppressing AA oxidation on the cathode.

![Figure 3. Cyclic voltammograms of (a) the anode for PCE, (b) GCE in a 200 mM AAS, and (c) PCE in a 50 mM pH 7.0 PBS.](image)

![Figure 4. Cyclic voltammograms of (a) the cathode for PCE in a 200 mM AAS, and (b) PCE in a 50 mM pH 7.0 PBS.](image)

Figure 5 shows the relationship between the current and voltage of the fuel cell during operation and the dependence of the power density on the output voltage. The maximum current density and power (power density) were 1.04 μA and 0.60 μW (1.83 μW/cm²) at 0.58 V in the AAS at room temperature. The current density of the cathode was lower than that of the anode. The electromotive force of the fuel cell is defined by the potential difference between the oxidation potential, 0.13 V of the anode and the reduction potential, 0.17 V of the cathode, and it was estimated to be 0.04 V. This may be the reason for the relatively low power generation of the cell investigated here. On the other hand, it was reported that the crossover current density of AA did not cause the reduction of the power generation performance since it was smaller (~1/100) compared to that of methanol [3]. However, it was presumed that AA was oxidized on the cathode and the crossover phenomenon should have occurred causing reduction of the electric power density based on the results of the cyclic voltammogram measurements of the electrodes.

![Figure 5. Current-voltage relationship during fuel cell operation and the dependence of power density on the output voltage.](image)
4. Conclusion

The AAFCs was fabricated on a flexible PI substrate using MEMS microfabrication processes. The fuel cell had a microchannel to introduce an aqueous of AAS. Al electrodes were formed on the PI substrate using photolithography and screen-printing. The porous carbon was deposited by screen-printing of carbon-black ink on the Al electrode surfaces in order to increase the effective electrode surface area. The microchannel with a depth of 200 μm was fabricated using a hot-embossing technique. The maximum power of 0.60 μW at 0.58 V that corresponds with the power density of 1.83 μW/cm² was realized by introducing AAS at room temperature.

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