

Glucose Fuel Cells with a Microchannel Fabricated on Flexible Polyimide Film

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Abstract. In this work, a glucose fuel cell was fabricated using microfabrication processes assigned for microelectromechanical systems. The fuel cell was equipped with a microchannel to flow an aqueous solution of glucose. The cell was fabricated on a flexible polyimide substrate, and its porous carbon-coated aluminum (Al) electrodes of 2.8 mm in width and 11 mm in length were formed using photolithography and screen printing techniques. 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 electrode surfaces. The microchannel with a depth of 200 μm was fabricated using a hot embossing technique. A maximum power of 0.45 μW at 0.5 V that corresponds to a power density of 1.45 $\mu\text{W}/\text{cm}^2$ was realized by introducing a 200 mM concentrated glucose solution at room temperature.

1. Introduction

Microelectromechanical systems (MEMS) have been extensively studied in recent years for biomedical applications such as diagnosis, treatment via targeted drug delivery [2] and embedded systems [1]. Amongst these, enzymatic biofuel cells that use glucose in a human body to produce electricity for embedded microsystems have been of special interest [3]. This is because they work under mild conditions of room temperature, neutral pH and atmospheric pressure, which make them amenable to the human body [4-19]. MEMS technologies are advantageous for biofuel cells as they enable miniaturization and mass production. Tago et al. have reported such a biofuel cell with microchannels and enzymes-modified platinum electrodes fabricated on a glass substrate [4]. However, when this device was used in vivo and subcutaneously, the fragile and inflexible glass substrate caused problems with biocompatibility. In comparison, polyimide (PI) as a substrate material offers good biocompatibility, high thermal stability, and flexibility. However, to transfer microstructures onto PI is not very easy. Nevertheless, recent reports on thermal nanoimprint techniques have shown to accurately transfer micropatterns onto PI substrates [20,21]. In this study, we report the fabrication and



characterization of glucose fuel cells with a microchannel fabricated on a PI substrate using a thermal nanoimprint technique. The fuel cell investigated here was composed of a bilirubin oxidase (BOD)-adsorbed cathode and a glucose oxidase (GOD) and osmium complex-adsorbed anode [8,9]. GOD immobilized on the anode oxidizes glucose molecules, as a result electrons and protons are produced. The electrons are transferred to the anode through an osmium complex mediator. Then they are conducted from the anode to the cathode via an external circuit generating electricity. Oxygen (O₂) in the fuel solution is reduced by BOD immobilized on the cathode to water on reaction with electrons and protons.

2. 2. Experimental

2.1 Design of glucose fuel cells with a microchannel.

Figure 1 shows the layout of the cathode and anode. The anode has a width of 2.8 mm and a length of 1 mm, and the cathode has a width of 2.8 mm and length of 10 mm. These electrodes were fabricated by photolithography on a PI sheet, coated with aluminum (Al) and then modified by carbon black and respective enzymes. The gap between the anode and cathode was 0.5 mm. The microchannel was fabricated on another PI sheet, and it was designed to have a width of 3 mm, a depth of 200 μ m, and a length of 11.5 mm. These two patterned PI substrates were stacked to form a fuel cell as shown in figure 2. The cathode was designed to be larger than the anode to account for the lower concentration of oxygen in comparison to that of glucose; to reduce the flux of oxygen in the upstream to the anode and consequently to improve the glucose oxidation performance [22]. 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.)

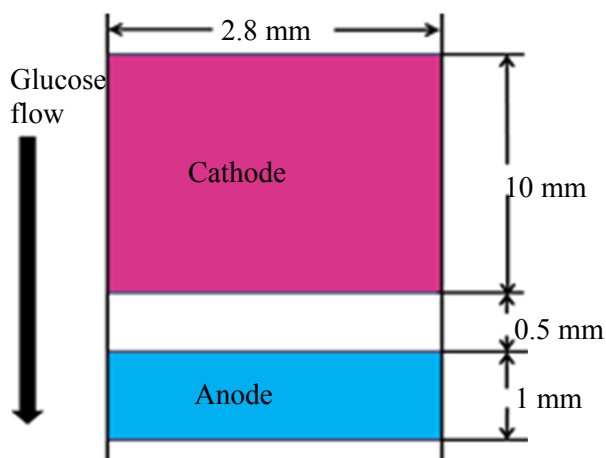


Figure 1. Layout of the electrodes on PI substrate.

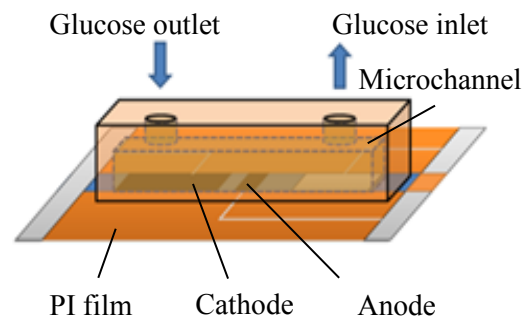


Figure 2. Design of glucose fuel cell with a microchannel

2.2 Fabrication processes

In order to increase the amount of enzymes adsorbed on the electrode surfaces, the effective surface area was increased by coating the electrode surfaces with a carbon black ink. The carbon-modified electrodes were fabricated on a PI sheet using conventional MEMS fabrication processes. Porous structures of the carbon-coated Al electrode surface were clearly observed by a scanning electron microscope (SEM), which suggest an increase in the effective electrode area.

1 mg of GOD was mixed with 25 μ l of phosphate buffer solution (PBS, 50 mM, pH 7.0). Then, 6 mg of the osmium complex mediator (Polyvinylimidazole -Os(2,2'-bipyridine)₂Cl) was mixed with 25 μ l of PBS. Finally, 2 μ l of the resulting solutions was dropped on the anode (surface area of 2.8 mm²), and left to dry for 20 min. Similarly, 1 mg of BOD was mixed with 25 μ l of PBS. 2 μ l of the resulting

solution was dropped on the cathode (surface area of 28 mm²) and left to dry for 20 min. The microfluidic channel was fabricated using hot embossing techniques as previously described in our previous report [23].

2.3 Measurements

Electrochemical measurements were performed in a 200 mM solution of glucose at room temperature. The electrochemical properties of the electrodes were characterized using a potentiostat (Electrochemical Analyzer, HA-1518, Hokuto Denko) 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 glucose solution was introduced 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:

$$W = V^2/R \quad (1),$$

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 the cathode, which was 30.8 mm².

3. Results and discussion

Figure 3 shows the cyclic voltammogram of the GOD/osmium complex-modified anode in 200 mM glucose solution. The catalytic oxidation of glucose can be clearly seen at potentials higher than 0.12 V. The maximum current density was 1457 μA/cm². This superior performance was due to the promotion of oxidation reactions by GOD and fast electron transfer by the mediator osmium complex [24,25]. The high current density saturated at a potential about 0.2 V and then showed a decrease from about 0.3 V. In this experiment, it is presumed that the reduction of the current density was due to the removal of the GOD/osmium complex mediator from the anode and the exhaustion of glucose near the surface of anode. Better immobilization of the enzymes to the electrode surface will help prevent their exfoliation.

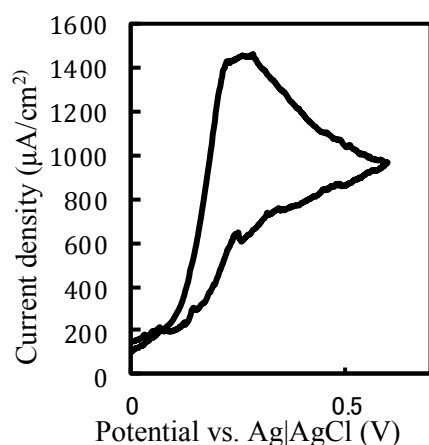


Figure 3. . Cyclic voltammogram of the GOD/ osmium complex -modified anode in 200 mM glucose solution.

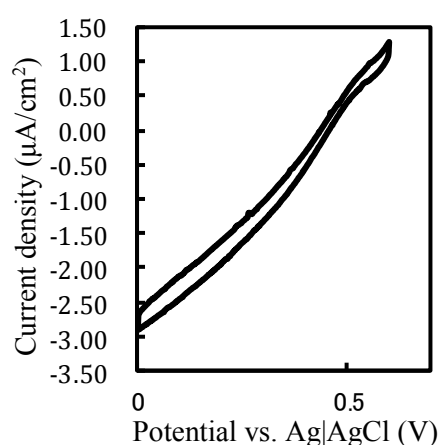


Figure 4. Cyclic voltammogram of the BOD- modified cathode in 200 mM glucose solution.

The cyclic voltammogram of the BOD-modified cathode in 200 mM glucose solution is shown in figure 4. The starting potential of the O_2 reduction current was about 0.5 V. The maximum current density was $1.45 \mu A/cm^2$. This value was almost three orders of magnitude lower than that of the anode. The stirring of fuel and bubbling of oxygen, have resulted in a high current density as reported before [6, 22, 26-29]. In this study, a high current density on reduction was not realized because the oxygen concentration in the fuel was probably low. Alternatively, perhaps the carbon ink did not increase the effective electrode surface area of the cathode. A low resistive Al film was used as the current collector for the glucose biofuel cells in this study to achieve a low cost of fabrication. However, it is possible that during the operation of the fuel cell, the Al electrodes might have eroded on interaction with the glucose solution. Al is considered to have a high ionization tendency for electrochemical corrosion. It may be necessary to use noble metals such as platinum (Pt) or gold (Au), which have low ionization tendency to keep the fuel cell performance from degrading. In this study, since we used Al as a current collector, it was presumed that the Al electrode was completely covered with the carbon ink.

The relationship between the current and voltage of the fuel cell during operation is shown in figure 5. While the dependence of the power density on output voltage is shown in figure 6. The maximum power density was $1.45 \mu W/cm^2$ at 0.5 V when the 200 mM glucose solution was introduced into cell by syringe pump. This maximum power density is lower by twenty factors when compared to the previously reported results [4]. This could be attributed to the extremely low current density at the cathode. In addition, the power measurements were made at room temperature, which could be another reason for the low value of the power generated in this study. Togo et al. have reported that the temperature of their fuel was maintained at $37^\circ C$ during power generation [4], which might have increased the catalytic activity of the enzymes

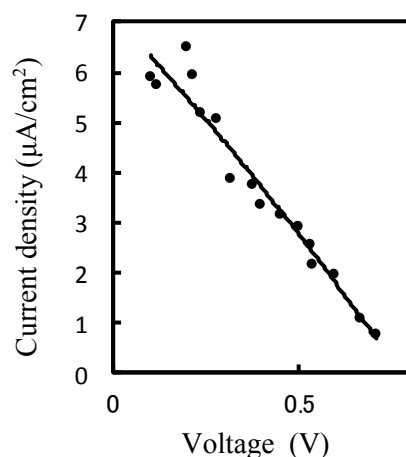


Figure 5. Current-voltage relationship during fuel cell operation.

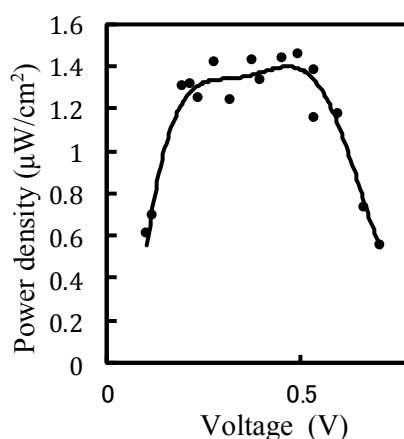


Figure 6. The dependence of power density on the output voltage.

4. Conclusion

A glucose fuel cell was fabricated on a flexible PI substrate using MEMS microfabrication processes. The fuel cell had a microchannel to introduce an aqueous glucose solution. Al electrodes of width 2.8 mm and length 11 mm were formed on the PI substrate using photolithography and screen printing. 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. The microchannel

with a depth of 200 μm was fabricated using a hot embossing technique. A maximum power of 0.45 μW at 0.5 V that corresponds with the power density of 1.45 $\mu\text{W}/\text{cm}^2$ was realized by introducing a 200 mM concentrated glucose solution at room temperature.

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