MINIATURED BIOFUEL CELLS AUTOMATICALLY RELAYED FOR LONGER-TERM POWER GENERATION

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Abstract: The present study reports a new stepwise power generation system for prolonging total lifetime of miniature biofuel cells. This system consists of parallelly-connected electrodes that were designed to be automatically activated at different timing after exposure to fuel solution by using a magnetic plastic cover and degradable glue. The timing of activaiton could be controlled by adjusting the weight ratio of Fe_3O_4 in the covers and the kind of degradable glues. The stepwisely increased power output of this system was eventually higher than the ordinary system.

Key words: biofuel cell

1. INTRODUCTION

Biofuel cells are promising for miniature power sources because of their specific characters such as high reaction selectivity and organic-based components, which enables to construct renewable, miniature and safe systems. In addition, biofuel cells are able to generate electricity from complex solution containing fuel and oxidant such as soft-drink, alcohol and blood. Despite these merits, there are some problems to be solved. The problematic lower power has recently been improved rapidly by using nano-materials as electrode. Another remaining problem is stability of the cell. The lifetime of an enzymatic biofuel cell is usually determined by enzyme stability which could be improved by protein engineering and immobilized state of enzymes. In recent days, some researchers suggested that the immobilized enzymes within a microstructure, such as a meso-porous carbon matrix [1] or Nafion membrane [2], showed higher stability.

We report here an attempt for prolonging total lifetime of miniature biofuel cells. Fig. 1 (a) shows the principle of our system, in which micro-biofuel cells protected with different kinds of degradable films are arrayed and connected in parallel. Each of the cells is designed to be activated at different time intervals after exposure to the fuel solution. The timing of activation will be controlled by the properties of the degradable films: the material used, molecular weight, composition, or thickness. Then, the total power output can be expected to be more stable than an ordinary system (Fig. 1 (b)).

We have demonstrated that the provisional protection of subsets of biofuel cells was effective in prolonging the total lifetime of the fuel cell system [3]. In the primary experiments, we fabricated the devices like fig. 1 with 70 μm-thick poly(lactic-co-glycolic acid) (PLGA) films as degradable protect membranes. After exposing to solution, PLGA cover films were swollen, lost its rigidity and attached to electrodes before the membranes were dissolved away. When the electrodes were wet with swollen membrane, the cell started generating electricity. Consequently it was difficult to control the exposure time of the stored electrode. Therefore, in this paper we used degradable materials as just glue not as the protect membrane itself. In addition, we thought that some additional forces might be required to peel off the protection

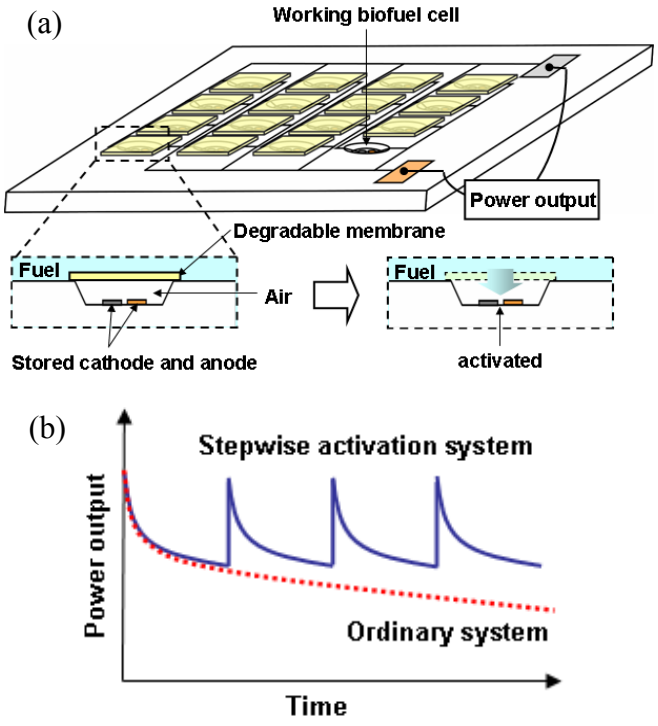

Fig. 1: (a) Schematic illustration of an array of miniature biofuel cells protected with degradable films that can be stepwisely degraded. (b) The image of the expected performance of the stepwise activation system.

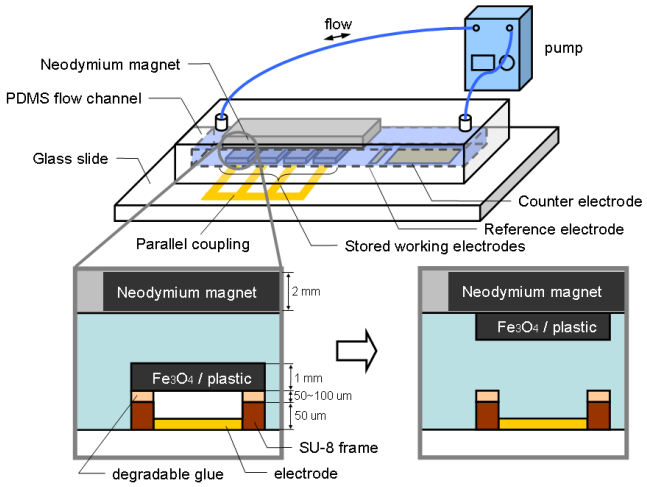

Fig. 2: Prototype of miniature biofuel cells.

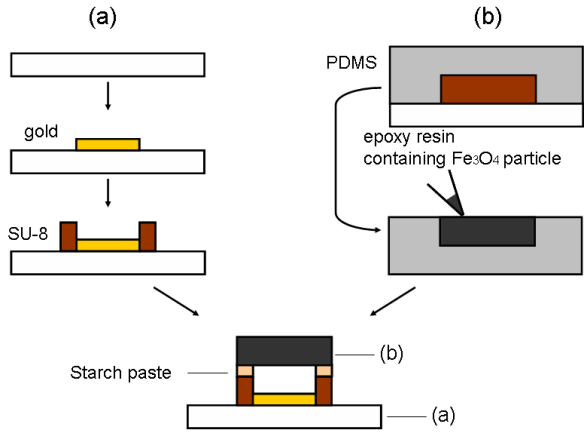

Fig. 3: Fabrication process of (a) electrode and SU-8 frame patterned on a glass slide, (b) magnetic plastic cover and their lamination.

membranes. As shown in fig. 2, we applied magnetic force to lift up the membrane from the electrodes area.

2. EXPERIMENTAL

2.1 Construction of the biofuel cell

We designed and tested a degradable device to investigate the feasibility of multi-pulse electrode activation without any external trigger. Fig. 2 shows the experimental system in this study. Electrodes covered with magnetic plastics which glued to the SU-8 frame were electrically connected in parallel. When whole cells were wetted by fuel solution, the glue films started to degrade and finally the magnetic cover peeled off from the frame and lifted up to the neodymium magnet set at the top of the flow channel. By changing the degradation rates of the glue and/or magnetic power, we adjusted the stored time of the electrodes for achieving multi-pulse electrode activation.

2.2 Fabrication procedure

Fabrication process of the electrode covered by magnetic plastic was briefly stated in fig. 3. Gold electrodes and SU-8 frames which made for being basis of the magnetic plastics were fabricated on a glass slide by photolithography and spattering (Fig. 3 (a)). Magnetic plastic covers were made using PDMS mold. A mixture of thermosetting epoxy resin and 10 ~ 60 wt. % of Fe_3O_4 particle was applied to PDMS mold and cured in a conventional oven for a few hours (Fig. 3 (b)). Finally, these two components described above were glued together by using starch paste which is common water-soluble glue. Here, the starch paste was stenciled on the magnetic cover so as to be ca. 100 μm-thick.

A 5 mm-height and 6 mm-wide PDMS flow channel was fabricated. As shown in fig. 2, a 2 mm-thick neodymium magnet plate was set at the roof of the flow channel. Glass layer and PDMS flow channel were laminated, and connected to peristaltic pump through silicone tube.

2.3 Preparation of electrocatalysts

When using an enzyme electrode as a working electrode, gold electrode was modified with carbon particle, electron mediator polymer and enzymes [4, 5]. A brief description of the preparation follows. An 8 μL PLL-VK_3 solution (4.83 mM VK_3) was mixed with a 2 μL Dp solution (14 μg μL^{-1}) and 1 μL of KB dispersed water (ca. 13 mg mL^{-1}). A 1.5 μL portion of the resulting solution was put onto a gold film electrode (surface area, 0.0225 cm^2) on a glass substrate, and was left to dry in air. To create the enzymatic bilayer, the surface of a PLL-VK_3/Dp-coated KB electrode was coated with 1.4 μL of a solution composed of equal volumes of a 16 μg μL^{-1} GDH solution and a 16 mg mL^{-1} PLL solution.

2.4 Electrochemical measurement

All electrochemical measurements were performed in 50 mM phosphate buffer solution (pH 7.0) containing 0.1 M NaCl at room temperature. The electrochemical output of the electrodes were collected using an Electrochemical Analyzer (Model 600S, BAS) with three electrode system containing an enzyme-modified electrode as the working electrode, an Ag|AgCl (0.1 M NaCl) reference electrode and a gold counter electrode. All measurements were conducted using constant voltage mode. A peristaltic pump (SJ-1220-2, ATTO) was used to make a controlled flow in the fluidic channel.

3. RESULTS AND DISSCUTTIONS

3.1 Parameters affecting storage time

We studied the effects of Fe_3O_4-contens in plastic cover and flow conditions on the time-delay for exposure of electrodes (storage time) by measuring the oxidation current of $Fe(CN)_6$. Fig. 4 shows the typical result of the stepwise electrode activation using the system described in 2.1. During the electrode was covered with the magnetic plastic, the observed current was nearly zero, and then the current was rapidly increased with lifting up of the magnetic plastic cover when the glue was degraded (gradually swelled and dissolved) and adhesion force was getting weaker than magnetic force (Fig. 4 (a)). In the following experiments, the exposure of the electrodes was judged from the electrical pulse like shown in fig. 4 (b).

At first, we found that the drying time of the starch paste was affected to the storage time of the electrode. Shorter drying time made the storage time shorter probably due to the residual water in a starch paste which will affect the adhesion force and its stability. These results indicate that the material property of the glue could control the storage time of the electrodes. The storage times of the electrodes were almost constant over 12 h of drying. In the following experiments, the drying time of the starch glue was set to around 24 h.

As shown in fig. 5 (a), the storage times were shorter when the used plastic covers contained larger amount of Fe_3O_4. Unfortunately averaged storage times of 40 and 20 wt. % Fe_3O_4-contained magnetic plastics did not show clear difference in the storage time. The data variation is thought to be causally related to unevenness of the starch glue coated on the magnet plastic. In fact, the viscosity of starch paste was too high to be coated thinly and evenly.

Fig. 5 (b) shows the relation between storage times and flow rates. Storage time at each flow velocity was around 0.2 hours. These results indicate that the degradation rate of the starch paste was not related to the flow velocity at least in this range. And the results also suggest that the flow direction and/or electrode arrangement might not be related to the degradation rate of the glue.

3.2 Stepwise electric power generation

Fig. 6 shows the time course of the output current from the prototype device shown in fig. 2. The device had parallelly-connected four enzyme electrodes which prepared as described in 2.3. Each electrode was covered with the magnetic plastic containing 60, 40, 20, and 10 wt. % Fe_3O_4 particle and glued with degradable starch paste (Fig. 6 (b)). We also prepared uncovered parallelly-connected four enzyme

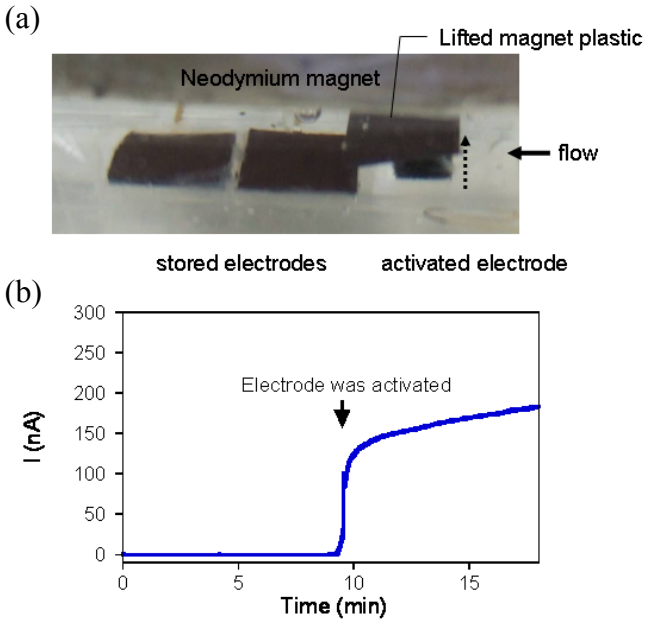

Fig. 4: Typical photograph and time course of current produced by the prototype device covered with the magnetic plastic.

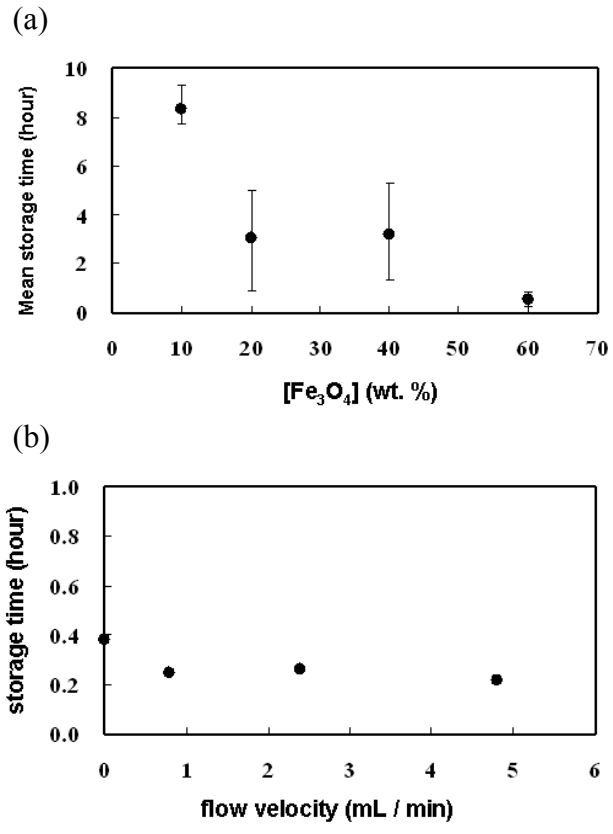

Fig. 5: Parameters affecting to storage time of electrodes (a) the mixture ratio of Fe_3O_4, (b) the flow rate. The measurements were performed three times in the phosphate buffer (pH 7) containing 5 mM $K_3[Fe(CN)_6]$, 0.1 M NaCl, at room temperature, with a flow rate of 0.8 mL min^{-1} (a).

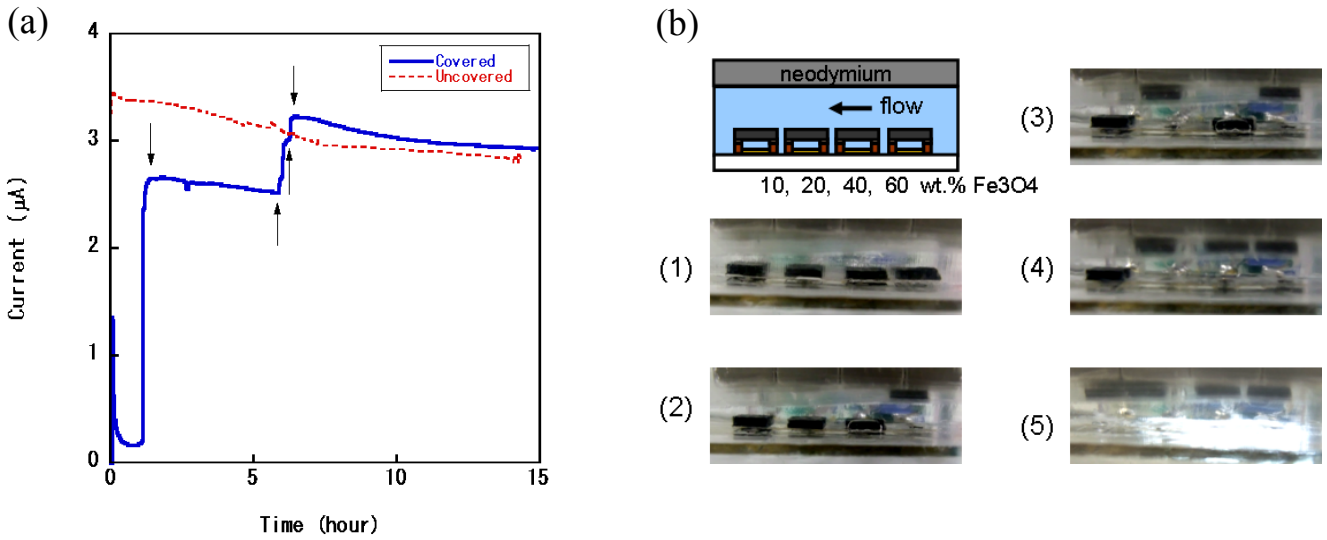

Fig. 6: Time course of (a) the current and (b) typical photographs produced by prototype of miniature biofuel cells covered with magnetic plastic and starch paste. The cell was working under 50 mM glucose, 5 mM NAD^+ and 0.1 M NaCl containing phosphate buffer solution (pH 7). The flow rate was 0.8 mL min^{-1}.

electrodes as the control. By using enzyme electrodes as anodes and Ag|AgCl electrode as a cathode, the output current of the glucose biofuel cell (R = 100 kohm) was measured in an air-saturated phosphate buffer (pH 7, 37°C) containing 50 mM glucose and 5 mM NAD^+. The solid line shows the output current of electrodes covered with magnetic plastics and the dotted line shows the current of uncovered electrodes. The observed small current of the covered cell at first stage (0 to 67 min) was produced from uninsulated lead wires. The current suddenly increased to 2.6 μA at 67 min due to lifting up of the magnetic cover containing 60 wt. % Fe_3O_4 (Fig. 6 (b)-(2)) and then the electrode was activated. In this term, the power output of uncovered electrodes was still higher than covered electrodes. Around 6 hours later, the power output of covered electrodes increased rapidly with lifting up of the magnetic cover (Fig. 6 (b)-(3), (4) and (5)). The difficulty in controlling the storage time was caused by the unevenness of starch glue as described 3.1. However, the power output of covered electrodes exceeded that of uncovered electrodes at 360 min (6 h). These results principly demonstrate that the stepwise power generation system was effective in prolonging the total lifetime of the biofuel cell.

4. CONCLUSION

We demonstrated that the provisional protection of subsets of biofuel cells is effective in prolonging the total lifetime of the fuel cell system. In this experiment, we obtained several hours of electrical pulse interval by using the magnetic cover glued with starch paste. Practically, much longer interval or precise control of the storage time should be obtained. In such case, PLGA glue is hopeful because the PLGA glue could store the electrode for a few days or more in other preparatory experiment. In addition, future work will be focused on replacing the magnet power to another power such as buoyancy of cover materials.

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