Supporting Information

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Toward Wearable Energy Storage Devices: Paper-Based Biofuel Cells based on a Screen-Printing Array Structure

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Single cell fabrication process.

A water-repellent-treated Japanese paper (Gasenshi Izumo, Keynote Planning Co., 120 mm thickness) was used as the printable substrate. This Japanese paper has a printable smooth surface and good oxygen permeability. One side of the paper surface was coated with a water repellent (Hajix, Comens Corp., Japan), the principal component of which consists of silicon nanoparticles. The water-repellent-treated Japanese paper showed good oxygen permeability.

The PBFC was fabricated using a screen printer (LS-150TV, NEWLONG SEIMITSU KOGYO Co. Ltd., Japan). Screen-printing techniques have been widely applied to the fabrication of enzyme electrodes because of the following advantages: (a) Precise patterns of the μm order can be drawn at high speed (~70 m min⁻¹), (b) a wide variety of inks can be used, (c) they provide high reproducibility, and (d) low cost. The screen-printed enzyme electrodes consist of several layers that are formed by the successive deposition of inks.

The PBFC was composed of bioanode and biocathode components in which porous carbon electrodes were constructed using porous carbon inks. A conductive carbon layer (5 mm x 10 mm) was printed using conductive carbon ink (JELCOM CH-10, Jujo Chemicals) onto the water-repellent Japanese paper, followed by curing at 120 °C for 30 min. To allow oxygen supply from the paper to the porous carbon layer, the biocathode conductive carbon layer had 25, 0.5 mm diameter, pores. A 5 mm square porous carbon layer was then printed onto the side containing the conductive carbon layer, followed by drying at 60 °C for 20 min. The porous carbon inks were prepared using Ketjen black (KB, 300-J, Lion Corporation, Japan), which has a high surface area and ideal mesopores for electro-enzymatic reactions. The porous carbon ink
was composed of 320 mg of KB and 80 mg of polyvinylidene difluoride (PVdF) binder (Kureha Corp.) in 5 mL of isophorone. The porous carbon ink was mixed by ultrasonic homogenization for 5 min, followed by planetary centrifugation for 2.5 min.

For glucose oxidation on the bioanode surface, 5 μL of glucose oxidase (GOx from Aspergillus niger, Cat. No: 599-04681, 100 U mg⁻¹, Wako Corp, Japan) solution (20 U μL⁻¹, dissolved in phosphate buffer solution at pH 7.0) and 5 μL of a saturated tetrathiafulvalene (TTF) solution in methanol, were added via syringe onto the porous anodic carbon layer, pre-treated with UV/ozone for 15 min. The biocathode was prepared by applying 5 μL of bilirubin oxidase (BOD from Myrothecium sp., Cat. No: BO-3, 1.2 U mg⁻¹, Amano Enzyme Inc.) solution (1 U μL⁻¹) containing 0.01% Triton X-100 onto the UV/ozone-pre-treated porous carbon layer.
Finite element method simulation of single cell of array-type PBFC.

The finite element method (FEM) is a numerical analysis technique that is widely used in the field of electrochemical research.\textsuperscript{[1]} In the present study, we simulated the current distributions and oxygen consumptions in three models of an array-type PBFC single cell. Figure S1(a) shows a schematic illustration of the theoretical model of a single cell.

We assumed that the single cell was composed of three parts:

1. The bioanode (1 cm\(^2\)), which consisted of a porous carbon electrode on a conductive carbon layer. The enzyme (0.01 mM) and mediator (0.5 mM) were assumed to be immobilized on the porous carbon electrode. The catalytic reactions obey the “Ping-Pong Bi-Bi Mechanism”, as shown in Fig. S1(a).\textsuperscript{[2]}

2. The electrolyte solution containing the required substances (0.25 mM) for the anode and cathode.

3. The biocathode (1 cm\(^2\)), which consisted of a porous carbon electrode on a conductive carbon layer. A direct-transfer-type enzyme (0.01 mM) is assumed to be immobilized on the porous carbon electrode.

Figure S1(b) depicts the three simulation models. We changed the ratio of width to length of the electrodes (\(r\)) from 0.04 to 36. The surface area of each model is the same (1 cm\(^2\)). A voltage of 0.2 V was applied between the bioanode and biocathode. The current densities and substrate concentrations were calculated using FEM. All calculations were performed using the finite element package COMSOL Multiphysics 5.1®. Table S1 shows the parameters for the simulations.

Figure S1(c) shows the current distributions and substrate concentrations on the biocathode, as simulated by FEM. It is noted that the simulated maximum output power and current density was 35 \(\mu\text{W cm}^{-2}\) and 300 mA cm\(^{-2}\), respectively. The red colored
arrows depict the current distributions, and the color gradations indicate the concentrations of the substrate on the biocathode. As shown in Figure S1(c), when $r = 0.04$, the current that flows from the bioanode was not uniform and collected only at the edge of the biocathode. In other words, the biocathode substance was consumed only at the edge of the biocathode. In this case, the current distribution is influenced by the internal resistance of the porous carbon electrode, solution resistance, and mass transfer of the fuel, which cannot be ignored as the electrode area expands. On the contrary, when $r = 4$ or 36, the current was found to distribute uniformly on the biocathode. From these results, it was concluded that current density is not improved by simply increasing the length (surface area) of the electrode. By calculating the normalized current density of the single cell, it was found to be almost constant at $r$-values greater than 4. Hence, each electrode was fabricated to be 0.5 cm wide and 2 cm long.
(a) Cross sectional view

\[ S + E_O \xrightarrow{k_1} SE \rightarrow P + E_R \]
\[ E_R + M_O \xrightarrow{k_2} EM \rightarrow E_O + M_R \]

Ping Pong Bi-Bi Mechanism\(^1\)

S : Substrate  
P : Product  
\(E_R\) : Enzyme (Reductant)  
\(E_O\) : Enzyme (Oxidant)  
\(M_R\) : Reduced mediator  
\(M_O\) : Oxidized mediator

(b) \( r = \frac{x}{y} \)

\[ r = 0.04 \quad r = 4 \quad r = 36 \]

(c)
Figure S1. (a) Schematic illustration of the theoretical modeling of an array-type PBFC single cell. (b) FEM simulation model designed by COMSOL Multiphysics 5.1. (c) Current distributions (red arrows) and concentration gradients of the substrate on the biocathode as simulated by FEM.
Table S1. Parameters for the FEM simulations.

| Parameters                                      | Values of parameters |
|------------------------------------------------|----------------------|
| Electric double layer capacitance of bioanode and biocathode | 20 $\mu$F cm$^{-2}$ |
| Diffusion coefficient of substances            | $1 \times 10^{-6}$ cm$^2$ s$^{-1}$ |
| Diffusion coefficient of mediator               | $1 \times 10^{-9}$ cm$^2$ s$^{-1}$ |
| $k_1$                                           | 1.75 m$^3$ s$^{-1}$ mol$^{-1}$ |
| $k_2$                                           | 350 s$^{-1}$          |
| $k_3$                                           | 4 m$^3$ s$^{-1}$ mol$^{-1}$ |
| $k_4$                                           | 675 s$^{-1}$          |
| $k_5$                                           | 20 s$^{-1}$           |
| $k_6$                                           | 80 s$^{-1}$           |
| Conductivity of electrolyte solution            | 0.1 S m$^{-1}$        |
| Conductivity of the carbon layer                | $1 \times 10^5$ S m$^{-1}$ |
| Temperature                                     | 300 K                 |
**Experimental set-up for the biocathode measurements using the three-electrode method.**

Figure S2 shows a schematic illustration of the experimental set-up for the evaluation of the biocathode.

![Schematic illustration of the experimental set-up for the investigation of the characteristics of the bioanode and biocathode (independently) using the three-electrode method.](image)

**Figure S2.** Schematic illustration of the experimental set-up for the investigation of the characteristics of the bioanode and biocathode (independently) using the three-electrode method.
Schematic illustration of the present PBFC.

Figures S3(a) and (b) depict schematic illustrations of a single PBFC: ((a) side view, and (b) cross sectional view). 1 M phosphate buffer solution (pH 7.0) containing 100 mM glucose was cast on the paper electrolyte layer. (c) Design concept from a single to a 3-series PBFC.

Figure S3. Schematic illustration of the PBFC. (a) Side view of a single PBFC. (b) Cross-sectional view of a single PBFC. (c) Design concept for the 3-series cell.
Power-potential curves of the single, 2-series and 3-series PBFCs.

Figure S4(a) shows the power-potential curves of the single, 2-series and 3-series PBFCs. Figure S4(b) shows the relationship between the number of cells and the maximum output power of the whole cell, showing that the maximum output power increases in proportion to the number of cells. Maximum power density of the fabricated single PBFC was 76 μW cm⁻².

Figure S4 (a) Power-potential curves of the single (blue line), 2-series (green line) and 3-series (red line) PBFCs. (b) Relationship between number of cells and maximum output power of the whole cell.
Computer Aided Data (CAD) of the 4-series/4-parallel PBFC

Figure S5 shows the CAD data of (a) the porous carbon layer, (b) the conductive carbon layer, and (c) the resist layer of the 4 series/4 parallel PBFC.

Figure S5. The CAD data of (a) the porous carbon layer, (b) the conductive carbon layer, and (c) the resist layer of 4-series/4-parallel PBFC.
**Performances of the paper-based biofuel cell**

The performance of the present paper-based biofuel cells are compared with those previously reported in Table S2.

**Table S2.** Performance of the paper-based biofuel cell compared to previously reported cells.

| REF | Cell Structure | Anode (enzyme/electrode material) | Cathode (enzyme/electrode material) | Open circuit voltage (V) | Maximum Current density (μA cm⁻²) | Maximum Current (μA) | Maximum Power density (μW cm⁻²) | Maximum Power (μW) | Fuel Concentration (mol dm⁻³) |
|-----|----------------|-----------------------------------|-------------------------------------|--------------------------|----------------------------------|---------------------|--------------------------------|-------------------|-----------------------------|
| 5   | 3-series cell  | GDH/MWCNT                         | BOD/Carbon black                    | 1.8                      | -                               | 1000                | -                              | 180 (per mg GDH)  | 100 mM glucose              |
| 7   | Single cell    | GOx/Ketjen black                   | BOD/Ketjen black                    | 0.55                     | 450                             | -                   | 120                            | -                 | 100 mM glucose              |
| 9   | Single cell    | GDH/MWCNT                         | BOD/MWCNT                           | 0.56                     | -                               | -                   | 13.5                           | 13.5              | 30 mM glucose               |
| 20  | 2-series cell  | FDH/MWCNT                         | BOD/MWCNT                           | 1.1                      | 129                             | 16.2                | 34                             | 7.9               | 200 mM fructose             |
|     | 2-parallel cell|                                   |                                     | 0.55                     | -                               | -                   | -                             | -                 |                            |
| 21  | 2-series cell  | GOx/MgOC                          | BOD/MgOC                            | 0.94                     | 480                             | 120                 | 180                            | 43                | 100 mM glucose              |
|     | This work      | 4-series/4-parallel                | GOx/Ketjen black                    | 2.3                      | 260                             | 1040                | 60                             | 970               | 100 mM glucose              |

*Abbreviation: ALDH (aldose dehydrogenase), BOD (bilirubin oxidase), FDH (fructose dehydrogenase), GDH (glucose dehydrogenase), GOx (glucose oxidase), MWCNT (multi-walled carbon nanotube), MgOC (MgO-templated mesoporous carbon).*
**LED illumination test using the PBFC**

We also applied an LED illumination test to our PBFC. As is clearly seen in Figure S6, the present PBFC is capable of illuminating an LED without the requirement of a booster circuit.

![LED illumination test using the present PBFC](image)

**Figure S6.** LED illumination test using the present PBFC.

**References**

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