

## Flexible and high-performance paper-based biofuel cells using printed porous carbon electrodes†

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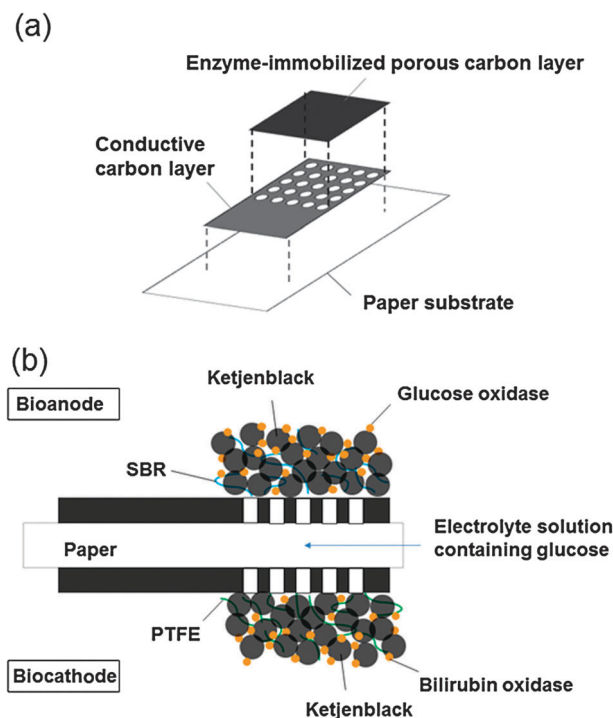
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Seiya Tsujimura<sup>\*b</sup>

**We demonstrate a flexible paper-based biofuel cell using porous carbon inks for high power output. The power density of the fabricated biofuel cell reached 0.12 mW cm<sup>-2</sup> (at 0.4 V), which is the highest output power reported to date, to the best of our knowledge.**

Biofuel cells (BFCs) are energy conversion systems that produce electricity from biological resources such as sugars and alcohols with the aid of specific enzymes. BFCs have shown potential for application as power sources for (implanted) biomedical devices, in addition to small electric devices.<sup>1–11</sup> Previously reported BFCs with high power densities are typically fabricated from carbon fiber-based electrode materials with the aim of increasing the surface area per cell volume;<sup>2</sup> however such devices have bulky and rigid structures. More recently, flexible, light, and thin BFC devices based on printing technologies have attracted increasing attention to address these drawbacks.<sup>12–16</sup> For example, Zhang *et al.* reported a paper-based printed BFC exhibiting a power density of 13.5  $\mu\text{W cm}^{-2}$  using carbon nanotubes (CNTs) as electrode materials.<sup>14</sup> The output power densities of other reported printed BFCs fall in the range of 3.5–13.5  $\mu\text{W cm}^{-2}$ .<sup>12–16</sup> Such relatively low output power densities may be ascribed to a lower effective electrode surface area, even though CNTs with high specific surface areas were used. The selection of a porous carbon material with large specific surface area that is compatible with

enzymatic reactions is crucial for improving the BFC output power density per unit of geometric surface area.<sup>11</sup>

In the present study, we demonstrate a high power paper-based BFC fabricated using a screen printer (LS-150TV, NEWLONG SEIMITSU KOGYO Co. Ltd., Japan). The BFC is composed of bioanode and biocathode components in which porous carbon electrodes were built using porous carbon inks (Fig. 1). The present BFC functions upon soaking the bottom of the printed-paper in an electrolyte solution to spread the electrolyte solution throughout the paper. We found Japanese paper to act as a suitable printable substrate since the Japanese paper has high water absorbency (Fig. S1, ESI†).<sup>17</sup>



**Fig. 1** Schematic illustration of (a) a screen-printed paper-based porous carbon electrode for bioanode and cathode, (b) a paper-based biofuel cell.

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† Electronic supplementary information (ESI) available: Performances of the paper-based biofuel cell in comparison with the others previously reported. SEM image and water absorbency of the Japanese paper. Experimental set-up. Cyclic voltammogram of a biocathode in the presence and absence of oxygen. Cyclic voltammograms of anode immobilized TTF without GO<sub>x</sub> and immobilized GO<sub>x</sub> without a mediator in the presence of glucose. Performance of the paper-based biofuel cell immersed in phosphate buffer (pH 7.0) in the presence of 100 mM glucose and absence of glucose at room temperature. See DOI: 10.1039/c3cc46644b

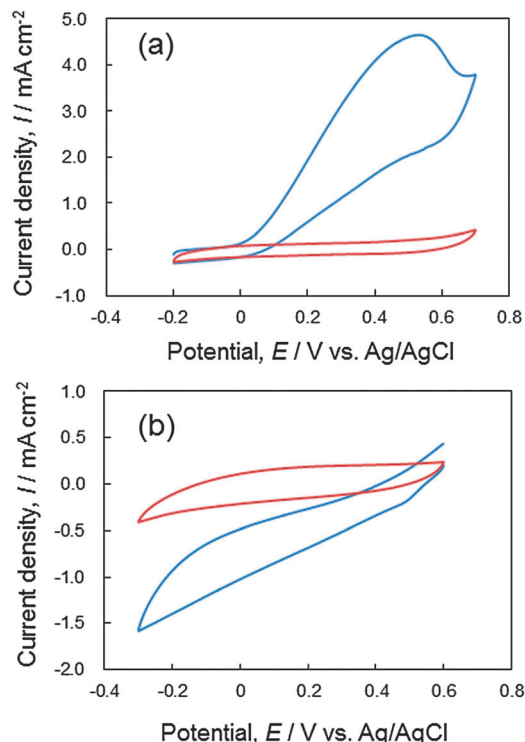
Firstly, a conductive carbon layer of 5 mm width  $\times$  10 mm length was printed using conductive carbon ink (JELCOM CH-10, Jujo Chemicals) on Japanese paper (Gasenshi Izumo, Keynote Planning Co., 120  $\mu\text{m}$  thickness), followed by curing at 120  $^{\circ}\text{C}$  for 30 min. Then, a 5 mm square of a porous carbon layer was printed on the side of the conductive carbon layer and dried at room temperature for 1 h. The conductive carbon layer has 25 pores of 0.5 mm in diameter to allow the infiltration of the electrolyte solution from paper to the porous carbon layer. The porous carbon inks were prepared using Ketjen black (KB, Lion Corporation, Japan), which has a high surface area, ideal mesopores for electro-enzymatic reactions, and specific binders.

Porous carbon ink for the anode was prepared by mixing 200 mg of KB and 15 mg of styrene butadiene rubber (SBR) binder (Zeon) in 5 mL of water, followed by ultrasonication for 5 min. Cathodic carbon ink was made by mixing 270 mg of KB and 180 mg of polytetrafluoroethylene (PTFE, 6-J, DuPont-Mitsui Fluorochemicals) in 5 mL of isophorone. For glucose oxidation on a bioanode surface, 5  $\mu\text{L}$  of glucose oxidase ( $\text{GO}_x$ , Wako) solution (20  $\text{U } \mu\text{L}^{-1}$ , dissolved in phosphate buffer solution at pH 7.0) and 5  $\mu\text{L}$  of tetrathiafulvalene (TTF) solution (saturated in methanol) were added *via* a syringe onto the porous anodic carbon layer, which had undergone UV/ozone pretreatment for 15 min. A biocathode was prepared by applying 5  $\mu\text{L}$  of bilirubin oxidase (BOD, Amano Enzyme) solution (1  $\text{U } \mu\text{L}^{-1}$ ) containing 0.01% of Triton X-100 on the UV/ozone-pretreated porous carbon layer.

Firstly, the characteristics of the bioanode and biocathode were investigated independently by the three-electrode method; the bioanode or biocathode was connected to a three-electrode potentiostat (ALS/CH Instruments, Model 802B). A  $\text{Ag}|\text{AgCl}$  reference electrode and Pt wire counter electrode were placed in the electrolyte solution. The edge of the paper was soaked in the electrolyte solution so that it spread throughout the paper during the measurements (Fig. S2a, ESI $^{\dagger}$ ). Fig. 2a shows cyclic voltammograms of the anode in the presence and absence of 100 mM glucose in 1 M phosphate buffer solution (pH 7.0) at room temperature. The cyclic voltammograms were recorded after 30 s of soaking the edge of the paper in the electrolyte solution. Although a clear redox wave of TTF was not observed on the printed anode in the absence of glucose, a clear catalytic wave for glucose oxidation was observed. The catalytic current for  $\text{GO}_x$  catalysis was mediated by TTF, which could be evidenced from the onset potential of the catalytic current (0 mV *vs.*  $\text{Ag}|\text{AgCl}$  sat. KCl). The catalytic current at 0.5 V was  $4.6 \text{ mA cm}^{-2}$ , which is more than 12 times higher than that for previously reported paper-based BFCs.<sup>12</sup> Without the porous carbon layer, the catalytic current was only  $0.1 \text{ mA cm}^{-2}$  for the same enzyme and mediator loadings. Therefore, the KB layer provides an efficient surface for the TTF-mediated bioelectrocatalytic reaction of  $\text{GO}_x$ .

It should be noted that a clear redox wave of glucose oxidation was not observed on a TTF-modified anode (without  $\text{GO}_x$ ) and a  $\text{GO}_x$ -immobilized anode (without TTF) (Fig. S4, ESI $^{\dagger}$ ).

Fig. 2b shows cyclic voltammograms of the cathode with and without BOD. No oxygen reduction current was observed in the absence of enzyme in this potential range. The oxygen reduction current clearly appeared in the presence of BOD, which corresponds to the catalytic reaction of BOD without a redox mediator.<sup>11</sup>

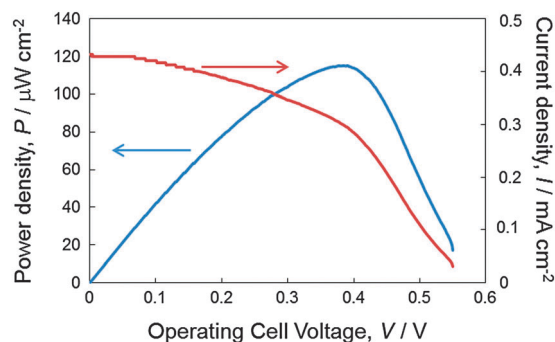


**Fig. 2** Cyclic voltammograms of (a)  $\text{GO}_x$  and a TTF-immobilized porous carbon electrode (bioanode) using 1 M phosphate buffer (pH 7.0) in the presence (blue line) and absence (red line) of 100 mM glucose at room temperature, (b) BOD-immobilized (blue line) and bare (red line) porous carbon electrode using 1 M phosphate buffer (pH 7.0) at room temperature. The scan rate was  $10 \text{ mV s}^{-1}$ . The edge of the paper was soaked in the electrolyte solution at room temperature during the measurement.

The catalytic reduction current of the biocathode was also not observed in the absence of oxygen (Fig. S3, ESI $^{\dagger}$ ). The catalytic current at  $-0.3 \text{ V}$  was  $-1.6 \text{ mA cm}^{-2}$ , and at  $0.15 \text{ V}$  was  $0.88 \text{ mA cm}^{-2}$ , which is more than 1.5 times higher than that of previously reported paper-based biocathodes.<sup>15</sup> It should be noted that optimization of the hydrophobicity of the porous carbon was essential for the production of oxygen reduction current. In the case of low hydrophobicity at a lower PTFE-to-KB ratio, the electrode was flooded with the electrolyte solution and thus the catalytic current was limited by the oxygen supply. On the other hand, no electrochemical response was obtained when the hydrophobicity was so high that the electrolyte did not penetrate the porous carbon layer.<sup>18</sup>

Electrochemical response of the BFC was examined (Fig. S2b, ESI $^{\dagger}$ ). In the BFC reported here, glucose and electrolyte are supplied to the enzyme electrode by capillary action. The biocathode is of passive type. Thus, oxygen is delivered to the cathodic enzyme from air. The current-potential and power-potential curves of the BFC are shown in Fig. 3.

The open circuit potential was 0.55 V, which is attributed to the difference in the onset potentials of the bioanode and biocathode. The maximum power density was  $0.12 \text{ mW cm}^{-2}$  at 0.4 V, which is nine times higher than that of the most powerful reported paper-based BFC (Table S1, ESI $^{\dagger}$ ).<sup>12</sup> Under these experimental conditions, the maximum current was  $0.45 \text{ mA cm}^{-2}$ , which would be mostly limited by the cathode performance. It should be



**Fig. 3** Performance of the paper-based biofuel cell. The edge of the paper was soaked in phosphate buffer (pH 7.0) containing 100 mM glucose at room temperature during the measurement.

noted that the maximum power density of the BFC in the absence of glucose was  $0.03 \text{ mW cm}^{-2}$  (Fig. S5, ESI†).

Further improvement in the power density of the BFC using  $\text{GO}_x$  and BOD could be achieved by: (1) increasing the porous carbon layer thickness with multiple printing; (2) reducing thermodynamic losses by selecting the more negative potential mediator for the anode, and; (3) lessening the concentration polarization through the anode carbon layers by introducing macropores for efficient glucose transport.

In summary, we have demonstrated a paper-based BFC using suitable porous anodic/cathodic carbon inks. The fabricated BFC exhibited a remarkable power output of  $0.12 \text{ mW cm}^{-2}$ ; this obtained maximum power is nine times higher than that of the previously described paper-based BFC, and is the highest output power reported to date, to the best of our knowledge. The present flexible paper-based biofuel cell is highly applicable to the development of low cost, flexible, ubiquitous energy devices.

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