Improved Power Capability with Pyrolyzed Carbon Electrodes in Micro Direct Photosynthetic/Metabolic Bio-fuel Cell

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As a biofuel source, direct photosynthetic/metabolic biofuel cells (DPBFC) use cyanobacteria whose photosynthesis and metabolization reactions can convert light energy to electricity. In our previous work, we fabricated a prototype micro-DPBFC that could generate a peak current density of 36 μA/cm^2 and a maximum power density of 270 nW/cm^2. In this study, we improve on the previous results by using carbon micro electromechanical systems (C-MEMS), formed from the pyrolysis of patterned photoresist, to fabricate carbon electrodes of an arbitrary shape and controlled porosity to increase the surface area. With these new C-MEMS electrodes, the maximum power density of the micro-DPBFC was 516 nW/cm^2, a performance twice as good as the results of our previous work.

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NOMENCLATURE

DPBFC = direct photosynthetic/metabolic biofuel cell
C-MEMS = carbon micro electromechanical system

1. Introduction

In our previous work, we developed a direct photosynthetic/ metabolic biofuel cell (DPBFC), a new biofuel cell based on the principle of photosynthesis of microorganisms.[1,2] The DPBFC has a modified polyaniline electrode that enhances the performance of the electrochemical reaction between the cyanobacteria and the electrode. We expect that electric power will be generated continuously as long as the bacteria are alive. The cell does not require any outside fuel, and is environmentally friendly. We would like to use DPBFCs in portable micro power sources to capitalize on these advantages. In our previous work, a 12 × 9 × 2-mm micro-DPBFC was designed and fabricated using micro fabrication technology[3-8] with an electrode made from SU-8 photoresist.[9] This micro-DPBFC had a peak current density greater than 36 μA/cm^2 and a maximum power density of 270 nW/cm^2. The power output was lower than expected due to the high internal electrical resistance caused by the small reaction area and the high electrical resistance of the electrodes. To improve on this, we require a material with a lower electrical resistance and a high specific surface area. For these reasons, many other developed fuel cells use a carbon cloth or paper.[10] However, it is difficult to fabricate a carbon electrode in an arbitrary shape and control its porosity with conventional direct machining. Therefore, carbon micro electromechanical systems (C-MEMS)[11-13] have been developed to create an arbitrary carbon structure shape using carbonized polymers. C-MEMS are obtained from the pyrolysis of patterned photoresist in a process that facilitates the precise fabrication of arbitrary shapes.

In this paper, we describe the use of C-MEMS to fabricate a high surface ratio electrode to improve the electrical performance of micro-DPBFCs. We also describe the fabrication process of the pyrolyzed carbon photoresist electrode.

2. Working Principle of DPBFCs

Cyanobacteria convert H_2O and CO_2 to glucose under light conditions through photosynthesis, and consume this glucose to survive under dark conditions through their normal metabolic function. They generate electrons during both processes, providing the basis for a fuel cell if those electrons can be gathered. Figure 1 is a schematic diagram of the DPBFC working principle with the anode chamber on the left, the cathode on the right, and a proton exchange membrane in between to separate them. The anode and cathode are made of polyaniline particles with a size of approximately 30 and 50 nm respectively; these particles are a known electro-conductive and biocompatible material.[14,15] The electrons generated during photosynthesis and metabolism are captured and transferred by the polyaniline anode.

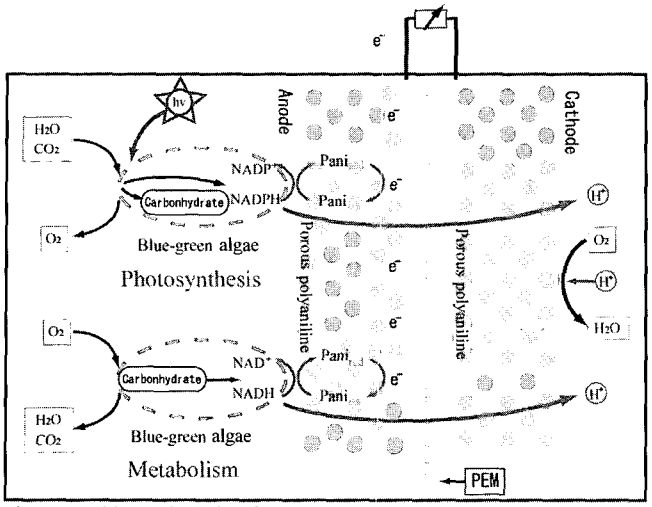


Fig. 1 Working principle of a DPBFC

3. Micro-DPBFC Structure and Fabrication

Figure 2 shows a photograph of the MEMS-based micro-DPBFC fabricated in our previous work. It was 12 mm long, 9 mm wide and 2 mm thick. The electrode was made of KMPR 1050 photoresist (Kayaku Microchem Corp., Tokyo, Japan) using a simple separation process.[9] To render the electrode conductive, an Au layer was sputtered on the photoresist surface. Then it was coated with polyaniline by soaking it in a polyaniline solution. This fabrication method is very simple but it produces an electrode with a high electrical resistance that reduces the performance of the fuel cell. We applied C-MEMS to the micro-DPBFC to overcome this drawback. Figure 3 shows the structure of the micro-DPBFC with a pyrolyzed carbon electrode. The size of this fuel cell is same as the previous one. The chamber was fabricated of KMPR 1050 photoresist with a simple separation technique using gelatin. This same separation technique was used to fabricate the electrode pattern on the photoresist to produce the pyrolyzed carbon electrode.

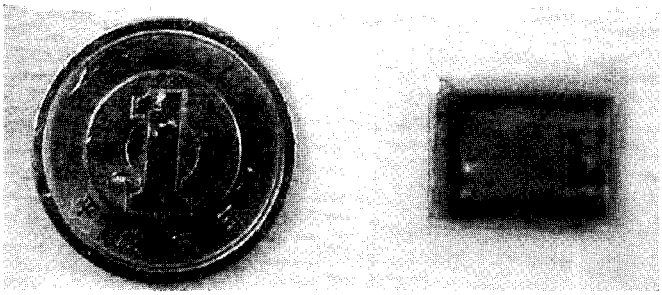


Fig. 2 Photograph of the previous micro-DPBFC[9]

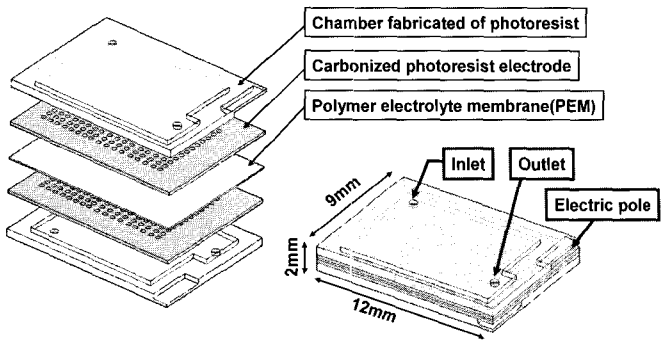


Fig. 3 Structure of the micro-DPBFC

3.1 Chamber Fabrication Using a Separation Method

We developed a simple separation method using gelatin to fabricate the components of the micro-DPBFC. Figure 4 shows the details of this separation process, which easily creates a removable micro-patterned structure. The gelatin solution was prepared by mixing gelatin and water at 1:7 by mass and heating it on a hot plate to 120°C to dissolve it before spin coating on the wafer. As shown in Fig. 4(1), the gelatin solution was spin coated on the wafer at 500 rpm for 15 s and at 1000 rpm for 30 s, and then baked on a hotplate at 120°C for 10 min to evaporate the water in the solution and create the gelatin layer. This gelatin layer served as a sacrificial layer for the next step, where the KMPR 1050 photoresist was spin coated on top of the gelatin layer. The pattern was then created on the photoresist, exposed, and developed. The wafer was boiled in water to dissolve the gelatin, leaving the removable patterned photoresist structure behind.

Figure 5 shows a photograph of the chamber for the micro-DPBFC fabricated using this separation technique. The chamber was 12 × 9 × 0.5 mm. The two holes in the chamber are the inlet and outlet for the bacteria.

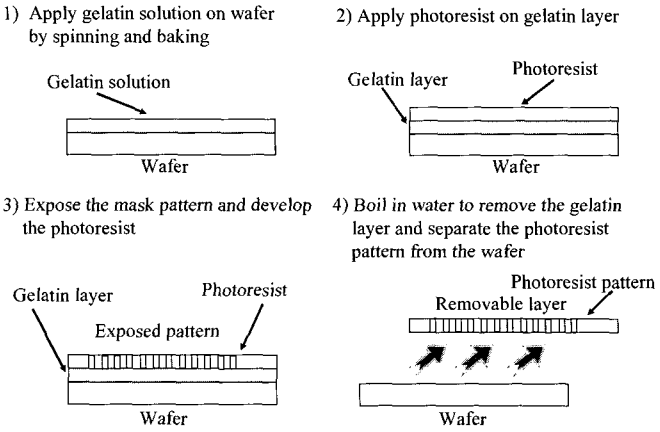


Fig. 4 Simple separation process using gelatin

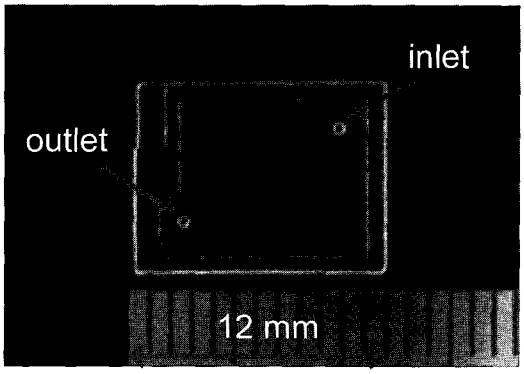


Fig. 5 Chamber for the fabricated micro-DPBFC

3.2 Carbon Electrode Fabrication Method Using C-MEMS

C-MEMS is a technology for fabricating highly precise micro-size carbon structures. The fabrication principle relies on the pyrolysis of organic materials in a vacuum or in an inert gas atmosphere such as Ar using an electrical furnace. The hydrogen and oxygen inside the photoresist are thermally decomposed, leaving high purity carbon behind in the photoresist. The fabrication details of our electrodes are as follows. First, the KMPR 1050 photoresist pattern was prepared using the normal procedure. Then, the patterned photoresist was post-baked in an Ar atmosphere (500 sccm) at 300°C for about 30 min, heated to 900°C for 1 h, and allowed to cool to room temperature. The heating rate was about 5°C/min; the electrical furnace used in this experiment was the FUA112DB (Advantec, Tokyo, Japan).

When using KMPR 1050 photoresist in this process, shrinkage was about 50%. Therefore, we started with a photoresist structure twice the size of the desired end result. Figure 6 shows the design of

the 24 × 18 mm electrode with a hole diameter of 240 μm before heat treatment. The electrode pattern was formed using the separation process with KMPR 1050 photoresist. First, the gelatin solution was spin coated on the Si wafer. Then, after baking, the KMPR 1050 was spin coated twice onto the gelatin layer at 500 rpm for 15 s and 1000 rpm for 30 s. After exposing and developing the electrode pattern, the wafer was put into boiling water for about 4 min to dissolve the gelatin layer and release the electrode-patterned photoresist. Figure 7 shows a photograph of the fabricated electrode pattern with a thickness of about 200 μm.

The next step is the pyrolysis of the electrode pattern to create the carbon electrode. During pyrolysis, if the photoresist pattern is placed in the electrical furnace directly, it will deform and become unusable because it will break down during the assembly process. For this reason, it was necessary to fabricate a plane carbon electrode by sandwiching the photoresist electrode between two carbon papers. Different weights were placed on the electrode to evaluate the deformation during carbonization. Figure 8 shows the experimental result of different stress conditions applied to determine the optimum condition for fabricating the plane electrode. When the stress was too small, the electrode deformed in the direction of thickness, and when the stress was too large, the pattern broke completely. A stress of approximately 43.1 Pa was most appropriate.

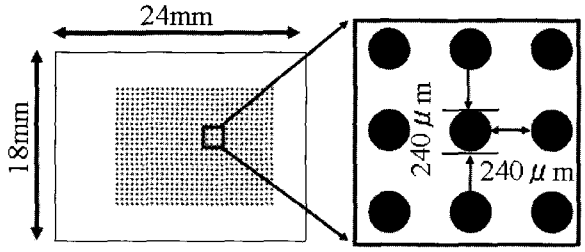


Fig. 6 Electrode design before heat treatment

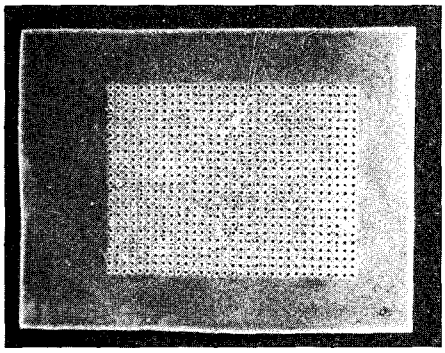


Fig. 7 Fabricated electrode-patterned photoresis

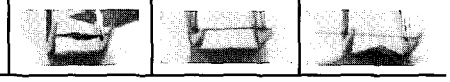
Experiment No.	1	2	3
Stress Pa(N/m²)	0	43.1	140.2
Photograph (top view)			
Photograph (side view)			

Fig. 8 Experimental result of different stress conditions

Figure 9 shows a photograph of the resulting pyrolyzed carbon photoresist electrode. It was 12 × 9 mm and the color had changed to black. The resistance in the direction of the film thickness was about 20 Ω. Figure 10 shows a SEM photograph of the fabricated electrode with a hole diameter of about 120 μm; this was fabricated according to the design.

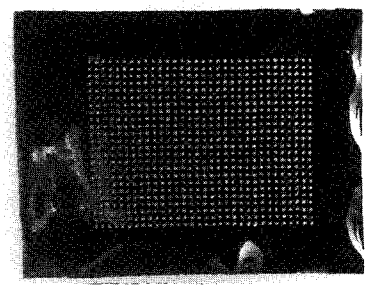


Fig. 9 Fabricated pyrolyzed carbon photoresist electrode

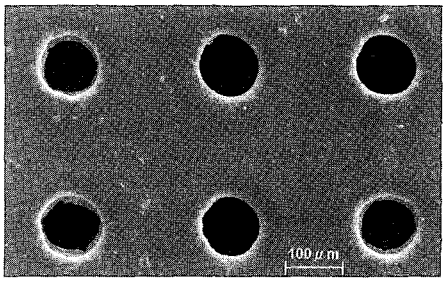


Fig. 10 SEM photograph of the fabricated electrode

3.3 Membrane Electrode Assembly Fabrication

We used Nafion117 (Dupont) for the polymer electrolyte membrane (PEM), after pretreating it with H_2O_2 (3–5 wt%) at 80°C for 1 h, followed by immersion in boiling distilled water for 1 h. Next, the carbon electrode was immersed in polyaniline solution to accumulate the polyaniline catalyst layer. The mass of polyaniline spread on the carbon electrode was about 1 mg. Figure 11 shows SEM photographs of the carbon electrode coated with polyaniline. A comparison of Figs. 10 and 11 shows that the polyaniline is efficiently coated on the carbon electrode and that the specific surface area of the result is much larger than the original. After the polyaniline coating, the two electrodes were hot-pressed together with the pretreated Nafion117 membrane at 140°C for 5 min to create the membrane electrode assembly (MEA) shown in Fig. 12.

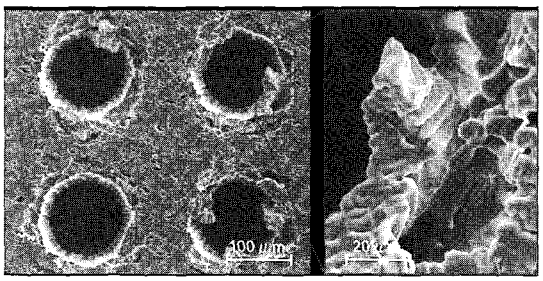


Fig. 11 SEM photograph after polyaniline coating

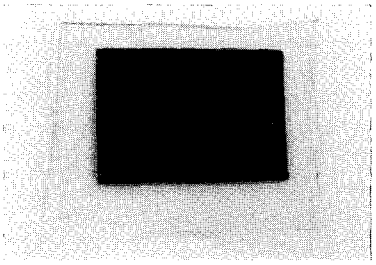


Fig. 12 Photograph of the fabricated MEA

3.4 Micro-DPBFC Fabrication

The chamber portion of the micro-DPBFC was made of KMPR 1050 photoresist, which becomes plastic when it is heated above 100°C. We used this characteristic to assemble the chamber and MEA by hot-pressing them together at 140°C for 2 min. Figure 13 shows a photograph of the assembled micro-DPBFC measuring 12 × 9 × 1 mm.

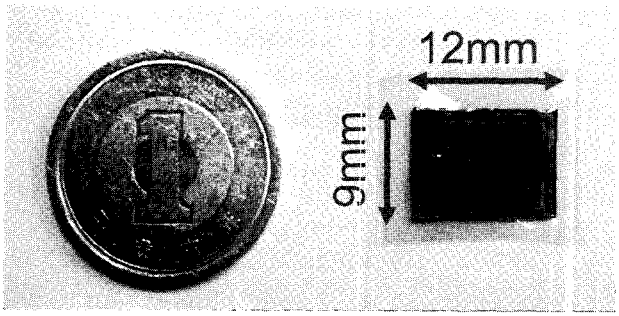


Fig. 13 Photograph of the fabricated micro-DPBFC

4. Experimental Results and Discussion about the Proposed Micro-DPBFC

We evaluated the performance of the micro-DPBFC we developed under normal room lighting conditions, and measured the electrical power with an electrochemical test system (1280Z, Solartron Co. Ltd., Farnborough, UK). Since a fuel cell has an arbitrary potential voltage, we added a forced voltage to gradually reduce it to zero while measuring the current between the anode and cathode. The power output was calculated from this voltage and current. We used *Synechococcus sp.* cyanobacteria as the biofuel source. This bacteria was cultured for 3 weeks and exposed to 8 hr under 2000 lux light and 16 hr of darkness every day.

Table 1 shows the experimental conditions for our electrical power evaluation, comparing our present work with our previous work.[9] The difference between the two experimental conditions is in the materials and the fabrication method of the electrode. Our new electrode is made of conductive pyrolyzed carbon while the previous electrode was made of a photoresist that required a sputtered Au layer to render it conductive. The different material and fabrication method for the new electrode produced a great improvement. Figure 14 shows the experimental power versus current curve of our new micro-DPBFC.

The volume of anolyte was about 11 μl. The maximum electrical power we obtained in this experiment was about 325 nW, and the maximum power density from the area inside the 9 × 7-mm chamber was about 516 nW/cm.[2] This is twice the density of the previous micro-DPBFC (270nW/cm^2), which demonstrates the superiority of the new micro-DPBFC with a pyrolyzed carbon electrode using C-MEMS.

Table 1 Experimental conditions for the micro-DPBFC evaluation

Experimental Condition	Anolyte	Catholyte	Material of MEA
No.1	Phosphate Buffer *Synechococcus.sp*	Air	Polyaniline **Pyrolyzed carbon electrode** Nafion117
No.2 (previous research)	Phosphate Buffer *Synechococcus.sp*	Air	Poly-aniline **Photoresist coated with Au** Nafion117

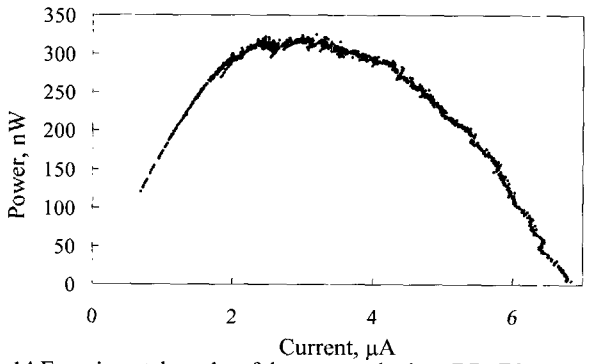


Fig. 14 Experimental results of the proposed micro-DPBFC

5. Conclusion

Our measurement of the electrical power confirmed the effectiveness of using a pyrolyzed carbon photoresist electrode in a micro-DPBFC. The pyrolyzed carbon electrode decreased the internal resistance of the fuel cell. It was easy to create an electrode of any arbitrary shape with controllable porosity using C-MEMS technology, which is not possible by conventional machining. The micro-pattered photoresist structure was created using photolithography. The performance of the DPBFC increased due the high-specific surface area of the electrode produced by C-MEMS. We also demonstrated a new and simple separation process using gelatin to fabricate a stand-alone microstructure. This technique can be applied to many other MEMS applications.

Future research areas include ensuring the long-term stability and activity of the bacteria, enhancing the activity of the bacteria, increasing the effective anode area, and miniaturizing the DPBFC for a wide range of applications. The developed DPBFC is a promising alternative to current fuel cells for micro power supply units.

ACKNOWLEDGEMENT

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