

Design Principle and Prototyping of Direct Photosynthetic/Metabolic Bio Fuel Cell (DPBFC)

Yuji Furukawa*¹, Takeyuki Moriuchi*² and Keisuke Morishima*²

PowerMEMS Conference

2-24-16 Nakacho, Koganeishi, Tokyo 184-8588, Japan

Tel +81-42-388-7105, Fax +81-42+388-7105, E-mail y-furuka@cc.tuat.ac.jp

*¹Professor, Graduate School of Technology Management,

*²Graduate School of Engineering,

Tokyo University of Agriculture & Technology

Abstract

A novel design of a photosynthetic/metabolic based bio-fuel-cell and fabrication processes to make it have been explored and developed. Novel nanostructure and modified Poly-aniline have been used to enhance the performance of the new bio-fuel cell. The mechanism of the electron transfer process and the electro-catalysis of Poly-aniline have been investigated. The developed Direct Photo-synthetic/metabolic Bio-Fuel Cells(DPBFC) succeeded in generating peak current density of more than $150\mu\text{A}/\text{cm}^2$ with a $100\text{-}\Omega$ load, $5.3\mu\text{W}/\text{cm}^2$ of max power density(using prototype fuel cell). As the final objective of this research is to apply DPBFC to micro energy source, one coin size($12\text{mm}\times 9\text{mm}$) micro DPBFC was developed and the fabrication method was shown.

Keywords: micro power source, biological-fuel cell, photosynthesis, metabolism, poly-aniline

1 INTRODUCTION

The availability of compact and high-efficient micro power sources is one of the most important key technologies in future autonomous and mobile integrated micro-systems. To realize this, various micro power-sources such as rotary engines, batteries, solar cells, and fuel cells have been developed [1-4]. Direct Methanol Fuel Cell(DMFC) is in the limelight, however, it needs fuel to be replenished periodically and also needs rare metals, further more, methanol is one of toxic materials as well known. These disadvantages are unlikely scenario for autonomous, mobile MEMS devices and implantable medical sensors. Biocatalysts (microorganism, enzymes) can be an alternative to the use of transition metal catalysts in fuel cells.

Professor Lin's group[5] has made it clear that a micro-photosynthetic/metabolic bio fuel cell composed of Cyano-Bacteria could make electricity by converting light energy into electricity whenever light is available and by metabolizing glucose while dark. This is a great breakthrough comparing with traditional bio-fuel cell, however, their mechanism to involve mediator such as Methylenblue inevitably lowers its durability and current density and limits its commercialization. It is required to remove the mediator and take out electricity directly from bio-cells by making anode contact to bacteria directly in order to overcome the above problems. As a solution, a new type of electrode using Poly-aniline which possesses either of electro-conductive and

bio-compatible characteristics for the bio-cells has been developed. Poly-aniline is very efficient in electro-catalysis and can be developed for a wide range of fuels. Based on priority technologies to make Poly-aniline with a particle size ranging from 30nm to 50 nm and electron conductivity ranging from 100 to 200 S/cm^2 , a mediator-less photo-synthetic/metabolic bio-fuel cell is possible by means of modified Poly-aniline acting as an electron transporting matrix.

The objective of this research is to confirm the principle of Direct Photo-synthetic/metabolic Bio-Fuel Cells(DPBFC) and to develop MEMS based DPBFC, utilizing novel fabrication processes and structures..

2 WORKING PRINCIPLE OF DPBFC

Figure 1 shows the outline of cyano-bacteria's photo-synthesis & metabolism reaction. Cyano-bacteria converts H_2O and CO_2 into glucose as the fuel source in the presence of light. In addition, cyano-bacteria metabolizes this glucose for its internal biological functions. Figure 2 is a schematic of the working principle of a developed Direct Photo-synthetic/Metabolic Bio Fuel Cell(DPBFC) with anode chamber on the left side, cathode on the right and a proton exchange membrane in between to separate the anode and cathode chambers. By employing Poly-aniline with a particle size either around 30 nm or 50 nm as an electron collector, electrons liberated during photo-synthesis and metabolism

are transported from cyano- bacteria cells to the anodic electrode to produce current.

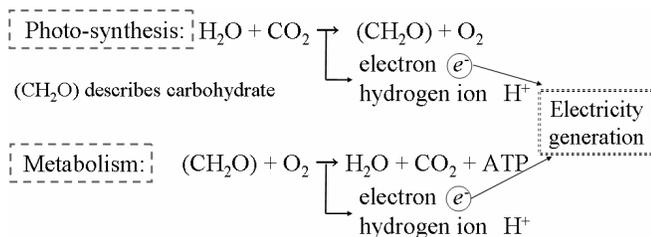


Figure 1. Bio-Chemical Reactions of Photosynthesis and Metabolism of Bacteria

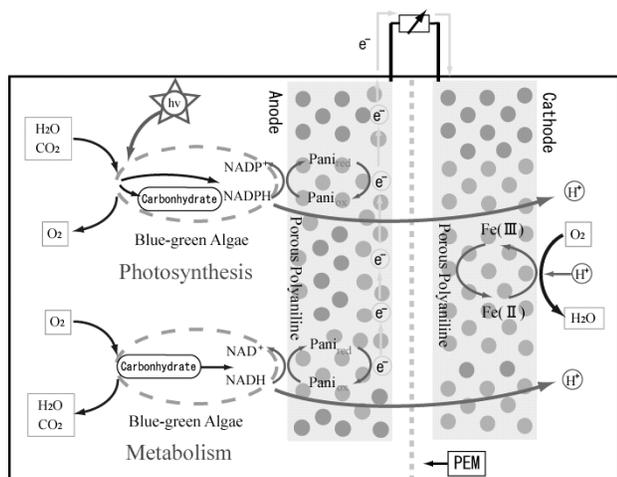


Figure 2. Working Principle of Developed DPBFC

3 STRUCTURE & FABRICATION OF DPBFC

The purpose of this research is to develop MEMS based miniature DPBFC. For this, the working principle and electro-chemical characteristics of DPBFC were evaluated first. Then, MEMS based miniature DPBFC was developed by using micro-fabrication process.

3.1 Structure & Fabrication Method of Prototype DPBFC

Figure 3 shows the schematic diagram of the prototype fuel cell. MEA(Membrane Electrode Assembly) was made by Nafion117 (Dupont Co. Ltd) and carbon cloth(0.33mm in thickness). For a current collector, two thin copper electrodes (0.3mm in thickness) manufactured by Electric Discharge Machining were used on the top and bottom face of MEA. To give enough room to insert the anolyte and catholyte, O-ring (internal diameter 24mm and 2mm in thickness) was used. Finally, the fuel cell was sandwiched by optical transparency material (acrylic or glass plate) from the top and the bottom. The entire size of DPBFC became 50mm×50mm and a reactive area (calculate simply from the area inside O-ring) became 4.5cm².

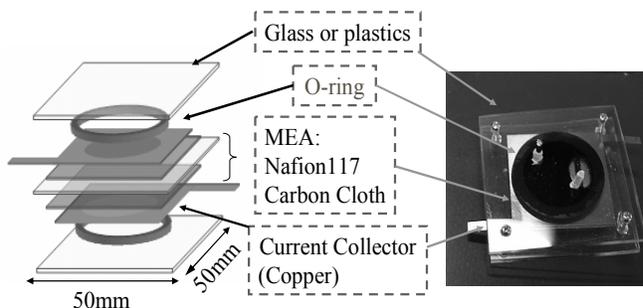


Figure 3. Schematic diagram of the prototype DPBFC

3.2 MEA Preparation for Prototype DPBFC

For the prototype DPBFC, carbon cloth was used for catalyst support material. Carbon cloth is widely used to MEA material for its excellent electric and structural characteristics. For PEM, Nafion117(Dupont) was used and pretreated by H₂O₂ (3-5wt. %) at 80°C for 1hour, followed by immersion in distilled water for 1hour. Then, the Nafion117 was treated with H₂SO₄ (0.5-1 M) at 80°C for 1 hour, followed by immersion in the distilled water for 1 hours. Next, the carbon cloth was immersed into Poly-aniline solution and the catalyst layer of Poly-aniline was accumulated. The mass of the Poly-aniline spread on the carbon cloth is about 0.07g (0.015g/cm²). Two electrodes were hot-pressed to one piece with pretreated Nafion117 membrane to make the MEA at 150, 50kg/cm² for 2 minutes. Then, it was clamped mechanically onto two cover plates via gasket.

3.3 Structure of Miniature DPBFC

MEMS based miniature DPBFC was made by micro fabrication process. Figure 4 shows the structure of miniature DPBFC. The size of the fabricated miniature DPBFC is 12mm × 9mm × 2mm(width × depth × thickness) and the reaction area is about 0.56cm²(calculated by chamber space). The whole structure is similar to the prototype fuel cell, Pyrex glass was used for light transparency cover, chamber and artificial porous electrode was made by different kind of SU-8(KAYAKU MICROCHEM). The miniature DPBFC has two ports (inlet & outlet) for inserting the cyano-bacteria solution and one electrical connection at each side to bring out electricity to external circuit.

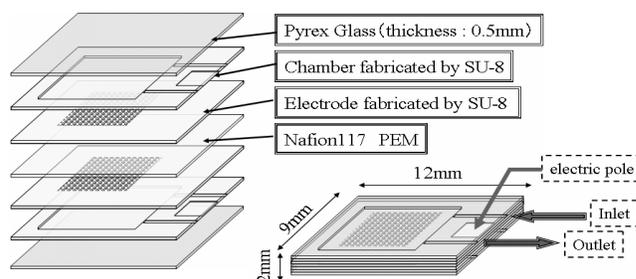


Figure 4. Structure of miniature DPBFC

3.4 Fabrication of Miniature DPBFC

MEMS based miniature DPBFC basically composed of three components. One is glass and chamber part which is made by Pyrex glass(500 μ m in thickness) and the chamber part is made by SU-8 photo-resist(about 200 μ m in thickness). The chamber has two ports to insert the anolyte, the width of the inlet/outlet channel is 1mm and the length is 3mm.

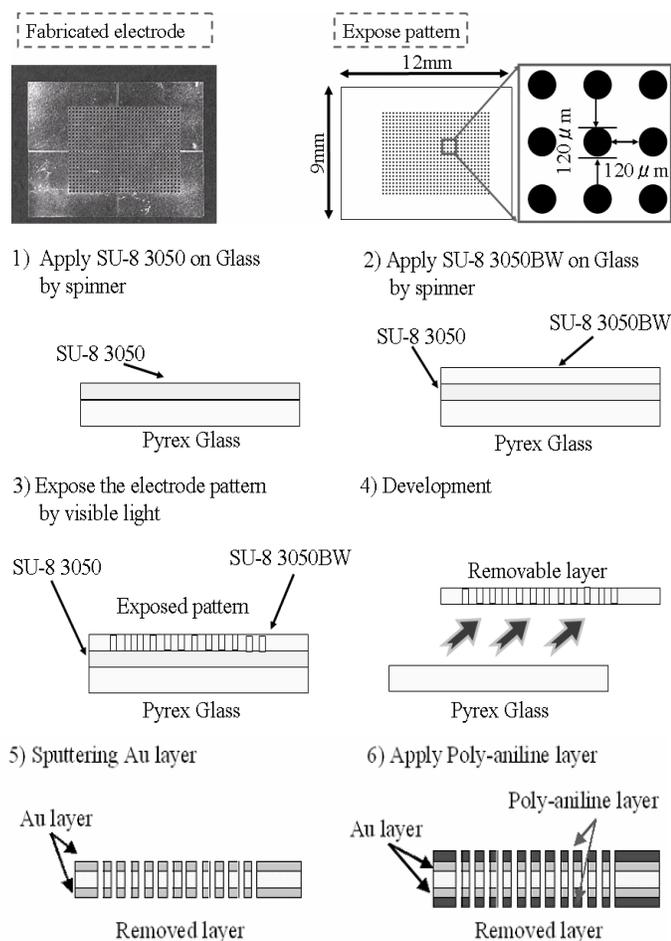


Figure 5. Fabrication method of Electrode

The second component is the electrode. Figure 5 shows the detail of the fabrication process of electrode using two types of SU-8 photo-resist. This process can make a removable micro patterned structure only by SU-8 photo-resist. As shown in Figure 5-1, Pyrex glass wafer(500 μ m in thickness) is used for substrate to spread photo-resist, SU-8 3050(KAYAKU MICROCHEM), which is ultra-violet light photosensitive positive type. SU-8 3050 was spin coated to Pyrex glass wafer by 500rpm for 15s and 1700rpm for 30s, 100 μ m in thickness. This layer is sacrificial for the next step. Then, SU-8 3050BW which is visible-light photosensitive positive type photo-resist was spin coated on SU-8 3050 layer to make the visible-light photosensitive layer. The next step is exposing the porous pattern of electrode as shown in Figure5,

whose size is 12m \times 9mm. Exposure equipment used in this process is a mask less one[6], which consists of a projector system and a digital pattern such as bitmap file prepared by PC. The feature is to be able to expose the pattern using only visible light and any ultra-violet light is not required because only SU-8 3050BW layer need to be exposed. Finally, the whole wafer was soaked into SU-8 Developer. In principle, SU-8 3050 layer is not exposed, it should work as sacrificial layer and dissolve and disappear in the developer. In fact, as shown in figure, SU-8 3050 layer works as sacrificial layer and SU-8 3050BW layer is removed from the glass wafer. This process is very useful because the same developer is able to use and no extra equipment or chemicals process is needed. To make the conductive layer on the electrode, Au thin layer was sputtered. Then, Poly-aniline layer was made by soaking the electrode into Poly-aniline solution. The weight of Poly-aniline coated on the electrode was about 1mg (1.8mg/cm²).

3.5 Assembly of Miniature DPBFC

The assembly of miniature DPBFC was made by hot pressing. Usually SU-8 structure needs hard bake process to secure the chemical & mechanical stability. Using this character, it is possible to make Pyrex glass with SU-8 chamber and electrode together by a hot pressing because both of the contact surfaces of SU-8 and Nafion117 are easily hot pressed to SU-8 electrode. Figure 6 shows the assembled miniature DPBFC.

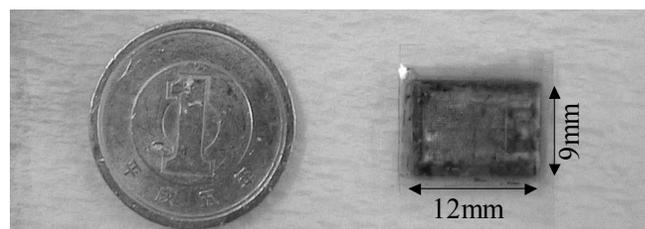


Figure 6. Miniature DPBFC assemble

4 EXPERIMENTAL RESULTS & DISCUSSIONS

The performance of developed DPBFCs were evaluated regarding their electric power, which was obtained by connecting electrical resistances, 10 Ω to 1000k Ω , to the fuel cell, while the voltage of the electrical resistance was measured by the data logger (Kyowa Co.Ltd, PCD320A) and the current value was measured by digital multi meter (Advantest Co0.Ltd, AD7461A).

4.1 Experimental Result of Prototype DPBFC

Two kinds of DPBFC were prototyped, the first one applied a mediator as the previous research by Lin in order to make it as a reference and the second one, nothing was inserted in the cathode side and applied Poly-aniline to make

the MEA. Other conditions such as anolyte, catholyte, material of MEA and used cyano- bacteria are listed in Table 1. Figure 7 shows an experimental result of voltage and power versus current curve. It is known that the bio-fuel cell with Poly-aniline (experimental condition No.2) shows better performance than conventional mediator based type. The maximum electric power obtained in the experiment condition No.2 was about $24\mu\text{W}$ ($5.3 \mu \text{ W}/\text{cm}^2$) at $680\mu\text{A}$ ($150\mu\text{A}/\text{cm}^2$). From these, the priority to adapt Poly-aniline to electrodes is verified.

4.2 Experimental Result of Miniature DPBFC

The developed miniature DPBFC was tested under the same condition of No.2 of Table 1, when the volume of the anolyte was $11.2\mu\text{l}$. Figure 8 shows the experimental result of power versus current curve. The maximum power was about 660nW ($1.2 \mu \text{ W}/\text{cm}^2$) at $20\mu\text{A}$ ($36\mu\text{A}/\text{cm}^2$) that is 1/4 of the power density of prototype DPBFC with a carbon cloth as electrode. The reason, the author considers, may come from the difference of electrode material. The carbon cloth is well known as highly porous and electrically conductive material. As electrons are extracted from bacteria cells through Poly-aniline surface, the proton is exchanged at PEM, and electrons are transferred to an external circuit through an electrode, these three components had better be placed spatially proximately in order to improve the efficiency.

5 CONCLUSION

Effectiveness of applying Poly-aniline to electrodes was verified from the developed prototype and miniature DPBFC. Poly-aniline is biocompatible, chemically stable and low cost material so that it may be possible for a practical use. Further more, novel and simple fabrication process using only hot press process has been developed to manufacture the miniature fuel cell. Additionally, new micro patterning process has been developed, in which only the top layer of pattern can be flaked off by the help of SU-8 photo-resist.

Future prospects are long-term stability of bacteria and its activity; enhance the activity of the bacteria, increase of effective anode area, miniaturization of DPBFC for wide range purpose and finding a proper solid electrolyte. The developed Direct Photosynthetic/ Metabolic Bio Fuel Cell is a promising alternative to current fuel cells to serve to a micro power supply unit.

Table 1 Experimental condition of Bio-Fuel Cell

Experimental Condition	Anolyte	Catholyte	Material of MEA
No.1	Methylene Blue Phosphate Buffer <i>Synechococcus.sp</i>	Potassium ferricyanide Phosphate Buffer	Carbon Cloth Nafion117
No.2	Phosphate Buffer <i>Synechococcus.sp</i>	Air	Poly-aniline Carbon Cloth Nafion117

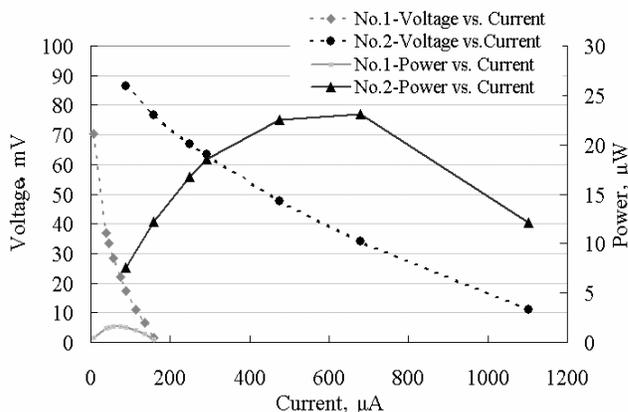


Figure 7. Voltage and Power versus Current Curve of Prototype DPBFC

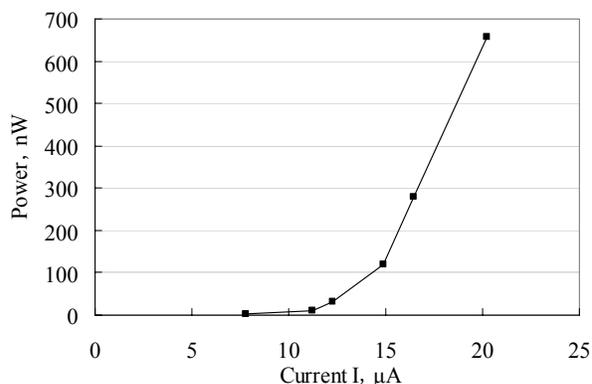


Figure 8. Power versus Current Curve of Miniature DPBFC

REFERENCES

- [1] J. B. Bates, N. J. Dudney, B. Neudecker, A. Ueda, and C. D. Evans, , 2000. "Thin-film batteries and lithium-ion batteries," Solid State Ionics, vol. 135, pp.33-45.
- [2] Jeremy P.Meyers, Helen L.Maynard, "Design considerations for miniaturized PEM fuel cells," J.Power Sources 109(2002), pp. 76-88.
- [3] R.Hahn, S.Wagner, A.Schmitz, H.Reichl, "Development of a planar micro fuel cell with thin film and micro patterning technologies," J.Power Sources 131(2004), pp.73-78.
- [4] G.Q.Lu, C.Y.Wang, T.J.Yen, X.Zhang, "Development and characterization of a silicon-based micro direct methanol fuel cell," Electrochimica Acta 49(2004), pp821-828.
- [5] K.B.Lam, M. Chiao, and L. Lin, 2003. "A micro Photosynthetic Electrochemical Cell," in Proc. IEEE Conf. on Micro Electro Mechanical Syst.(MEMS 2003), Kyoto, Japan, Jan. 19-23, 2003, pp. 391-394.
- [6] K.Itoga, M.Yamato, J.Kobayashi, A.Kikuchi, T.Okano, "Cell micropatterning using photopolymerization with a liquid crystal device commercial projector," Biomaterials 25(2004), pp2047-2053.