# Development of Low Crystalline Carbon Anode for Microbial Fuel Cells

Kaho YAMADA\* Kenichi FUJINO Toshikazu FUKUSHIMA Katsuhiro YAMADA

# Abstract

The activated sludge process, which exploits aerobic microbes to remove pollutants from wastewater, has been used for the treatment of domestic and industrial wastewater. However, much energy is required for the aeration and treatment of excess sludge. On the other hand, microbial fuel cells (MFCs) are expected to treat wastewater with less energy consumption. For their practical application, we must improve treatment efficiencies, reduce material costs, and establish reliable operation. In this study, we have developed a highperformance and low-cost material for MFC anodes. We made a low crystalline carbon electrode and graphite electrode and evaluated their performances. As a result, the low crystalline carbon electrode showed higher maximum power density due to its biocompatibility. In addition, it has the advantage of relatively low cost and higher strength. These results demonstrated the utility of the low crystalline carbon electrode.

## 1. Introduction

The activated sludge process (**Fig. 1**) is currently the most widely used technology for treating domestic and industrial wastewater. It is also used in the steel industry for treating coke-oven wastewater. The activated sludge process is a technology for removing pollutants in the wastewater by aerobic microbes and shows good treatment efficiency. However, there are two problems. First, it is necessary to aerate the treatment tank to provide oxygen to microbes. The aeration requires a large amount of electric energy. Next, the excess sludge, which is the carcasses of actively grown microbes, is generated as industrial waste in a large amount. A large amount of electric energy is also required to treat the excess sludge (dewater, dry, transport, incineration, and otherwise). To solve the problems, new wastewater treatment technologies have been developed. A microbial fuel cell (MFC) is attracting attention as one of such technologies.

The MFC has emerged as a potentially interesting technology for the production of energy from wastewater (**Fig. 2**).<sup>1)</sup> The electroactive bacteria on the anode degrade the organic matter in an anaerobic condition and the electrons generated at that time are donated to the anode. The electrons are transferred to the cathode and consumed by the reduction reaction. In other words, the bacteria on the anode are degrading the pollutants in the wastewater and generating the electric energy at the same time. A cathode chamber filled with an aqueous solution is used as the cathode in one case. An air-cathode is used as the cathode in another. The former is called a doublechamber MFC (Fig. 2(A)). The latter is called a single-chamber (Fig. 2(B)). The single-chamber MFC uses the oxygen in air as the oxidant and thus does not require aeration. MFCs have a lower cell yield compared to aerobic processes. This is caused by the reduced energy available for biomass growth as a significant part of the substrate energy is converted to electrical power.<sup>2)</sup> This is considered to reduce the energy and cost required for the excess sludge disposal. When the MFC is applied to sewage treatment, an energy saving of



Fig. 1 Wastewater treatment process by activated sludge process

 <sup>\*</sup> Environment Research Lab., Advanced Technology Research Laboratories 20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511



Fig. 2 MFC configurations

(A) A double-chamber MFC; (B) A single-chamber air-cathode MFC. CEM: cation exchange membrane.

90% or more and waste reduction can be expected when the reduction in the power consumption for aeration and other operations, the reduction in the sludge, and the power generation from pollutants are combined.<sup>3)</sup> In this way, the MFC has advantages such as: (1) Part of the chemical energy of the pollutants in the wastewater can be recovered as electrical energy; (2) The electric energy required for aeration can be reduced by using the air-cathode; and (3) The amount of excess sludge generated can be reduced. In view of advantages (2) and (3), the MFC technology can be expected as a next-generation energy-saving wastewater treatment technology. In recent years, MFCs that can treat wastewater with the same efficiency as that of the activated sludge process have been reported.<sup>4)</sup> MFC technology has been actively developed.

The MFC technology has not been used for actual wastewater treatment systems yet since the solving of problems such as efficiency enhancement, cost reduction, and scale-up structure research is required. MFCs for wastewater treatment must use naturally formed microbial communities. To improve efficiency, therefore, electrodes and device structures must be improved. To obtain economic benefits from the MFCs, it is also necessary to reduce the electrode cost.<sup>5)</sup>

For practical use, we have been studying low-cost and high-performance MFC anode electrodes. In this paper, we report the results<sup>6)</sup> on the superiority of low crystalline carbon electrodes with relatively low manufacturing cost as MFC anodes.

# 2. Main Subjects

We focused on low crystalline carbon as a low-cost electrode material and evaluated its performance by measuring its physical properties and evaluating its power generation capacity when it was used as an MFC anode material. Since the magnitude of the current is proportional to the reaction rate of the anode, the wastewater treatment capacity can be evaluated by evaluating the power generation capacity. Details are described below.

#### 2.1 Microbial fuel cell anode materials

Carbon materials are most often used as MFC anode materials. This is because the carbon materials have properties such as electrical conductivity, microbial decomposition resistance, large surface area, high porosity, and relatively low cost. Many carbon anodes have a high degree of graphitization. Carbon fiber anodes are representative of this. Among them are carbon cloth electrodes, carbon felt electrodes, and carbon brush electrodes.<sup>7</sup>

Graphitic carbon electrodes are electric arc furnace electrodes. They are produced by adding coal-based or petroleum-based pitch as a binder for aggregation like coke breeze and then by kneading, molding, firing, and graphitizing. Electrodes thus produced consist of a particle-bonded porous structure, have low volume resistance, and are relatively strong. However, a high temperature of 3 000°C or more is required to obtain a graphite material. This increases the manufacturing cost. When the electrode is thinned to increase output, for example, some concern remains about the strength of the electrode. In addition, graphite is highly crystalline and is hydrophobic on the surface. The adhesion and growth of microbes is hence not very fast.<sup>6)</sup>

We focused on porous and low crystalline carbon as an MFC anode electrode material that can solve the above-mentioned problems. The porosity was expected to increase the surface area, the amount of microbial adhesion, and the wastewater contact area. The low crystallinity was considered to improve surface hydrophilicity and microbial adhesion efficiency. The lack of the need for hightemperature firing provides another advantage of low manufacturing cost. To evaluate the performance of low crystalline carbon as an MFC anode material, we operated MFCs with low crystalline carbon electrodes, graphitic carbon electrodes, and carbon felt electrodes as anodes. We compared the performance of the respective electrodes by the power generating capacity. We produced low crystalline carbon electrodes and graphitic carbon electrodes as described in the next section. Commercial carbon felts were used.

# 2.2 Method for producing low crystalline carbon electrodes and graphitic carbon electrodes

Pitch coke with a true density of 1.82 g/cm<sup>3</sup> was pulverized and blended to a particle size distribution of 25 wt% of 0.250 to 0.500 mm particles, 45 wt% of 0.075 to 0.249 mm particles, and 30 wt% of 0.074 mm and smaller particles. To 100 parts by mass of pitch coke particles prepared in this way was added 40 parts by mass of a binder pitch (with a softening point of 97°C) obtained from coalbased heavy oil. The mixture was heated at 200°C for 20 min and kneaded. The kneaded preform was extruded into a 20 mm in diameter bar and fired in a non-oxidizing atmosphere at 900°C to obtain a carbon preform. The carbon preform was cooled to room temperature in a non-oxidizing atmosphere, removed from the furnace, and machined into a cylinder with a diameter of 20 mm and a height of 48 mm to obtain a low crystalline carbon electrode. The low crystalline carbon electrode was graphitized in a non-oxidizing atmosphere at 2550°C to obtain a graphitic carbon electrode.

# 2.3 Physical property measurement methods

To compare the physical properties and performance of the electrodes thus prepared and to determine which electrodes have better properties, we performed their surface analysis by X-ray diffraction (XRD) and measured their bulk density, open porosity, bending strength, and water absorbency. The measurement methods are described below.

Each carbon preform was turned to remove about 0.1 mm of the surface. The XRD parameters of the powder samples thus prepared, or the (002) plane interlayer distance d002 and crystal size Lc002 of carbon crystals, were measured using a Rigaku x-ray diffractometer and according to a method specified by the Japan Society for the Promotion of Science.

The diameter 2r and length L of the carbon electrodes were measured with a caliper. The mass of the carbon electrodes was measured. The bulk density was calculated by

Bulk density  $(g/cm^3) = Mass of carbon electrode/(\pi r^2L)$ 

The open porosity was determined according to JIS R 1634:1998 - Test methods for density and apparent porosity of fine ceramics. The dry mass, mass in pure water, and saturated mass of cylindrical

carbon preform samples (with a diameter of 20 mm and a length of 48 mm) were measured. The saturated mass was determined by vacuuming the sample and allowing the sample to absorb water. The open porosity was calculated from these mass values by:

Open porosity (%)

= (Saturated mass - Dry mass)/(Saturated mass - Mass in water) × 100

The bending strength was measured according to the bending strength test method specified in JIS R 7222 and using a Shimadzu AGS-500A desktop universal tester. The above-mentioned cylindrical carbon preforms were loaded at a constant rate of 50 N/s. The obtained maximum load was used to calculate the bending strength by

#### Bending strength

=  $8 \times$  Maximum load  $\times$  Gauge length/( $\pi \times$  cylinder diameter)

The dry mass of the cylindrical carbon preform sample was first determined. The sample was then immersed in pure water at 23°C and 1 atm, removed after 24 h, and left to stand for 3 min. When the sample was fully dried without any water drops, the saturated mass was measured again. The increase in the saturated mass over the dry mass was calculated as water absorbency by

 $\label{eq:linear} \begin{array}{l} \mbox{Water absorbency (wt\%) = (Saturated mass-Dry mass)/(Dry mass) \times 100 \\ \mbox{2.4 Electrode performance evaluation methods} \end{array}$ 

# 2.4.1 Microbial fuel cell operating method

We operated three 500 mL single-chamber MFCs, each with a low crystalline carbon electrode, graphitic carbon electrode, or carbon felt electrode as the anode. The performance of these electrodes as MFC anodes was evaluated from their power generation capacity. A photo of the MFC reactor is shown in Fig. 3. The carbon felt electrode was 5 cm long, 5 cm wide, and 1 cm thick. As shown in Fig. 4, the low crystalline carbon electrode and the graphitic carbon electrode were each wound with a 0.3 mm in diameter titanium wire. A hooked wire with a diameter of 1.2 mm was inserted into the carbon felt electrode. The generated current was collected through these titanium wires. Electrochem EC-20-10-7 carbon paper coated with 1.0 mg/cm<sup>2</sup> of platinum catalyst was used as the cathode electrode. The cathode electrode measured  $2.5 \times 2.5$  cm. An external resistor was placed between the electrodes. A Graphtec mini LOGGER GL840 data logger was installed to measure the voltage between the electrodes.

When evaluating the MFCs, we operated them using simulated wastewater with acetic acid as a main source of organic matter.<sup>6)</sup> At the start-up, 100 mL of the solution in the running MFC was added to 400 mL of simulated wastewater as a microbial seeding source. Twice a week, 100 mL of the 500 mL simulated wastewater in the MFC was replaced with fresh simulated wastewater. The external resistor was set to 1000  $\Omega$  at the start of operation and to 470  $\Omega$  on the 43rd day of operation.

#### 2.4.2 Power generation capacity evaluation method

After the MFCs were operated for 42 days, their current densitypower density curves (power curves) and current density-voltage curves (polarization curves) were measured. The maximum power density was obtained from the maximum value of the power curve. The internal resistance was obtained from the slope of the polarization curve. The power generation capacity of each electrode was evaluated from the magnitude of the maximum power density and the internal resistance.

The maximum power density indicates the maximum power generation capacity of the MFC and is a parameter often used when comparing the power generation capacity of the electrodes. The internal resistance is the resistance value of the MFC. The correlation





Fig. 4 Photographs of electrodes (A) Low crystalline carbon electrode; (B) Graphite electrode; (C) Carbon felt.

among the internal resistance, voltage, and current is expressed by  $E_{\text{cell}}(V) = \text{OCV}(V) - I(A) \cdot R_{\text{int}}(\Omega)$ 

where  $E_{\text{cell}}(V)$  is the voltage when the current is I(A), OCV is the open circuit voltage (OCV), and  $R_{\text{int}}(\Omega)$  is the internal resistance of the MFC. That is, the internal resistance can be calculated from the slopes of the current and voltage plots.<sup>1)</sup> The lower the internal resistance, the higher the voltage that can be maintained in the high current range.

One hour before the start of the measurement, the external resistor was removed from the MFC to leave the circuit open. Using a BAS ALS1000C potentiostat, the voltage was maintained for 1 min with the potential difference between the anode and cathode set at OCV and then swept at a speed of 1 mV/s from OCV to 0 V. The power P(W) was calculated from the relationship (P = IE) between the obtained voltage  $E_{cell}(V)$  and current I(A). The current density and the power density were obtained by dividing the current and the power by the anode surface area, respectively. The anode surface area was calculated by the cylinder surface area formula for the low crystalline carbon electrodes and the graphitic carbon electrodes and by the rectangular parallelepiped formula for the carbon felt electrodes. The obtained current density, power density, and voltage were plotted to obtain power and polarization curves.

# 2.5 Results and discussion

# 2.5.1 Physical property measurement results

**Table 1** shows the physical properties of the prepared electrodes. It was confirmed that the graphitic carbon electrode was graphitized with the interlayer distance d002 close to the interlayer distance 0.3354 nm of graphite. On the other hand, the low crystalline carbon electrode was confirmed to be low in crystallinity from its d002 value. The low crystalline carbon electrode has higher bending strength than the graphitic electrode. It has a high degree of shape freedom. When it is used as a thin plate electrode, for example, it is very strong. The low crystalline carbon electrode has excellent water absorbency. This can be expected to improve the microbial adhesion and the electron transfer efficiency between the microbes and the electrodes. The low crystalline electrode has high resistivity. This

Table 1	Physical	properties	of low	crystalline	carbon	electrode	and
	graphite	electrode <sup>6)</sup>					

	Low crystalline carbon electrode	Graphite electrode
Baking temperature	900°C	900°C
Graphitizing temperature	_	2550°C
XRD d002 (nm)	0.344	0.335
Lc002 (nm)	5.462	43.320
Bulk density	1.40 g/cm <sup>3</sup>	1.31 g/cm <sup>3</sup>
Open porosity	18.0 %	18.6 %
Bending strength	17.6 MPa	13.0 MPa
Resistivity	$78 \ \mu\Omega m$	$12 \ \mu\Omega m$
Water absorptivity	8.9 wt%	2.2 wt%

effect was examined from electrochemical measurement results. **2.5.2 Power generation capacity evaluation results** 

Figure 5 shows the changes in voltage over time. The voltage rose sharply from immediately after the start of the MFC to the third day and then gradually rose. There were no significant differences in voltage among the three MFCs during the period when they were run with an external resistance of 1 000  $\Omega$ . The low crystalline carbon electrodes showed the highest voltage during the period of operation with an external resistance of 470  $\Omega$ .

**Figure 6** shows the power curves and polarization curves measured on the 42nd day of the operation. The power curves show that the maximum power density was 88.1, 69.5, and 62.7 mW/m<sup>2</sup> for the low crystalline carbon, graphitic carbon, and carbon felt electrodes, respectively, and that the maximum power density of the low crystalline carbon electrodes was 1.3 and 1.4 times that of the graphitic carbon electrodes and the carbon felt electrodes, respectively. That is, the low crystalline carbon electrodes displayed a higher power generation capacity than that of the graphitic carbon electrodes.

The reason why the low crystalline carbon electrodes showed an excellent power generation capacity was attributed to the shape of their polarization curves (Fig. 6). It was confirmed that the low crystalline carbon electrodes showed a sharp decrease in voltage in the region where the current density was higher than that of the graphitic carbon electrodes. The sharp voltage drops in the high-current ranges are caused by the diffusion control of the organic matter or by the reaction control by the microbes. The diffusion control of the organic matter is a state in which the organic matter is decomposed as soon as it diffuses and reaches the electrodes and in which the concentration of organic matter on the electrode surface is zero. The reaction control by the microbes is a state in which the reaction does not proceed any further due to the limit of the decomposition ability of microbes on the electrode. Since there was considered to be no significant difference in the ease of diffusion of the organic matter among the electrodes, the decomposition ability of the microbes on the electrodes was considered to be higher for the low crystalline carbon electrodes than for the graphitic carbon electrodes. It was speculated that this is because the high water absorbency of the low crystalline carbon electrodes increased the electron transfer efficiency between the microbes and the electrodes. The internal resistances calculated from the slopes of the polarization curves were 105, 110, and 140  $\Omega$ , respectively. The low crystalline carbon electrodes had higher resistivity than the graphitic carbon electrodes, but their internal resistance was equal to that of the graphitic carbon electrodes.



Fig. 5 Time courses of voltage of three MFCs (GP: graphite electrode, LC: low crystalline carbon electrode, CF: carbon felt)



Fig. 6 Power and polarization curve of three MFCs (GP: graphite electrode, LC: low crystalline carbon electrode, CF: carbon felt)

Since the reaction by the microbes became the rate controlling step, the resistivity of the low crystalline carbon electrodes was considered to be sufficiently small. Namely, the resistivity of the low crystalline carbon electrodes is inferior to that of the graphitic carbon electrodes but is sufficient enough. Since the low crystalline carbon electrodes have water absorbency, they are superior in the ease of microbial adhesion and the electron transfer efficiency between the microbes and the electrodes. As a result, the low crystalline carbon electrodes were considered to have shown a high power generation capacity.

The above-mentioned physical property measurement and power generation capacity assessment results show that the low crystalline carbon electrodes have higher power generation capacity than the graphitic carbon electrodes and the carbon felt electrodes. This is probably because they have low crystallinity and hence have high water absorbency. In addition, the low crystalline carbon electrodes are fired at a lower temperature than the graphitic carbon electrodes and thus can be produced at a lower cost than the graphitic carbon electrodes. Therefore, the use of low crystalline carbon electrodes as high-performance and low-cost MFC anodes can be expected.

# 3. Conclusions

We studied low-cost and high-performance MFC electrode materials and found that the low crystalline carbon electrodes are superior. The low crystalline carbon electrodes are inferior in electrical conductivity but superior in water absorbency as compared to the

graphitic carbon electrodes. The higher water absorbency was presumed to have improved the adhesion of microbes to the electrode surface and hence the electron transfer efficiency between the microbes and the electrodes. The low crystalline carbon electrodes are also stronger than the graphitic carbon electrodes and have a higher degree of shape freedom. They need not be fired at high temperature and thus are less costly to make. Our results showed that the low crystalline carbon electrodes are superior to the graphitic carbon electrodes and carbon felt electrodes, which are widely used for the MFC anode, in terms of performance, strength, and cost. Therefore, the use of the low crystalline carbon electrodes as high-performance and low-cost MFC electrodes can be expected.

In the future, we will continue our electrode development to achieve higher performance and lower cost for the practical use of MFCs.

#### References

- 1) Watanabe, K.: Recent Developments in Microbial Fuel Cell Technologies for Sustainable Bioenergy. Journal of Bioscience and Bioengineering. 106 (6), 528–536 (2008)
- 2) Rabaey, K., Verstraete, W.: Microbial Fuel Cells: Novel Biotechnology for Energy Generation. Trends in Biotechnology. 23 (6), 291-298 (2005)
- 3) Kouzuma, A., Miyahara, M., Watanabe. K.: Possibility of Microbial Fuel Cell. KAGAKU TO SEIBUTSU. 50 (3), 150–152 (2012)
- 4) Miyahara, M., Hashimoto, K., Watanabe, K.: Use of Cassette-Electrode Microbial Fuel Cell for Wastewater Treatment. Journal of Bioscience and Bioengineering. 115 (2), 176-181 (2013)
- 5) Rozendal, R.A., Hamelers, H.V., Rabaey, K., Keller, J., Buisman, C.J.: Towards Practical Implementation of Bioelectrochemical Wastewater Treatment. Trends in Biotechnology. 26 (8), 450-459 (2008)
- 6) Nippon Steel Chemical & Material Co., Ltd., Nippon Steel Corporation: Microbial Fuel Cell for Wastewater Treatment and the Carbon Anode Electrode. Japanese Unexamined Patent Application Publication No. 2019-164978
- 7) Wei, J., Liang, P., Huang, X.: Recent Progress in Electrodes for Microbial Fuel Cells. Bioresource Technology. 102 (20), 9335-9344 (2011)



Kaho YAMADA Environment Research Lab. Advanced Technology Research Laboratories 20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511



Toshikazu FUKUSHIMA Senior Researcher, Ph.D. (Environmental Studies) Environment Research Lab.

Advanced Technology Research Laboratories







Kenichi FUJINO Senior Researcher Carbon Materials Center (Currently Epoxy Resin Materials Center) Research & Development Div. Nippon Steel Chemical & Material Co., Ltd.

Katsuhiro YAMADA Senior Researcher Carbon Materials Center Research & Development Div. Nippon Steel Chemical & Material Co., Ltd.