

Construction and Operation of a Scaled-up Microbial Fuel Cell

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Microbial fuel cells (MFCs) are electrochemical devices that use microorganisms as biocatalysts for generating electricity from the degradation of organic matter as fuel.¹⁻⁴ Since MFCs satisfy 'carbon neutral' and a variety of wastewaters such as domestic,⁵ winery,⁶ and swine⁷ wastewater can be utilized, MFCs are considered to be a possible solution to the global warming and energy shortage as well as to the water and environmental problems, though partially. Pollutant removal is another major target of MFCs.⁸ Increasing demand for safer removal of pollutants to keep the environment clean and sustainable considers the MFC to be a promising technology.

Most MFC studies have been limited to the laboratory scale mainly because of their low power densities when applied in large scale. It is generally agreed that power density rapidly drops with increasing MFC size. For example, maximum power density of 6.86 W m^{-2} was obtained with a 1 cm^2 . But only 2.77 W m^{-2} was resulted with a 14 cm^2 anode, although reactions conditions were different.⁹ Lewandowski *et al.* systematically examined the effect of the anode surface area on power density while maintaining the cathode surface area quite large. They found that power density was inversely proportional to the logarithm of the anode surface area.¹⁰ Expressed in power per volume, power density also rapidly decreases with the increase in cell volume. Very high power densities up to 2.1 kW m^{-3} were reported with milliliter scale reactors. However, in a liter scale operation, power density dropped to several tenths of watt or several watts. Therefore, it is a big issue to increase the MFC scale while maintaining adequate performance.¹¹⁻¹⁴

In this research, we have developed a hexagonal prism-shaped MFC of a large volume, aiming at practical application. Specifically, the effect of temperature and substrate loading on the performance has been evaluated in relation to the coulombic efficiency and chemical oxygen demand (COD) removal. The long-term stability over a period of more than five months was also tested.

Experimental Section

Construction of a Scaled-up MFC. Figure 1 shows a schematic diagram of a large scale MFC used in this study. It was a single-chamber cell of a hexagonal prism shape with 1.29 L internal cell volume. The frame was made of Plexiglas and each window served as an air-cathode ($6 \text{ cm} \times$

12 cm). 30 wt % wet-proofed carbon cloths (type B, E-TEK, USA) were used as cathode material. The catalyst layer was formed by spreading Pt/C powder (0.5 mg cm^{-2} , 20% Pt on Vulcan XC-72, De Nora North America, Inc.) over the carbon cloth surface facing the solution. The gas-diffusion layer was formed on the opposite side. First, carbon black (1.56 mg cm^{-2} , Vulcan XC-72) was mixed with PTFE (polytetrafluoroethylene) solution ($12 \mu\text{L}$ per mg carbon black), and spread over the surface.¹⁵ After drying for 2 h, the carbon cloth was heated in a furnace at $370 \text{ }^\circ\text{C}$ for 30 min. Then PTFE coating was done on the surface and dried in air and in a furnace for 15 min. This PTFE coating was repeated four times. By taking this cell geometry, we tried to keep the cathode area

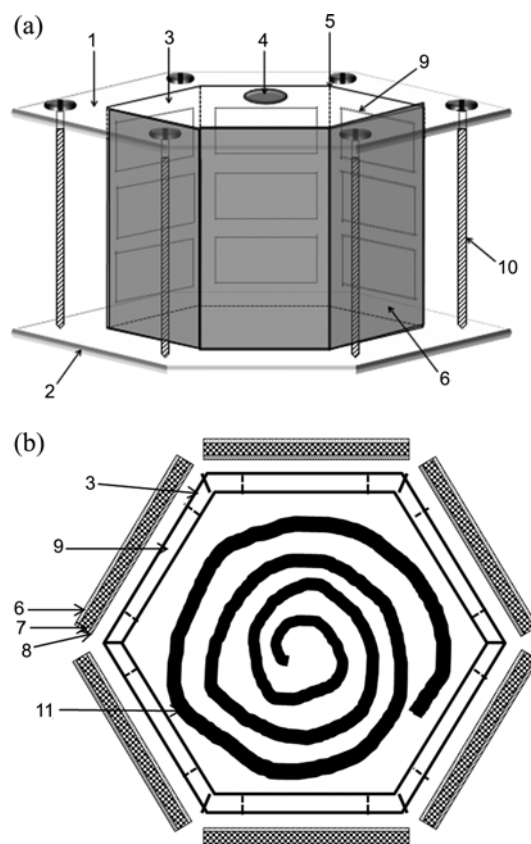


Figure 1. Schematic diagrams of the hexagonal prism-shaped cell used in the experiments: overview (a) and top view (b). 1) Upper panel, 2) lower panel, 3) cell body, 4) hole for substrate injection, 5) nickel wire, 6) gas diffusion layer, 7) carbon cloth, 8) catalyst layer, 9) window, 10) fastening screw, 11) carbon fiber.

as large as possible because the cathode size have more significant effect on the power than the anode size.¹² In the meantime, carbon fiber bundle (PANEX-35, ZOLTEK, USA) was used as anode material. It consisted of 50 K filament fibers manufactured from polyacrylonitrile precursor with a diameter of 7.2 μm for each filament. The total length of carbon fiber bundle was 6 m. It was located in the middle of the solution. Six cathode plates were tied together with nickel wires and the nickel wires were connected to the anode through the external load. Different loads were attached to construct polarization curve.

MFC Operation. For the MFC start-up, the anode chamber was inoculated with a 1:3 mixture of activated sludge (Jungnang Sewage Treatment Center, Seoul, Korea) and a medium solution. The basic composition of the medium solution was prepared according to the literature.¹⁶ Sodium acetate substrate solutions (1, 2, 3 and 4 g L^{-1}) and phosphate buffer solution (50 mM, pH 7) containing mineral (12.5 mL L^{-1}), vitamin (12.5 mL L^{-1}), NH_4Cl (0.31 g L^{-1}), and KCl (0.13 g L^{-1}) were mixed. All the solutions were prepared using deionized water purified from water purification system (aquaMAX-Ultra, Younglin, Korea). During the start-up period, the biofilm was formed on the anode surface under the closed circuit discharging using a 100 Ω external resistor. After about 20 days' inoculation period, the anode chamber was fed with a medium solution and discharged under a 100 Ω external resistor until stable voltage was reached. Polarization curves were then constructed using different resistors for different substrate concentrations. The feeding solution was replaced when the voltage was dropped below 50 mV. For the long term stability test, we simply exchanged the substrate solution. All the measurements were done either at room temperature or at elevated temperature. For the precise temperature control at 30, 35 and 40 $^\circ\text{C}$, a drying oven (Model FO-600M, Jeio Tech, Korea) was used.

Measurements and Analysis. The cell voltage (V) was measured using an automatic battery cycler (WBCS 300, WonAtech, Korea). Power (P) was calculated from $P = V^2/R$, where R is the external resistance value. Power was normalized by the anode surface area (m^2) or the reactor volume (m^3). The coulombic efficiency (CE) was calculated according to the equation, $\text{CE} (\%) = (Q_{\text{Act}}/Q_{\text{Theo}}) \times 100$, where Q_{Act} is actual charge obtained from the experiments and Q_{Theo} is theoretical charge calculated from the substrate amount using $Q_{\text{Theo}} = (F b S V)/M$, where F is Faraday constant (96485 C mol^{-1}), b number of moles of electrons produced per mole of substrate (acetate = 8), S the substrate concentration, V the reactor volume, and M the molecular weight of the substrate (for acetate, 60.05 g mol^{-1}).

Chemical oxygen demand (COD) was measured as COD removal is commonly used to evaluate the MFC performance. We measured COD before and after the MFC operation based on colorimetry in which organic compounds are decomposed to CO_2 by $\text{Cr}_2\text{O}_7^{2-}$ leaving Cr^{3+} . Absorbance increase at 600 nm for Cr^{3+} was monitored and related to COD. Chemical treatment and decomposition was done using a

water test kit (HS-COD-MR, Humas, Korea).

Anode surface morphology after experiments was collected with SEM (JSM-6380, JEOL, Japan) and optical microscope (Icamscope, Sometech, Korea). For the better images, carbon fiber bundle was immersed in 3% glutaraldehyde solution for 2 h and washed in 50 mM phosphate buffer for 15 min twice. For dehydration, the samples were successively treated with 10, 25, 50, 75, 90, and 100% ethanol for 20 min for each treatment, and then subjected to drying overnight.

Results and Discussion

Figure 2 shows voltage generation with time during start-up period under the closed circuit condition at room temperature. During this period, electroactive biofilms containing exoelectrogens are formed. Until ten days the voltage was remained about 0.2 V at 500 Ω external load and then rapidly increased to 0.6 V, indicating that a stable biofilm was beginning to be formed. However, when 100 Ω was attached, sudden voltage drop to 0.2 V was observed. This is because the system was not fully stabilized to bear the sudden current withdrawing. It is believed that electrons produced from the substrate oxidation were not effectively transferred to the anode. A new batch containing only medium solution was supplied to the anodic compartment after 42 days under the 100 Ω load. Cell voltage rapidly increased to about 0.8 V and stayed there. After this, reproducible charging-discharging patterns were resulted under which condition polarization curves were collected. It should be noted, however, that maximum power density calculated from the polarization curve steadily increased as we changed the batch solution. With a second batch, the maximum power density was only 0.82 W m^{-3} . This value increased to about 2 W m^{-3} after many charging-discharging cycles for 1 g L^{-1} acetate concentration.

Figure 3 is the plot of power density vs current density for different substrate concentrations at room temperature. The general trend is that power density increases with concent-

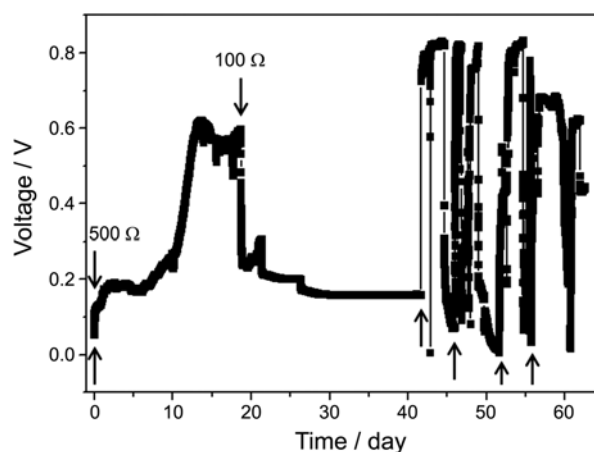


Figure 2. Cell voltage variation during a start-up period while discharging through the external circuit at room temperature. Arrows indicate a new batch addition.

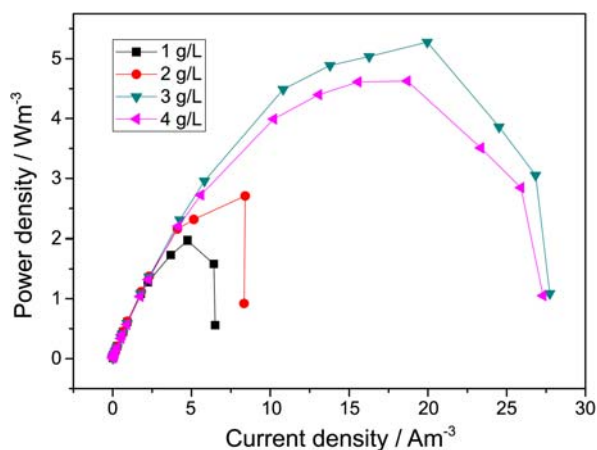


Figure 3. Plot of power density vs current density at different acetate concentrations at room temperature.

ration. Maximum values are 1.97, 2.71, 5.27 W m⁻³ for 1, 2, and 3 g L⁻¹ acetate concentrations, respectively. However, at higher concentration the power density rather decreased contrary to our expectation. Cheng *et al.* also observed similar effect in their small MFC experiments.¹² With an MFC of 28 mL capacity, negligible increase in power density was resulted for 2 g L⁻¹ substrate concentration compared to 1 g L⁻¹.

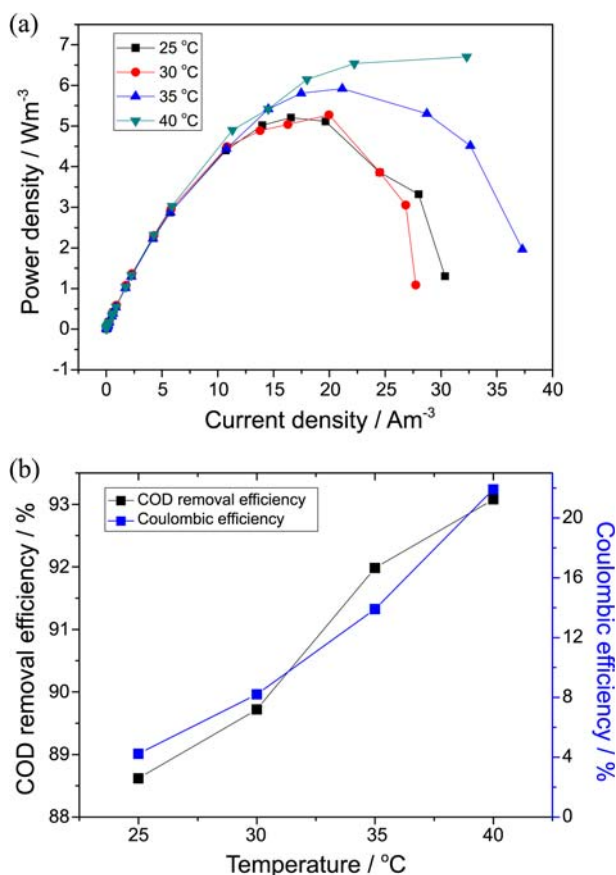


Figure 4. Plot of power density vs current density (panel A) and plot of COD removal efficiency and coulombic efficiency (panel B) at different temperatures with 3 g L⁻¹ acetate concentration.

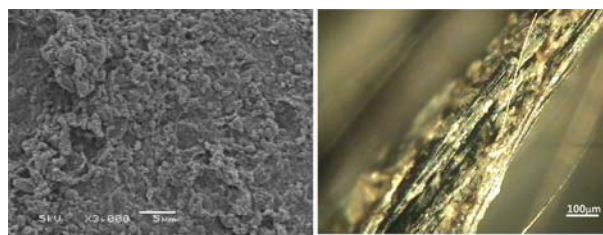


Figure 5. SEM (left) and optical (right) images of anode surfaces after the long term operation.

But for lower concentrations, there was large increase with concentration. These results imply an important point for the MFC operation that COD of wastewater needs to be optimized. For example, since COD of animal wastewater easily exceed several tens of thousands ppm, it should be diluted before feeding it to the MFC.

The temperature effect on power density, COD removal, and coulombic efficiency was also investigated (Fig. 4). In general, as temperature increases, the MFC performance also increases. The maximum power density of about 6 W m⁻³ was observed between 35 °C and 40 °C (panel A). But the difference was not much at low current densities. The COD removal efficiency gradually increased with temperature from 88.5% to 93%, indicating that acetate was well utilized by the bacteria consortium. This means that at elevated temperature bacterial metabolic activity becomes higher. Contrast to high COD removal efficiency, coulombic efficiency was rather low with only about 22% at 40 °C. This could be attributed to the fact that only the small percentage of produced electrons were transferred to the anode although the biofilm was well formed on the anode surface and thus the substrate removal could be very effective.

Figure 5 is the SEM and optical images of the anode surface taken after the 160 days operation. Bacteria cover the whole surface and the biofilm thickness is several tens of micrometers. With this thickness, the direct electron transfer from the outer part of the biofilm is very difficult, although several electron transfer mechanisms have been proposed. Nevertheless, more than 20% coulombic efficiency was observed at 40°C. The long term operation test (data not shown) was performed for 160 days. Under 100 W polarization, the cell voltage was maintained near 0.54 V and showed no indication of any decrease.

In conclusion, we constructed a scaled-up MFC cell and operated it under various conditions for the practical application. As temperature increased the MFC performance also increased. High COD removal efficiency indicates that this system is effective in reducing organic substances but low coulombic efficiency implies that some effective means of electron transfer should be developed to translate organic decomposition to electricity. Low maximum power density of *ca* 6 W m⁻³ compared to the small size MFCs teaches that decreasing overpotentials contributing to the internal resistance is crucial for implementing MFCs in the real world.

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