

Improvement of Cathode Reaction of a Mediatorless Microbial Fuel Cell

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Abstract Oxygen diffuses through the cation-specific membrane, reducing the coulomb yield of the fuel cell. In the present study, attempts were made to enhance current generation from the fuel cell by lowering the oxygen diffusion, including the uses of ferricyanide as a cathode mediator and of a platinum-coated graphite electrode. Ferricyanide did not act as a mediator as expected, but as an oxidant in the cathode compartment of the microbial fuel cell. The microbial fuel cell with platinum-coated graphite cathode generated a maximum current 3–4 times higher than the control fuel cell with graphite cathode, and the critical oxygen concentration of the former was 2.0 mg l^{-1} , whilst that of the latter was 6.6 mg l^{-1} . Based on these results, it was concluded that inexpensive electrodes are adequate for the construction of an economically feasible microbial fuel cell with better performance as a novel wastewater treatment process.

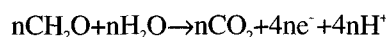
Key words: Mediatorless microbial fuel cell, cathode reaction, ferricyanide, platinum-coated electrode, wastewater treatment, BOD sensor

A microbial fuel cell (MFC) is a device that converts chemical energy to electrical energy with the aid of the catalytic reaction of microorganisms [1, 9, 14]. A MFC consists of anode and cathode separated by a cation-specific membrane [9]. Microbes in the anode oxidize fuel, and the resulting electrons and protons are transferred to the cathode through the circuit and the membrane, respectively. Electrons and protons are consumed in the cathode, reducing oxidant, usually oxygen.

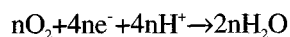
Since the microbial cells are electrochemically inactive due to the nonconductive cell surface structure, mediators are employed to facilitate electron transfer from the microbial cells to the anode in MFCs [6, 18]. Most of the mediators used are toxic water-soluble phenolic compounds.

For this reason mediated MFCs have been applied to very limited areas. In our laboratory, a mediatorless microbial fuel cell has been developed using an electrochemically active bacterium or microbial consortium [15, 16]. In the fuel cell, electrochemically active bacteria, some of which have been isolated and identified [14, 20], are believed to have direct electrochemical reactions, which lead to the operation of a mediatorless MFC [13]. Since a large part of energy carried by the organic contaminants in wastewater is converted to electricity, MFC might produce far less excess sludge, when used as a wastewater treatment process, than the conventional aerobic process. For this reason, MFC was proposed as a novel wastewater treatment process [15]. Another area of MFC application would be as a BOD (biological oxygen demand) sensor, since the current generated is directly proportional to the strength of the wastewater [9].

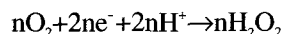
The electron donors are oxidized in the anode compartment of a microbial fuel cell (anode reaction);



The electrons are transferred to the cathode compartment through the circuit, because of the potential difference developed between the reducing anode and cathode supplied with air. The protons are transferred to the cathode through the membrane. The electron and proton are consumed, reducing oxygen in the cathode compartment (cathode reaction);



or



Previous studies showed that the performance of a mediatorless MFC is determined by several factors [9]. They are: 1) microbial activities oxidizing fuels in the anode, 2) electron transfer from microbial cells to the anode, 3) proton transfer from the anode to cathode through the cation-specific membrane, 4) resistance of the

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circuit used to transmit electrons from the anode to the cathode, and 5) oxygen consumption in the cathode, which is also called cathode reaction. Among them, oxygen consumption is considered to be the most serious factor to limit the performance of MFC, due mainly to the poor oxygen-reducing catalytic activity of the electrode used as the cathode [9].

The low catalytic activity of the cathode influences the performance of MFC in several ways. A coulomb yield of around 30% was obtained from a mediatorless MFC with graphite as the cathode, using starch-processing wastewater as fuel [9]. This low coulomb yield is believed to be due to oxygen limitation in the cathode and to fuel consumption to reduce oxygen diffused into the anode through the membrane. Oxygen diffusion through the cation-specific membrane from the cathode compartment to the anode compartment, affecting the anode reaction, has been reported to occur in some biofuel cells [19, 22].

In order to eliminate the oxygen limitation, the dissolved oxygen concentration in the cathode should be kept high, which requires increased power consumption, and results in more oxygen diffusion into the anode. A cathode with improved catalytic activity has been proposed to solve this problem.

The cathode reaction can be improved through electrode modification with metals, surfactants, or organic materials [5, 7, 23], or by using cathode mediators such as methylene blue, viologens, thionines, ferricyanides, and quinoid compounds [1, 6, 10, 11, 18].

In this study, the use of potassium ferricyanide as a mediator and electrode modification with platinum were investigated to enhance the cathode reaction of a mediatorless MFC. Ferricyanide is known to function as a mediator in electrode reactions reduced at the electrode surface and re-oxidized by oxidant [12, 21]. Platinum has been well known as a very good catalyst for oxygen reduction, which is the cathode reaction of many fuel cell types [17]. As a consequence, platinum-coated electrodes have popularly been used as the cathodes in chemical fuel cells.

To the best of our knowledge, this is the first report on oxygen diffusion through the membrane and the use of a platinum-coated electrode as the cathode in a mediatorless microbial fuel cell.

MATERIALS AND METHODS

Wastewater

Wastewater used in this study was described earlier [9]. The wastewater (SPW) was collected from a starch processing plant (Samyang Genex Co., Korea). The chemical oxygen demand (COD_c) of the wastewater was around $1,100 \text{ mg l}^{-1}$, and the wastewater contained $25 \pm 7.7 \text{ mg l}^{-1}$ total nitrogen and $10.7 \pm 1.7 \text{ mg l}^{-1}$ total phosphorus.

Inorganic nitrogen was less than 5 mg l^{-1} . SPW was diluted with phosphate buffer (pH 7.0, 50 mM) containing 100 mM NaCl to designated COD concentrations of 400 mg l^{-1} or 800 mg l^{-1} depending on each experimental purpose.

Artificial wastewater containing glucose and glutamate (GGAW) [4] was also used in some experiments. The BOD of the wastewater was 113.5 mg l^{-1} . Glucose and glutamate solution was filter-sterilized before being added to the autoclaved inorganic salt solution. The GGAW was prepared using a carboy, and purged with oxygen-free nitrogen gas before use. The carboy was connected to a gas-tight bag containing oxygen-free nitrogen gas to keep it under anaerobic conditions.

Microbial Fuel Cell System

Batch mode experiments employed an NCBE-type microbial fuel cell described earlier [1, 9] and is available from National Center for Biotechnology Education (Reading, U.K., <http://www.ncbe.reading.ac.uk>). For continuous runs, a sensor-type microbial fuel cell was used [4]. Each fuel cell consisted of anode and cathode compartments, which were separated by a cation-specific membrane (Nafion® 450, Dupont Co., Wilmington, DE, U.S.A.). Graphite (GF series, Electrosynthesis, Amherst, NY, U.S.A.) was used as the electrode. In some experiments, modified graphite was used as the cathode.

The NCBE-type MFCs used in the batch experiments had been running for over 4 years using diluted SPW. The void volumes of the anode and cathode compartments were 25 ml each. The cathode compartment was filled with 50 mM phosphate buffer (pH 7.0) containing 100 mM NaCl as an electrolyte. The anode content was completely replaced with diluted SPW, when the current dropped to the background level. In some experiments, potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ (6–100 mM) was added to the cathode electrolyte as a mediator. Nitrogen was gassed through the anode at the rate of 10 ml min^{-1} , and the cathode was aerated at the same rate.

GGAW with 113.5 mg l^{-1} BOD was fed to the anode compartment, and air-saturated tap water to the cathode compartment of sensor-type MFCs using peristaltic pumps at the rate of 1.37 ml min^{-1} for continuous experiments. The void volume of the anode and cathode compartments was 20 ml. The sensor-type MFCs had been enriched and run for over a year using GGAW as the fuel [4].

The MFCs were run at 30°C with an external resistance of 10Ω to monitor the current. All experiments were conducted with at least 3 separate MFCs, and mean values or a typical result are presented.

Preparation of Pt-Coated Graphite Electrodes

Platinum powder (2 nm diameter) was mixed with 1.5 parts of Vulcan XC72 carbon (E-TEK, Somerset, NJ, U.S.A.) and 1/3 parts of Nafion ionomer (Dupont Co., Wilmington,

DE, U.S.A.) before being spray coated onto graphite at the ratio of 0.28 mg platinum per cm² graphite surface.

Dissolved Oxygen (DO) Monitoring System

DO was measured using a DO meter (Orion Model 850, Beverly, MA, U.S.A.). DO of the cathode electrolyte was monitored not in the cathode compartment but in a gas-tight glass vessel, because current could not be measured with the DO electrode placed in the cathode, probably due to high potential being used for the DO measurement. The electrolyte was circulated at the speed of 2 ml min⁻¹ through the gas-tight glass vessel (working volume of 20 ml), in which the DO electrode was placed. Connections were made using butyl rubber tubing [9].

To determine the oxygen diffusion rate through the membrane, an empty fuel cell was used. The DO electrode was placed in one side of the membrane (assumed as the anode compartment of the MFC), gassed using oxygen-free nitrogen, and the other side (assumed as the cathode compartment) using air-nitrogen mixed gas of different ratio to obtain desired DO. Increase of DO in the nitrogen gassed side was monitored as the initial oxygen diffusion rate after the nitrogen gassing had been stopped.

Instrumentation and Analyses

The potential was measured using a multimeter (Keithley Instruments, Inc., Cleveland, OH, U.S.A.) and recorded every minute through the data acquisition system (Testpoint®, Capital Equipment Co., Richmond, VA, U.S.A.), as described earlier [9]. The measured potential was converted to current according to the relationship of potential=current×resistance.

Coulomb was calculated by integrating the current over the time in batch experiment. Theoretical coulomb was calculated based on the chemical oxygen demand (COD) consumed in the MFCs. One mg of COD is equivalent to 12 C. Coulomb yield was referred as the fraction of coulomb obtained over theoretical coulomb.

COD of samples was measured by the closed reflux titrimetric method, using chromate as the oxidant [8]. Ferricyanide in the catholyte was analyzed spectrophotometrically at the wavelength of 420 nm (extinction coefficient=1,040 M⁻¹cm⁻¹) [24].

RESULTS AND DISCUSSION

Oxygen Diffusion Rate Through the Membrane

An empty fuel cell was used to measure the oxygen diffusion rate through the membrane with various DO gradients across the membrane. As shown in Table 1, a significant amount of oxygen diffused through the membrane. The higher the DO gradient, the higher the diffusion rate.

Table 1. Oxygen diffusion rate through the cation-specific membrane in an MFC.

DO in the cathode compartment (mg l ⁻¹)	Diffusion rate (μg cm ⁻² h ⁻¹)
6.56	5.20±0.01
5.85	3.12±0.01
3.91	2.91±0.02
1.86	2.70±0.01
0.86	2.49±0.02

Effects of Aeration on the Anode Compartment

NCBE-type MFCs were operated with 400-mg l⁻¹-COD SPW as fuel and the anode compartment was gassed with nitrogen containing different amounts of air (5–20%) to measure current (Table 2). Three MFC showed similar results, and the figures in the table are their mean values. As shown in the table, the maximum current and coulomb yield decreased as more air was gassed through the anode compartment. These results suggest that oxygen is reduced in consuming electron in the anode compartment. The coulomb yield in the control experiment (gassing with 100% nitrogen) was around 30%. Since SPW contains low concentration of possible electron acceptors such as nitrate and sulfate, the low coulomb yield might be due to oxygen diffused into the anode compartment through the sampling port and others.

Use of Pure Oxygen to Gas the Cathode Compartment

NCBE-type MFCs were operated by using pure oxygen to gas the cathode compartment, and the maximum current and coulomb yield were compared with the control run. As shown in Fig. 1, the maximum current was lower when the cathode compartment was gassed with pure oxygen (1 mA) than those obtained using air (1.3 mA). The coulomb yield was less than one-third of the control run. These results were unexpected, because oxygen supply to the cathode compartment was the most serious limiting factor [9]. These results show that more oxygen diffused to the anode compartment and encouraged aerobic respiration when pure oxygen was used, because of the higher DO gradient across the membrane. Microbes

Table 2. Current and coulomb yield obtained from mediatorless NCBE-type MFCs gassed with different air-nitrogen mixtures.

Ratios of gas mixture gassed into the anode (N ₂ :Air)	Current (mA)	Coulomb yield (%)
100%:0%	1.2±0.1	35±3
95%:5%	1.0±0.12	15±3
90%:10%	0.9±0.1	7±2
85%:15%	0.6±0.05	6±0.5
80%:20%	0.5±0.03	5±1

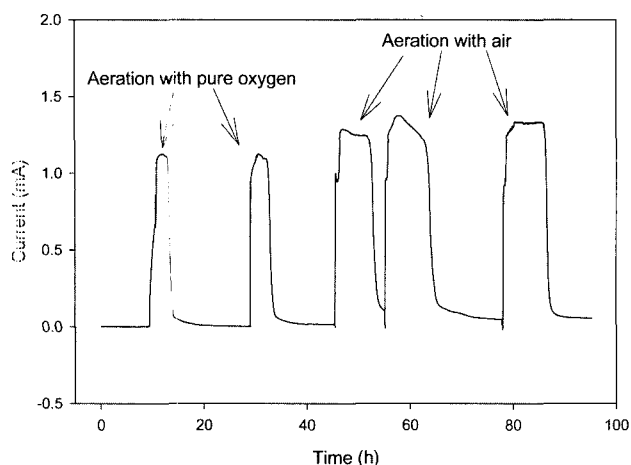


Fig. 1. The performance of NCBE-type MFCs gassed with pure oxygen or air to the cathode compartment. The fuel cells were run with SPW of 400 mg l⁻¹ COD as fuel. The coulomb yields were 9.9±2.7% with pure oxygen and 30.9±3.6% with air.

enriched in the anode compartment are probably facultative anaerobes.

Critical Oxygen Concentration of the MFC with Graphite Cathode

Sensor-type MFCs were used to measure critical oxygen concentration ($[O_2]_{crit}$) through monitoring current and DO concentration of electrolyte from the cathode compartment by assuming that the anode reaction is dependent on the cathode reaction, and that the cathode reaction follows the Monod equation. As expected, the current increased as the cathode flow rate increased from 5 to 20 ml min⁻¹, and the current did not increase further at the cathode flow rate

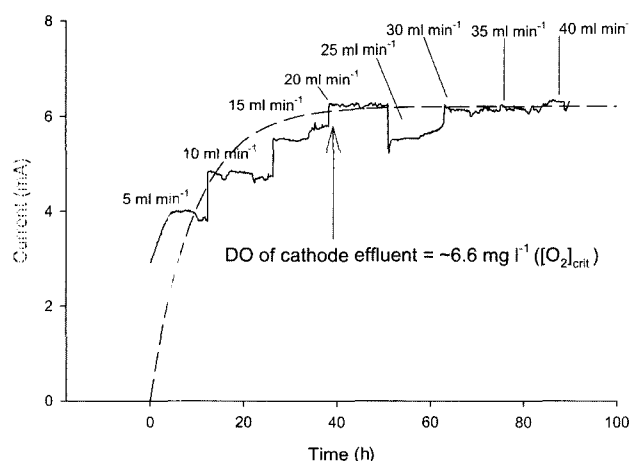


Fig. 2. Determination of critical oxygen concentration ($[O_2]_{crit}$) by monitoring current and DO in the cathode effluent of sensor-type MFCs at different flow rates of air-saturated electrolyte into the cathode compartment. The MFCs operated in a continuous mode.

higher than 20 ml min⁻¹ (Fig. 2). At the cathode flow rate of 20 ml min⁻¹, DO concentration was 6.6 mg l⁻¹ and this concentration was determined as the $[O_2]_{crit}$ of the fuel cell (Fig. 2). A $[O_2]_{crit}$ value of 6.6 mg l⁻¹ is very high in comparison with aerobic bacterial cultures, whose values are less than 1.0 mg l⁻¹ (http://www.np.edu.sg/~dept-bio/biochemical_engineering/lectures/oxy/oxy16.htm). This result confirms that graphite is an inert material with low catalytic activity for the cathode reaction [9]. For an efficient MFC, the cathode reaction should be improved by using either a cathode with better oxygen reducing activity or a cathode mediator.

Use of Ferricyanide as a Cathode Mediator

NCBE-type MFCs were used to test the chemical as a cathode mediator in batch-mode experiments. MFCs were run after the cathode compartments were filled with 50 mM phosphate buffer (pH 7.0) containing 100 mM NaCl and 6 mM potassium ferricyanide, and the current generated was compared with that of a control run (Fig. 3). When the chemical was added, MFCs generated a current of 2.5 mA for about 2 h before the current dropped to the control level and eventually to the background level with the depletion of fuel. Absorbance of the cathode electrolyte was monitored at 420 nm during the run, and absorbance was over 2.5, when the current started to decrease, and stayed lower than 0.1 throughout the run (Fig. 3). A slightly higher coulomb (56.4 C) was obtained from the run, when ferricyanide was added, than the control (49.6 C). It was shown in a separate experiment that the coulomb yield increased as the function of ferricyanide concentration (data not shown).

These results show that ferricyanide functions as an oxidant but not as a mediator, probably because ferrocyanide

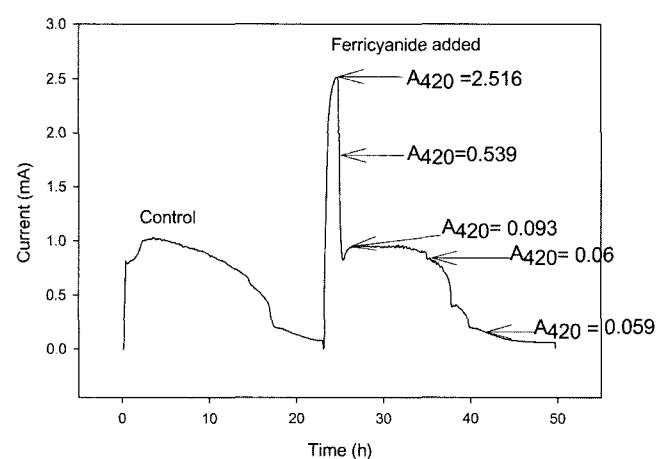


Fig. 3. The effects of ferricyanide being added to the cathode electrolyte on the current generation by MFCs. NCBE-type MFCs were used. The numbers in the figure are the absorbance values (at 420 nm) of the cathode electrolyte after 6 mM potassium ferricyanide had been added.

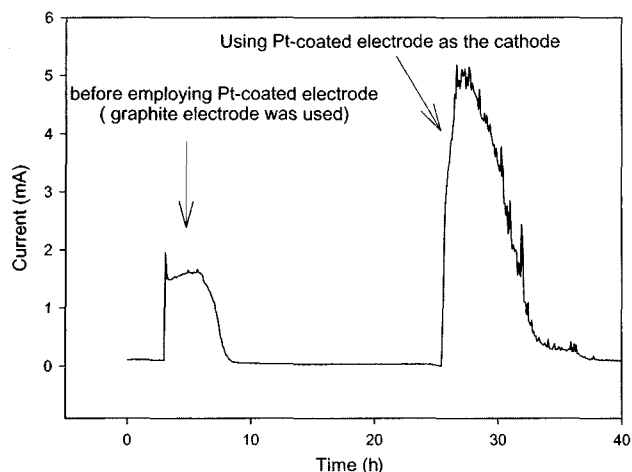


Fig. 4. The performance of NCBE-type MFCs with graphite or with platinum-coated graphite as the cathode.

The fuel cells were run with SPW of 400 mg l^{-1} COD as fuel. The coulomb yields were $27.3 \pm 3.3\%$ with graphite cathode and $78.3 \pm 7.3\%$ with platinum-coated graphite cathode.

is re-oxidized by oxygen in the cathode compartment at much lower rate than reduction in the mediatorless microbial fuel cell system. Ferricyanide is also known to act as oxidants in some electrochemical systems [2, 3, 6]. To confirm this, an empty fuel cell was used to measure the oxidation rate of ferrocyanide. The empty fuel cell containing 20 mM potassium ferrocyanide dissolved in normal electrolyte was aerated at the rate of 10 ml min^{-1} , and ferrocyanide was found to be oxidized to ferricyanide at the rate of about $0.015\text{--}0.02 \text{ mM h}^{-1}$. This is much lower than the reduction rate observed in the above experiments.

Platinum-Coated Graphite Electrode as the Cathode

The cathode of NCBE-type MFCs was replaced with the same size platinum-coated graphite electrode, carefully so as not to disturb the microbial population in the anode compartment. The microbial fuel cell with platinum-coated cathode generated the over 5 mA maximum current, whilst that in the control case (before the electrode was used) was 1.5 mA (Fig. 4). Repeated operation showed similar results. In addition, the coulomb obtained from the microbial fuel cell with platinum-coated electrode was about 3 times higher than the control (Fig. 4). These results showed that platinum-coated cathode is better for the cathode reaction in a mediator-less microbial fuel cell than the graphite one.

$[\text{O}_2]_{\text{crit}}$ value was determined to be 2 mg l^{-1} (Fig. 5), which is much lower than that of bare graphite electrode, but higher than that of aerobic bacteria. Since the oxygen diffusion rate through the membrane is gradient dependent (Table 1), low $[\text{O}_2]_{\text{crit}}$ value of the cathode can reduce

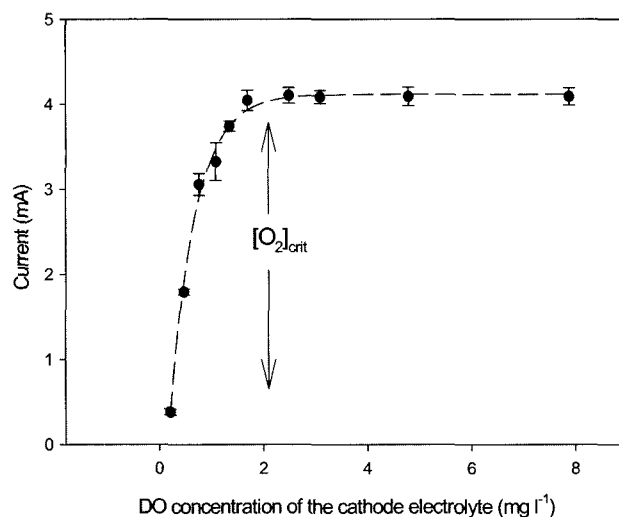


Fig. 5. Determination of $[\text{O}_2]_{\text{crit}}$ of the MFC with platinum-coated cathode, using NCBE-type MFCs.

oxygen diffusion to the anode compartment thus improving the performance of an MFC without oxygen limitation. Such a cathode with a low $[\text{O}_2]_{\text{crit}}$ also helps solve the problem of power consumption for cathode aeration, as mentioned earlier. This is very important in the application of an MFC as a BOD sensor [4] as well as a novel wastewater treatment process. For this reason, inexpensive electrodes with the $[\text{O}_2]_{\text{crit}}$ value similar to or equal to that of aerobic bacteria are desirable.

CONCLUSIONS

In a mediatorless microbial fuel cell, oxygen diffuses through the cation-specific membrane, and the diffusion rate is dependent on dissolved oxygen concentration gradient. Oxygen is actively consumed in the anode compartment, reducing coulomb yield. Microbes enriched in the anode compartment are probably facultative anaerobes. Ferricyanide cannot be used as a cathode mediator, since the substance is reduced much faster than being oxidized by oxygen. Graphite electrode needs dissolved oxygen concentration over 6.6 mg l^{-1} for the maximum cathode reaction. At this dissolved oxygen concentration in the cathode compartment, a considerable amount of oxygen is diffused into the anode compartment, significantly reducing coulomb yield of the fuel cell. Platinum-coated electrode, which gives lower critical oxygen concentration of 2.0 mg l^{-1} , can be used instead of bare graphite electrode as the cathode to improve the performance of the fuel cell. Inexpensive modified electrodes are needed for the construction of an economically feasible microbial fuel cell as a BOD sensor and also as a novel wastewater treatment process.

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