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Improved Performance of Microbial Fuel Cell Using Membrane-Electrode Assembly

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Abstract A mediator-less microbial fuel cell (MFC) was used to determine the performance effects of a membrane-electrode assembly (MEA). The MFC with an MEA generated a higher current with an increased coulomb yield when compared to an MFC with a separate cathode. Less oxygen was diffused through an MEA than through a Nafion membrane. The MFC performance was improved with a buffer, although a high-strength buffer reduced the performance.

Key words: Bioelectrochemistry, mediator-less microbial fuel cell, cathode reaction, oxygen, membrane-electrode assembly

It has already been shown that the Fe (III)-reducing bacteria *Shewanella putrefaciens* [6] and *Geobacter sulfurreducens* [1] can use an electrode as their electron acceptor/sink. Consequently, this property has been exploited to generate electricity coupled to the oxidation of fuel as electron donors [1, 9]. A microbial consortium has been enriched in a fuel cell-type electrochemical device using wastewater as the fuel [8]. Such an MFC can be used as a BOD sensor, as the current generated is directly proportional to the amount of electron donors supplied [5, 7]. MFCs have also been proposed as a novel wastewater treatment process, with the advantage of reduced sludge generation, since a large part of the energy carried by the electron donors in wastewater is converted to electricity [8].

Several operational factors limiting the performance of an MFC have been identified [3], including proton permeability through the membrane, and oxygen supply limitations for the cathode reaction. Thus, several studies have developed a novel type of MFC without a membrane, which is more efficient than the conventional type [4].

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As such, a coulomb yield of around 30% has been obtained from a mediator-less MFC with graphite as the cathode when using starch-processing wastewater as fuel [3]. This low coulomb yield is the result of fuel consumption to reduce oxygen, which is diffused into the anode through the membrane. Graphite as the cathode shows a critical oxygen concentration of around 6 mg l^{-1} [13]. But, when the oxygen concentration in the cathode compartment is kept higher than this value to avoid oxygen limitation, a considerable amount of oxygen is diffused into the anode compartment. Thus, an MFC with platinum-coated graphite as the cathode has been found to have an improved cathode reaction [13] with a coulomb yield over 70% due to its low critical oxygen concentration (around 2.2 mg l^{-1}), resulting in less oxygen diffused into the anode compartment [13]. This improvement in the cathode reaction can reduce the power needed for cathode aeration; meanwhile, an MFC that uses oxygen directly from air can eliminate the need for cathode aeration. This can actually be achieved using a structure called membrane-electrode assembly (MEA), which is widely used in chemical fuel cells [10]. Thus, Park and Zeikus [11, 12] proposed a model of a single-compartment biofuel cell that does not require cathode aeration. As such, the use of an MEA would seem to be more advantageous than MFCs with two compartments separated by a membrane, as a modified electrode can remain more stable under dry conditions than in an aqueous catholyte, and the performance should be better with close contact between the cathode and the membrane.

Accordingly, this study tested mediator-less MFCs to compare the differences in performance between MFCs with an MEA, and MFCs with a separate cathode compartment.

Wastewater

Starch-processing wastewater (SPW) described earlier [3, 13] was used throughout the study. The chemical oxygen

demand (COD_{Cr}) of the wastewater was around 2.3 g l^{-1}, and the wastewater contained significant amounts of total nitrogen and total phosphorus [13]. The SPW was diluted using a phosphate buffer (pH 7.0, 50 mM) containing 100 mM of NaCl to a COD concentration of 900 mg l^{-1}.

Microbial Fuel Cell System

The MFCs used in this study were NCBE-type microbial fuel cells that had been operated for over 4 years using diluted SPW [3]. The fuel cells consisted of anode and cathode compartments separated by a cation-specific membrane. Graphite was used as the electrode material. The cathode compartment was filled with a 50 mM phosphate buffer (pH 7.0) containing 100 mM NaCl as the electrolyte. The MFC was operated in a batch mode, based on completely replacing the anode content with diluted SPW when the current dropped to the background level. Nitrogen gas was passed through the anode at a rate of 10 ml min^{-1}, and the cathode was aerated at the same rate. In some experiments, the membrane and cathode compartment, including the graphite cathode, were replaced with an MEA prepared as below.

The MFCs were placed in a temperature-controlled chamber kept at 30°C. Each MFC was loaded with an external resistance of 10 Ω to monitor the current. All experiments were conducted with at least 3 separate MFCs, and the mean values or typical results are presented.

Preparation of MEAs

The MEAs were prepared according to the methods described by Larminie and Dicks [10]. Teflonized (20%) carbon paper (E-TEK, Somerset, NJ, U.S.A.) coated with a platinum/carbon powder/Nafion mixture was used as the cathode. The platinum/carbon powder/Nafion mixture was made by mixing 5/24 weight parts of the Nafion ionomer (5%, Dupont Co., Wilmington, DE, U.S.A.) dissolved in isopropanol (1 g Nafion in 5 g solvent) with a suspension of 1 weight part of platinum powder (2 nm diameters) and 1.5 weight parts of Vulcan XC72 carbon (E-TEK). The platinum/carbon powder was suspended in isopropanol at a ratio of 300 ml solvent to 1 g platinum/carbon powder mixture. The mixture was then sonicated for 30 min before being spray-coated onto carbon paper at a ratio of 0.28 mg platinum per cm^2 surface. The platinum-coated electrode was sprayed with 5/8 weight parts of the Nafion ionomer dissolved in isopropanol (3 g isopropanol/1 g Nafion). Electrode sheets 5×5 cm^2 in size were then prepared from the coated carbon papers.

The electrodes were hot pressed at 140°C, 200 atm for 2 min onto a Nafion 117 membrane (Dupont Co.), which was then cleaned by successively boiling in 3% hydrogen peroxide for 1 h, in 1 N sulfuric acid for another 1 h, and in boiling deionized water for 1 h.

MFCs with MEA

The membrane and cathode of each NCBE-type MFC were carefully replaced with an MEA, so as not to disturb the microbial population in the anode compartment. The MFCs with an MEA were operated in a similar way to the NCBE-type MFCs. The cathode was directly exposed to air in the MFCs with MEAs.

Determination of Oxygen Diffusion Through MEA

The MFCs with MEAs were set up without an electrode in the anode compartment, which had 3 ports: 1 for nitrogen gassing, and the other two for connecting to the butyl rubber tubing of the DO monitoring system. The anode compartment was filled with 50 mM of a phosphate buffer containing 100 mM NaCl as the electrolyte.

The DO was measured using a DO meter (Orion Model 850, Beverly, MA, U.S.A.). The electrolyte from the anode compartment was pumped through the butyl rubber tubing to a gas-tight glass vessel with a DO probe to measure the DO concentration before being pumped back to the compartment. The electrolyte was circulated at a speed of 2 ml min^{-1}. The working volume of the gas-tight glass vessel was 5 ml.

The anode electrolyte was first gassed with air at a rate of 50 ml min^{-1} to achieve an air-saturated state (DO= around 7-8 mg l^{-1}). Thereafter, it was gassed with nitrogen at the same rate until the DO of the anode electrolyte almost reached the bottom level, then the nitrogen gassing was stopped and the anode compartment tightly closed at the same time. The DO concentration of the anode electrolyte was monitored throughout the experimental process using the system described above. Any increase in the DO concentration was regarded as the result of oxygen diffusion through the MEA.

Instrumentation and Analyses

The potential was measured using a multimeter (Keithley Instrument Inc., Cleveland, OH, U.S.A.) and recorded every 5 min through a data acquisition system (Testpoint®, Capital Equipment Co., U.S.A.). The measured potential was converted to a current according to the relationship of potential=current×resistance. The coulomb yield, expressed as current×time, was calculated by integrating the current over the time from the start point of the experiment, to the time where the current was decreased to 5% of the maximum current. The Chemical Oxygen Demand (COD) was measured using the closed reflux titrimetric method with chromate as the oxidant [2]. The cations were quantified using an X-Ray Fluoresence Spectrometer (Model RIX2100, Rigacu, Tokyo, Japan).

Electricity Generation

The NCBE-type MFCs had been enriched and operated for over 4 years with a graphite cathode before the membranes

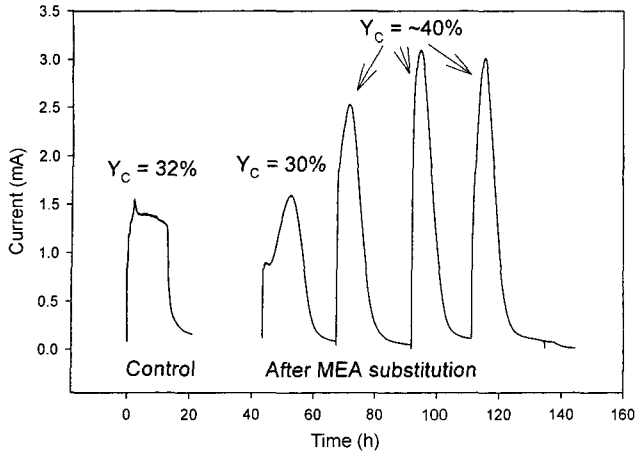

Fig. 1. Electricity generation from mediator-less MFC before (control experiment) and after substituting MES for membrane and cathode (Y_C: Coulomb yield of MFC).

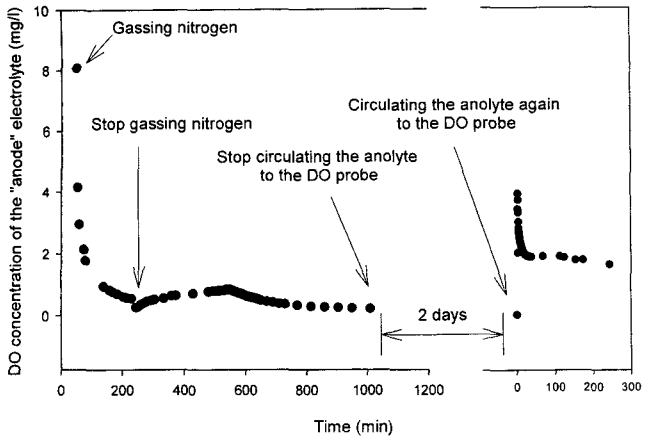

Fig. 2. Changes in DO concentration of anolyte in MFC with MEA.

and cathodes were replaced with MEAs. The MFCs before the replacement generated a maximum current of around 1.5–2 mA with a coulomb yield of 30±2%. However, a maximum current of over 3 mA was obtained with a coulomb yield of 40±5% after the membrane and cathode were replaced with the MEA (Fig. 1). When the membrane and cathode were restored, the current and coulomb yield were similar to those for the MFCs before the replacement. The changes in the current and coulomb yield were not due to the disturbance caused during the replacement.

COD Removal Efficiency of MFCs with MEA

The COD concentration of the anode content for the MFC with an MEA decreased from 900 mg l^{-1} to around 350 mg l^{-1} after one operational batch. The COD removal efficiency did not change after the replacement of the cathode with an MEA.

Water Formation on Electrode Surface of MEA

Water drops accumulated on the surface of the cathodes of the running MFCs, however, this phenomenon was not observed in the control fuel cell with a fresh anode not enriched with microbes. This result shows that the MEA functioned properly.

Oxygen Diffusion Through MEA

Oxygen diffusion is known as a serious factor that reduces the coulomb yield of the conventional mediator-less MFC [13]. Therefore, the oxygen diffusion through the MEA was measured (Fig. 2). As shown in Fig. 2, the DO increased slightly after the nitrogen gassing was stopped for about 5 h before decreasing to the minimum level. When the circulation pump was reactivated after 2 days of inactivation, the DO increased to about 4 mg l^{-1} before it decreased again. The initial increase in the DO after the nitrogen gassing was stopped was probably due to the residual oxygen in the system, while the subsequent decrease shows that the oxygen consumption in the system was higher than its diffusion into the system. The increase in the DO while the circulation pump was inactivated shows that oxygen was diffused through the MEA, and that this diffusion was less than the oxygen consumption in the system, probably by the oxygen electrode. In a separate experiment, the oxygen consumption by the oxygen electrode was measured as 1.44±0.24 mg h^{-1}. Thus, the oxygen diffusion through the MEA was likely less than in this figure.

Effect of Buffer as Anode Electrolyte

It has also been shown that the addition of a buffer to the anode compartment improves the performance of MFCs [3]. Therefore, the MFCs with the MEA were operated using wastewater diluted with a phosphate buffer (pH 7.0) of differing strengths, ranging from 50 to 200 mM, containing 100 mM NaCl. Table 1 shows that the higher the strength of the buffer, the higher the coulomb yield. Yet the maximum current showed a different pattern from that of the coulomb yield. The highest current of around 3.2 mA was obtained from the MFC fed with wastewater diluted with a 50 mM buffer, whilst maximum current was approximately 2.25 mA when the MFCs fed with the fuel were diluted with a 100 or 200 mM buffer. When the

Table 1. Effect of buffer strength on the performances of MFC with MEA.

Buffer strength (mM)	Maximum current (mA)	Coulomb yield (%)
50	3.15±0.3	40±5
100	2.25±0.15	52±5
200	2.25±0.2	65±5.5

MFCs were operated using wastewater diluted with a 100 or 200 mM buffer, white crystals formed on the MEA that were carbonate salts of sodium (23.50%) and potassium (8.36%), and other elements at less than 0.01%, including Fe, Pt, Si, Mg, Pb, Mn, P, Cu, Sn, Ca, Al, Cl, and S. Therefore, these results show that the cations crossed the MEA competitively with protons. Meanwhile, the low current with the high strength buffer may have been the result of reduced cathode reactions due to the reduced proton permeability, and from salt accumulation.

In conclusion, an MEA has advantages over a separate cathode and membrane in terms of the coulomb yield and current generation that are probably due to the reduced oxygen diffusion into the anode compartment. In addition to the better performance, the use of an MEA can save energy needed to supply air into the cathode compartment. When an electrolyte with a high salt concentration is used, precautions should also be made to avoid the accumulation of salts on the cathode surface, which reduces the cathode reaction.

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