Microbial Fuel Cells with a Mediator-Polymer Modified Anode

Masanori ADACHI*, Ryotaro YAMAMOTO, Tatsuo SHIMOMURA, and Akiko MIYA

Ebara Research Co., Ltd. (4-2-1 Honfujisawa, Fujisawa-shi 251-8502, Japan)

Received February 27, 2009; Accepted August 12, 2010

The electrical performance of microbial fuel cells (MFCs) using a modified anode consisted of anthraquinone-2,6-disulfate as a mediator, polyethyleneimine as a functional polymer and graphite felt as a base material was studied. The performance of an MFC was improved using the mediator-polymer modified graphite felt anode. The maximum power density of the mediator-polymer modified MFC was reached 1.0 mW cm⁻² (per geometric anode surface area), it was 2.7 times higher than that of an mediator-less MFC. The power generation of mediator-polymer modified MFC was stable for more than 10 days.

Key Words: Microbial Fuel Cells, Mediator, Modified Electrode, Biomass

1 Introduction

Energy production technologies from biowaste, such as methane generation, ethanol fermentation, etc., have been studied intensively for the last decade.¹ In particular, microbial fuel cells (MFCs) are expected as an innovative apparatus for biowaste treatment systems.² In general, an accumulation of acetate is observed for the anaerobic degradation of biowaste. Therefore, acetate-utilizing extracellular material-reducing bacteria (EMRB) are suitable for use in MFCs. The minimum system components of an MFC are an anode, a cathode, a membrane and EMBR. The simplest MFC is referred to as a mediator-less MFC.³ Many research groups have studied mainly mediator-less MFCs, due to their expected stability and high current efficiency.⁴ Recently, the anodic current density of mediator-less MFCs has been successfully increased; Torres et al. (2008) reported a stable current density of 1.1 mA cm⁻² (per geometric area of anode) for a mediator-less MFC with acetate and Geobacter sulfurreducens.⁵ However, faster oxidation processes are required on the anode to realize MFCs for practical applications, because the estimated oxidation of organic matter using MFC is slower than that of existing biowaste treatment systems. It has been suggested that anodic current in MFC increased by a mediator.⁶,⁷ Anthraquinone-2,6-disulfate (AQDS) as the mediator is known to serve as a bio-active electron acceptor and an electrode-active electron donor with low overpotentials.⁸ On the other hand, use of free mediator entails two issues that, high concentration is needed because of diffusion, and that the mediator is washed out. Therefore we have proposed that a mediator-polymer modified anode with EMBR has the potential to increase anodic current density.⁹ On the modified anode, EMBR can use the oxidized form of the fixed-mediator as an electron accepter and convert it to the reduced form, and the reduced form fixed-mediators can then be oxidized back by the anode. It is estimated that the electron transfer via a fixed-mediator is smoother than mediator-less electron transfer, because the fixed-mediator is reacted immediately with EMRB or the anode. In this work, the performance of a MFC consisting of a modified anode and a Pt-coated Ti mesh cathode was evaluated by linear sweep voltammetry.

2 Experimental

2.1 Preparation and characterization of anodes

A derivative of AQDS (Aldrich) was used as an electron mediator, polyethyleneimine (PEI; Nippon Shokubai Co., Ltd., EPOMIN® P-1000, MW = 320,000) was used a base polymer, and graphite felt (GF; Nippon Carbon Co., Ltd., Carbolon) was used as an electrode. The AQDS-PEI modified GF electrode (E1) was prepared as detailed in our previous report.⁹ The E1 was prepared in order to compare the electrical characteristics and the amounts of immobilized AQDS contained therein. A PEI cross-linked GF electrode with 1,5-pentanediolic acid (E2) and an unmodified GF electrode (E3) were used as control electrodes. For electrochemical characterization of the modified electrodes, differential pulse voltammetry (DPV) was performed to investigate the oxidation-reduction properties of the electrodes, and chronocoulometry (CC) was carried out to determine the amount of AQDS present in the electrodes.⁶ Both of these operations were carried out in 0.1 M phosphate buffer (pH 7.0, RT).

2.2 The anode performance with EMRB

The electrodes (anode, E1, E2 or E3 [geometric area 8 cm²]; cathode consisting of a Pt-coated Ti mesh [Tanaka Kikinzoku Kogyo K. K., geometric area 120 cm²]; reference electrode [standard calomel electrode, DKK-TOA Corp., HC-205C]) were connected to a potentiostat (Hokuto Corp., HA-151). The reactor was make up of an anode compartment filled with an anaerobic medium and a cathode compartment filled with phosphate buffer. The liquid in the two compartments was separated by a proton exchange membrane (Dupont Nafion® NX 424, geometric area of 25 cm²). The anode and reference electrodes were immersed in the anaerobic medium containing sodium acetate (48 mM) as the main organic substrate (concentration of soluble chemical oxygen
demand (C<sub>COD</sub>) was 3.7 g L<sup>-1</sup>, pH 7.5, 1.2 L). The inoculum liquid<sup>60</sup> (10 mL) containing <i>G. sulfurreducens</i> was injected into the anaerobic medium. The anode compartments of the reactor were not sterilized prior to inoculation. The anode potential was maintained at 0.0 V vs. NHE using the potentiostat. The cathode was immersed in the 0.1 M phosphate buffer (pH 7.5, 0.7 L), and the buffer was purged with air (2 L min.<sup>-1</sup>). The medium in the anode compartment was usually sampled twice a week and C<sub>COD</sub> was determined using a COD test kit (Hach Co., COD systems). The concentration was maintained at over 2 g L<sup>-1</sup> by injection of 10 to 20 mL of sodium acetate solution (pH 7.0, C<sub>COD</sub> 150 g L<sup>-1</sup>), or by renewing half of the anaerobic medium. The reactor was kept at 37°C in a large-size incubator (Yamato Science Co. Ltd., IN802). After the 20 day incubation period, the anode performance was measured by linear sweep voltammetry (LSV) using an electrochemical analyzer (BAS Inc., ALS 660C).

2.3 Electrical performance measurements of MFCs

The microbial fuel cells consisted of the E1 or E3 anodes, the Pt-coated Ti mesh cathode and the reactors used for evaluation of electrical cell performance. The conditions for operation of the reactor and the anaerobic medium condition were the same as that for evaluation of the anodes. The performance of MFCs with E1 (mediator-fixed MFC) and E3 (mediator-less MFC) anodes were measured using the electrochemical analyzer. Power output was calculated from current-MFC voltage curve measured by LSV (scan rate: 5 mV s<sup>-1</sup>). The internal resistance of the two MFCs was measured by AC impedance method with the electrochemical analyzer. For both MFCs, the anode and the cathode had been connected via a 50 Ω resistor and an ammeter (Hokuto Co. Ltd., HM-103) for 10 days. The steady-state current of the two MFCs was measured.

3 Results and Discussion

3.1 Electrical characterization of the anodes

Figure 1 shows differential pulse voltammograms for the three electrodes. For the E1 electrode, a large peak of 0.4 mA cm<sup>-2</sup> was clearly observed at ~0.15 V vs. NHE. For the E2 and E3 electrodes, both of the measured currents were below the detection limits. Therefore, the large peak was considered to be due to AQDS immobilized on the modified electrode. The density of AQDS per geometric unit area of the modified electrode was determined by CC as 0.5 μmol cm<sup>-2</sup>

Figure 2 shows LSVs of the three incubated anodes. The scan rate was so slow that the anodic current density was approximated as the steady state anodic current density at each potential. For the E1, E2 and E3 anodes, the spontaneous potential was ~0.3 V vs. NHE.

For the E1 electrode, the maximum current density was 4.3 mA cm<sup>-2</sup> at a potential of 0.3 V vs. NHE. The shape of the current density-potential curve for the E1 electrode displayed a diffusion-limited current under the condition that potential of the electrode was over 0.2 V vs. NHE. For E2 and E3 electrodes, the current densities of both were over 1.2 mA cm<sup>-2</sup> at a potential of 0.1 V vs. NHE. The current of both electrodes was limited by diffusion under the condition that the potential was over ~0.1 V vs. NHE. The performance of the E3 electrode was similar to that reported for an unmodified carbon rod and <i>G. sulfurreducens</i>.<sup>5</sup> It would be simple to assume that the specific surface area of the unmodified graphite felt is much larger than that of the carbon rod; however, the anodic current densities of both were almost of the same magnitude. For practical application of the MFCs, the bio-film was covered with the whole electrode. Therefore, the geometric area of the electrode was important to compare performance of electrodes.

The steady-state current density of the AQDS-PEI modified GF anode (E1) was demonstrated to be higher than that of the E2 and E3 anodes. The maximum current density of the E1 electrode was higher than that we previously reported.<sup>60</sup> Torres <i>et al.</i> (2008) reported that the anodic current density with 100 mM phosphate buffer (1.1 mA cm<sup>-2</sup>) was two times higher than that with a 50 mM phosphate buffer (0.5 mA cm<sup>-2</sup>). Therefore, it was suggested that use of 100 mM phosphate buffer enhanced the current density (43 mA cm<sup>-2</sup>) of the mediator-polymer modified anode. In our previous report, the concentration of the phosphate buffer used was 50 mM.

3.2 Power output and stability of the MFC

The power output of the mediator-fixed and mediator-less MFCs were measured electrochemically, and the results are shown in Fig. 3. The power output of the
mediator-fixed MFC displayed a clear peak, with maximum power at 8.0 mW (20 mA, 0.4 V), and the power density of the anode (E1) was 1 mW cm⁻². However, the maximum power output of the mediator-less MFC was only 3.0 mW, and the power density of the anode (E3) was 0.37 mW cm⁻². The maximum power output of the mediator-fixed MFC was 27 times higher than that of the mediator-less MFC. The internal resistance of both MFCs was measured at 7-8 Ω, and the ohmic loss was estimated to be less than 2.5 mW. The cathode used in this study was sufficiently large to consume electrons from the anode; therefore, these results suggest that the performance of the two MFCs was affected by the performance of the two anodes, and the performance of the MFC was improved by using the mediator-polymer modified anode.

Figure 4 shows the power output of the mediator-fixed MFC and the mediator-less MFC over time. For the mediator-fixed MFC, the power output was stable in the range of 4-5 mW for 10 days. The power output of the mediator-less MFC was stable at 2.4 mW for 10 days. During the experiment, the power output of both MFCs was stable, despite the anode potential not being controlled. The C_{COD} of the anaerobic medium was kept high at over 2 g L⁻¹. The results suggested the possibility that mediator-fixed MFC is as stable as the mediator-less MFCs in long-term operation.¹⁰

In conclusion, 10 consecutive days of high power generation was successfully achieved with the mediator-fixed MFC and G. sulfurreducens. The performance of the AQDS-PEI modified GF anode was superior to that of the PEI-1,5-pentanediol acid modified GF anode and the unmodified GF anode. The power output of the mediator-fixed MFC reached 8 mW and the performance was stable for at least 10 days in the batch reactor. These results suggest that the use of MFCs with mediator-polymer modified anode-systems could contribute to significant progress in the oxidation of organic matter. This MFC has potential for power generation using acetate that is produced from biowaste containing a high concentration of organic matter, such as food waste and sewage.

Acknowledgement
The authors wish to thank Dr. T. Osa (Professor emeritus of Tohoku Univ.) for helpful advice, and Y. Saijyo, R. Yamada and K. Oishi for their contribution to operating the MFCs and performing the electrochemical measurements.

References