Article

Microbial Fuel Cell Equipped with Bipolar Membrane Using Iron (III) Hydroxide as Final Electron Acceptor

Iori Kazama [ID], Yuji Aso [ID], Tomonari Tanaka [ID] and Hitomi Ohara *[ID]

Department of Biobased Materials Science, Kyoto Institute of Technology, Hashigami-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
* Correspondence: ohara@kit.ac.jp; Tel.: +81-75-724-7689

Abstract: In this paper, we presented a novel microbial fuel cell (bMFC) structure, with a bipolar membrane separating the anode and cathode chambers. A bipolar membrane divides the bMFC into anode and cathode chambers. The bipolar membrane comprises anion and cation exchange layers. The anode chamber side has the cation exchange layer, while the cathode chamber side has the anion exchange layer. The anode chamber of the bMFC was loaded with *Shewanella oneidensis* MR-1 and lactic acid, while the cathode chamber was loaded with pure water and iron (III) hydroxide. The bMFC generated electrons for 20 days at a maximum current density of 30 mA/m^2 and the ohmic resistance value was estimated to be 500 Ω. During the operation of the bMFC, both the anode and cathode chambers kept anaerobic conditions. There was no platinum catalyst in the cathode chamber, which is required for the reaction of protons with oxygen. Therefore, oxygen could not serve as an electron acceptor in the bMFC. We considered a bMFC mechanism in which protons produced by *S. oneidensis* react with hydroxide ions, the counter anions of Fe^{3+}, inside the bipolar membrane to produce water. In other words, the electron acceptor in bMFC would be Fe^{3+}.

Keywords: bipolar membrane; iron (III) hydroxide; lactic acid; microbial fuel cell; *Shewanella oneidensis*

1. Introduction

There is a need to increase electricity generation while controlling carbon dioxide in the atmosphere for the sustainable development of society. As a result, microbial fuel cells (MFCs) based on biomass are actively researched. MFCs produce electricity by supplying electrons obtained from the process of metabolizing organic matter by certain microorganisms to electrodes. Water-rich biomass is not suitable as a fuel for thermal power generation. However, because microorganisms survive in water, MFCs can use biomass in water. On the other hand, wastewater treatment employs microorganisms to reduce biochemical oxygen which demands BOD, which is the same reaction used in MFC electricity generation. Therefore, an application of MFC was proposed in which organic-containing wastewater was simultaneously treated and used as fuel to generate electricity [1].

Conventional MFCs consist of an anaerobic anode chamber and an aerobic cathode chamber isolated by a cation exchange membrane. Each chamber has electrodes installed, and the cathode chamber contains a catalyst such as platinum for the reaction of oxygen and proton. In the anode chamber, microorganisms metabolize organic matter and biomass to produce electrons and protons. Electrons are transferred from the anode via an outer circuit to the cathode, while protons are transferred from the anode chamber via the cation exchange membrane to the cathode chamber. Protons and electrons react with dissolved oxygen in the cathode chamber to produce water through the catalytic action of platinum. In previous studies, cathodic reduction using non-platinum catalysts rather than platinum catalysts was reported [2–11]. For example, iron (II) phthalocyanine and cobalt tetra-methoxyphenyl-porphyrin [3] and ferricyanide [7] were used as catalysts when conducting

such experiments. However, when these MFCs are used in wastewater treatment, a large amount of these chemicals are discharged into the environment, which is a problem.

Bipolar membranes consisting of a cation-exchange membrane and an anion-exchange membrane [12,13] can dissociate water into H^+ and OH^- when used in electrodialysis. Therefore, bipolar membranes are used in large-scale desalination processes in the industry [14]. Recently, studies were published on the use of MFCs equipped with bipolar membranes in wastewater treatment systems [15,16]. A new type of MFC with a bipolar membrane to reduce iron (III) oxide to iron (II) oxide was also reported [17]. In this report, microorganisms metabolized acetic acid into electrons, protons, and carbon dioxide in the anode chamber, and the generated electrons reduced iron (III) oxide to iron (II) oxide in the cathode chamber. *Acidithiobacillus ferrooxidans* then oxidized iron (II) oxide and then, again to iron (III) oxide. Finally, *A. ferrooxidans* respiration produced water. The cation exchange layer of the bipolar membrane was installed in the cathode chamber of this MFC, and the anion exchange layer was installed in the anode chamber. The MFC's final electron acceptor was oxygen, and the cathode chamber must remain aerobic. Other bipolar membranes MFCs were reported, using sodium acetate as fuel and wastewater containing hexavalent chromium from a plating factory as an electron acceptor [18]. A microbial electrolysis method that produced electricity and hydrogen from acetic acid using bipolar membranes was also reported, but it used platinum as a catalyst [19].

S. oneidensis MR-1 has excellent properties suitable for MFCs [20] because the strain can be used with several compounds, including manganese (IV) oxide, cobalt, and uranium, as terminal electron acceptors. Particularly, the strain can be used with iron (III) oxide as an electron acceptor, implying that this microorganism can transfer electrons to solid electrodes [21–23].

In this report, we propose a bipolar membrane-equipped bMFC with a bipolar membrane separating the anode and cathode chambers. In this bMFC, the cation exchange layer of the bipolar membrane is installed on the anode chamber side, while the anion exchange layer is installed on the cathode chamber side. This installation is the inverse of previous reports using bipolar membranes [17–19]. The bMFC uses *Shewanella oneidensis* MR-1 and lactic acid, produced from biomass, as fuel. The cathode chamber was kept in an anaerobic condition, and iron (III) hydroxide was placed there. Therefore, oxygen cannot function as an electron acceptor in the cathode chamber. These findings imply that the current bMFC employs a different electron acceptance mechanism than previously reported MFCs. The goal of this report is to demonstrate that the bMFC structure can generate electricity continuously, evaluate its performance, and clarify the bMFC reaction mechanism.

2. Materials and Methods

2.1. Bacterial Strain and Seed-Culture

In this study, the strain of *Shewanella oneidensis* MR-1 was used. The Luria–Bertani (LB) medium contained 5 g/L yeast extract (Nacalai Tesque Inc., Kyoto, Japan), 10 g/L Tryptone (Nacalai Tesque), and 10 g/L sodium chloride (Nacalai Tesque). The LB medium was first dissolved in distilled water before being placed in a 500 mL Sakaguchi flask and cultured at 30 °C for 24 h while being shaken at 120 rpm. Yeast extract in LB medium contains NADH and NADPH, which produce electrons, and affect the accurate measurement of electricity generation. Hence, to remove the LB medium component in the seed culture, *S. oneidensis* was washed three times with saline solution before being added to the fuel solution.

2.2. Fuel Solution

To make 1 L of fuel solution (pH7.0), 12.4 g of sodium lactate (70% aqueous solution, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was mixed with pure water and autoclaved at 121 °C for 20 min.

2.3. bMFC Configuration

Figure 1 depicts the bMFC configuration used in this study. The bMFC has two chambers made of 2 cm-thick polycarbonate plates with 8 cm diameter holes. A bipolar membrane (Neosepta BP-1E, Astom Co., Tokyo, Japan) divided the bMFC into anode and cathode chambers. The bipolar membrane comprised anion and cation exchange layers. The anode chamber side had the cation exchange layer, while the cathode chamber side had the anion exchange layer. Each chamber had a volume of 100 cm^3. The bipolar membrane and cathode of the carbon plate (Toyo Tanso Co., Ltd., Osaka, Japan) had effective areas of 50 cm^2. A 0.3 g iron (III) hydroxide (Kojundo Chemical Laboratory Co., Saitama, Japan) was placed in the cathode chamber. The anode contained carbon-felt (LFP-210, Osaka Gas Chemicals Co., Osaka, Japan). The electric current produced by the bMFC was evaluated using multiple data logger sets (NR-600, NR-TH08, and NR-U60, Keyence Co., Osaka, Japan). The electric current was processed by application software (NR-H8W, Keyence). A digital current meter (A6122-04, Watanabe Electric Industry Co. Ltd., Tokyo, Japan) was connected between the various data logger sets and bMFC. Data logging time was 15 min, and data was plotted every 4 h.
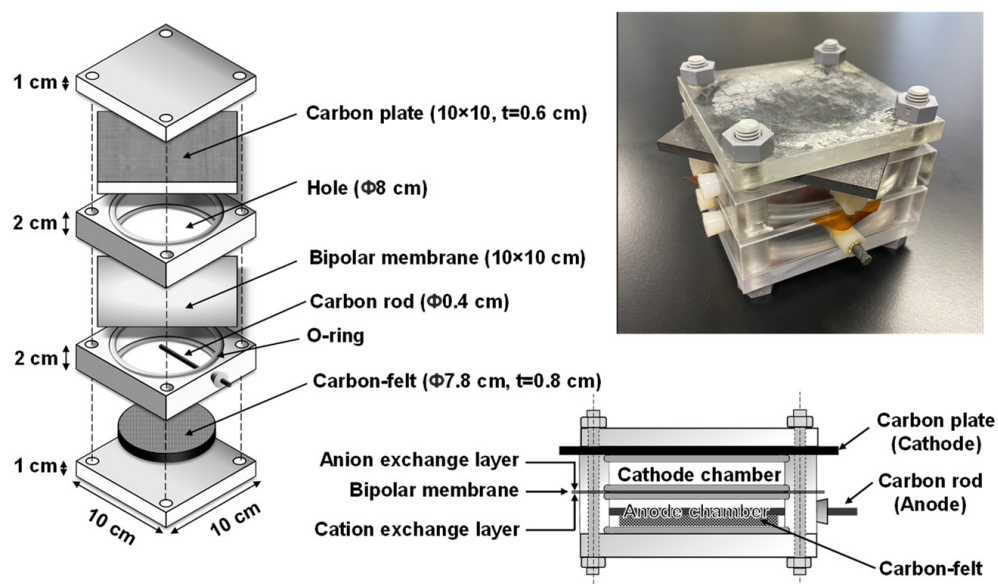

Figure 1. Assembly and cross-section of bMFC. The vessel parts were made of polycarbonate. The anode chamber's carbon rod was connected to carbon felt, and 0.3 g iron (III) hydroxide was applied to a carbon plate.

2.4. bMFC Operation

Before assembling the bMFC, the chamber components were sterilized by exposing UV light on the detached components on a clean bench for 60 min. The anode chamber was filled with fuel solution before seed-cultured *S. oneidensis* at an optical density (OD_{600}) of 0.2 was added and the pH of the anode solution was 7.0. To promote the anaerobic respiration of *S. oneidensis*, nitrogen gas (N_2) was bubbled (100 cm^3/min for 3 min) into the solution in the anode chamber. Meanwhile, the cathode chamber was filled with autoclaved pure water and bubbled with N_2 (at the same ratio as before) to rule out oxygen as the final electron acceptor. The bMFC was incubated at 30°C with the anode chamber upside down.

2.5. Reference Experiments

In this study, four types of reference experiments were carried out (Table 1). In the first type, the anode chamber did not contain any microorganisms. In the second type, no iron (III) hydroxide was used in the cathode chamber. In the third type, a cation exchange membrane (Selemion HSF, AGC Co., Tokyo, Japan) was used instead of a bipolar membrane.

This type was similar to the conventional types, in that it employed a cation exchange membrane, but it did not employ a catalyst and kept the cathode chamber in an anaerobic state. In the fourth type, the bipolar membrane was used in the opposite direction as in the bMFC. Therefore, the cation exchange layer was placed on the cathode chamber side and the anion exchange layer on the anode chamber side.

Table 1. Conditions for four control experiments.

Experiment	*S. oneidensis*	Iron (III) Hydroxide	Membrane	Results
bMFC	With	With	Bipolar	Figure 2
First type	Without	With	Bipolar	Figure 3A
Second type	With	Without	Bipolar	Figure 3B
Third type	With	With	Cation exchange	Figure 3C
Fourth type	With	With	Bipolar (Opposite direction)	Figure 3D

2.6. Analysis of Lactic Acid

The lactic acid concentration was determined using high-performance liquid chromatography with a UV detector monitored at 210 nm (Prominence, Shimadzu Co., Kyoto, Japan) and an SCR-102H column (Shimadzu). The elution solvent was 0.1 v/v% perchloric acid (70% aqueous solution, Wako Pure Chemical Industries) at a flow rate of 0.9 mL/min.

2.7. Ohmic Resistance

The electric circuit designed for polarization in this report was the same as in our previous report. Figure A1 depicts this electric circuit [24].

Through this report, the error bars in figures represent the standard deviations of the three-time experiments independently.

3. Results and Discussion

3.1. bMFC Operation

The bMFC generated electricity continuously for 20 days at maximum current density 33.2 ± 14.6 mA/m^2 at day 9.75 during that period (Figure 2). The final pH values of anode and cathode cambers changed to 7.6 ± 0.2 and 7.5 ± 0.5 from 7.0, respectively. The lactic acid in the fuel solution was completely consumed at the end of the operation. However, it is believed that power was still generated on day 20 because reducing substances such as NADH remained in the cells after being reduced by the consumed lactic acid, and electricity was generated through their oxidation. Microorganisms require a certain amount of time to adapt to new environments, and that time is variable. Therefore, when seed culture is inoculated in bMFC, which is a new environment, there is variation in activity. On the other hand, during the later stages of bMFC operation, the microorganisms acclimated to the environment and the variability reduced. For example, the current density of 9.5 ± 10.1 mA/m^2 at day 0.25 had almost the same value of 11.9 ± 3.4 mA/m^2 at day 20, which may explain why the standard deviation was reduced.

The conditions of four types of reference experiments were summarized in Table 1.

Figure 3A depicts the electricity generation result for the bMFC in Figure 2 under identical conditions except for the absence of microorganisms. In this case, the maximum current density observed was less than 10% when compared to using *S. oneidensis*. This fact demonstrates that the electricity generation in Figure 2 was demonstrated by the function of *S. oneidensis*.

Figure 3B depicts the electricity generation result for the bMFC in Figure 2 under the same conditions except without iron (III) hydroxide. The electricity generation in this figure was less noticeable than in Figure 2. The generated electrons moved from the anode chamber to the cathode chamber via the external circuit, but there were no electron acceptors in the cathode chamber, which is thought to be why power generation did not

continue in this case. This finding implies that Fe^{3+} dissociated from iron (III) hydroxide could act as an electron acceptor.
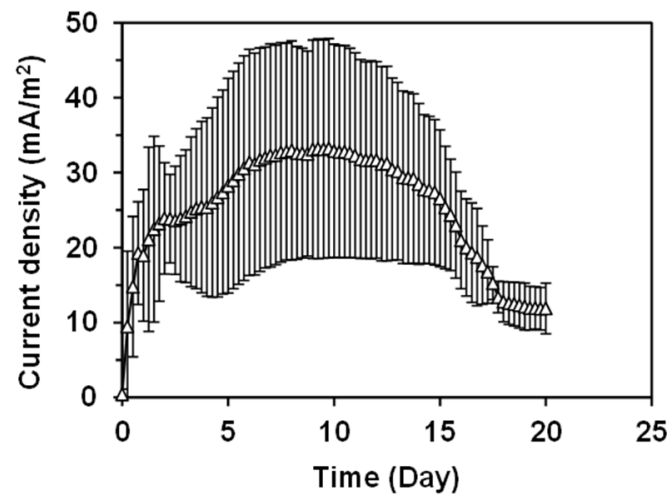

Figure 2. The current density of bMFC operation. *S. oneidensis* MR-1 served as the microorganism, and lactic acid served as the fuel. The bipolar membrane's cation exchange layer and anion exchange layer were placed on the anode and cathode chamber sides, respectively. Iron (III) hydroxide was put onto the carbon plate. Both the anode and cathode chambers remained anaerobic.
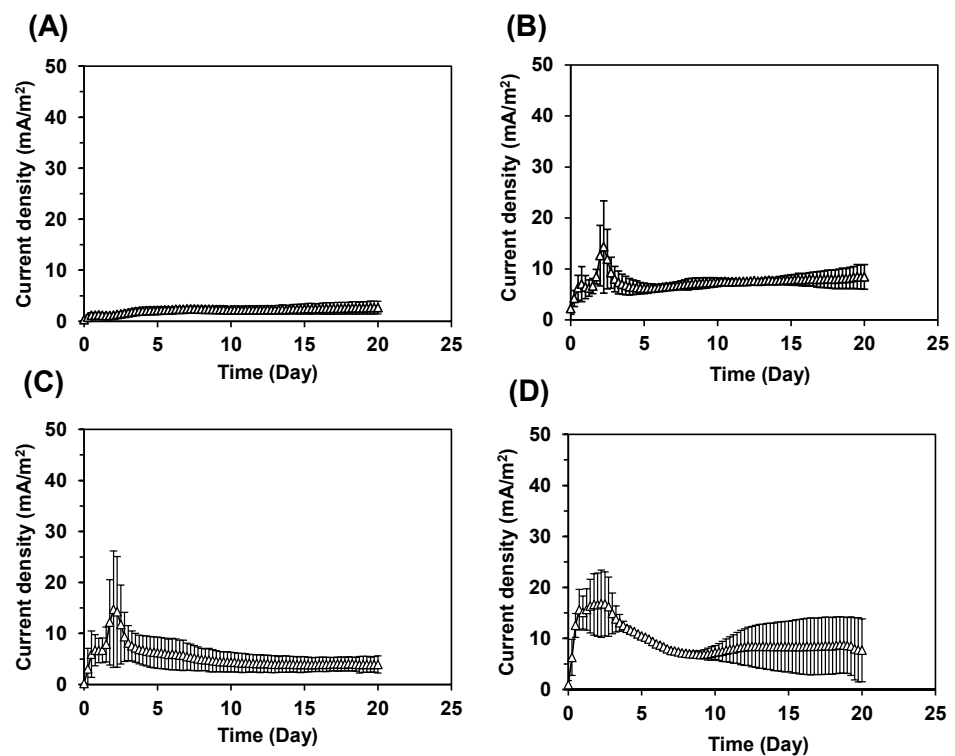

Figure 3. The current density of reference experiments. Compared to the bMFC used in Figure 2; (**A**) without any microorganism, (**B**) without iron (III) hydroxide, (**C**) using cation exchange membrane instead of the bipolar membrane, (**D**) opposite direction of bipolar membrane.

Figure 3C depicts the result of using a cation exchange membrane instead of the bipolar membrane of the bMFC shown in Figure 2. In this case, the protons generated moved from the anode chamber to the cathode chamber via the cation exchange membrane, as in conventional MFCs [5]. However, power electricity did not continue because, unlike

conventional MFCs, the protons were unable to react with the electrons flowing from the external circuit because there was no oxygen or catalyst in the cathode chamber. This finding suggests that the anion layer of a bipolar membrane is important for electricity generation.

Figure 3D depicts the outcome of reversing the orientation of the bMFC bipolar membrane used in Figure 2. The failure of electricity generation is thought to have occurred because protons in the anode chamber were unable to move into the cathode chamber. This result shows that the surface charge of the bipolar membrane was essential for generate electricity.

These findings suggest that the bipolar membrane and its orientation, as well as the presence of iron (III) hydroxide in the anode chamber, are required in generating electricity continuously from *S. oneidensis*.

3.2. Mechanism of bMFC

The bMFC reaction mechanism will be distinct from that of conventional MFCs. The abovementioned reference experiments point to the following bMFC reactions. The fuel of lactic acid was metabolized to H^+ and electrons by *S. oneidensis* in the anode chamber [25] (Equation (1)).

$$C_3H_6O_3 + 2H_2O \rightarrow C_2H_4O_2 + H_2O + CO_2 + 4H^+ + 4e^- \tag{1}$$
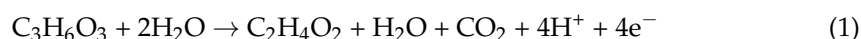
The electrons moved from the anode chamber via the external circuit to the cathode chamber, whereas the H^+ was drawn to the bipolar membrane's cation exchange layer, which had a negative charge.
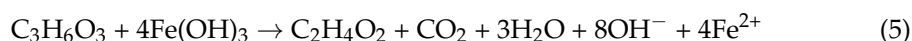
In the cathode chamber, $Fe(OH)_3$ was dissociated to OH^- and Fe^{3+} (Equation (2)), and then, Fe^{3+} was reduced to Fe^{2+} by an electron from the external circuit (Equation (3)).

$$4Fe(OH)_3 \rightleftarrows 4Fe^{3+} + 12OH^- \tag{2}$$

$$4Fe^{3+} + 4e^- \rightarrow 4Fe^{2+} \tag{3}$$

The OH^- was drawn to the bipolar membrane's anion exchange layer, which had a positive charge. Additionally, the H^+ was drawn to the bipolar membrane's cation exchange layer. Then, H^+ and OH^- reacted to form water on the interface of the anion and cation layers (Equation (4)).

$$4H^+ + 4OH^- \rightarrow 4H_2O \tag{4}$$

The total reaction is summarized in Equation (5).

$$C_3H_6O_3 + 4Fe(OH)_3 \rightarrow C_2H_4O_2 + CO_2 + 3H_2O + 8OH^- + 4Fe^{2+} \tag{5}$$

In this reaction mechanism, $Fe(OH)_3$ is the final electron acceptor.

The above mechanism of bMFC is represented as an illustration (Figure 4).

3.3. Coulombic Efficiency

The Coulombic efficiency (ε) is the percentage ratio of the measured actual generated electron charge to the theoretical electron charge calculated from the consumed fuel, and it can be calculated using Equation (6).

$$\varepsilon = \frac{\int_0^t It\,dt}{nFS}\,100\% \tag{6}$$

where I (A) represents the generated current value, t (sec) represents the operation time, n represents the number of electrons per mole of consumed fuel, F represents Faraday's constant (96,485 C/mol), and S (mol) represents the amount of consumed fuel.
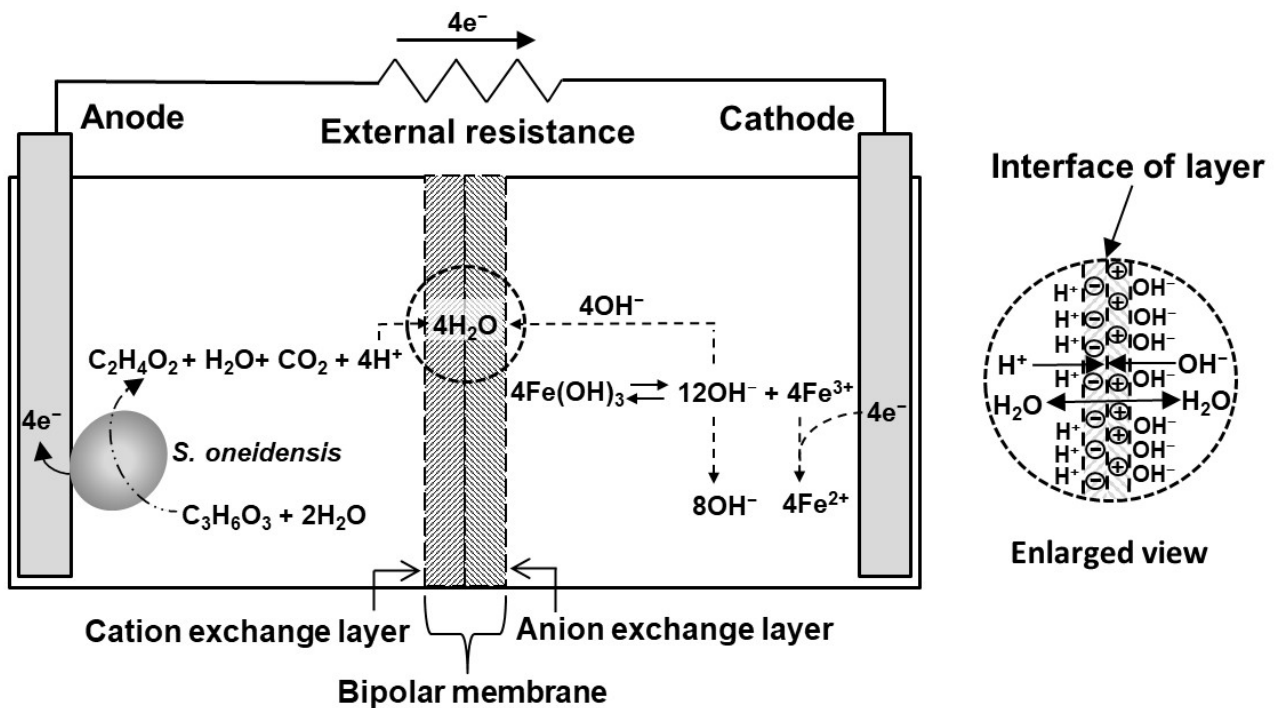
Figure 4. Reaction mechanism of bMFC-equipped bipolar membrane with $Fe(OH)_3$. In the anode chamber, the lactic acid is metabolized to H^+ and electrons by *S. oneidensis*. The electrons are moved to the cathode chamber. The H^+ drawn to the bipolar membrane's cation exchange layer. In the cathode chamber, $Fe(OH)_3$ is dissociated to OH^- and Fe^{3+}, and then, Fe^{3+} is reduced to Fe^{2+} by an electron. The OH^- is drawn to the bipolar membrane's anion exchange layer. Additionally, the H^+ is drawn to the bipolar membrane's cation exchange layer. Then, H^+ and OH^- react to form water on the interface of the anion and cation layers.

In Figure 2, 1 g (11.1 mmol) of lactic acid was initially poured into the anode chamber (100 cm^2), and the lactic acid was consumed completely at the end of the operation, and so, the value of S was 11.1×10^{-3}. Additionally, n was 4 from Equation (1). The theoretically generated electron charge was then calculated to be 4284 C. On the other hand, the current density (mA/m^2) in Figure 2 was converted to I (A) by multiplying by the effective area of the bipolar membrane (50 cm^2), and the actual generated electron for the 20-day operation period (1728×10^3 s) was calculated. The numerator of the fraction in Equation (6) was then calculated to be 219 C. Thus, based on these estimates, the Coulombic efficiency was calculated to be 5.1%.

Succinic acid, fumaric acid, and acetic acid other than lactic acid were determined by HPLC, and 0.51 mmol of acetic acid was detected in the anode chamber (100 mL), no lactic acid, succinic acid, or fumaric acid was detected at the end of the operation [25,26]. This result suggests that the low Coulombic efficiency was not due to the metabolism of lactic acid into organic acids other than acetic acid. On the other hand, the electrons generated by the consumed lactic acid were thought to remain in the bacteria as reducing substances such as NADH at the end of the operation. The fact that electricity generation continues even after the lactic acid has been completely consumed is thought to be due to the oxidation of these reducing substances. The Coulombic efficiency is expected to improve with continued operation. Furthermore, in this study, the number of components in the fuel solution was kept as low as possible to comprehend the reaction mechanism. It is expected that the Coulombic efficiency can be further improved by adding nitrogen sources and vitamins that are beneficial to microbial metabolism. Furthermore, the concentration of microorganisms in the anode chamber in this study was OD_{600} of 0.2. This is a relatively low concentration, and it is thought that increasing the concentration of the microorganisms could result in even higher Coulombic efficiency within the same operating period.

3.4. Ohmic Resistance

The ohmic resistance was estimated using polarization analysis, which measures the current-voltage curve. The analysis was carried out when the maximum current was shown in Figure 2. The resistance was gradually increased from 0 to 10 kΩ (Figure A1), and the values of the current-voltage curves were measured at the point of stability at each step (approximately 1 min) (Figure 5). All measurements were completed within one hour to minimize the impact of changes in the state of the bMFC during the measurement.
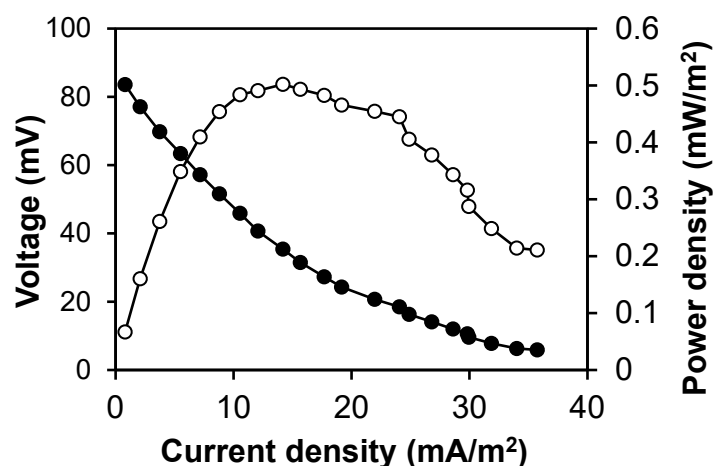

Figure 5. Polarization curve of the bMFC. The analysis was conducted when the maximum current occurred in Figure 2. Voltage (closed circles) and power density (open circles) against the current density of bMFC. The electromotive force calculated from the vertical axis intercept was 71 mV. The maximum power density was 0.5 mW/m^2. The ohmic resistance value was 500 Ω (2.5 Ωm^2) estimated from the linear portion of the curve (10.5–19.2 mA/m^2).

A typical fuel cell polarization curve has three regions: the cell voltage drops rapidly and nonlinearly in the activation region, followed by a slow and near-linear drop in the ohmic region. The continuous current increase could be due to a concentration polarization region or a condition in which reactant mass transport becomes the limiting factor [27].

In Figure 5, based on a linear relationship of current density against voltage between 10.5 and 19.2 mA/m^2, the ohmic resistance value was estimated to be 500 Ω, and the electromotive force calculated from the vertical axis intercept was 71 mV. Furthermore, the maximum power density was 0.5 mW/m^2. This value, as well as Coulombic efficiency, was expected to improve as the concentration of the microorganisms increased.

Figure 5 shows a polarization curve with a small voltage drop in the concentration polarization region that was not distinguished from the ohmic resistance region. These characteristics were because cations (H$^+$) and anions (OH$^-$) did not pass through the bipolar membrane but instead penetrated and reacted at the layer interface, as illustrated in Figure 4. In other words, the mass transport loss was minimal.

The ohmic resistance of MFCs with air cathodes is generally thought to be low [28]; we reported an ohmic resistance of 16.3 kΩ (81.3 Ωm^2) for an MFC with the same air cathode membrane area and anode chamber volume, using *S. oneidensis* as in this study. In contrast, the ohmic resistance of bMFCs was even lower than 500 Ω, indicating the high potential of bMFCs.

Ohmic resistance measures how difficult it is for protons and other ions to move [29]. In conventional MFCs with cation exchange membranes, the protons generated must pass through the cation exchange membrane to the cathode solution, where they react with the oxygen by the cathode catalyst to continuously generate electricity. In MFCs with an air cathode, the cation exchange membrane is integrated with the cathode where the platinum catalyst is immobilized. Therefore, protons do not need to pass through the cathode solution, but oxygen must pass through the air cathode's PTFE and carbon paper

layers [24]. On the other hand, the low internal resistance of bMFC can be attributed to the mechanism that neither protons nor OH^- must pass through the membrane, but only react at the interface of the anion and cation layers of the bipolar membrane (Figure 4). The reduced $Fe(OH)_2$ at the end of the operation can be oxidized to $Fe(OH)_3$ again by blowing air through the solution and can be used repeatedly. In this experiment, a paste of $Fe(OH)_3$ powder with water was added to the cathode. This paste had poor dispersibility in water. It was expected that adding $Fe(OH)_3$ as a colloid to the cathode solution may have further increased the efficiency.

4. Conclusions

The newly developed bMFC employed bipolar membranes, which are already used in industrial seawater desalination, and are inexpensive and environmentally friendly iron oxide catalysts rather than expensive catalysts such as platinum or other harmful chemicals, and have a low internal resistance. It is also advantageous for scale-up because there is no need to keep the cathode chamber aerobic. Furthermore, in MFCs with air cathodes, one side of the membrane surface must be open to supply oxygen. However, in bMFCs, the structure shown in Figure 1 can be stacked. In this report, a fuel solution with few components was used to clarify the reaction mechanism. Further investigation of the fuel solution's components is expected to yield even higher performance. Furthermore, by selecting microorganisms, a wide range of biomass can be used as fuel. The range of applications for bMFC is expected to expand in the future.

Author Contributions: Conceptualization, H.O.; methodology and analysis, H.O. and I.K.; writing—original draft preparation, H.O. and I.K.; review and editing, H.O., Y.A. and T.T. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.
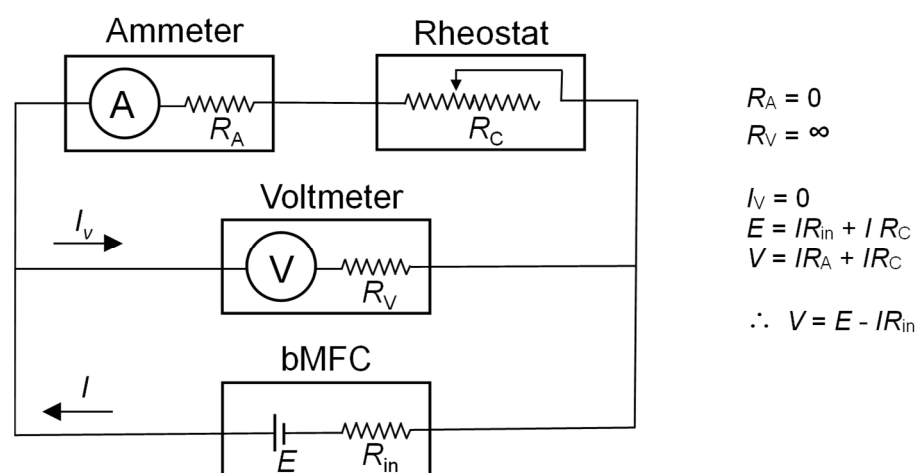
Appendix A

Figure A1. Circuit for determining the internal resistance and electromotive force of bMFC. The electric circuit was designed to estimate the internal resistance of the bMFC. R_A, R_V, R_C, and R_{in} denote the internal resistance values of the ammeter, voltmeter, rheostat, and bMFC, respectively. "*I*" denotes the current value in the line and "*E*" denotes the electromotive force. In the apparatus, R_A was considered negligibly small and R_V was considered infinite.

This resulted in the following equation:

$$E = I\,R_{in} + I\,R_{C}$$

Conversely, the indicated value of the voltmeter (*V*) is given by the following equation:

$$V = I\,R_{C}$$

Substituting the second equation into the first equation results in the following equation:

$$V = E - I\,R_{in}$$

The last equation implied that the internal resistance of the bMFC could be estimated by the slope of the graph of *V* with respect to *I*. In this study, the R_{C} changed from 0 to 10 kΩ. *E* was plotted with respect to *I*, and the ohmic resistance of the bMFC linear portion of the graphs was estimated.

References

1. Liu, H.; Ramnarayanan, R.; Logan, B.E. Production of Electricity during Wastewater Treatment Using a Single Chamber Microbial Fuel Cell. *Environ. Sci. Technol.* **2004**, *38*, 2281–2285. [CrossRef] [PubMed]
2. Oh, S.; Min, B.; Logan, B.E. Cathode Performance as a Factor in Electricity Generation in Microbial Fuel Cells. *Environ. Sci. Technol.* **2004**, *38*, 4900–4904. [CrossRef]
3. Zhao, F.; Harnisch, F.; Schröder, U.; Scholz, F.; Bogdanoff, P.; Herrmann, I. Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. *Electrochem. Commun.* **2005**, *7*, 1405–1410. [CrossRef]
4. Zhao, F.; Harnisch, F.; Schröder, U.; Scholz, F.; Bogdanoff, P.; Herrmann, I. Challenges and Constraints of Using Oxygen Cathodes in Microbial Fuel Cells. *Environ. Sci. Technol.* **2006**, *40*, 5193–5199. [CrossRef]
5. Rabaey, K.; Verstraete, W. Microbial fuel cells: Novel biotechnology for energy generation. *Trends Biotechnol.* **2005**, *23*, 291–298. [CrossRef]
6. Rabaey, K.; Lissens, G.; Siciliano, S.; Verstraete, W. A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. *Biotechnol. Lett.* **2003**, *25*, 1531–1535. [CrossRef] [PubMed]
7. Rabaey, K.; Clauwaert, P.; Aelterman, P.; Verstraete, W. Tubular Microbial Fuel Cells for Efficient Electricity Generation. *Environ. Sci. Technol.* **2005**, *39*, 8077–8082. [CrossRef] [PubMed]
8. Liu, H.; Logan, B.E. Electricity Generation Using an Air-Cathode Single Chamber Microbial Fuel Cell in the Presence and Absence of a Proton Exchange Membrane. *Environ. Sci. Technol.* **2004**, *38*, 4040–4046. [CrossRef]
9. Cheng, S.; Liu, H.; Logan, B.E. Power Densities Using Different Cathode Catalysts (Pt and CoTMPP) and Polymer Binders (Nafion and PTFE) in Single Chamber Microbial Fuel Cells. *Environ. Sci. Technol.* **2005**, *40*, 364–369. [CrossRef]
10. Topcagic, S.; Minteer, S.D. Development of a membraneless ethanol/oxygen biofuel cell. *Electrochim. Acta* **2006**, *51*, 2168–2172. [CrossRef]
11. Palmore, G.R.; Kim, H.-H. Electro-enzymatic reduction of dioxygen to water in the cathode compartment of a biofuel cell. *J. Electroanal. Chem.* **1999**, *464*, 110–117. [CrossRef]
12. Simons, R.; Khanarian, G. Water dissociation in bipolar membranes: Experiments and theory. *J. Membr. Biol.* **1978**, *38*, 11–30. [CrossRef]
13. Hurwitz, H.; Dibiani, R. Investigation of electrical properties of bipolar membranes at steady state and with transient methods. *Electrochim. Acta* **2001**, *47*, 759–773. [CrossRef]
14. Tongwen, X. Electrodialysis processes with bipolar membranes (EDBM) in environmental protection—A review. *Resour. Conserv. Recycl.* **2002**, *37*, 1–22. [CrossRef]
15. Li, X.; Jin, X.; Zhao, N.; Angelidaki, I.; Zhang, Y. Efficient treatment of aniline containing wastewater in bipolar membrane microbial electrolysis cell-Fenton system. *Water Res.* **2017**, *119*, 67–72. [CrossRef]
16. Chacón-Carrera, R.; López-Ortiz, A.; Collins-Martínez, V.; Meléndez-Zaragoza, M.; Salinas-Gutiérrez, J.; Espinoza-Hicks, J.; Ramos-Sánchez, V. Assessment of two ionic exchange membranes in a bioelectrochemical system for wastewater treatment and hydrogen production. *Int. J. Hydrogen Energy* **2018**, *44*, 12339–12345. [CrossRef]
17. ter Heijne, A.; Hamelers, H.V.M.; de Wilde, V.; Rozendal, R.A.; Buisman, C.J.N. A Bipolar Membrane Combined with Ferric Iron Reduction as an Efficient Cathode System in Microbial Fuel Cells. *Environ. Sci. Technol.* **2006**, *40*, 5200–5205. [CrossRef]
18. Kim, C.; Lee, C.R.; Song, Y.E.; Heo, J.; Choi, S.M.; Lim, D.-H.; Cho, J.; Park, C.; Jang, M.; Kim, J.R. Hexavalent chromium as a cathodic electron acceptor in a bipolar membrane microbial fuel cell with the simultaneous treatment of electroplating wastewater. *Chem. Eng. J.* **2017**, *328*, 703–707. [CrossRef]
19. Wang, Y.-H.; Wang, B.-S.; Liu, Y.-P.; Chen, Q.-Y. Electricity and hydrogen co-production from a bio-electrochemical cell with acetate substrate. *Int. J. Hydrogen Energy* **2013**, *38*, 6600–6606. [CrossRef]

20. Oram, J.; Jeuken, L.J. *Shewanella oneidensis* MR-1 electron acceptor taxis and the perception of electrodes poised at oxidative potentials. *Curr. Opin. Electrochem.* **2017**, *5*, 99–105. [CrossRef]
21. Shi, L.; Rosso, K.M.; Zachara, J.M.; Fredrickson, J.K. Mtr extracellular electron-transfer pathways in Fe(III)-reducing or Fe(II)-oxidizing bacteria: A genomic perspective. *Biochem. Soc. Trans.* **2012**, *40*, 1261–1267. [CrossRef]
22. Wu, D.; Xing, D.; Lu, L.; Wei, M.; Liu, B.; Ren, N. Ferric iron enhances electricity generation by *Shewanella oneidensis* MR-1 in MFCs. *Bioresour. Technol.* **2013**, *135*, 630–634. [CrossRef] [PubMed]
23. Phansroy, N.; Aso, Y.; Sasaki, S.; Aoki, T.; Ohara, H. Immobilization of the iron on the surface of non-woven carbon fiber for use in a microbial fuel cell. *Mater. Renew. Sustain. Energy* **2016**, *5*, 16. [CrossRef]
24. Takeuchi, Y.; Khawdas, W.; Aso, Y.; Ohara, H. Microbial fuel cells using *Cellulomonas* spp. with cellulose as fuel. *J. Biosci. Bioeng.* **2017**, *123*, 358–363. [CrossRef] [PubMed]
25. Lanthier, M.; Gregory, K.B.; Lovley, D.R. Growth with high planktonic biomass in *Shewanella oneidensis* fuel cells. *FEMS Microbiol. Lett.* **2008**, *278*, 29–35. [CrossRef] [PubMed]
26. Tang, Y.J.; Hwang, J.S.; Wemmer, D.E.; Keasling, J.D. *Shewanella oneidensis* MR-1 Fluxome under Various Oxygen Conditions. *Appl. Environ. Microbiol.* **2007**, *73*, 718–729. [CrossRef]
27. Fan, Y.; Sharbrough, E.; Liu, H. Quantification of the Internal Resistance Distribution of Microbial Fuel Cells. *Environ. Sci. Technol.* **2008**, *42*, 8101–8107. [CrossRef]
28. Logan, B.E.; Regan, J.M. Electricity-producing bacterial communities in microbial fuel cells. *Trends Microbiol.* **2006**, *14*, 512–518. [CrossRef] [PubMed]
29. Liang, P.; Huang, X.; Fan, M.-Z.; Cao, X.-X.; Wang, C. Composition and distribution of internal resistance in three types of microbial fuel cells. *Appl. Microbiol. Biotechnol.* **2007**, *77*, 551–558. [CrossRef]