

A Bipolar Membrane Combined with Ferric Iron Reduction as an Efficient Cathode System in Microbial Fuel Cells[†]

ANNEMIEK TER HEIJNE,[‡]
 HUBERTUS V. M. HAMELERS,^{*,‡}
 VINNIE DE WILDE,[‡]
 RENÉ A. ROZENDAL,^{‡,§} AND
 CEES J. N. BUISMAN^{‡,§}

Sub-Department of Environmental Technology, Wageningen University, Bomenweg 2, P.O. Box 8129, 6700 EV Wageningen, The Netherlands, and Wetsus, Centre for Sustainable Water Technology, Agora 1, P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands

There is a need for alternative catalysts for oxygen reduction in the cathodic compartment of a microbial fuel cell (MFC). In this study, we show that a bipolar membrane combined with ferric iron reduction on a graphite electrode is an efficient cathode system in MFCs. A flat plate MFC with graphite felt electrodes, a volume of 1.2 L and a projected surface area of 290 cm² was operated in continuous mode. Ferric iron was reduced to ferrous iron in the cathodic compartment according to $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ ($E_0 = +0.77$ V vs NHE, normal hydrogen electrode). This reversible electron transfer reaction considerably reduced the cathode overpotential. The low catholyte pH required to keep ferric iron soluble was maintained by using a bipolar membrane instead of the commonly used cation exchange membrane. For the MFC with cathodic ferric iron reduction, the maximum power density was 0.86 W/m² at a current density of 4.5 A/m². The Coulombic efficiency and energy recovery were 80–95% and 18–29% respectively.

Introduction

The microbial fuel cell (MFC) is a device in which microorganisms produce electricity from biodegradable material. In this way, chemical energy is converted directly into electrical energy (1–3). The MFC consists of two compartments: an anoxic compartment with an anode and an aerobic compartment with a cathode. At the anode, bacteria oxidize organic material to carbon dioxide, protons, and electrons. Electrons are released to the anode and go through an electrical circuit to the cathode. There the electrons reduce oxygen, together with protons, to water. Protons migrate from anode to cathode through a cation exchange membrane, which separates both compartments. In the overall reaction, organic material and oxygen are converted into carbon dioxide, water, and electricity.

Overall MFC performance is, among others, limited by the unfavorable reaction kinetics of oxygen reduction (4, 5).

To drive the oxygen reduction at the desired rate, a large part of the available energy is needed to establish the necessary overpotential. This problem has already been recognized earlier in the field of chemical fuel cells (6, 7).

Different approaches are currently explored to improve the performance of the cathode in MFCs. Aeration into the cathodic compartment and lowering the catholyte pH have been shown to increase cathode performance (8–10), but are insufficiently effective to take away the limitation. The use of hexacyanoferrate as an electron acceptor improves cathode performance considerably (1, 10, 11), but this compound is not suitable for application in practice because of its toxicity and its inability to be regenerated with oxygen (12). The use of platinum as a catalyst on carbon electrodes clearly improves cathode performance (9, 10). Air cathodes, covered with platinum, give good results because of the improved oxygen transfer (13).

Although platinum is a good catalyst, it is expensive and there is a need for alternatives (14). One alternative is to replace platinum by chemical catalysts which are based on cheaper metals. Fe(II)- and cobalt-based cathodes, for example, show similar performance as compared to platinum (14, 15). Besides chemical catalysts, biological catalysts, combined with redox mediators, can also facilitate oxygen reduction. Biological catalysts are attractive as they are active at ambient temperatures and are renewable (4). Biological catalysts can be applied in the form of enzymes (4, 16), or using microorganisms. Microorganisms have the additional benefit that they produce the desired enzymes in situ.

Bergel et al. (17) found that a seawater biofilm on a stainless steel cathode increased cathode performance. They suggested that the biofilm directly reduced oxygen, although the mechanism was not elucidated. Rhoads et al. (18) used biomineralized manganese oxides as cathodic reactants. Manganese dioxide (MnO₂) was reduced to soluble Mn²⁺ at the cathode. Mn²⁺ was subsequently reoxidized with oxygen to manganese dioxide and deposited on the electrode by microorganisms. The redox couple Mn²⁺/MnO₂ thus acted as a mediator for electron transport from the electrode to the oxygen reducing (Mn²⁺-oxidizing) microorganisms.

The objective of this study was to investigate the feasibility of using the redox couple Fe³⁺/Fe²⁺ as a cathodic electron mediator for oxygen reduction. The redox couple Fe³⁺/Fe²⁺ was selected for three reasons: (i) it is known for its fast reaction at carbon electrodes (7), (ii) it has a high standard potential (+0.77 V vs NHE for equal concentrations of Fe³⁺ and Fe²⁺ at low pH), and (iii) ferrous iron can be biologically oxidized to ferric iron with oxygen as the electron acceptor up to high potentials of +850 to +950 mV vs NHE (19).

Earlier tests in our laboratory with ferric iron had indicated that a cation exchange membrane could not maintain the low catholyte pH required to keep ferric iron soluble. Cation exchange membranes transport other cations than protons as well, which can cause a pH rise in the cathodic compartment (20). This pH rise caused extensive iron precipitation that damaged the membrane (see Figure S1, Supporting Information). The focus of this study was to devise an MFC with sufficiently low catholyte pH (<2.5) to keep ferric iron soluble without external acid dosing. To achieve this, a bipolar membrane was used instead of the commonly used cation exchange membrane. A bipolar membrane has, to our knowledge, never been applied in MFCs before. It consists of cation and anion exchange sections joined together in series (21, 22). A phenomenon that occurs in a bipolar membrane is water dissociation via electro dialysis. When applying an electric field, water dissociates into H⁺ and OH⁻

* Corresponding author phone: +31 317 483447; fax: +31 317 482108; e-mail: Bert.Hamelers@wur.nl.

[†] This article is part of the Microbial Fuel Cells Focus Group.

[‡] Wageningen University.

[§] Centre for Sustainable Water Technology.

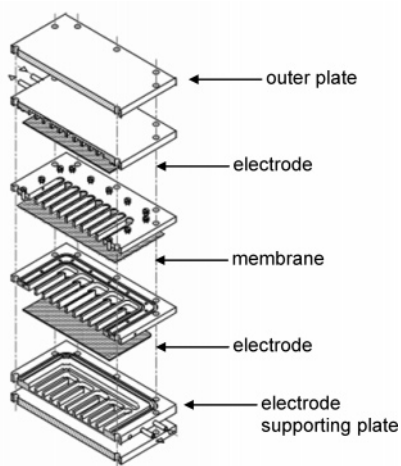


FIGURE 1. The flat plate microbial fuel cell.

at the membrane junction, followed by proton migration through the cation exchange membrane (facing the cathode) and hydroxide migration through the anion exchange membrane (facing the anode). This study investigates the performance of the MFC with the bipolar membrane combined with ferric iron reduction on the graphite cathode. As ferrous iron oxidation has been studied extensively and has been shown to operate efficiently at a high rate, e.g., refs 23–26; the performance of the MFC was investigated without regeneration of ferric iron. This enabled us to quantify ferric iron reduction and its effect on pH and to analyze the behavior of the membrane.

Materials and Methods

Microbial Fuel Cell Setup. The flat plate MFC, comparable to the one previously used in ref 27, consisted of 6 Plexiglas plates sized 28.0 × 28.0 cm bolted together (Figure 1). The four middle plates contained channels for solution transport. The membrane (fumasep FBM, FuMA-tech GmbH, St. Ingbert, Germany) was placed between the two middle plates (thickness and channel depth: 1.2 cm). Against these plates, the electrodes were placed. The electrodes were kept in position by the electrode supporting plates with a thickness of 1.5 cm and a channel depth of 1.2 cm. The two outer plates (thickness 1.5 cm) were massive and served as a physical support. Cathode and anode both had a channel volume of 0.62 L.

The electrodes consisted of graphite felt sized 19.0 cm × 19.0 cm (thickness: 3 mm, FMI Composites Ltd., Galashiels, Scotland) having, following Min et al. (27), an effective geometric channel surface of 290 cm², which is 80% of the total surface area.

A gold wire was pressed on the electrode and served as current collector. The cathode and anode electrodes were connected via the gold wire to a resistor with a range of 0–100 Ω. The reference electrodes were Ag/AgCl, 3 M KCl electrodes (+205 mV vs NHE, ProSense QiS, Oosterhout, The Netherlands). The catholyte was recirculated continuously via an open bottle for passive oxygen supply. This was done to be able to compare the results from the Coulombic efficiency tests with other studies. The oxygen level was continuously measured. The oxygen concentration was always around 20%, the concentration in ambient air. The anolyte was recirculated at a rate of 10 L/h to prevent diffusion limitations for acetate, buffer and nutrients to the bacteria. Both anode and cathode potential were constantly logged, as well as catholyte pH, conductivity and temperature. Data were collected on a PC via a FieldPoint FP-AI-110 module. Anolyte pH was constantly monitored without logging. The program LabVIEW was used for data acquisition.

Microorganisms and Medium. The anodic compartment was inoculated with effluent from another operating MFC run on acetate. The feeding to the anodic compartment contained a potassium acetate solution which was fed at a rate of 250 mL/d (HRT = 2.5 days), with varying acetate concentrations in the range of 8–40 mM, based on the expected current. Every 4 days, 1 mL of a macronutrient solution (consisting of 4.31 g/L NH₄Cl, 5.39 g/L CaCl₂·2H₂O, 4.31 g/L MgSO₄·7H₂O, and 54 mg/L FeCl₃) and 10 mmol potassium phosphate buffer at pH = 7 was supplied to the anodic compartment (concentration = 10 mM).

Microbial Fuel Cell Operation. The MFC was operated in a temperature-controlled room at T = 303 K. It was operated in continuous mode, except during start-up and when performing Coulombic efficiency tests.

The MFC was started in batch mode with a fumasep FKB cation exchange membrane and deionized water in the cathodic compartment. After stable operation in continuous mode, the cation exchange membrane was replaced by a fumasep FBM bipolar membrane. At this point, the power production was 22 mW/m². The bipolar membrane was placed in the MFC with the cation exchange side facing the cathodic compartment and the anion exchange side facing the anodic compartment. The catholyte was first a 0.017 M ferric iron chloride (Fe(III)Cl₃) solution. Thereafter, the catholyte was replaced with a 0.017 M ferric iron sulfate hydrate (Fe(III)₂(SO₄)₃·xH₂O) solution and the MFC was operated with anolyte pH 7 and 6. For experiments with a longer duration, the catholyte was recirculated via a storage vessel, resulting in a total catholyte volume of around 17 liters.

The open circuit voltage (OCV) and open circuit potential (OCP) were measured by disconnecting the electrodes so that there was no current. Power density curves were generated by varying the circuit load of the resistor between 5 and 100 Ω. Coulombic efficiency was determined in batch mode by addition of potassium acetate after all acetate was removed from the anodic compartment. This was assumed to be the case after the cell voltage decreased below 5% of the maximum voltage, following Gil et al. (8).

Analyses. Anode and cathode potential were measured versus Ag/AgCl reference electrodes (+205 mV vs NHE). The voltage across the membrane was defined as the potential difference between the cathode reference electrode and the anode reference electrode. All potentials are reported versus Ag/AgCl reference electrodes.

Power density P (W/m²) and current density j (A/m²) were calculated from cell voltage E (V), circuit load R (Ω), and anode electrode surface area A (m²) according to the following:

$$P = \frac{E^2}{RA} \quad (1)$$

and

$$j = \frac{E}{RA} \quad (2)$$

The internal resistance R_i (Ω) was calculated from the slope of the polarization curves (28).

Coulombic efficiency η_C (%) was calculated from the charge in the produced current relative to the charge of the electrons present in the substrate:

$$\eta_C = \frac{\int_0^t I dt}{nFm_{Ac,in}} \cdot 100\% \quad (3)$$

where I = current (A), n = number of electrons involved per

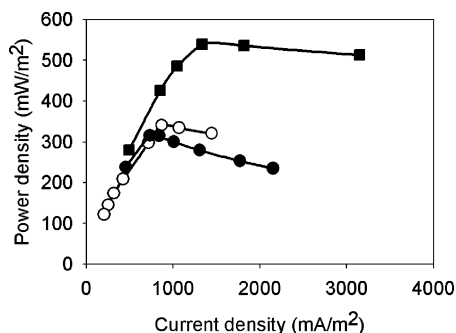


FIGURE 2. Power density curves for the MFC with cathodic ferric iron reduction using ferric iron chloride (○) and ferric iron sulfate with anolyte pH 7 (●) and anolyte pH 6 (■). Catholyte pH was between 2.0 and 2.5 in all experiments.

reaction ($n = 8$), $F =$ Faraday's constant (96 485 C/mol), and $m_{Ac,in} =$ amount of acetate added (mol).

Energy recovery η_E (%) was calculated from the measured cell voltage as compared to the maximum voltage from Gibb's free energy change ΔG (kJ/mol) for the overall reaction, multiplied with the Coulombic efficiency:

$$\eta_E = \frac{E}{E_{max}} \eta_C \text{ with } E_{max} = \frac{-\Delta G}{nF} \quad (4)$$

The overall reaction in the MFC is $CH_3COO^- + 2 O_2 \rightarrow 2 HCO_3^- + H^+$ with $E_{max} = 1.09$ V, standard conditions (29).

Total iron concentrations were measured using Hach Lange tests LCK 320.

A concept used in bipolar membrane studies is the water-splitting efficiency or the proton transport number t_w (22). At 100% water splitting efficiency (proton transport number = 1), one mol of water is split into protons and hydroxides inside the membrane per mol of electrons traveling from anode to cathode, followed by migration into the adjacent solutions. The proton transport number is defined as the current carried by protons relative to the total current:

$$t_w = \frac{I_{protons}}{I_{total}} \quad (5)$$

where $I_{protons}$ is the current carried by protons. The current carried by protons was calculated from the increase in proton concentration in time, multiplied with Faraday's constant.

Results

Power Density and Internal Resistance. Power density curves are shown in Figure 2. The maximum power density was 341 mW/m² ($E = 0.39$ V, $R = 15 \Omega$) for the MFC with cathodic ferric iron reduction using ferric iron chloride. A similar result was obtained using ferric iron sulfate, which gave a maximum power density of 298 mW/m² ($E = 0.30$ V, $R = 10 \Omega$). The maximum power density increased to 539 mW/m² ($E = 0.40$ V, $R = 10 \Omega$) after lowering the anolyte pH to 6.

The internal resistance was 10.3 Ω for the MFC with the cathodic ferric iron reduction using ferric iron chloride and 7.1 Ω and 8.4 Ω using ferric iron sulfate with anolyte pH 7 and 6, respectively.

Electrode Potentials. The performance of the anode, cathode, cell and membrane were analyzed by $E-j$ curves. The voltages and potentials in an open circuit ($j = 0$ A/m²) indicate the maximum voltage or potential which is feasible under the existing experimental conditions. After connecting the resistor, thus allowing an electrical current through the system, it can be seen to what extent this maximum voltage or potential is reached.

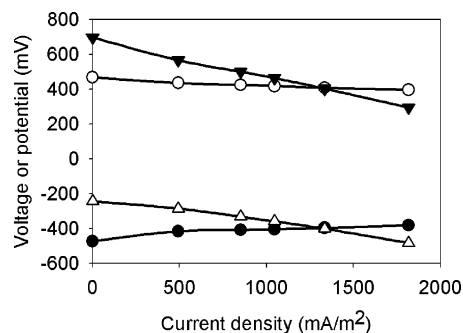


FIGURE 3. Anode potential (●), cathode potential (○), cell voltage (▼), and voltage across the membrane (△) as a function of current density (circuit load was varied between 5 Ω and 40 Ω) for the MFC with cathodic ferric iron reduction using ferric iron sulfate. Anolyte pH = 6. Anode and cathode showed low overpotential, whereas the voltage loss across the membrane increased with increasing current density.

For the MFC with cathodic ferric iron reduction using ferric iron sulfate, the anode and cathode potential as well as cell voltage and voltage across the membrane are shown in Figure 3. The OCV was 679 ± 5 mV using ferric iron chloride and 698 ± 9 mV using ferric iron sulfate. The open circuit cathode potential was $+456 \pm 4$ mV using ferric iron chloride and $+469 \pm 9$ mV using ferric iron sulfate. The cathode potential decreased slightly with increasing current density at a rate of 0.04 mV/(mA/m²). The anode potential showed similar behavior. Cell voltage decreased with increasing current density as the voltage loss across the membrane increased.

Coulombic Efficiency and Energy Recovery. Coulombic efficiency and energy recovery were determined at the circuit load at which the maximum power density was found.

The Coulombic efficiency for the MFC with cathodic ferric iron reduction using ferric iron chloride was 80% ($j = 920$ mA/m², addition of 1 mmol acetate). The energy recovery was 29%.

The Coulombic efficiency for the MFC with cathodic ferric iron reduction using ferric iron sulfate was 85% ($j = 1028$ mA/m², addition of 1 mmol acetate). The energy recovery was 21%.

The Coulombic efficiency increased to 95% after lowering the circuit load to 5 Ω and addition of both 1 and 5 mmol acetate ($j = 1383$ mA/m² and $j = 1744$ mA/m² respectively) using ferric iron sulfate. The energy recovery was 18 and 23% respectively.

Continuous Low Load Power Production. The MFC with cathodic ferric iron reduction was operated for a period of almost 3 months at varying circuit loads, while the ferric iron solution was regularly refreshed. Finally, we investigated electricity production at constant low circuit load (1.5 Ω) to confirm that not only instantaneous power was measured (30). During an operation period of over 50 h, power density increased from 0.5 to 0.86 W/m², which was the highest power density found in this study. This latter value corresponds to a volumetric power production of 42 W/m³, normalized to the channel volume of the anodic compartment. Current density increased from 3.4 to 4.5 A/m². Cell voltage was stable at 190 mV (see Figure S2, Supporting Information). The total iron concentration was measured at regular intervals during the experiment and was found to be always between 16.3 and 16.4 mM. This concentration was 3.5% lower than the expected concentration, but within accuracy of the measurement method and the purity of the iron sulfate.

Discussion

Bipolar Membrane. The design for the MFC with cathodic ferric iron reduction and regeneration of ferric iron by the

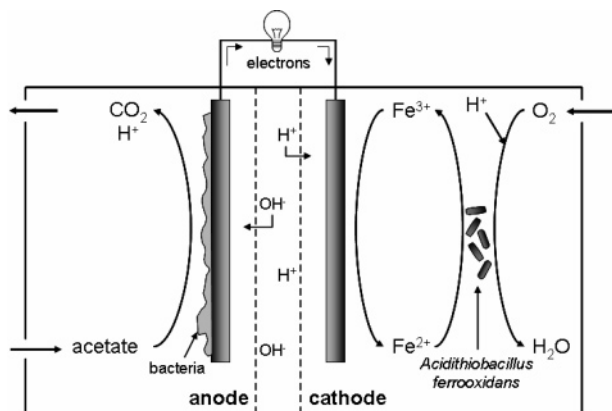


FIGURE 4. Design for the MFC with the iron-mediated cathode. Anodic and cathodic compartment are separated by a bipolar membrane with the cation exchange side facing the cathode and the anion exchange side facing the anode. The bipolar membrane maintains the low catholyte pH required to keep ferric iron soluble by means of water dissociation into H^+ and OH^- . The redox couple Fe^{3+}/Fe^{2+} acts as a mediator for electron transport from the electrode to the oxygen reducing (ferrous iron oxidizing) microorganism *A. ferrooxidans*.

microorganism *Acidithiobacillus ferrooxidans* is shown in Figure 4. The low catholyte pH (<2.5) required to keep ferric iron soluble was maintained by using a bipolar membrane. The bipolar membrane provides the cathodic compartment with protons and the anodic compartment with hydroxides as a result of water dissociation. The low catholyte pH can be maintained in this way without the need of acid dosage. The bipolar membrane showed no detectable loss of iron.

A cation exchange membrane, as normally used in an MFC, would fail in this respect as had been observed in earlier experiments with Nafion 117. These experiments show that the cathode performed well for only several hours. Catholyte pH increased rapidly, while anolyte pH decreased. Due to low solubility of ferric iron at pH > 2.5, ferric iron hydroxide precipitates were found inside the membrane as a result of ferric iron migration (see Figure S1, Supporting Information). The pH drop in the anodic compartment and the pH increase in the cathodic compartment were due to migration of protons and other cations through the cation exchange membrane. Not only protons but also other cations are likely to migrate through cation exchange membranes when present in higher concentrations (20).

Voltage Across the Bipolar Membrane. The voltage across the membrane was defined as the potential difference between the cathode reference electrode and the anode reference electrode. Ohmic losses can be expected as a result of the distance between the membrane and the electrodes. The measured voltage across the membrane thus consists of both ohmic losses and a true voltage across the membrane. The ohmic voltage drop ΔV_{Ω} (V) was calculated at both sides of the membrane, according to the following:

$$\Delta V_{\Omega} = \frac{dj}{\sigma} \quad (6)$$

where d = distance between the membrane and the reference electrode (cm), j = current density (A/cm^2), and σ = conductivity (S/cm).

The measured voltage across the membrane was corrected for the ohmic voltage drop using $d = 2.1$ cm, $\sigma_{\text{anolyte}} = 2.5$ mS/cm, and the logged value for $\sigma_{\text{catholyte}}$. The result is shown in Figure 5 for the MFC with cathodic ferric iron reduction using ferric iron sulfate and anolyte pH 6. The corrected (true) voltage across the membrane was between -200 and -250 mV.

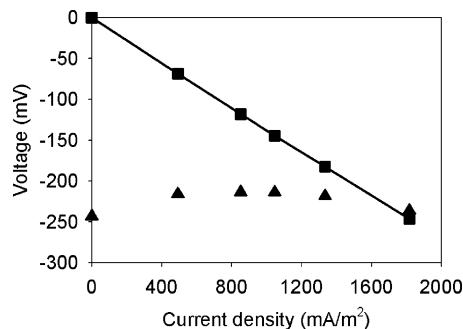


FIGURE 5. Voltage across the membrane (▲) corrected for the ohmic voltage drop (■) for the MFC with cathodic ferric iron reduction using ferric iron sulfate. The ohmic voltage drop increased with increasing current density, whereas the voltage across the membrane was between -200 and -250 mV, independent of current density. Ohmic losses limited MFC performance.

A voltage drop across the bipolar membrane is required to start the water splitting reaction. This voltage drop was calculated to be 0.83 V for a 100% selective bipolar membrane for the generation of a one molar acid and base solution at 298 K (22) using the following:

$$\Delta V = \frac{-2.3RT}{F} \Delta pH \quad (7)$$

The pH difference between the anodic and the cathodic compartment in our MFC was 3.5. According to eq 7, this results in a voltage drop of -0.21 V. The observed voltage across the membrane was thus sufficient to allow water splitting. The occurrence of water splitting was confirmed by the decrease in catholyte pH during ferric iron reduction. Bipolar membranes have never been characterized under the specific conditions in our MFC: low current densities, different anolyte and catholyte, low conductivity, and a small pH gradient across the membrane. Further research is necessary.

From our findings it turns out that that the ohmic losses make up a substantial part of the energy losses. MFC performance can be considerably improved by reducing the ohmic losses. This can be done by placing the electrodes and the membrane in close contact.

Ferric Iron Reduction. The measured cathode potential turned out to be proportional to the natural logarithm of the ratio Fe^{3+}/Fe^{2+} , as would be expected from the Nernst equation:

$$E_{\text{cathode}}(Fe^{2+}, Fe^{3+}) = E_{\text{cathode}}^0 + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

with $E_{\text{cathode}}^0 = 0.77$ V vs NHE

The measured cathode potential was corrected for the conductivity as the conductivity increased proportionally with increasing Fe^{2+} concentration. The ferric and ferrous iron concentrations at each point were calculated from the initial amount of ferric iron and the produced current. The measured cathode potential was found to be $E_{\text{cathode}} = 424 + 18.4 \ln [Fe^{3+}]/[Fe^{2+}]$ ($R^2 = 0.9953$). Analysis of other experimental data showed similar behavior. The slope, being 18.4 mV, is lower than the theoretical value of $RT/F = 26.1$ mV. This could be an effect of diffusion limitation.

The formal (measured) potential is influenced by other substances in the solution and by the ionic strength of the solution (31). As a result, the measured E^0 value (424 mV) can be lower than the theoretical value (565 mV vs Ag/AgCl).

Proton Transport Number. For the MFC with cathodic ferric iron reduction, a decrease in catholyte pH was observed.

The increase in proton concentration was in the order of magnitude of 2 mM/h. Two processes that would lead to a pH decrease in the cathodic compartment are (i) proton supply by the bipolar membrane as a result of water dissociation in the membrane and (ii) transport of alkalinity from the cathodic to the anodic compartment.

The water-splitting efficiency or proton transport number indicates the current carried by protons compared to the total current (22). The proton production by the bipolar membrane was calculated from the pH drop in the cathodic compartment.

Preliminary calculations showed a proton transport number of 0.6–0.7. This transport number however should be considered as an indication only, as the decrease in pH was small. This subject needs further investigation.

Perspectives for Practical Application. Ferric iron should be regenerated from ferrous iron to make the MFC with cathodic ferric iron reduction suitable for practical application. Chemical ferrous iron oxidation at low pH is very slow, as it is proportional to the squared OH^- concentration (32). Microorganisms such as *A. ferrooxidans* are capable of oxidizing ferrous iron to ferric iron at low pH, using oxygen as the terminal electron acceptor. Biological ferrous iron oxidation at low pH has been studied extensively and has been shown to operate efficiently at a high rate, e.g., refs 23–26. Ebrahimi et al. (23) studied ferrous iron oxidation by the chemolithoautotrophic microorganisms *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*. In their biofilm airlift reactor, ferrous iron was reoxidized by *A. ferrooxidans* and *L. ferrooxidans* to ferric iron at a rate of 145 mol Fe^{2+} /m³h. The optimal performance was obtained at 100 mol Fe^{2+} /m³h with 98% conversion efficiency. If a similar setup is used for the MFC, assuming a current density of 4.5 A/m² and a ferrous iron conversion rate of 100 mol/m³h with 98% efficiency, the reactor size required to ensure complete regeneration of ferric iron would be 50 mL, which is only 4% of the reactor volume. The most suitable way in which ferric iron can be regenerated in this system will be investigated in further study.

The energetic efficiency of acetate conversion to electricity via combustion of methane gas after anaerobic treatment is up to 35% (1). To make the MFC a good alternative for conventional wastewater treatment techniques, its energy recovery should be comparable. The energy recovery in the MFC with cathodic ferric iron reduction was 18–29% at the maximum power density. In studies that used platinum-based cathodes with similar power densities, the energy recovery was 2–15% (28, 33). For a continuous system, energy recovery was 2–26% as found by Rabaey et al. (34) with the use of hexacyanoferrate in the cathodic compartment.

The Coulombic efficiency in this study was considerably higher than that found in other studies: 80–95% in comparison to 40–75% at similar power densities (12, 13, 27, 28, 34).

The MFC with a bipolar membrane combined with ferric iron reduction on a graphite cathode is shown to have a high Coulombic efficiency and energy recovery. Further research into the reactor design for ferric iron regeneration and into reduction of the internal resistance of the MFC is needed to further improve MFC performance.

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Supporting Information Available

Picture of the damaged Nafion cation exchange membrane as a result of ferric iron migration, and figure of the stable power production of the MFC with cathodic ferric iron reduction at the maximum performance. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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