



Performance of a scaled-up Microbial Fuel Cell with iron reduction as the cathode reaction

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ABSTRACT

Scale-up studies of Microbial Fuel Cells are required before practical application comes into sight. We studied an MFC with a surface area of 0.5 m² and a volume of 5 L. Ferric iron (Fe³⁺) was used as the electron acceptor to improve cathode performance. MFC performance increased in time as a combined result of microbial growth at the bio-anode, increase in iron concentration from 1 g L⁻¹ to 6 g L⁻¹, and increased activity of the iron oxidizers to regenerate ferric iron. Finally, a power density of 2.0 W m⁻² (200 W m⁻³) was obtained. Analysis of internal resistances showed that anode resistance decreased from 109 to 7 mΩ m², while cathode resistance decreased from 939 to 85 mΩ m². The cathode was the main limiting factor, contributing to 58% of the total internal resistance. Maximum energy efficiency of the MFC was 41%.

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1. Introduction

Wastewaters are being recognized as a renewable energy source in the form of biodegradable organic matter. Extracting energy from wastewaters is a valuable contribution to the production of renewable energy and the reduction of greenhouse gas emissions. Microbial Fuel Cells (MFCs), using microorganisms as the catalyst, are regarded as a promising technology for the production of electricity from wastewater [1]. Advantage of the MFC compared to current technologies like anaerobic digestion, is the potentially high energy efficiency, as electricity is produced directly without an energy inefficient combustion step. Unlike anaerobic digestion however, the feasibility of MFC technology has not been proven on a commercial scale yet [2]. From a technological and energetic point of view, the maximum power production is limited by ohmic losses in the solution, electrochemical losses at the electrodes, and bacterial metabolic losses [1–3]. Essential measures to overcome energy losses in the MFC are to maintain short internal distances to reduce the ohmic resistance, to choose highly conductive electrodes [4], and to improve the cathode as largest part of the energy losses in an MFC occurs at the cathode.

Small-scale MFCs with volumes ranging between 10 mL and 1 L and projected surface areas between 1 cm² and 400 cm² have been

tested worldwide for many years now. However, larger-scale MFC research has been lagging behind. The first successful attempt for scaling up the MFC was published by Dekker et al. [5]. It was shown that a scaled-up system consisting of four stacked cells, with a total volume of 20 L and a projected surface area of 5000 cm², using oxygen reduction at pH = 4 on a Pt-catalyzed electrode, achieved 144 W m⁻³. MFC performance was limited by the cathode, contributing to >80% of the total energy losses even at an oxygen concentration of 34.7 mg L⁻¹ and pH = 4 [5]. Even when Pt was used as a catalyst, the cathode was the main limiting factor in MFC performance. The MFC to be sustainable, however, should not contain noble metals. A renewable non-noble metal based alternative for oxygen reduction is the reduction of ferric iron (Fe³⁺) to ferrous iron (Fe²⁺), and simultaneous biological re-oxidation of the formed ferrous iron [6,7]. The objective of this study was to improve cathode performance in the scaled-up MFC by replacing oxygen as the electron acceptor with ferric iron (Fe³⁺). We operated a single scaled-up cell instead of four cells, so that scaling up could be studied without the effect of cell reversal. In this setup, the MFC was operated during 37 days, and performance was analyzed by development of current and power production with time and by polarization curves.

2. Materials and methods

2.1. Reactor configuration

The scaled-up MFC was previously described in Dekker et al. [5]. The two electrodes were made of two layers of titanium mesh

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coated with platinum and iridium (330 mm × 1500 mm) on a flat plate, resulting in a projected surface area of 0.5 m². The Pt–Ir coating was used to reduce the internal resistance and overpotentials of the cell [5]. While Pt is a good catalyst for oxygen reduction, previous study showed that still large overpotentials existed for oxygen reduction at pH=4 [5]. Therefore, ferric iron was used as electron acceptor at the cathode, combined with biological ferrous iron oxidation [6] to regenerate the ferric iron. In this study we used the same Pt–Ir coated electrodes to be able to compare MFC performance with the previous study. In order to maintain the low catholyte pH required to keep ferric iron soluble, a bipolar membrane (Fumasep FBM, Fumatech, Germany) was used to separate anolyte and catholyte. The thickness of the anode and cathode compartment was 5 mm, which led to a total cell volume of 5 L and a volumetric surface area of 100 m² m⁻³. The flow in both anode and cathode side was directed from three inlets on the bottom to three outlets on the top. This was done to improve the flow characteristics compared to previous study, where an S shape flow path from the inlet at the bottom to the outlet at the top was used [5], which lead to possible dead zones in the cell. Both anode and cathode compartment contained Ag/AgCl reference electrodes connected to the top of the cell (PreSense QiS, Oosterhout, the Netherlands). The potential of these reference electrodes were regularly checked vs. an SCE reference electrode (+0.241 V vs. NHE). The potentials of anodes and cathodes were converted and expressed vs. SCE throughout.

2.2. Start-up and operation

Sludge from an anaerobic digester was used to inoculate the anode. Acetate was used as a carbon and energy source in a nutrient solution containing 10 mM macro-nutrients, 1 mM micro-nutrients, 1 mM vitamins and 20 mM phosphate buffer as previously described [5]. Acetate concentration in the medium was calculated from the produced current as described in Dekker et al. [5], and the resulting minimum acetate concentration in the MFC was 20 mM so that no acetate depletion would occur. This synthetic medium was continuously fed into the anode recirculation vessel with a feeding rate of 54 mL h⁻¹. The system was operated at 30 °C in a constant temperature chamber.

Both anolyte and catholyte were recirculated at a flow rate of 70 L h⁻¹. The anode recirculation vessel had a volume of 1 L, whereas the cathode recirculation vessel had a volume of 30 L. The anolyte was controlled at pH 7 with 3 M KOH, and the catholyte was controlled at pH 1.6 with 1.8 M H₂SO₄. The catholyte consisted of ferric iron sulfate solution (1 g L⁻¹), and was inoculated with biomass support particles (BSPs) containing ferrous iron oxidizing bacteria. These BSPs were used to concentrate the biomass, while in the course of time, ferrous iron oxidation was not limited to the BSPs but occurred also in the solution [6]. Before inoculation, these iron oxidizers were grown from Rio Tinto sediment following the procedure described in [6]: the biomass support particles were placed in a Fe²⁺ containing medium (3.3 g L⁻¹ Fe²⁺), and incubated on a rotary shaker at 175 rpm. After several replacements of the medium, the BSPs were placed in the recirculation vessel of the cathode. The standard nutrients for the iron oxidizers (0.4 g L⁻¹ (NH₄)₂SO₄, 0.4 g L⁻¹ KH₂PO₄ and 0.4 g L⁻¹ MgSO₄) were supplied to the cathode compartment only at the beginning of the experiment. Air was continuously sparged in the cathode recirculation vessel through four porous Teflon cylinders.

The strategy for MFC operation was the following. The first 7 days were used for start-up, until anode potential became stable at a value of -0.47 V vs. SCE. During these 7 days, the external resistance was decreased from 50 Ω to 2 Ω in several steps. From day 7 on, the resistor was removed and the cell voltage of the MFC was potentiostatically controlled in a 2-electrode setup using a HP 96-20 potentiostat (Bank Elektronik – Intelligent Controls GmbH,

Pohlheim, Germany). The operating mode was changed from using an external resistance to potentiostatic control, because a too low resistance would be needed for the high currents produced. For example, at a cell voltage of 0.475 V, the maximum current was 2.8 A, which means that a resistor as low as 0.475/2.8 = 0.17 Ω would be required. As the contact resistances of wiring and connections in this case is already larger than the resistor needed, and also heat production at the resistor may result in unstable resistance, this would result in large inaccuracies (overestimations) in the current. To be able to measure the correct current, and to enable a further increase in current density, potentiostatic control was thus required.

From day 7 to 12, the current density was increased by decreasing the controlled cell voltage from 0.575 V to 0.47 V. From day 12 to 37, MFC performance was further improved by increasing the iron concentration in the catholyte in 5 steps from 1 g L⁻¹ to measured concentrations of 2 g L⁻¹, 3 g L⁻¹, 5 g L⁻¹, 5.5 g L⁻¹, and 6 g L⁻¹. This was done at constant controlled cell voltage of 0.475 V until day 28, where cell voltage was decreased to 0.45 V until the end of the experiment. The cell voltage was thus always controlled at a positive value between 0.45 and 0.575 V. Combined with the fact that electrons flowed from anode to cathode, this means that the MFC produced power throughout the whole experiment.

On day 37, the experiment was ended because a technical failure occurred, which resulted in acidification of the anolyte and consequently inactivity of the anodic microorganisms.

2.3. Measurements and analyses

During the experiment, cell voltage, electrode potentials, and the voltage across the membrane (potential difference between the reference electrodes) were collected every 60 s via a Fieldpoint data acquisition system, connected to a PC. Current density and power density were normalized to the projected surface area of 0.5 m² or to the total cell volume of 5 L.

Anolyte and catholyte were sampled every two or three days and analyzed for their iron concentration. The ratio of ferrous and ferric iron was measured using Dr. Lange test LCK 320 (Hach Lange GmbH, Düsseldorf, Germany).

Acetate concentrations were measured with gas chromatography as described in [8].

Polarization curves were recorded using dc-voltammetry with the HP 96-20 potentiostat. For this, cell voltage was decreased stepwise from open circuit voltage down to 0 V in steps of 0.025–0.1 V. At each voltage, current was stabilized for at least 10 min.

The volumetric resistance was calculated from the anode and cathode overpotentials (V) divided by the current density (A m⁻²). Anode overpotential was calculated as the measured anode potential minus the thermodynamic anode potential of -0.535 V vs. SCE (at 20 mM acetate, 50 mM bicarbonate, pH=7). Cathode overpotential was calculated as the thermodynamic cathode potential of +0.581 V vs. SCE (at Fe³⁺/Fe²⁺ = 90%) minus the measured cathode potential. Resistances were expressed in Ω m², and can be converted into volumetric resistance (Ω m³) by dividing by the specific surface area of 100 m² m⁻³.

3. Results and discussion

3.1. MFC performance in time

The performance of the scaled-up MFC during the 37 days of operation is shown in Fig. 1. Fig. 1A shows the cell voltage, potentials of anode and cathode, and the membrane potential as a function of time. Fig. 1B shows the related development in current density and power density. Anode potential became stable at -0.47 V vs. SCE after 7 days. At this point, current density was

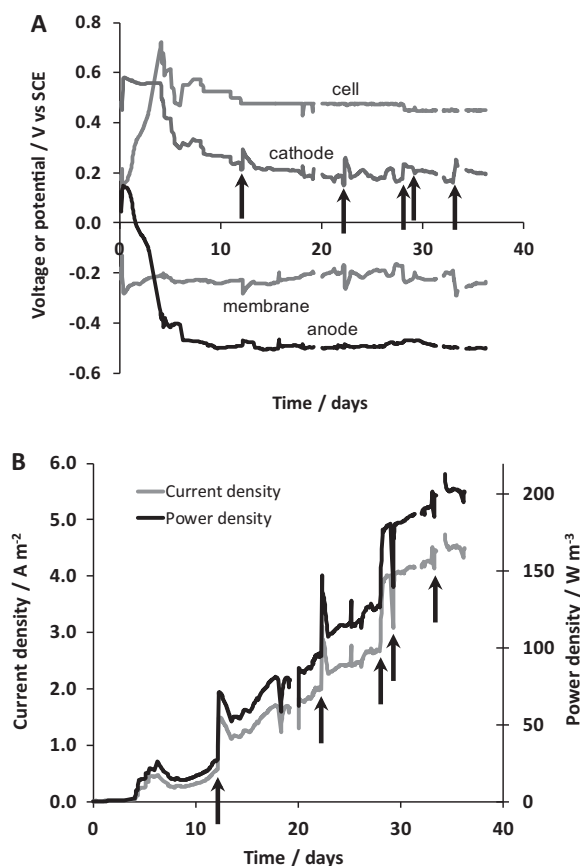


Fig. 1. Performance of the MFC using acetate as electron donor and ferric iron (Fe^{3+}) was reduced at the cathode. Anode and cathode were separated by a bipolar membrane. Anolyte pH was 7, while catholyte pH was 1.6. The MFC was operated for 37 days, and its performance is shown in terms of cell voltage, cathode potential, anode potential, and voltage across the membrane (A), and in terms of current and power density (B). Additions of iron to the catholyte are indicated with arrows.

0.36 A m^{-2} . During the rest of the experiment, the bio-anode maintained a low and stable anode potential around -0.5 V vs. SCE.

From day 7 on, the operation mode was switched from using an external resistance to potentiostatic control. This resulted in quite stable potentials of anode, cathode, and membrane throughout the remainder of the experiment. Although the potentials were stable, the current density and power density continuously increased in time. Increase in current density combined with no change in overpotential means that MFC performance improved in time. This improvement in performance can for example be the result of better catalysis or better mass transfer. This resulted in an increase in power density in time.

For the cathode, sudden increases in current density were found when the iron concentration was increased, as indicated by arrows in Fig. 1. This jump in current density after each addition of iron, means that the iron concentration was one of the factors limiting MFC performance. The continuous increase in current density in time is probably a combined effect of the growth and development of the bio-anode with time, higher iron concentrations, and increased activity of the iron oxidizers with time, resulting in more available Fe^{3+} , which is favorable for the reduction reaction. While the first three additions of iron were done in the form of Fe^{3+} , the last two additions of iron were done in the form of Fe^{2+} (sulfate). Whereas addition of Fe^{3+} resulted in a positive peak in current density, the addition of Fe^{2+} resulted first in a decrease in current density, but as soon as the iron oxidizers had oxidized the added Fe^{2+} into Fe^{3+} , current density started increasing. The voltage across the membrane stayed constant throughout the experiment,

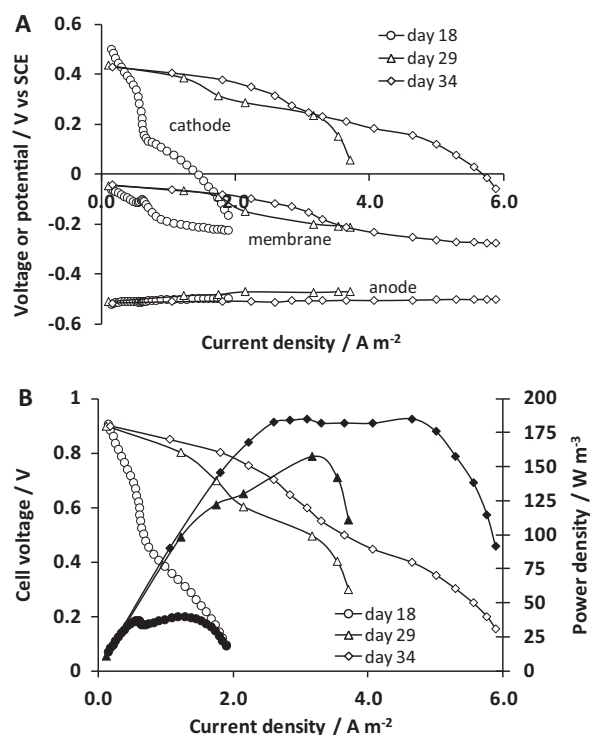


Fig. 2. Polarization curves of scaled-up MFC with time, for anode, cathode, and membrane (A) and cell voltage (open symbols) and power density (closed symbols) (B).

although current density increased. This is in accordance with previous findings [7] and can be explained by the fact that the voltage loss over the bipolar membrane is a function of the pH difference between both compartments, and this pH difference was constant throughout the experiment.

During the last 5 days of the experiment, at an iron concentration of 6 g L^{-1} , the maximum power density of 2.0 W m^{-2} was found, corresponding with 200 W m^{-3} , at a current density of 4.2 A m^{-2} , while cell voltage was controlled at 0.475 V . At this point, the experiment was ended due to a technical failure. As power density was still increasing, it can be expected that power densities higher than 2.0 W m^{-2} can be reached.

The electrical current can be produced via two reactions: (i) reduction of Fe^{3+} to Fe^{2+} , and (ii) direct oxygen reduction. It is likely that largest part of the current was produced by reduction of Fe^{3+} , as an increase in iron concentration resulted in an increase in current. Furthermore, previous experiments for oxygen reduction at an oxygen concentration of 5.8 mg L^{-1} at $\text{pH}=4$ produced a current density of only 0.5 A m^{-2} , at the same cathode potential and Pt-coated electrode and in the absence of iron. This current was likely to be oxygen limited, as an increase in oxygen concentration resulted in an increase in current density.

3.2. Polarization curves

The increasing performance of the scaled-up MFC with time is also reflected in the polarization curves, which were recorded on day 18, 29, and 34 (Fig. 2A and B). On day 18, the iron concentration in the catholyte was 1.7 g L^{-1} . The maximum power density was 40 W m^{-3} at a current density of 1.3 A m^{-2} . On day 29, after the third increase in iron concentration, the maximum power density in the polarization test reached 157 W m^{-3} at a current density of 2.1 A m^{-2} and an iron concentration was 5.2 g L^{-1} . On day 34, the iron concentration was 5.7 g L^{-1} , and this resulted in a maximum power density of 185 W m^{-3} at a current density of 4.6 A m^{-2} .

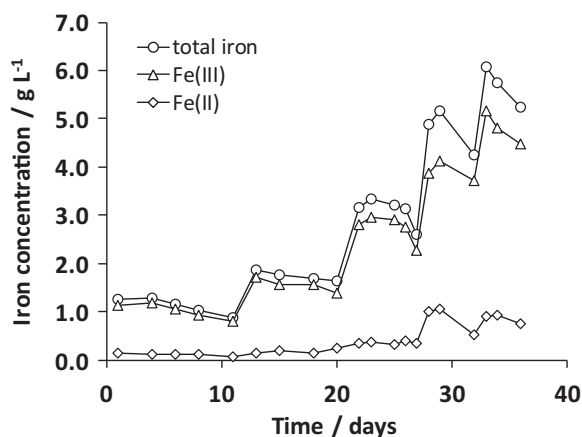


Fig. 3. Iron concentration in the catholyte, at pH = 1.6. The ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ was always >80%, showing enough capacity of the iron oxidizing microorganisms.

Whereas the anode overpotential was stable with increasing current density, reflecting the ability of the bio-anode to adapt to higher current densities without additional energy losses, both the cathode and the membrane showed considerable overpotentials. With time, performance of the cathode improved as a result of the higher Fe^{3+} concentration.

Strikingly, the maximum power density in the polarization curves was lower than the power produced during potentiostatic control at a fixed potential (Fig. 1). This seems to be caused by the time chosen for each step of the polarization curve. We used a time of 10 min for each potential step. This was not enough for the current to stabilize, as cell voltage and current density still gradually increased after 10 min. Due to this short time period for each cell voltage, MFC performance was underestimated in the polarization curve. This may be a result of the large electrodes used in this study compared to other studies, that may need longer time to reach equilibrium. In smaller systems on the other hand, usually performance is overestimated when recording polarization curves [8,9]. Still, polarization curves provide essential information on the response of electrode potentials and cell voltage to a change in current density. For characterization of MFCs, it is therefore important to combine results of long-term operation with polarization curves.

3.3. Iron concentration decreased with time

The iron concentrations in the catholyte are shown in Fig. 3. Overall, most iron was in the form of Fe^{3+} , and thus the biological ferrous iron oxidation rate was high enough to sustain the produced current. In the first half of the experiment, the ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ was always >90%, while the ratio slightly decreased in the second half of the experiment, with ratios between 80% and 90%. The lower ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ during the second half of the experiments may be caused by (i) the higher current density, for which a higher oxidation rate of Fe^{2+} is needed, and this may lead to limitations in oxygen availability, or (ii) limited activity of the iron oxidizers as a result of higher Fe^{2+} concentrations, which can have an inhibitory effect on growth and oxidizing capacity at concentrations in the range of 2–5.6 g L⁻¹ [10]. After each addition of iron, the iron concentration did not stay constant but decreased with time. It is unlikely that iron diffused through the membrane to the anolyte, as samples of the anolyte showed no iron, as also observed in previous study [6]. Precipitation of iron seems the most reasonable explanation for the decrease in iron concentration, as it was observed on the cathode when dis-

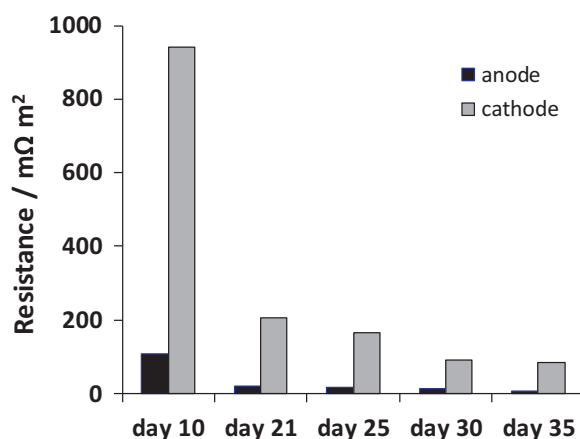


Fig. 4. Resistance of anode and cathode throughout the operation period. Total resistance decreased a factor 10, while cathode resistance was considerably higher than anode resistance.

assembling the MFC. Inspection of these precipitates under the microscope showed that they consisted of yellow/orange rod-shaped microorganisms in combination with salt structures. These yellow precipitates were probably a combination of the iron oxidizers with iron salts. The risk of iron precipitation is an important point of attention for further development of scaled-up systems using Fe^{3+} .

3.4. Analysis of internal resistances

When looking at the performance of the MFC during the operation time in Fig. 1A, on first sight it seems that no considerable changes occur; all potentials are more or less constant and the highest peaks correspond with a potential change of about 0.1 V. Only when combining the potentials in Fig. 1A with the current density in Fig. 1B, it can be seen that big changes occur with time. The reason that this change is not seen in Fig. 1A is partly a result of the potentiostatic operation mode, where the cell voltage is kept constant. In this way, there is not much room for the potentials to change; instead, current density changes. To visualize the changes in performance, it is useful to express the energy losses in the system in terms of their internal resistances (in $\Omega \text{ m}^2$ or $\Omega \text{ m}^3$). This resistance is calculated as the overpotential (difference between theoretical potential and measured potential) divided by current density. In this way, the effect of current density is taken into account, and it makes comparison with other systems with different electrode sizes possible [4,11].

The three parts of the MFC where we measured the energy losses were anode, cathode, and membrane. The resistance for anode and cathode at each iron concentration was averaged during the most stable 24 h (Fig. 4). As the voltage loss over the membrane was independent of current density, its resistance is not shown. Anode resistance decreased from 109 to 7 mΩ m² in the course of the experiment, reflecting the increase in activity of the electroactive biofilm. Cathode resistance decreased from 939 to 85 mΩ m² as a result of the increase in Fe^{3+} concentration (Fig. 3). So, both anode and cathode resistance decreased almost a factor 10 within the operating period, resulting in the increase in MFC performance with time. Total cell resistance (anode, cathode, and membrane) decreased from 1756 mΩ m² in the beginning of the experiment to 146 mΩ m² in the final stage of the experiment. At maximum performance, the cathode contributed to 58% of the total resistance, which shows that the cathode was still the main factor limiting MFC performance. At the same time, the membrane contributed to 37% of the total internal resistance.

3.5. Outlook

The obtained power density of 200 W m^{-3} (2.0 W m^{-2}) is a next achievement in scaling-up MFCs. It is a factor 1.4 higher than the 140 W m^{-3} previously obtained in the same scaled-up MFC [5], and illustrates again that it is possible to reach power densities similar to those obtained in lab experiments. While the anode had a low resistance of $7.5 \text{ m}\Omega \text{ m}^2$ ($0.075 \text{ m}\Omega \text{ m}^3$), the cathode resistance was $84 \text{ m}\Omega \text{ m}^2$ ($0.84 \text{ m}\Omega \text{ m}^3$) and made up 58% of the total resistance caused by anode, cathode and membrane together. The replacement of oxygen reduction by ferric iron reduction resulted in a decrease in cathode resistance from (on average) $1.3 \text{ m}\Omega \text{ m}^3$ [5] to $0.85 \text{ m}\Omega \text{ m}^3$. This demonstrates the superior performance of ferric iron reduction compared to oxygen reduction, even for oxygen reduction on a Pt-coated electrode at pH 4 using pure oxygen. In this study, we used Pt catalyzed cathode for the reduction of iron in order to be able to compare performance with previous study. Ideally, however, non-noble metals would be used as an electrode material. It is therefore interesting to compare the overpotentials for iron reduction on graphite and on Pt. The cathode potential for iron reduction on graphite was $+0.33 \text{ V}$ vs. Ag/AgCl at a current density of 4.4 A m^{-2} [7], while the cathode potential for iron reduction on Pt, $+0.21 \text{ V}$ vs. Ag/AgCl at a current density of 4.5 A m^{-2} . We therefore expect higher, or at least comparable performance when graphite would be used instead of Pt as an electrode material.

An important parameter to consider besides power density, and resistances, is the energy efficiency. The energy efficiency reflects which part of the energy in the carbon source is converted into electrical energy, and is the product of Coulombic efficiency and voltage efficiency. The Coulombic efficiency was determined between day 20 and 30 and was found to be 65%. The theoretical maximum cell voltage of acetate oxidation in combination with iron reduction, assuming that 90% of the iron is present in the form of Fe^{3+} , is 1.12 V . The applied cell voltage of 0.475 V then results in a voltage efficiency of 43%. This combination of coulombic efficiency and voltage efficiency results in an energy efficiency of 28%. In the polarization curve on day 34, voltage efficiency was considerably higher. This polarization curve (Fig. 2B) showed a maximum power density of 180 W m^{-3} at a current density of 2.6 A m^{-2} . At this point, the cell voltage was 0.7 V , resulting in a voltage efficiency of 63%. Combined with a coulombic efficiency of 65%, this results in an energy efficiency of 41%.

In terms of power production and energy efficiency, it is interesting to compare the MFC with anaerobic digestion, the only other biotechnology in which similar wet organic waste streams are converted into electricity. For comparison, we assume that all COD in the anaerobic digester is present in the form of acetate. The energy content of the acetate can be calculated similarly to the MFC: with oxygen as the final electron acceptor, the Gibb's free energy is -844 kJ mol^{-1} . The energy content of the formed CH_4 can be calculated from the reaction $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$, and is -810 kJ mol^{-1} . This means, that 34 kJ mol^{-1} of the energy in acetate is lost in the conversion to CH_4 . This corresponds with an energy loss of roughly 5%.

Furthermore, we assume that 5% of the energy in acetate is not converted to methane and ends up in the sludge, so that the overall efficiency of conversion of acetate into methane is 90%, and an average combustion efficiency of CH_4 of 33% [12], we find an overall energy efficiency of acetate into electricity of 30%. The power that can be produced in the anaerobic digestion, based on a conversion rate of $25 \text{ kg COD m}^{-3} \text{ d}^{-1}$, a lower heating value of $50.1 \text{ MJ (kg CH}_4\text{)}^{-1}$, and an overall energy efficiency of 30%, is 1087 W m^{-3} . In terms of power production, the performance of this scaled-up MFC is still a factor 5 away from anaerobic digestion. It should be noted, that the conversion rate in the MFC at a current density of 4.2 A m^{-2} is only $3 \text{ kg COD m}^{-3} \text{ d}^{-1}$, while the power produced in the anaero-

bic digester was based on a conversion rate of $25 \text{ kg COD m}^{-3} \text{ d}^{-1}$. While in anaerobic digesters an increase in conversion rate results in an increase in power, this does not hold for MFCs, in which the balance between voltage and current determines at which conversion rate maximum power is reached.

In terms of energy efficiency, MFCs should be comparable to anaerobic digestion to become a competitive technology. Although the calculated energy efficiency of the MFC of 28–41% seems comparable to the energy efficiency of anaerobic digestion, several factors were not taken into account in the calculation of the energy efficiency of the MFC. First, the energy requirement for aeration was not included in the energy balance. A typical oxygen transfer rate for mechanical aerators is $2.0 \text{ kg O}_2 \text{ kW}^{-1} \text{ h}^{-1}$ [13]. This would mean that at the highest current of 2.8 A (5.5 A m^{-2}), which corresponds with an oxygen transfer rate of $0.82 \text{ g O}_2 \text{ h}^{-1}$, the power requirement for aeration would be 0.41 W . This is 41% of the produced power of 1.0 W (2.0 W m^{-2}). It is clear that including the energy requirement for aeration in the energy balance results in a major decrease in energy efficiency. For the MFC to become competitive with anaerobic digestion, energy efficient ways to convert ferrous iron to ferric iron need to be found. Air cathodes, which are based on passive aeration for oxygen transfer, are an energy efficient alternative approach to oxidize the ferrous iron. Secondly, energy requirement for input of chemicals to maintain stable pH at anode and cathode were not included in the calculation. Although not determined in this study, previous study showed that the bipolar membrane had a proton transport number of 0.65–0.76 [7]. This means that the remainder of protons (and hydroxides), 24–35% of the electrons produced, needs to be supplied via addition of chemicals. An approach to reduce the energy requirement for chemicals would be to increase the proton transport number of the bipolar membrane. Analysis of the system with these improvements could then indicate if the MFC with iron reduction can become competitive with anaerobic digestion.

Which issues need to be further addressed to bring application of MFCs closer?

First of all, there is need for a well-functioning cathode if MFC performance is to be further improved. This study again showed that the cathode resistance was considerably higher than the anode resistance, and until today, the limit of the bio-anode has not been reached. For this to happen, we need a strong cathode that can accept the electrons from the anode at a similar rate, or we need to increase the cathode surface area several times compared to the anode surface area. We showed that reduction of ferric iron resulted in superior performance compared to oxygen reduction. The scaled-up MFC with ferric iron reduction was operated during 37 days with continuous increase in performance. A further increase in iron concentration may result in higher cathode potential and improved MFC performance. On the other hand, higher iron concentrations may inhibit the iron oxidizers. Another limitation to ferric iron reduction may be the risk of precipitation. These issues need to be further studied and addressed. Besides the use of iron as electron acceptor, several other routes are possible to improve the cathode, for example the application of oxygen reducing biocathodes [14–16]. Testing these alternatives in a scaled-up system will show their feasibility for practical application.

Secondly, this study aimed at characterization and improvement of a single cell, whereas as part of scaling-up, also stacking is an important point of attention to achieve high voltages. Still little research has been done on stacking. When stacking cells in series, cell reversal, which happens when one cell is not strong enough to maintain the current produced by the other cells, has been shown to be a major bottleneck [5,17]. Ways to overcome cell reversal need to be further studied, for example by analyzing flow characteristics to ensure that all cells become reliable, and by developing strategies to keep an MFC in operation when cell reversal occurs. Thirdly, it is

important that these phenomena are studied in scaled-up systems, as these may reveal other limiting factors not encountered in lab-scale systems. These scaled-up MFCs should further demonstrate the applicability of MFCs in practice. Finally, new challenges arise when using real wastewater as the substrate instead of acetate. These new challenges are related to the presence of particulate matter, hydrolysis of more complex substrates than acetate, fluctuating concentrations of organics, and the need for sufficient buffer capacity to reach the desired activity at the bio-anode.

4. Conclusions

In this continued study on scaling-up MFCs, the cathode reaction was improved by replacing oxygen reduction with ferric iron reduction. This resulted in a maximum power density of 200 W m^{-3} at a current density of 4.2 A m^{-2} . Analysis of anode and cathode resistances revealed that MFC performance increased as a result of development of the electroactive biofilm on the anode, increase in Fe^{3+} concentration in the cathode, and increased activity of the iron oxidizers. The cathode remained the main limiting factor.

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