Microbial Electrolysis Cells for production of methane from CO$_2$: long-term performance and perspectives

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ABSTRACT.

A methane producing Microbial Electrolysis Cell (MEC) is a technology to convert CO$_2$ into methane, using electricity as an energy source and microorganisms as the catalyst. A methane producing MEC provides the possibility to increase the fuel yield per hectare of land area, when the CO$_2$ produced in biofuel production processes is converted to additional fuel methane. Besides increasing fuel yield per hectare of land area, this also results in more efficient use of land area, water, and nutrients. In this research, the performance of a methane producing MEC was studied for 188 days in a flat plate MEC design. Methane production rate and energy efficiency of the methane producing MEC were investigated with time to elucidate the main bottlenecks limiting system performance. Using water as the electron donor at the anode during continuous operation, methane production rate was 0.006 m$^3$/m$^3$ per day at a cathode potential of -0.55 V vs. NHE with a coulombic efficiency of 23.1%. External electrical energy input was 73.5 kWh/m$^3$ methane, resulting in a voltage efficiency of 13.4%. Consequently, overall energy efficiency was 3.1%. The maximum achieved energy efficiency was obtained in a yield test and was 51.3%. Analysis of internal resistance showed that on the short-term, cathode and anode losses were dominant, but with time, also pH gradient and transport losses became more important. The results obtained in this study are used to discuss the possible contribution of methane producing MECs to increase in fuel yield per hectare of land area.

KEY WORDS

Microbial Electrolysis Cell, CO$_2$ reduction, methane, biomass efficiency, land use
Introduction

There is a societal need for the production of fuels from alternative, renewable energy sources to substitute fossil fuels. Organic material (biomass) is an attractive feedstock for the production of biofuels, as it is often locally available, it could contribute to reducing greenhouse gas emissions when produced and utilized in a sustainable way, and biomass can be easily stored [1]. The current biofuel debate, however, shows that it is questionable whether sufficient biomass can be produced in a sustainable way to cover all the world’s fuel needs [2, 3]. To achieve a higher and more sustainable biofuel production, it is therefore of importance that the fuel yield per hectare of the available land area should be increased, while water and nutrients should be used as efficiently as possible [4, 5].

The amount of biomass used for energy production has increased considerably from 648 Mtoe in 1973 to 1179 Mtoe in 2007 [6]. In the conversion of biomass into biofuel, e.g. fermentation of sugars into ethanol or anaerobic digestion of acetate into methane, most of the oxygen atoms present in organic material need to be removed to produce a high energy density fuel. These oxygen atoms are removed in the form of CO$_2$ [7]. For example, in case of fermentation of sugars into ethanol, for each mole of ethanol produced, 1 mole of CO$_2$ is formed. Similarly, in case of anaerobic digestion of acetate into methane, for each mole of methane produced, 1 mole of CO$_2$ is formed. In this process of removing oxygen atoms in the form of CO$_2$ part of the carbon present in biomass is lost [7]. If the by-product CO$_2$ is converted into additional fuel, this would increase the fuel yield per hectare of land area. This increases not only the fuel yield land use efficiency, but also the efficiency of use of nutrients and water. This research therefore investigates whether a Microbial Electrolysis Cell (MEC) is a suitable technology to convert CO$_2$ to additional fuel.

An MEC is a novel technology that uses renewable electricity as the energy source for the production of fuels and chemicals, such as hydrogen [8], ethanol [9], and hydrogen peroxide [10]. A recently developed application for MECs is to produce methane from CO$_2$ using microorganisms as the catalyst, with input of electrical energy [11]. A methane producing MEC consists of two electrodes, anode and cathode, separated by a membrane. The membrane is essential to produce pure products [12]. At the anode, an oxidation reaction takes place, e.g. the oxidation of acetate or water,
yielding CO$_2$ or O$_2$ respectively, and protons and electrons. Electrons are released to the anode and flow through an external electrical circuit to the cathode, while protons and cations migrate through the membrane to the cathode to maintain electroneutrality. At the cathode, the protons and electrons are used to produce methane. The reaction at the cathode is catalyzed by electrochemically active microorganisms, i.e. hydrogenotrophic methanogens [11], and the cathode is therefore called a biocathode. In a methane producing MEC, the overall reaction is thermodynamically not favorable and needs electrical energy to drive the reaction [13].

Hydrogenotrophic methanogens can catalyze methane production from CO$_2$ in an MEC via two mechanisms: (i) direct extracellular electron transfer (eq. 1), i.e. the electrons are directly taken up from the electrode and used to reduce the CO$_2$ to methane,

$$\text{CO}_2 + 8 \text{H}^+ + 8 \text{e}^- \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad (E_{\text{cat}} = -0.24 \text{ V vs. NHE [11]}) \quad (1)$$

All reported potentials are standard potentials under biological relevant conditions at pH 7 and 25$^\circ$C.

and (ii) indirect extracellular electron transfer (eq. 2 and 3), i.e. with intermediate production of hydrogen [11, 14]. In this mechanism first hydrogen is produced at the cathode either electrochemically or bio-electrochemically (eq. 2).

$$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \quad (E_{\text{cat}} = -0.41 \text{ V vs. NHE [15]}) \quad (2)$$

This hydrogen is used together with CO$_2$ to produce methane (eq. 3).

$$\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad (3)$$

Methane production via direct extracellular electron transfer is considered the most energy-efficient process, as the standard potential of hydrogen production via indirect extracellular electron transfer ($E_{\text{cat}} = -0.41 \text{ V vs. NHE}$) is lower than of methane production via direct extracellular
electron transfer ($E_{\text{cat}} = -0.24 \text{ V vs. NHE}$). The protons and electrons needed for the reduction reaction at the cathode are produced by oxidizing water at the anode (eq. 4).

4 \text{ H}_2\text{O} \rightarrow 2 \text{ O}_2 + 8 \text{ H}^+ + 8 \text{ e}^- \quad (E_{\text{an}} = 0.81 \text{ V vs. NHE [13]}) \quad (4)

The overall process is the production of methane from CO$_2$ and water (eq. 5).

CO$_2$ + 2 H$_2$O $\rightarrow$ CH$_4$ + 2 O$_2$ \quad (E_{\text{cell}} = -1.05 \text{ to } -1.22 \text{ V vs. NHE}) \quad (5)

The minimum thermodynamic energy input required is thus achieved when employing direct reduction of CO$_2$ to methane, and is 32.7 MJ electrical energy per m$^3$ of methane (9.1 kWh/m$^3$ methane) under biologically relevant conditions (pH 7 and 25°C).

This paper studies whether a methane producing MEC is a suitable technology for increasing the fuel yield per hectare of land area. Previous studies on methane producing MECs focused on the mechanism of methane production and showed that direct reduction of CO$_2$ to methane coupled to water oxidation is feasible with an additional energy input on top of the thermodynamic energy input [11, 14]. However, the different types of energy losses occurring in the MEC that lead to this additional energy input were not extensively studied. Insight in these energy losses is essential to improve the performance of methane producing MECs, and consequently to increase the fuel yield per hectare of land area. This study therefore investigated the nature and extent of energy losses in a methane producing MEC and their effects on MEC energy efficiency and methane production rates.

The oxygen produced at the anode could negatively affect the performance of methane producing MECs. The oxygen might diffuse to the cathode [16] and could lead to parasitic reactions either via direct reduction to water at the cathode or via oxidizing the methane produced. Oxygen is also known to inhibit hydrogenotrophic methanogens [17] and might decrease the methane production rate. To understand a possible negative role of oxygen, the methane producing MEC was first operated for 83 days using hexacyanoferrate(II) oxidation at the anode and subsequently for 105
days using water oxidation at the anode. The performance of the biocathode in both periods was analyzed using polarization curves and yield tests. The overall performance of the methane producing MEC was determined by analyzing the resistances of the different elements of the methane producing MEC, i.e. anode, cathode, membrane, and electrolyte, and by analyzing the overall energy efficiency. The results obtained in this study were finally used to discuss the possible contribution of methane producing MECs to increase in fuel yield per hectare of land area.

Materials and methods

Experimental set-up

The experiment was performed in the same electrochemical cell as described in Sleutels et al. [18] with a total volume of 0.56 L using a cation exchange membrane (0.7 mm, Ralex CM, Mega a.s., Czech Republic). The anode was made of platinum coated (50 g/m²) titanium mesh (projected surface area 250 cm², thickness 1 mm, specific surface area 1.7 m²/m² – Magneto Special Anodes BV, The Netherlands). The cathode was made of graphite felt (projected surface area 0.025 m², thickness 3 mm – FMI Composites Ltd., Scotland). Both the anode and cathode compartment were equipped with an Ag/AgCl 3 M KCl reference electrode (+0.205 V vs. NHE; ProSense QiS, The Netherlands). The electrochemical cell was connected to a PC via a Fieldpoint FP-AI-110 module (National Instruments, United States) and every 60 seconds cell voltage, current, and cathode and anode potential were recorded using LabVIEW 7.1 (National Instruments, United States). A luminescent dissolved oxygen probe (LDO10101, Hach, USA) was installed in the catholyte, and every 30 minutes dissolved oxygen in the catholyte was measured. The system was operated in a temperature controlled chamber at 30°C.

Electrolytes and microorganisms

Oxygen, product of water oxidation at the anode, can possibly affect methanogens at the cathode [17]. To prevent oxygen to affect biofilm development at the cathode at the start of the experiment, hexacyanoferrate(II) was oxidized at the anode. Because hexacyanoferrate(II) is not sustainable as it
is not self-regenerating [13], it was changed to water oxidation on day 83. At start, anolyte consisted of 100 mM potassium hexacyanoferrate(II) and was circulated at 1.5 mL/s. The anolyte was refreshed regularly to avoid depletion of electron donor. The anolyte was changed to demineralized water containing 20 mM potassium phosphate buffer on day 83. The catholyte influent consisted of a 20 mM potassium phosphate buffer, macronutrients (280 mg/L NH₄Cl, 5.7 mg/L CaCl₂, 10 mg/L MgSO₄·7H₂O, 90 mg/L MgCl₂·6H₂O), and 1 mL/L of a micronutrients and vitamin solution same as [19]. The catholyte influent was supplemented with 5 g/L NaHCO₃ as carbon source, as at operating pH 7 CO₂ is mainly present as HCO₃⁻, and circulated at 1.5 mL/s. The catholyte was continuously refreshed at a rate of 0.1 mL/min (Stepdos 03RC, KNF, Germany). 5 gram of anaerobic sludge, obtained from an UASB treating distillery wastewater (Nedalco, The Netherlands), was used as inoculum and the electrochemical cell was flushed with pure nitrogen (>99.9992%) for 30 minutes before applying a cell voltage. pH of the catholyte was controlled at pH 7±0.1 through a pH controller (Liquisis M CPM 253, Endress+Hauser, Switzerland) using 1 M HCl.

**MEC operation**

During long-term MEC operation there is a risk on malfunctioning of the reference electrodes in the electrochemical cell. To prevent damage to the methane producing biocathode as a result of malfunctioning of the reference electrode, cell voltage was controlled instead of cathode potential. The electrochemical cell was connected to a power supply (MCP94, Bank Elektronik, Germany). Cell voltage was adjusted to obtain the desired cathode potential, when cathode potential deviated >20 mV from the desired cathode potential.

The experiment was started using a biocathode from an already running MEC using hexacyanoferrate(II) oxidation at the anode. This biocathode had a current density of 0.3 A/m² and was operated at an E_cat of -0.8 V vs. NHE. At the start of the experiment (day 0) this biocathode was inoculated to make sure that sufficient biomass was present. From day 0 to day 83, with hexacyanoferrate(II) as the anolyte, the cathode potential was controlled at -0.7 V vs. NHE. After switching the anolyte to water (day 83 to 177), the cathode potential was -0.55 V vs. NHE. This
potential was higher than with hexacyanoferrate(II), and is the result of the maximum range in applied cell voltage of the potentiostat, which was limited to -2 V. This range limited the cathode potential as the anode potential required for water oxidation was higher than the anode potential required for hexacyanoferrate(II) oxidation. On day 188, the experiment was finished due to leakages in the MEC.

Polarization tests

Polarization tests were made using an IviumStat potentiostat with a Peripheral Port Expander (Ivium Technologies, Eindhoven, The Netherlands). The applied cathode potential was decreased from -0.4 V to -1.0 V with steps of 0.1 V, each step lasting 10 minutes, using hexacyanoferrate(II) oxidation at the anode. When using water oxidation at the anode, the cell voltage was controlled instead of cathode potential. In this case, the applied cell voltage was decreased from -1.0 V to -2.0 V with steps of 0.1 V, each step lasting 10 minutes, and cathode potential was continuously recorded versus a reference electrode. This resulted in a cathode potential at highest -0.21 V vs. NHE and at lowest -0.78 V vs. NHE using water oxidation at the anode. Current was recorded each second and the last ten data points at each cathode potential were averaged and plotted in the polarization curve.

Gas analysis

Gas composition of the cathode gas phase was measured with two different gas chromatographs, same as [20], to measure all gasses present. Gas production was measured with a gas flow meter (Milligascounter®, Ritter, Germany).

Methane production rate was calculated from the measured gas production and gas composition using the mass balance equation described by [21]:

\[
V_{CH_4,t} = V_{CH_4,t-1} + (V_{T,t} - V_{T,t-1}) \cdot \frac{c_{CH_4,t} + c_{CH_4,t-1}}{2} + V_{cat} \cdot (c_{CH_4,t} - c_{CH_4,t-1})
\]  

(6)

with \(V_{CH_4,t}\) and \(V_{CH_4,t-1}\) the cumulative methane gas production (L CH\(_4\)) on sample time \(t\) and previous sample time \(t-1\), respectively, \(V_{T,t}\) and \(V_{T,t-1}\) the total gas production measured with a gas flow meter (L) on sample time \(t\) and previous sample time \(t-1\), respectively, \(C_{CH_4,t}\) and \(C_{CH_4,t-1}\) the
measured methane fractions in the cathode gas phase (-) on sample time t and previous sample time t-1, respectively, and $V_{\text{cat}}$ the cathode headspace volume (0.7 L).

Yield tests

To compare performance of the methane producing biocathode between the two anolytes hexacyanoferrate(II) and water, a methane yield tests of 8h was performed on day 70 (13 days before switching anolytes), and day 101 (18 days after switching anolytes). Before the yield test was started, the cathode compartment was flushed with pure nitrogen (>99.9992%) for 30 minutes. During the yield test, the cathode potential was controlled at -0.7 V vs. NHE using an IviumStat potentiostat. Catholyte was continuously refreshed as described for continuous operation, and at the start and end of the yield test the cathode gas phase was analyzed for methane as described.

Energy efficiency

The two most important parameters to describe performance of the MEC are methane production rate and energy efficiency. Methane production rate was determined as described in yield tests. Energy efficiency (eq. 7) of a methane producing MEC is the product of coulombic efficiency (eq. 8) and voltage efficiency (eq. 9) [12].

$$\eta_{\text{energy}} = \eta_{\text{CE}} \cdot \eta_{\text{voltage}} = \frac{-\Delta G_{\text{CH}_4} \cdot V_{\text{CH}_4}}{V_m \cdot E_{\text{cell}} \cdot \int_{t=0}^{t} I dt}$$  \hspace{1cm} (7)

Coulombic efficiency ($\eta_{\text{CE}}$, %), the efficiency of capturing the electrons from the electric current in methane, was calculated via

$$\eta_{\text{CE}} = \frac{V_{\text{CH}_4} \cdot F \cdot n}{V_m \cdot \int_{t=0}^{t} I dt}$$ \hspace{1cm} (8),

with $V_{\text{CH}_4}$ the cumulative methane gas production (m$^3$ CH$_4$), F the Faradays constant (96485 C/mole e$^-$), n the moles of electrons per mole of methane (8 mole e$^-$/mole CH$_4$), $V_m$ the molar volume (0.0252 m$^3$/mole), I the current (A), and t the time (s).
Voltage efficiency, the amount of external electrical energy that ends up in methane, was calculated via the Gibb’s free energy of oxidation of methane over the electrical energy input of the MEC

$$\eta_{\text{voltage}} = \frac{E_{\text{emf}}}{E_{\text{cell}}} = \frac{-\Delta G_{\text{CH}_4}}{E_{\text{cell}} \cdot n \cdot F}$$ \hspace{1cm} (9),

with $E_{\text{emf}}$ the so called reversible energy loss (V), i.e. the electrical energy converted into chemical energy in the form of methane, $E_{\text{cell}}$ the energy input of the MEC, i.e. the applied cell voltage (V), and $\Delta G_{\text{CH}_4}$ the Gibb’s free energy of oxidation of methane (890.4 kJ/mole CH$_4$ [22]).

To improve the performance of the methane producing MEC, factors that affect the energy efficiency should be identified. Therefore, the effect of oxygen diffusion through the membrane on MEC performance was calculated, and an internal resistance analysis of the methane producing MEC was performed as described hereafter.

Oxygen diffusion through membrane

The coulombic efficiency reflects to which extent other electron consuming reactions, so called parasitic reactions, than the preferred CO$_2$ reduction reaction take place in the electrochemical cell. Parasitic oxidation occurs when oxygen produced at the anode diffuses to the cathode, where it oxidizes methane and/or hydrogen to CO$_2$ and/or water. This results in a decrease in methane production rate and a lower coulombic efficiency (smaller part of the electrons ending up in methane). Parasitic reduction occurs when oxygen is directly reduced to water at the cathode. The contribution of parasitic oxidation or reduction to coulombic efficiency can be estimated by calculating the oxygen diffusion flux ($J_{O_2}$ in mole O$_2$/m$^2$/per second) over the cation exchange membrane using Fick’s law

$$J_{O_2} = D_{O_2} \cdot \frac{(c_{O_2,\text{cat}} - c_{O_2,\text{an}})}{\delta}$$ \hspace{1cm} (10),

with $D_{O_2}$ the diffusion coefficient of oxygen determined for a CMI-7000 cation exchange membrane (Membrane International Inc., USA) ($4.3 \cdot 10^{-10}$ m$^2$/s) [16], $c_{O_2,\text{an}}$ and $c_{O_2,\text{cat}}$ the dissolved oxygen concentration at the anode and cathode (mole O$_2$/m$^3$), respectively, and $\delta$ the thickness of the
membrane as supplied by the manufacturer (0.7·10⁻³ m). The oxygen diffusion flux is inversely proportional to the thickness of the membrane. The estimated rate of methane oxidation ($r_{CH_4,ox}$ in m³ CH₄/m³ per day) due to this flux of oxygen is

$$r_{CH_4,ox} = \frac{J_{O_2} \cdot A \cdot V_m \cdot t}{2 \cdot V_{reactor}}$$  \hspace{1cm} (11)$$

with $A$ the membrane surface area (0.025 m²), $t$ the time (d), $V_{reactor}$ the total reactor volume (0.56 L), and taking into account that 2 moles of oxygen are consumed per mole methane.

**Internal resistance analysis**

The applied cell voltage consists of a thermodynamically calculated cell voltage needed to produce methane under biologically relevant conditions, the reversible energy loss $E_{emf}$, and internal energy losses, the so called irreversible energy losses [18]. Irreversible energy losses, energy lost as a result of the resistances of different parts of the MEC, consist of the pH gradient over the membrane ($E_{\Delta pH}$), cathode overpotential ($\eta_{cat}$), anode overpotential ($\eta_{an}$), ionic losses ($E_{ionic}$), and transport losses ($E_T$), that were calculated according to [18]

$$E_{cell} = E_{emf} - E_{\Delta pH} - \eta_{cat} - \eta_{an} - E_{ionic} - E_T$$  \hspace{1cm} (12)$$

with $E_{emf} = E_{cat} - E_{an}$ (V). Cathode ($E_{cat}$) and anode ($E_{an}$) potential were calculated using the Nernst equation under experimentally relevant conditions ($E^{0}_{Fe(II)} = 0.361$ V vs. NHE, $T = 303$ K, $[Fe(CN)_6]^{4-}$ is assumed on average to be equal to $[Fe(CN)_6]^{3-}$ [13], $E^{0}_{H_2O} = 1.229$ V vs. NHE, pO₂ = 0.28·10⁵ Pa (average measured liquid dissolved oxygen concentration cathode was 12.4 mg O₂/L (day 83-177)), $E^{0}_{cat} = 0.169$ V vs. NHE, pCH₄ = 0.075·10⁵ Pa (pressure cathode compartment was 1.005 bar with an average measured methane concentration of 8.78% (day 0-188)), $[HCO_3^-] = 0.06$ M, $[H^+] = 10^{-7}$ M).

As anolyte and catholyte pH changed with time, these were included in the irreversible energy losses calculations.

$$E_{an,Fe(II)} = E^{0}_{Fe(II)} - \frac{R \cdot T}{F} \cdot \ln \left( \frac{[Fe(CN)_6]^{4-}}{[Fe(CN)_6]^{3-}} \right) = 0.36V$$ vs. NHE  \hspace{1cm} (13)$$
\[ E_{\text{an,}H_2O} = E_{H_2O}^0 - \frac{R \cdot T}{4 \cdot F} \cdot \ln\left( \frac{1}{pO_2 \cdot [H^+]^4} \right) = 0.87V \text{ vs. NHE} \] (14)

\[ E_{\text{cat}} = E_{\text{cat}}^0 - \frac{R \cdot T}{8 \cdot F} \cdot \ln\left( \frac{[CH_4]_{\text{cat}}}{[HCO_3^-] \cdot [H^+]^3} \right) = -0.34V \text{ vs. NHE} \] (15)

Ionic and transport losses were calculated from all other potential losses using equation 12. Parameters measured in time to calculate potential losses were anode and cathode potential, catholyte and anolyte pH, and cell voltage. At a constant applied cell voltage, the current density that is produced by MECs depends on the internal resistance of the MEC. Partial resistances (R_i in Ω·m^2) were calculated by dividing the calculated potential loss by the current density, and total internal resistance was the sum of the partial resistances [18].

For analysis of internal resistance during continuous operation, six representative periods were chosen. These six periods were:

1) at the start of the experiment using hexacyanoferrate(II) oxidation (days 2-6, indicated as ‘start Fe’),

2) in the middle of stable operation using hexacyanoferrate(II) oxidation (days 50-57, indicated as ‘middle Fe’),

3) before switching anolytes (day 83, indicated as ‘end Fe’),

4) after switching anolytes (day 83, indicated as ‘start water’),

5) in the middle of stable operation using water oxidation (days 125-132, indicated as ‘middle water’), and

6) at the end of the experiment using water oxidation (days 167-176, indicated as ‘end water’).
Results and discussion

Figure 1. Polarization tests give insight in the performance of a methane producing biocathode in time (operation day indicated in figure) using hexacyanoferrate(II) (grey dashed line) or water (black solid line) oxidation at the anode.

Biocathode performance

Polarization tests are a useful tool to give insight in the development of the methane producing biocathode with time. A higher current density at the same cathode potential indicates an increase in performance. When using hexacyanoferrate (day 0-83) at the anode, during continuous operation cathode potential was controlled at -0.7 V vs. NHE, and current density was on average 0.78±0.20 A/m². The polarization curves as shown in Figure 1 show that the biocathode had similar performance on days 6 and 83, indicating stable performance. The current density obtained in the polarization curves at -0.7V vs. NHE is well within the range obtained during continuous operation. After changing the anode reaction to water oxidation and increasing the cathode potential to -0.55 V vs. NHE during continuous operation, current density was on average 0.25±0.04 A/m². Similar to using hexacyanoferrate(II) oxidation at the anode, the polarization curves show that the biocathode
had similar performance on days 132 and 177, indicating stable performance, and the current density obtained in the polarization curves at -0.55 V vs. NHE is in line with the current density obtained during continuous operation.

Figure 1 also shows that at the same cathode potential the biocathode performed better when using water oxidation compared to hexacyanoferrate(II) oxidation. The higher current density using water oxidation compared to hexacyanoferrate(II) oxidation could be the result of oxygen diffusion over the membrane resulting in parasitic reactions at the cathode, or the result of better performance of the biomass on the biocathode. Presence of oxygen at the cathode could lead to increased current production through direct oxygen reduction at the cathode. Whether parasitic reactions at the cathode are a plausible explanation for the better performance using water oxidation can be verified by calculating the oxygen flux over the cation exchange membrane (eq. 10 and 11). Dissolved oxygen concentration at the anode was on average 0.95 mg/L using hexacyanoferrate(II) oxidation, and 12.4 mg/L using water oxidation, while dissolved oxygen concentration at the cathode was always 0 mg/L. This leads to an oxygen flux over the membrane of $1.8 \times 10^{-9}$ mole O$_2$/m$^2$ per second using hexacyanoferrate(II) oxidation, and $2.4 \times 10^{-7}$ mole O$_2$/m$^2$ per second using water oxidation. This flux of oxygen can consume electrons at a rate of 0.007 A/m$^2$ using hexacyanoferrate(II) oxidation, and 0.09 A/m$^2$ using water oxidation. This is equal to 0.6% of the measured current density at cathode potential -0.7 V vs. NHE during the polarization test using hexacyanoferrate(II) oxidation and 37% of the measured current density at cathode potential -0.55 V vs. NHE during the polarization test using water oxidation (Figure 1). These calculations show that oxygen diffusion over the membrane can explain part of the higher current density using water oxidation.

After correction for the additional current density caused by possible oxygen diffusion over the membrane, current density using water oxidation was still higher than when using hexacyanoferrate(II) oxidation (Figure 1). This suggests that the higher controlled cathode potential during continuous operation also lead to an increased current density. Using water oxidation, during continuous operation cathode potential was -0.55 V vs. NHE, while during hexacyanoferrate(II) oxidation the cathode potential was -0.7 V vs. NHE. The cathode potential of -0.55 V vs. NHE was
higher than used in previous studies, where potentials below -0.7 V vs. NHE were investigated [11, 14, 22, 23]. At this high cathode potential, direct CO₂ reduction to methane is energetically more favorable than CO₂ reduction via hydrogen: eq. 1 and 2 show a higher potential for direct CO₂ reduction compared to CO₂ reduction via hydrogen, meaning that at -0.55 V vs. NHE more energy is to be gained by the microorganisms via direct reduction of CO₂. Previous study indeed revealed that at cathode potentials higher than -0.75 V vs. NHE, methane was mainly produced via direct CO₂ reduction, while at lower cathode potentials methane can also be produced indirectly via hydrogen [14]. In this study, at a cathode potential of -0.55 V vs. NHE, direct reduction of CO₂ was the most likely process, although we did not further investigate the mechanisms.

To further study the performance of the biocathode when using water oxidation at the anode compared to hexacyanoferrate(II) oxidation, yield tests were performed, in which the cathode potential was controlled at the same value of -0.7 V vs. NHE. This was done on day 70 (13 days before switching anolytes) and day 101 (18 days after switching anolytes). Table 1 shows that during the yield test, the current density was 40% higher when using water oxidation compared to hexacyanoferrate(II) oxidation. This is in agreement to what was found during polarization tests (Figure 1). Methane production rate was 30% higher when using water oxidation compared to hexacyanoferrate(II) oxidation, and this was confirmed by the slightly lower coulombic efficiency for water oxidation compared to hexacyanoferrate(II) oxidation in the yield tests. The coulombic efficiency of hexacyanoferrate(II) oxidation in the yield test being higher than 100% could be a result of biomass degradation and oxidation or storage of electrons in the microorganisms [24]. The better performance of the biocathode when using water oxidation could also be a result of the lower applied cathode potential in the yield test (-0.7 V vs. NHE) compared to the potential at which the biofilm was acclimatized during continuous operation (-0.55 V vs. NHE). This change in cathode potential could have affected the functioning of the biocathode.

The polarization curves and yield tests reveal that oxygen via parasitic reactions decreases the coulombic efficiency of the biocathode, however, it has no obvious negative effect on the methane production rate. This might be explained by the fact that the oxygen reacts away either via direct
reduction to water at the cathode or via oxidizing the methane produced, and therefore cannot affect the methanogens present at the biocathode.

Long-term current generation and methane production in flat plate MEC

![Graph showing cumulative methane production with time. The black diamonds indicate methane production calculated from the current, while the grey squares indicate measured methane production. Anolyte was changed from hexacyanoferrate(II) to water on day 83, as indicated by the dashed line.](image)

**Figure 2.** Cumulative methane production with time. The black diamonds indicate methane production calculated from the current, while the grey squares indicate measured methane production. Anolyte was changed from hexacyanoferrate(II) to water on day 83, as indicated by the dashed line.

Current and methane were produced continuously in the flat plate MEC for 188 days (Figure 2). When using hexacyanoferrate (day 0-83), cathode potential was controlled at -0.7 V vs. NHE, and current density ranged between 0.4 A/m² and 2.5 A/m², being on average 0.78±0.20 A/m². Methane production ranged between 0.01-0.10 m³ CH₄/m³ per day, being on average 0.05±0.03 m³ CH₄/m³ per day. After changing the anode reaction to water oxidation and increasing the cathode potential to -0.55 V vs. NHE, current density decreased and ranged between 0.2 A/m² and 0.6 A/m² (day 83-188), being on average 0.25±0.04 A/m². Methane production ranged between $3\times10^{-4}$-0.025 m³
CH₄/m³ per day, being on average 0.006±0.008 m³ CH₄/m³ per day. This decrease in gas production rate when switching the anolyte from hexacyanoferrate(II) to water is in line with the lower current density (Figure 2).

Methane production rate was on average a factor 8 higher using hexacyanoferrate(II) as electron donor compared to water during continuous operation (Table 1). Part of the explanation for the lower methane production rate when using water oxidation is the higher cathode potential and consequently the lower current density, however, this cannot be the only explanation, as the current density was only a factor 3-4 lower. Parasitic reactions that consume electrons will also lead to a lower methane production rate. These parasitic reactions are reflected in the coulombic efficiency, which was about a factor 1.5-4 lower when using water oxidation compared to hexacyanoferrate(II) oxidation during continuous operation (Table 1). Whether parasitic reactions are a plausible explanation for the lower coulombic efficiency can be verified by calculating the oxygen diffusion flux over the cation exchange membrane. Average dissolved oxygen concentration at the anode was 12.3 mg/L using water oxidation, while dissolved oxygen concentration was always 0 mg/L at the cathode. This leads to an oxygen flux over the membrane of 2.4·10⁻⁷ mole O₂/m² per second. This flux of oxygen can oxidize methane at a rate of 0.012 m³ CH₄/m³ per day. If we calculate the expected methane production rate using the measured methane production rate in Table 1, and taking into account the methane lost due to oxidation by oxygen, then the methane production rate using water oxidation was 0.005 + 0.012 = 0.017 m³ CH₄/m³ per day (middle water) and 0.006 + 0.012 = 0.018 m³ CH₄/m³ per day (end water). This would result in a maximum coulombic efficiency of 57.8% (middle water) and 67.5% (end water), which is comparable to the coulombic efficiency for hexacyanoferrate(II) oxidation. These calculations show that parasitic reactions can explain part of the differences in coulombic efficiency between both anolytes.

Parasitic reactions alone, however, cannot explain why coulombic efficiency is considerably lower than 100% for both anolytes during continuous operation. It is believed that part of the methane is lost due to diffusion from the cathode to the anode, similar to hydrogen losses in MECs [15, 25], and therefore less methane is measured in the cathode gas phase than expected from the measured...
current. The coulombic efficiency can likely be improved by using a membrane that is less permeable for gases. This results in less methane diffusion from the cathode to the anode, and less oxygen diffusion from the anode to cathode, and consequently in less parasitic reactions.

Methane production rates reported for methane producing bio-electrochemical systems using water oxidation are 0.012-0.015 m³ CH₄/m³ per day for two-compartment MECs at cathode potentials between -0.8 V and -0.9 V vs. NHE [11, 14]. The methane production rates during continuous operation using hexacyanoferrate(II) oxidation, 0.033-0.071 m³ CH₄/m³ per day, were higher than previously reported methane production rates. Methane production rates during continuous operation using water oxidation were somewhat lower, 0.005-0.006 m³ CH₄/m³ per day, however, this is expected as the results are obtained at a cathode potential of >0.25 V higher than used in other studies.

Voltage efficiency and energy efficiency

During continuous operation using hexacyanoferrate(II) oxidation at the anode, the energy input was 15.4 kWh/m³ methane (start Fe; based on Eₜₐₜₛ = -1.21 V) and 31.6 kWh/m³ methane (middle Fe; based on Eₜₐₜₛ = -1.23 V) (Table 1). Using water oxidation at the anode, the energy input was 97.2 kWh/m³ methane (middle water; based on Eₜₐₜₛ = -1.99 V) and 73.5 kWh/m³ methane (end water; based on Eₜₐₜₛ = -1.99 V) (Table 1). Gibb’s free energy of methane oxidation is 9.8 kWh/m³ methane [22], so voltage efficiency was 63.7% (start Fe) and 31.1% (middle Fe) using hexacyanoferrate(II) oxidation, and 10.1% (middle water) and 13.4% (end water) using water oxidation.

Energy efficiency (eq. 7) is the product of coulombic efficiency (eq. 8) and voltage efficiency (eq. 9) [12]. The energy efficiency was 42.6% (start Fe) and 10.3% (middle Fe) using hexacyanoferrate(II) oxidation, and 1.8% (middle water) and 3.1% (end water) using water oxidation (Table 1).

It should be noted that the energy efficiency using hexacyanoferrate(II) oxidation at the anode does not include the energy required for regeneration of hexacyanoferrate(II), which is essential for hexacyanoferrate(II) to be a sustainable electron donor for use in practical applications [13].
energy efficiency using hexacyanoferrate(II) oxidation at the anode, however, reveals the potential performance of a methane producing biocathode using an efficient anode, and is useful to study the effect of oxygen diffusion over the membrane on the performance of a methane producing MEC.

The yield tests show the maximum achieved voltage efficiency and energy efficiency. The energy input in a yield test using hexacyanoferrate(II) oxidation was 16.6 kWh/m³ methane (day 70), leading to a voltage efficiency of 59.3% and an energy efficiency of 62.0% (Table 1). The energy input in a yield test using water oxidation was 18.2 kWh/m³ methane (day 101), leading to a voltage efficiency of 53.9% and an energy efficiency of 51.3% (Table 1).

**Identifying sources of irreversible energy losses**

To study how energy efficiency can be improved, analysis of irreversible energy losses during continuous operation of the methane producing MEC is essential. At a constant applied cell voltage, the current density that is produced by MECs depends on the internal resistance of the MEC [18]. Therefore, partial resistances were calculated to identify which processes contributed most to the total internal resistance of the MEC. These partial resistances represent cathode losses, anode losses, losses due to the pH gradient over the membrane, and transport & ionic losses.

Figure 3 shows an increase in total internal resistance with time for both anolytes. This causes a decrease in current density with time. Current density decreased from 1.15 A/m² to 0.30 A/m² (from start Fe to end Fe) using hexacyanoferrate(II) oxidation, and from 0.30 A/m² to 0.25 A/m² (from start water to end water) using water oxidation. From Figure 3, also two main effects can be seen: (i) in case of hexacyanoferrate(II) oxidation, the total internal resistance was considerably lower than with water oxidation, and was mainly caused by the cathode, and (ii) in case of water oxidation, in the beginning anode and cathode contributed most to the total internal resistance, while pH and transport & ionic losses increased with time.
Figure 3. Total internal resistance, and partial resistances were measured in time for hexacyanoferrate(II) and water oxidation at the anode for continuous operation. Anolyte was changed from hexacyanoferrate(II) to water on day 83, as indicated by the dashed line. Anolyte was refreshed on day 115, as indicated by the solid line.

In case of hexacyanoferrate(II) oxidation, the cathode resistance was at least 0.43 \( \Omega \cdot m^2 \) (start Fe). Immediately after switching anolyte hexacyanoferrate(II) for water, both the cathode and anode contributed most to total internal resistance (Figure 3). Cathode resistance was at least 1.04 \( \Omega \cdot m^2 \) (end water), while anode resistance was at least 1.33 \( \Omega \cdot m^2 \) (start water). The sudden increase in anode resistance after switching anolytes could be attributed to the poor catalytic properties of graphite for water oxidation [26]. The increase in anode and cathode resistances with time may be caused by increasing product concentrations (O\(_2\), methane, and protons) near or inside the electrode. This could negatively affect reaction kinetics, and gas accumulation inside the electrode could result in less available effective cathode surface area. Transport & ionic resistances increased with time from 0.015 \( \Omega \cdot m^2 \) (start water) to 0.83\( \Omega \cdot m^2 \) (end water), despite refreshing the anolyte (day 115). In
this same time period, anolyte conductivity increased from 0.3 S/m (start water) to 0.7 S/m (end water), while catholyte conductivity decreased from 2.1 S/m (start water) to 1.0 S/m (end water). This is equal to a decrease in ionic resistance from 0.01 $\Omega \cdot m^2$ (start water) to 0.006 $\Omega \cdot m^2$ (end water), using the equation described by Sleutels et al. [18] and assuming the distance between the electrodes and the membrane is 5 mm. These calculations show that the transport & ionic resistance mainly consists of transport losses, and not so much of ionic losses due to limited conductivity of the electrolyte, which is in line with Sleutels et al. [18]. The resistance due to the development of a pH-gradient over the membrane increased in the same time period from 0.17 $\Omega \cdot m^2$ (start water) to 0.94 $\Omega \cdot m^2$ (end water), with the most prominent increase at the end using water oxidation, as the anolyte acidified due to proton production from pH 6.25 (start water; cathode pH 7.09) to 3.37 (end water; cathode pH 7.10). At the end using water oxidation, all resistances contributed to a similar extent to the total internal resistance.

Increased methane yield per hectare of land area

At this point, the methane producing MEC is still in its early stage of development. For an estimation of the potential of a methane producing MEC, two crucial inputs need to be considered: renewable electrical energy and CO$_2$. There are several possible sources and technologies for renewable electricity production: PV cells using solar energy, wind turbines using wind energy, or reverse electrodialysis using the energy from mixing salt and fresh water [27]. A suitable source of CO$_2$ should (i) be of renewable origin to be independent of fossil fuels, and (ii) contain high concentrations of CO$_2$, preferably without oxygen present. Gas streams of fermentation processes (renewable fuel production technologies) are therefore an attractive CO$_2$ source for methane producing MECs. As an example, we will discuss biogas produced via anaerobic digestion of biomass. Biogas consists of both CH$_4$ and CO$_2$, which are produced in a 1:1 ratio. To add a higher energetic and economic value to the biogas, it needs to be upgraded, which means that the CO$_2$ content needs to be lowered, and the methane content needs to be increased. Conventionally, CO$_2$ is removed by scrubbing the CO$_2$-rich gas with an aqueous solution containing chemicals (hydroxide,
amines, etc.) [28]. By contrast, a methane producing MEC does not only lower the CO$_2$ content of biogas, but furthermore, converts CO$_2$ into additional methane. As roughly half of the biogas consists of CO$_2$, the methane yield from anaerobic digestion could be doubled using a methane producing MEC.

Figure 4. Combining anaerobic digestion and methane producing MECs leads to an improved methane yield per hectare of land area. The energy efficiency ($\eta_e$) of the methane producing MEC is calculated as the ratio between the thermodynamic energy input based on the Gibb’s free energy of the reaction (9.8 kWh/m$^3$ methane) divided by the actual electrical energy input. A relative methane yield $>1$ indicates that more methane is produced than via anaerobic digestion alone. Thus, at an energy efficiency above 5.5%, the combination of anaerobic digestion and methane producing MECs leads to an increased methane yield per hectare of land per year compared to anaerobic digestion.

Figure 4 shows the relative methane yield per hectare of land area per year for combined anaerobic digestion and methane producing MECs using electricity from PV cells. A relative methane yield $>1$ indicates that more methane is produced via the combined processes compared to anaerobic digestion alone. The relative methane yield is shown as a function of the surface area used for PV
cells in combination with a methane producing MEC, and the energy efficiency of a methane producing MEC. We assume that PV cells convert the incoming solar radiation of 150 W/m² [29] into electricity at an efficiency of 10% [30], and that biogas consists of equal parts of methane and CO₂. In the hypothetical situation of 100% energy efficiency, which means that no energy losses occur in the MEC system and the energy input consists only of the reversible thermodynamic energy input, to double the methane yield, 5% of the land area needs to be covered with PV cells in combination with methane producing MECs (meaning that 95% of the surface area is used for biomass growth, resulting in a lower CO₂ yield per hectare, and a relative methane yield <2). The methane producing MEC should have an energy efficiency higher than 5.5% to increase methane yield per hectare of land area compared to anaerobic digestion alone (Figure 4).

It is important to note that the use of water oxidation at the anode is essential for reaching an additional methane yield compared to existing biomass conversion technologies. Methane producing MECs that use biomass in the form of acetate as the electron donor at the anode, and that recycle the produced CO₂ from the anode to the cathode, produce the same mix of CO₂ and methane as anaerobic digestion. Oxidation of one mole of acetate at the anode results in 8 moles of electrons and 2 moles of CO₂, the latter being present in the form of bicarbonate at biologically relevant pH 7 (eq. 16). The formed 8 moles of electrons can be used to reduce only one mole of CO₂ (or bicarbonate) to methane (eq. 17). The overall reaction in a methane producing MEC using acetate oxidation at the anode is thus limited by the 8 moles of electrons present in one mole of acetate. Overall, 1 mole of acetate results in 1 mole of methane produced at the cathode, and 1 mole of CO₂ produced at the anode (eq. 18).

Organic matter oxidation at anode [13]:

\[ \text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^- \] (16)

Carbon dioxide reduction at cathode:

\[ \text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 3\text{H}_2\text{O} \] (17)

Overall reaction methane producing MEC using organic matter oxidation at the anode:
In contrast, when using water oxidation at the anode, the amount of electrons is in principle unlimited, meaning that sufficient electrons can be produced to reduce all the CO$_2$ present into methane, leading to a theoretically double methane yield. Methane producing MECs that use an electron source other than biomass are therefore the only way to achieve higher methane yields per hectare of land area compared to anaerobic digestion.

**Perspectives**

This study showed that an MEC is suitable to convert CO$_2$ to methane, with a biocathode that continuously converted CO$_2$ to methane for 188 days. The maximum achieved energy efficiency in this study was 51.3%, obtained during the yield test using water oxidation. An energy efficiency of 51.3% would increase the methane yield per hectare of land area by a factor 1.8 when covering 10% of the land area with PV cells (Figure 4). For these calculations, it is assumed that the methane production rate of methane producing MECs is the same as the CO$_2$ production rate of anaerobic digestion (5 m$^3$/m$^3$ per day), whereas the maximum achieved methane production rate in this study was still a factor 25 lower. A considerable reduction in internal resistance is still needed to reach sufficiently high conversion rates. The internal resistance analysis shows that several improvements can be made to reduce the internal resistance and to increase energy efficiency. First, high-surface electrode materials with good catalytic properties for water oxidation and with good properties for biofilm development [19] for catalysis of CO$_2$ reduction should be used to decrease cathode and anode losses [13]. Second, by directing the flow through the porous electrode, the surface area can be effectively used and mass transfer losses are decreased [13, 31]. Third, decreasing the distances between membrane and electrodes minimizes mass transfer losses even further [13, 32]. Finally, to increase the coulombic efficiency and the methane content of the gas, a membrane that is less permeable for gases should be used. Implementing these improvements will bring a methane
producing MEC closer to its potential for increasing the methane yield land use efficiency, and consequently to increase water, and nutrient efficiency.

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Table 1. Performance of a methane producing biocathode with hexacyanoferrate(II) or water oxidation at the anode during continuous operation and for yield tests.

<table>
<thead>
<tr>
<th>Operation period</th>
<th>Hexacyanoferrate(II) oxidation</th>
<th>Water oxidation</th>
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<tbody>
<tr>
<td></td>
<td>Continuous</td>
<td>Yield test</td>
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<tr>
<td></td>
<td>Start Fe</td>
<td>Middle Fe</td>
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<tr>
<td>$E_{\text{cat}}$ (V)</td>
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<td>-0.71</td>
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<td>$j$ (A/m$^2$)</td>
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<td>$r_{\text{CH}_4}$ (m$^3$/m$^3$ per day)</td>
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<td>Energy input (kWh/m$^3$)</td>
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<tr>
<td>$\eta_{\text{voltage}}$ (%)</td>
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<td>$\eta_{\text{energy}}$ (%)</td>
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