



Microbial fuel cells operated with iron-chelated air cathodes

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ABSTRACT

The use of non-noble metal-based cathodes can enhance the sustainability of microbial fuel cells (MFCs). We demonstrated that an iron-chelated complex could effectively be used as an aerated catholyte or as an iron-chelated open air cathode to generate current with the use of MFCs. An aerated iron ethylenediaminetetraacetic acid (Fe-EDTA) catholyte generated a maximum current of 34.4 mA and a maximum power density of 22.9 W m⁻³ total anode compartment (TAC). Compared to a MFC with a hexacyanoferrate catholyte, the maximum current was similar but the maximum power was 50% lower. However, no replenishment of the Fe-EDTA catholyte was needed. The creation of an activated carbon cloth open air cathode with Fe-EDTA-polytetrafluoroethylene (PTFE) applied to it increased the maximum power density to 40.3 W m⁻³ TAC and generated a stable current of 12.9 mA (at 300 mV). It was observed that the ohmic loss of an open air cathode MFC was dependent on the type of membrane used. Moreover, increasing the anode electrode thickness of an open air cathode MFC from 1.5 to 7.5 cm, resulted in a lowering of the power and current density.

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1. Introduction

In a microbial fuel cell (MFC), the chemical energy comprised in various organic substrates such as acetate, glucose but also organic waste streams [1–3], is converted into electrical energy with the aid of microorganisms [4]. Both mixed bacterial communities and pure cultures can oxidize organic substrates at the anode to yield electrons, protons and oxidized products [5]. At the cathode, the electrons react with a final electron acceptor such as oxygen. Due to the positive potential difference between the electrodes and the flow of electrons, electrical energy is generated [6]. Improvements of the reactor designs and its components have increased the power output to values up to 2.2 kW m⁻³, but these systems are limited in size to a volume of about 1 cm³ and use an unsustainable catholyte [7]. In contrast, the power output of dm³ sized reactors amounts to values of 28 W m⁻³ [8], which is about 2 orders of magnitude lower. The internal ohmic voltage losses and overpotentials of the reactor are believed to be important physical determinants for the achievable power output in MFCs [9,10], especially when the size of the reactor increases. In addition, there is a need for a robust and effective cathode reaction.

The non-catalyzed cathodic oxygen reduction at graphite granules with high available surface areas supports volumetric power

densities of up to 11 W m⁻³ MFC [11]. However, commonly a microbial or chemical catalyst is applied to facilitate the cathodic oxygen reduction in MFCs and to increase the power generation. Platinum is frequently applied on graphite or carbon cathodes to catalyze the oxygen reduction reaction in MFCs resulting in power densities of up to 115 W m⁻³ MFC [6,12]. However, platinum is expensive and prone to poisoning [6]. Instead, non-noble metal catalysts such as pyrolysed iron(II) phthalocyanine (Pyr-FePc) and cobalttetramethoxyphenylporphyrin (CoTMPP) applied on graphite cathodes have been proposed as a cheaper alternative to catalyze the oxygen reduction reaction [13]. Recently, the use of a mixed microbial community has been shown to catalyze the oxygen reaction on a graphite felt cathode [14]. This truly sustainable MFC system resulted in an open circuit potential of 0.93 V and a power output of up to 83 W m⁻³ MFC but needs to be operated under steady operating conditions and might be prone to a difficult start-up due to the microbial nature of both the anode and cathode process [14]. The use of modified porous carbon materials has been described as a catalytic support for the cathodic reduction of oxygen [15], but has to our knowledge not been implemented in MFCs.

Instead of directly using oxygen as a final electron acceptor, a ferric iron solution can be used as an intermediate electron acceptor if its precipitation is prevented. ter Heijne et al. [16] used a bipolar membrane to maintain a pH of 2.0–2.5 to prevent the precipitation of the ferric catholyte in the cathode compartment. To increase the rate of the aerobic chemical re-oxidation of iron, an *Acidithiobacillus ferrooxidans* species was used [8]. However, in order to prevent the iron precipitation at a neutral pH value, the addition of a chelating

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agent is needed. The iron complex potassium hexacyanoferrate is commonly used as a final electron acceptor in MFC cathodes, but due to the very slow re-oxidation rate by oxygen, it is not regarded as sustainable [6]. Ethylenediaminetetraacetic acid (EDTA) is well known for its iron-chelating properties [17]. Moreover, the reactivity of a Fe-EDTA couple towards the oxygen reduction reaction has been reported [18], which makes it a possible catalyst for the oxygen reduction reaction in MFCs.

In this paper, we investigate the use of various iron-chelating molecules to operate MFCs with an iron-based chelated catholyte which is reversibly re-oxidized by oxygen. Subsequently, we investigated the adsorption of an iron-chelating mixture on activated carbon. Its properties as an open air cathode have been compared to activated carbon cloth. In addition, the effect of increasing the anodic reactor volume for a given cathode surface and the influence of the membrane was investigated. Both are important factors for a future scaling up of MFCs.

2. Experimental

2.1. Reactor setup

The reactors were constructed by using perspex frames, as previously described by Aelterman et al. [19]. Each frame (both anode and cathode) had a thickness of 1.5 cm and the total empty volume of one frame was 156 cm³. The anode frames were completely filled with a packed bed of graphite granules (5 mm, Le Carbone, Belgium) and a graphite rod (5 mm diameter, Morgan, Belgium) was used to collect the electrons. The total anode compartment (TAC) volume was 156 cm³. To obtain a homogenous liquid upflow through the anode compartment, a perforated tube was installed in the anode compartment inlet. Each anode compartment had a hydraulic circuit containing an individual influent tubing, outlet tubing and a recirculation loop. A cation exchange membrane (CEM 1 or 2 – see below) or a proton exchange membrane (PEM – see below) was used to separate the anode and cathode of a MFC unit. The cathode preparation, construction and operation are discussed below.

2.2. MFC aerated with iron-chelating catholytes

Several iron-chelating catholytes were prepared in demineralized water: iron ethylenediaminetetraacetic acid (Fe-EDTA – 50 mM Fe₂(SO₄)₃, 100 mM EDTA-4S), iron nitrilotriacetic acid (Fe-NTA – 50 mM Fe₂(SO₄)₃, 100 mM NTA), Fe-succinate (50 mM Fe₂(SO₄)₃, 100 mM C₄H₆O₄) and Fe-citrate (100 mM C₆H₅FeO₇). In the cathode frame, a 2.5 mm graphite felt electrode (Sigraterm, SGL Carbon) and a stainless steel mesh current collector were installed. The cathode compartment was filled with 60 mL catholyte and aerated at a rate of 190 L h⁻¹ at the bottom with humidified air. Humidification was accomplished by bubbling air through a washing bottle containing demineralized water at room temperature. For the graphite control, i.e. a reference system not containing a Fe-chelated solution, a mineral M9-medium not containing a carbon source [20] was used as catholyte. The hexacyanoferrate catholyte consisted of a 50 mM K₃Fe(CN)₆ aqueous solution in a 100 mM KH₂PO₄ buffer (Merck, Belgium) [19]. A cation exchange membrane (CEM-1 – Ultrex™ CMI7000, Membranes International Inc., USA) was used to separate the compartments in all these tests. In case of the Fe-EDTA catholyte and graphite control, an additional MFC was operated with a proton exchange membrane (PEM – Fumapem F-930, FuMA-Tech, Germany).

2.3. MFC with open air cathodes

Activated cloth (Zorflex, Chemviron Carbon, UK) was used as base material for all open air cathodes. In the case of the oxidized

activated carbon cloth, an oxidation treatment was applied by submerging it in a mixture of concentrated HNO₃ and concentrated H₂SO₄ (1/1 ratio) for 60 min after which it was rinsed intensively with water [21]. The Fe-EDTA activated carbon cloth cathode was prepared by submerging a piece of activated cloth for the duration of 4 h in a 100 mM EDTA-4S solution, after which it was dried at 40 °C and submerged for 1 h in a 50 mM Fe₂(SO₄)₃ solution. After this step it was dried again at 40 °C. A third system, the Fe-EDTA-PTFE open air cathode, was prepared by uniformly applying a mixed solution of Fe₂(SO₄)₃, EDTA-4S and PTFE on the activated carbon cloth. The mixture was created by combining 56.25 μL cm⁻² of a 200 mM Fe₂(SO₄)₃ solution, 56.25 μL cm⁻² of a 210 mM EDTA-4S solution (prepared in 0.05 M H₂SO₄) and 5.6 μL cm⁻² of a (60%, w/w dispersion) polytetrafluoroethylene (PTFE)-solution [22]. After the application of this mixture, the activated carbon cloth was dried at 40 °C. The open air cathodes consisted of 2 layers of activated carbon cloth (the projected surface was 104 cm²) and were clamped against a proton exchange membrane (PEM) (Fumapem F-930, FuMA-Tech, Germany). A set of carbon fibres (SGL, Germany) was used as a current collector. The open air cathode frames contained an inlet and outlet to which an individual cathode sprinkling loop was connected in order to continuously sprinkle a 0.5 dm³ 0.7% (w/w) NaCl solution over the cathode surface at a rate of 100 cm³ h⁻¹.

2.4. Anode compartment thickness

By the addition of additional frames to the anode compartment, the volume and thickness of the anode compartment could be increased stepwise (per 156 cm³ or 1.5 cm thickness) from 156 to 780 cm³ anode volume or from 1.5 to 7.5 cm anode thickness. The anode was completely filled with homogenized pre-inoculated graphite granules, as a consequence, the volume and thickness of the electrode also increased from 156 to 780 cm³ or from 1.5 to 7.5 cm, respectively. The addition of an additional frame took about 30 min and during this period, the anode was exposed to oxygen. However, this did not negatively affect the anodic microbial activity and the voltage increased to its original level within a couple of hours. The cathode consisted of a Fe-EDTA treated open air cathode (see above) and was not changed during the course of the experiment. A proton exchange membrane (PEM – Fumapem F-930, FuMA-Tech, Germany) or a cation exchange membrane (CEM-2 – Ionac, Sybron Chemicals, USA) was used. The current generation for each anode compartment thickness was recorded at an external resistance of 7.8 mΩ m³ TAC (the applied external resistances ranged from 50 Ω (156 cm³) to 10 Ω (780 cm³)) during at least 15 h. The volumetric resistance is calculated by multiplying the applied external resistance and the total anode compartment (TAC) volume. By applying a constant volumetric external resistance (mΩ m³), a constant current density was expected as the volume of the reactor was increased.

2.5. Operational conditions and inoculation

All MFCs were operated in a continuous mode and an external resistance of 3.9–7.8 mΩ m³ TAC was used. In order to inoculate the MFCs, the effluent of an active acetate-fed MFC was fed to the MFC during a period of 6 h. Afterwards, a sterile synthetic influent (M9-medium) containing 1.0 g dm⁻³ sodium acetate prepared as previously described [20] was continuously fed to the individual anode frames by a peristaltic pump (Watson Marlow, Belgium) at a flow rate of 13.3 cm³ h⁻¹ corresponding to a volumetric loading rate of 1.6 kg chemical oxygen demand (COD) m⁻³ TAC d⁻¹. Each anode frame had an individual recirculation loop with a flow rate of 100 cm³ h⁻¹, the volumetric recirculation rate was kept constant during all the experiments. The MFCs were operated at a room temperature of 22 ± 2 °C.

2.6. Data acquisition and (electro)chemical analysis

The data acquisition, the calculation of the average current generation, the recording of the polarization curves (recorded in triplicate, scan rate 1 mV s^{-1}) and the determination of the ohmic losses with the current interrupt method was as previously described in Aelterman et al. [19]. The polarization of electrode samples was performed in a half cell at the water-air inter-phase of a 100 mM phosphate buffer solution at pH 7 versus a Ag/AgCl reference electrode (RE-5B, BASi, UK) while a platinum strip served as the counter electrode. The analysis was performed in triplicate and at a scan rate of $10 \mu\text{A s}^{-1}$. In case a polarization curve of the anode (working electrode) and cathode (counter electrode) was recorded during MFC operation, an Ag/AgCl reference electrode was installed close to the anode electrode in the sidewall of the anode frame facing the membrane. In case the open air cathodes were tested in a MFC, a 81 h test procedure was applied consisting of 14 repetitive cycles of, respectively, 1 h open circuit voltage (OCV), the recording of a polarization curve, the current interrupt method and a period of 4 h current generation at 300 mV cell voltage. The redox potential of the catholytes was determined with a glassy carbon electrode versus a Ag/AgCl reference electrode (197 mV versus standard hydrogen electrode (SHE)).

The iron desorption of the open air cathodes was determined in a specific separate desorption experiment. The total iron concentration of a control and iron-treated activated cloth samples (4 cm^2)

were determined by a complete destruction of the samples with aqua regia. During a 14 h desorption experiment, cathode samples (4 cm^2) were shaken in demineralized water (19 mL). When the samples were removed, 1 mL of 12N HCl was added to the liquid to prevent precipitation. By measuring the iron concentration of the liquid phase by atomic absorption (Aanalyst 200, PerkinElmer, VS), the iron desorption could be calculated.

3. Results

3.1. Aerated liquid catholytes

The poor solubility of ferrous and ferric iron at a pH above 2.5 hampers the use of this redox couple as a catholyte in MFCs. By administering iron-chelating molecules, the solubility of the ferric/ferrous couple can be significantly increased even at a neutral pH. Four different iron-chelated catholyte solutions were applied in a MFC with CEM-1. After an initial lowering of the current generation during a period of 1–2 h, the continuous current generation settled at a stable level and lasted for at least a period of 6 days without a need to replenish the cathode liquid for all iron-chelated catholytes (Fig. 1). The Fe-EDTA chelated catholyte generated the highest continuous current of $6.6 \pm 0.7 \text{ mA}$. The ratio of the cumulative charge production and the single oxidation capacity of the iron catholytes varied from 1.95 (Fe-citrate) to 6.86 (Fe-EDTA) (Fig. 1) and was indicative for a reversible iron oxidation reaction. As a

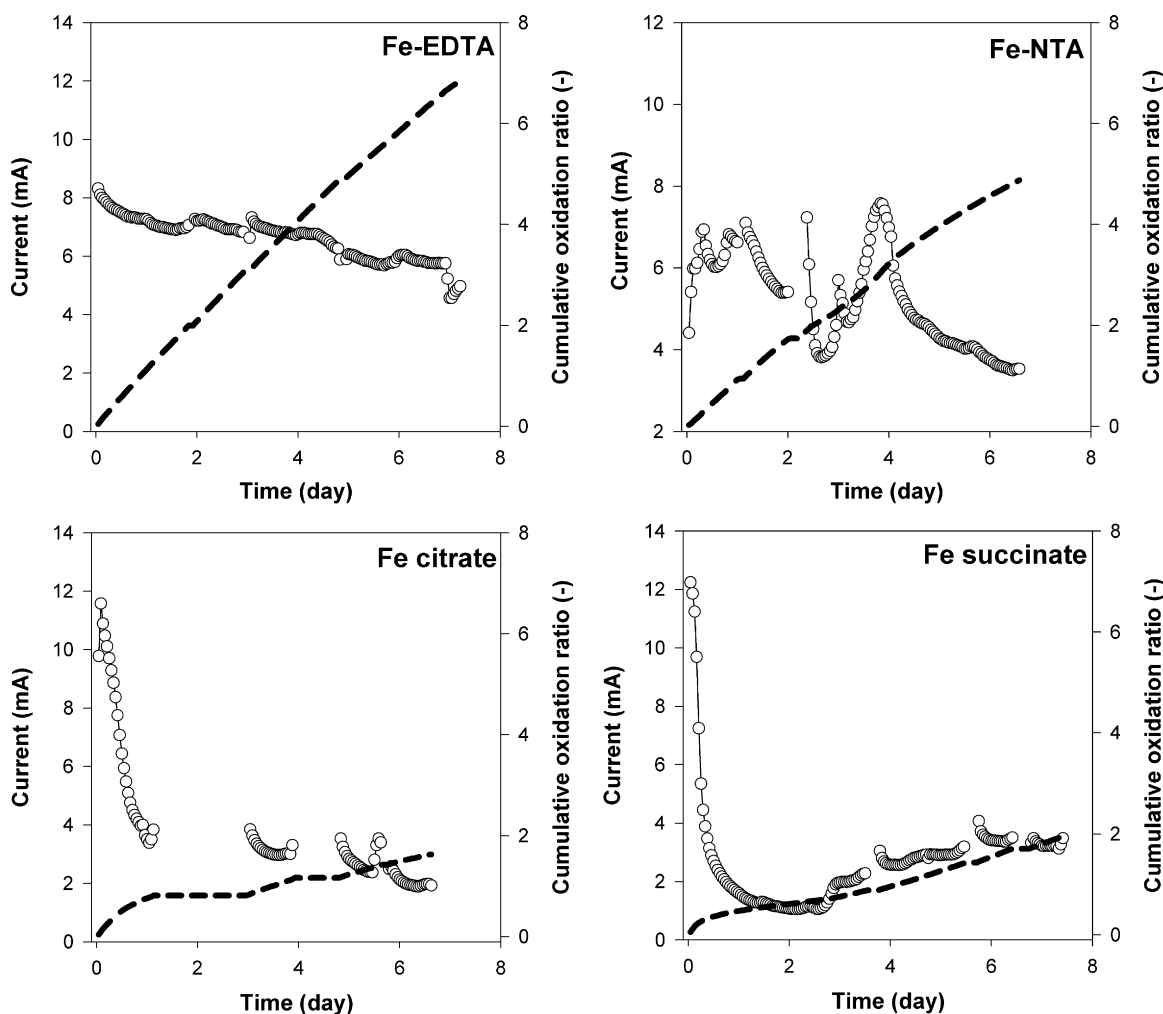


Fig. 1. Overview of the continuous current generation (○) generated by a MFC with a CEM-1 and the ratio of the cumulative charge production and the single oxidation capacity (cumulative oxidation ratio – striped line) for the four iron catholytes.

Table 1

Overview of the equilibrium potential of the catholyte solution (E_h) and operational parameters of the MFCs operated with CEM-1. The reported parameters are: pH (start and end), maximum open circuit potential (OCV_{max}), continuous current generation at 25Ω ($I_{25\Omega}$) ($3.9 \text{ m}\Omega \text{ m}^3$), maximum current generation (I_{max}) and volumetric power generation ($P_{v,max}$) during polarization. The geometric cathode surface area was 104 cm^2 and the total anode compartment (TAC) volume was 156 cm^3 .

Cathode system	E_h^a (mV)	pH		OCV_{max} (mV)	$I_{25\Omega}$ (mA)	I_{max} (mA)	$P_{v,max}$ (W m^{-3} TAC)
		Start	End				
Fe-EDTA	440	3.4	9.5	457	6.6 ± 0.7	34.4 ± 4.3	22.9 ± 10.6
Fe-NTA	479	3.8	9.0	454	5.2 ± 1.3	25.6 ± 3.4	9.9 ± 2.8
Fe-citrate	466	1.9	8.5	452	3.8 ± 1.3	7.8 ± 1.8	2.9 ± 0.8
Fe-succinate	661	1.6	9.3	874	2.6 ± 1.7	9.0 ± 2.8	4.4 ± 1.8
Hexacyanoferrate	384	7.0	7.0	655	12.1 ± 3.1	35.4 ± 7.2	47.1 ± 17.3
Plain graphite	n.a.	7.0	9.3	256	3.8 ± 1.4	20.8 ± 3.0	5.8 ± 1.3

n.a.: not applicable.

^a Expressed versus standard hydrogen electrode (SHE).

comparison, two reference systems were tested: a cathode with a hexacyanoferrate (HCF) solution and a plain graphite cathode operated with a buffer solution. The HCF system outperformed all the tested systems both in terms of current generation and power production but required a regular replacement of the catholyte. Yet, the Fe-EDTA catholyte system generated a comparable maximum current as the HCF system during polarization (Table 1). Fe-citrate and Fe-succinate had a remarkable higher (respectively, factors 2 and 3) open circuit voltage (OCV) compared to the graphite control but nevertheless both the current and power output were a factor 2 lower compared to the control. Moreover, after 6 days a red-dish precipitation was noted in case of the Fe-succinate catholyte, whereas for the other chelating agents no visual Fe-precipitation was observed. Therefore, both the Fe-citrate and Fe-succinate were not regarded as suitable catholytes for MFCs. During the current generation, the pH of all the catholytes of the MFCs with CEM-1 gradually increased to values of up to 9.5 (Table 1). However, when a PEM was used instead of CEM-1, the pH raise of the Fe-EDTA catholyte was limited to 8.7. Moreover, the continuous current generation of the Fe-EDTA system ($8.1 \pm 0.6 \text{ mA}$) was a factor 1.2 higher compared to a similar MFC using CEM-1. Compared to a graphite control with a PEM-MFC the current of the Fe-EDTA PEM-MFC was a factor 1.6 higher (Fig. 2). During a 15-day period of continuous current generation, the cumulative charge production exceeded the single oxidation capacity of the catholyte by a factor 18.3, indicating that the Fe-EDTA was used as a catalyst rather than as a final electron acceptor.

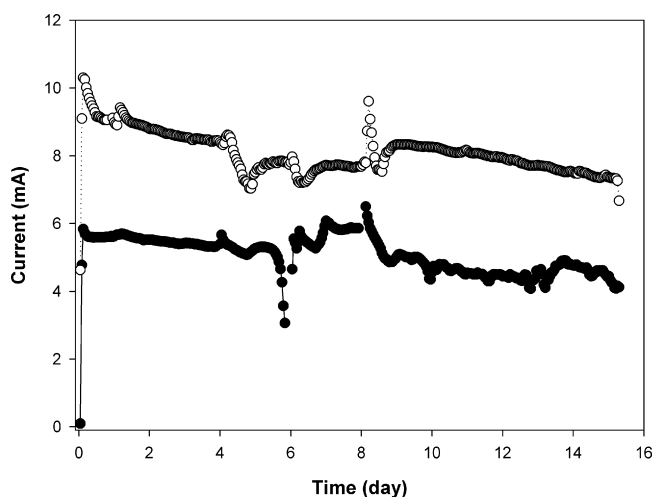


Fig. 2. The continuous current generation by a MFC with a PEM and a graphite electrode in case of an aerated Fe-EDTA catholyte (○) and an aerated mineral medium (●) during a period of 15 days without the replacement of the catholytes.

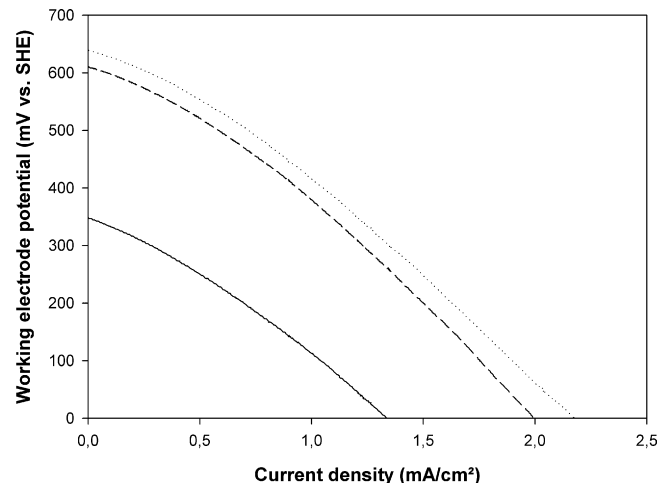


Fig. 3. The polarization curves of freshly prepared air cathode samples: unmodified activated carbon cloth sample (—), the oxidized activated carbon cloth sample (---) and the Fe-EDTA adsorbed activated carbon (···) ($n=3$, scan rate $10 \mu\text{A s}^{-1}$).

3.2. Open air cathodes

The feasibility to adsorb iron chelates on an activated carbon cloth for the application as an open air cathode in a MFC has been tested. Based on the previous results, an open to the air chemical cathode by adsorbing Fe-EDTA on an activated carbon cloth was prepared. This system was compared to an activated carbon

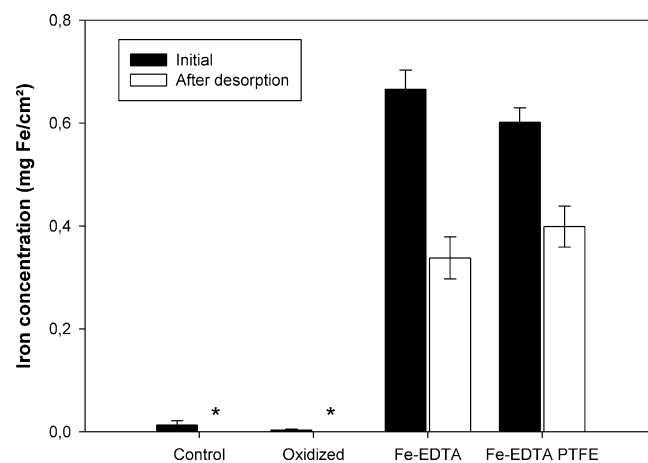


Fig. 4. The initial iron concentration (mg Fe cm^{-2}) determined by a total destruction and the remaining iron concentration after a desorption (14 h) in demineralized water of the control, the oxidized, the Fe-EDTA and the Fe-EDTA-PTFE activated carbon cloth samples ($n=3$) (*not applicable).

Table 2
Open circuit voltage (OCV), continuous current (I_{cont}), continuous power density ($P_{\text{v,cont}}$) and maximum current (I_{max}), and maximum power density (P_{max}) as recorded during polarization for MFCs operated with an open to the air Fe-EDTA–PTFE activated carbon cloth cathode (Fe-EDTA–PTFE), a Fe-EDTA activated carbon cloth cathode (Fe-EDTA) and an oxidized activated carbon cloth cathode (oxidized control).

	OCV (mV)	I_{cont}^a (mA)	I_{max} (mA)	$P_{\text{v,cont}}^a$ (W m^{-3} TAC)	P_{max} (W m^{-3} TAC)
Fe-EDTA–PTFE	613	12.9 ± 1.8	35.4 ± 3.3	3.9 ± 0.5	40.3 ± 2.3
Fe-EDTA	619	8.9 ± 0.4	25.5 ± 2.1	4.0 ± 0.4	33.5 ± 3.5
Oxidized control	636	7.2 ± 0.5	17.8 ± 1.6	2.1 ± 0.2	17.6 ± 1.7

^a Measured at a fixed cell voltage of 300 mV in case of Fe-EDTA–PTFE and oxidized cathodes and at a external resistance of 50 Ω (average 440 mV) in case of a Fe-EDTA cathode.

cloth control which was chemically oxidized with strong acids to induce the formation of catalytic centers on the surface. The electrochemical properties of freshly prepared samples of, respectively, an unmodified activated carbon cloth, an oxidized activated carbon cloth and a Fe-EDTA absorbed activated carbon cloth are shown in Fig. 3. Both the oxidative and the Fe-EDTA treatment resulted in a remarkable increase of the OCV (factor 2) and the maximum current density (factor 1.4) compared to an original untreated activated carbon cloth sample. The initial iron concentrations present on both the untreated control, the oxidized control and the Fe-EDTA treated activated carbon cloth are shown in Fig. 4. Up to 0.6 mg Fe cm^{-2} could be retained on the activated carbon cloth by applying an adsorption of Fe-EDTA. However, by shaking a sample in demineralized water during a period of 14 h, 49% of the iron was found to be desorbed. By supplementing PTFE to the Fe-EDTA mixture, the desorption of iron could be decreased to 37%, although the final iron concentration on the Fe-EDTA–PTFE sample was not significantly higher compared to the Fe-EDTA sample. Table 2 gives an overview of the performance of the oxidized, the Fe-EDTA and the Fe-EDTA–PTFE activated carbon cathodes when applied in a MFC. The three open air cathodes systems proved to generate a stable current generation during a period of at least 6 days without a need to replenish the catalyst. The maximum OCV was comparable for the three systems, but the maximum power density during polarization of the two iron-treated activated carbon samples was about twice that of the oxidized activated carbon cloth (Table 2). The continuous current generation of the Fe-EDTA–PTFE cathode was 1.8 times higher compared to the oxidized control cathode. Analogous to the iron-chelated catholytes, an increase of the pH cathodic sprinkling liquid to values of up to 8.6 was noted.

3.3. Anode thickness

The spacing of the electrodes is an important issue for the future scale-up of MFCs. By increasing the anode compartment thickness (resulting in an increased three dimensional electrode thickness), the influence on the volumetric current and power generation for a given open air cathode surface was investigated. The continuous current generation of a MFC with a Fe-EDTA activated carbon open air cathode and PEM during subsequent periods of 15 h gradually increased from 8.9 ± 0.4 to 22.5 ± 1.0 mA when the thickness of the anode compartment was increased from 1.5 to 6.0 cm at an equivalent external resistance of $7.8 \text{ m}\Omega \text{ m}^3$ TAC. However, when the anode compartment thickness measured 7.5 cm, the current generation lowered to 16.4 ± 2.6 mA. The continuous current of the CEM-2 operated MFC, only increased when the anode thickness was enlarged from 1.5 till 4.5 cm (7.8 ± 0.4 to 15.2 ± 0.9 mA) after which the continuous current generation leveled off to about 10.8 mA (6.0 and 7.5 cm anode compartment thickness). Thus, the addition of additional anode units did not result in a proportional increase of the current generation and as a consequence a decrease of the volumetric current density was noted. The maximum volumetric power density measured during polarization also decreased when

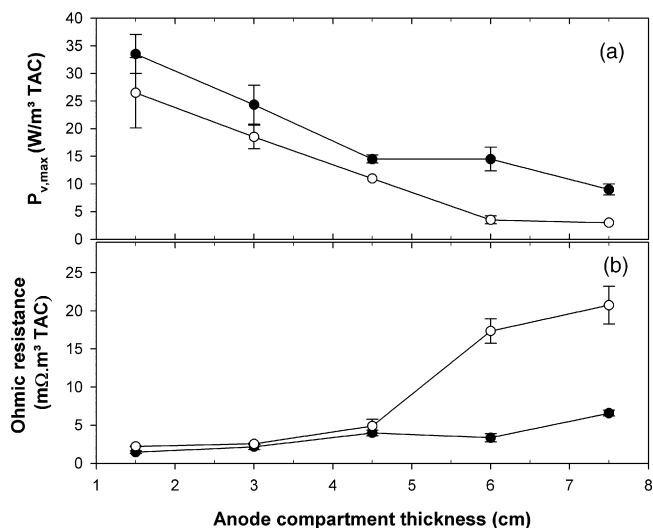


Fig. 5. Maximum volumetric power density (W m^{-3}) and ohmic resistance ($\text{m}\Omega \text{ m}^3$) in function of an increasing anode compartment thickness (cm) (equivalent volume of 156–780 cm^3 in steps of 156 cm^3) of two MFCs with an open air Fe-EDTA cathode and a proton exchange membrane (●) and a cation exchange membrane (CEM-2) (○) ($n=3$), respectively.

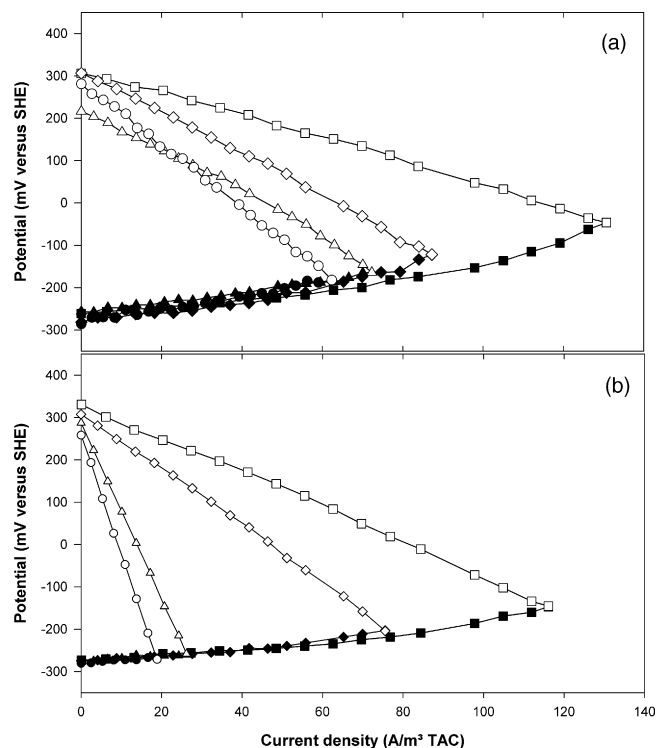


Fig. 6. Overview of the polarization curves of the anode (black symbols) and cathode (white symbols) of MFCs operated with a Fe-EDTA cathode and, respectively (a) a proton exchange membrane (PEM) and (b) a cation exchange membrane (CEM-2) in function of the anode compartment thickness (square: 3 cm, diamond: 4.5 cm, triangle: 6 cm, circle: 7.5 cm) ($n=3$, scan rate 1 mV s^{-1}).

the thickness of the anode compartment was increased (Fig. 5). Moreover, an increase of the ohmic losses was noted and, in case of the CEM-2 operated MFC, a sharp rise of the ohmic losses was noted to $20.7 \text{ m}\Omega \text{ m}^3 \text{ TAC}$ from an anode thickness of 6 cm on (Fig. 5). Overall, the MFC with the PEM membrane yielded the highest power output and the lowest ohmic losses. Fig. 6 shows the polarization curves of the anode and the cathode of the PEM and CEM-2 operated MFC in function of the anode compartment thickness. The slope of the anode polarization curve was indifferent of the anode thickness and membrane type. However, the slope of the cathode polarization curve (which included the electrolyte and membrane losses) decreased when the anode thickness was increased. Also a sharp decrease of the slope of the cathodic polarization was noted when the anode thickness was increased from 4.5 to 6.0 cm. Even with the PEM membrane, the pH of the cathodic sprinkling liquid increased to a pH of up to 9.6, in case of the CEM-2 membrane the pH increased to 10.3.

4. Discussion

4.1. A sustainable cathode reaction

There is a need for a sustainable and economic cathode reaction for MFCs. We demonstrated that an iron-chelated complex could effectively be used as a catholyte or as an iron-chelated open air cathode to generate current with the use of MFCs. The setups enabled a stable continuous current generation of up to 12.9 mA without a need to replenish the catalyst. Overall, the Fe-EDTA complex yielded the best results although a substantial difference was noted between the catholyte and the absorbed open air system. While both systems generated a similar maximum current, the OCV and maximum power output of the open air system were considerably higher. This was probably due to the higher oxygen concentration present in the open air system or due to an additional reactivity of activated carbon towards oxygen [15]. Moreover, if the volume of the open air cathode compartment is neglected, the power density based on the total MFC reactor of the open air systems ($156 \text{ cm}^3 \text{ MFC}$) was about four times higher compared to the catholyte system ($312 \text{ cm}^3 \text{ MFC}$). Alternative non-noble metal-based open air cathodes such as pyr-FePc and pyr-CoTMPP have been reported by Zhao et al. [13] and generated, respectively, up to 13.9 and $14.3 \text{ W m}^{-3} \text{ MFC}$ in a $0.5 \text{ dm}^3 \text{ MFC}$. A MFC operated with a bipolar membrane and using an iron catholyte which was biologically re-oxidized, generated a maximum power density of up to $28 \text{ W m}^{-3} \text{ MFC}$ [8]. Compared to these results, the Fe-EDTA-PTFE open air MFC enabled a higher power density of $44 \text{ W m}^{-3} \text{ MFC}$ but it must be noted that the latter reported reactors were not designed for high volumetric power outputs. However, both a platinum catalyzed [12] and a biological cathode [14] operated MFC enabled a threefold higher power output compared to a MFC with a Fe-EDTA cathode. Nevertheless, these MFCs, respectively, required a costly precious metal or a careful operation to maintain an active cathodic microbial community. Therefore, the Fe-EDTA cathode represents a cost-effective cathode for MFCs.

4.2. Chelating system: type and application

The equilibrium redox potential of the different chelating systems (Eh – Table 1) was not representative for the corresponding MFC performance, e.g. Fe-succinate had the highest Eh and OCV but yielded the lowest current and power output. Although, Freguia et al. [11] demonstrated that plain graphite electrodes are able to catalyze the oxygen reduction in MFCs resulting in a power generation of up to $11 \text{ W m}^{-3} \text{ MFC}$, in the case of Fe-citrate and Fe-succinate, a steep drop of the current to levels below the current generated by

a graphite control was noted. The initial drop was probably related to a lowering of the Fe(III)/Fe(II) ratio due to an insufficient re-oxidation of these iron chelates by oxygen. In addition, the type of chelating agent can have an influence on the oxidation of Fe(II) by oxygen. Santana-Casiano et al. [18] reported that alanine and glutamic acid did not affect the oxidation kinetics of Fe(II) while ethylenedioxidiethylenedinitrioxetetra-acetic acid (EGTA) formed a strong ferrous complex that inhibited the oxidation of Fe(II). In contrast, EDTA increased the oxidation rate of Fe(II) to Fe(III) and due to a photoreduction of Fe(III)-EDTA in the presence of light, Fe(II)-EDTA was even regenerated [18]. Our results also indicated an enhanced oxidation of Fe-EDTA and Fe-NTA by oxygen compared to Fe-citrate and Fe-succinate. In addition, we demonstrated the feasibility to electrochemically reduce iron-chelated solutions on an electrode surface. The combination of these two factors resulted, especially in the case of Fe-EDTA, in a suitable catholyte for MFCs. However, it must be noted that although only in the case of Fe-succinate a loss of the chelating capacity was noted, a loss of the chelating properties of the recalcitrant Fe-EDTA complex due to biodegradation [23] or photochemical degradation [24] might occur on the long term.

The Fe-EDTA system was successfully applied on an open air cathode, and based on the polarization curves of freshly prepared cathode samples (Fig. 3), similar current densities as described for pyr-CoTMPP modified graphite foil were obtained [22]. Although, modifying the activated carbon support by an oxidative treatment resulted in a higher reactivity towards oxygen [15], its performance during fuel cell operation was lower compared to an iron treatment. Afkhami et al. [25] reported that the adsorption of EDTA on activated carbon increased its capacity to adsorb various metals, including iron. Our results indicate the feasibility to adsorb up to $16.7 \text{ mg Fe g}^{-1}$ activated carbon cloth although a desorption of 49% was noted during the specific desorption experiment. According to Afkhami et al. [25], concentrations of up to $44.6 \text{ mg Fe g}^{-1}$ on an EDTA pretreated activated carbon adsorbent are achievable. Increasing the amount of iron on the open air cathodes or lowering its desorption, might further enhance its catalytic activity and hence boost the power output of MFCs.

4.3. Anode thickness and membrane type

Both the conductivity of the medium and the ohmic losses of the reactor seriously hamper the practical implementation of MFCs [9,10]. The electrode spacing is an important parameter for future upscaling of MFCs. Our results indicate that increasing the thickness of the anode compartment and resulting electrode of a three dimensional anode did not result in an increase of the absolute power generation proportional to an increase of the anode compartment volume. As a consequence the power density lowered and a maximum attainable absolute power output was found. The type of membrane used had a significant influence on the reactor performance, although in both cases a considerable increase of the pH in the cathode compartment was noted. The latter could account for a lowering of the current (Figs. 1 and 2) as reported by Zhao et al. [22], although recently He et al. [26] reported a decrease of the cathodic polarization resistance with increasing pH, indicating that the oxygen reaction rate increased at a higher pH. The precise effect of the pH on the reactivity of the cathode warrants further research. Even though, compared to other ions, protons and hydroxide ions exhibit anomalously high mobilities in aqueous solutions which have been explained as structural diffusion, thermal hopping, proton tunneling or solvation effects [27], the relatively higher concentration of other ions in the electrolyte favors their transfer compared to protons, and as a result, independent of the type of membrane used, an increase of the pH in the cathode compartment has been reported [28,29]. Therefore, to further increase the

performance of MFCs, there is a need for a membrane specifically designed for the conditions at which MFCs work, i.e. neutral pH and aqueous electrolytes. The optimization of the membrane cathode inter-phase could result in a further improvement of the cathode reaction and in an omission of the sprinkling loop which was used to humidify the cathode. Moreover, to obtain the maximum power densities for a given reactor volume, multiple thin units are preferred over one thick reactor system. However, when the costs are taken into account, the price per unit of power generated will define the most economical solution.

5. Conclusions

The use of the Fe-EDTA complex enabled the operation of MFCs with either a sustainable catholyte or with an iron loaded open air cathode. During the operation of the MFC, a stable current generation of up to 15 days was achieved and no regeneration of the catalyst was required although an increase of the pH in the cathode compartment was noted. The maximum power output was comparable to that of previously described MFCs with non-precious metal catalysts cathodes, although a biological and a platinum cathode had a threefold higher power output. An increase of the anode electrode volume did not result in an improvement of the power density. Therefore, to maximize the power output for a given reactor volume, it is suggested to use multiple small systems of about 1.5 cm thickness, rather than one thick anode compartment.

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