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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.

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 cm^3 and use an unsustainable catholyte [7]. In contrast, the power output of dm^3 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 cobalttetramethoxyphenylporphyin (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 cm^3. 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 cm^3. 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 $Fe_2(SO_4)_3$, 100 mM EDTA-4S), iron nitrilotriacetic acid (Fe-NTA – 50 mM $Fe_2(SO_4)_3$, 100 mM NTA), Fe-succinate (50 mM $Fe_2(SO_4)_3$, 100 mM $C_4H_6O_4$) and Fe-citrate (100 mM $C_6H_5FeO_7$). 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 $K_3Fe(CN)_6$ aqueous solution in a 100 mM KH_2PO_4 buffer (Merck, Belgium) [19]. A cation exchange membrane (CEM-1 – Ultrex^{TM} 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 HNO_3 and concentrated H_2SO_4 (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 $Fe_2(SO_4)_3$ 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 $Fe_2(SO_4)_3$, EDTA-4S and PTFE on the activated carbon cloth. The mixture was created by combining 56.25 $\mu L\,cm^{-2}$ of a 200 mM $Fe_2(SO_4)_3$ solution, 56.25 $\mu L\,cm^{-2}$ of a 210 mM EDTA-4S solution (prepared in 0.05 M H_2SO_4) and 5.6 $\mu L\,cm^{-2}$ 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 cm^2) 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 dm^3 0.7% (w/w) NaCl solution over the cathode surface at a rate of 100 $cm^3\,h^{-1}$.

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 cm^3 or 1.5 cm thickness) from 156 to 780 cm^3 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 cm^3 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 $m\Omega\,m^3$ TAC (the applied external resistances ranged from 50 Ω (156 cm^3) to 10 Ω (780 cm^3)) 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 ($m\Omega\,m^3$), 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 $m\Omega\,m^3$ 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 $cm^3\,h^{-1}$ 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 $cm^3\,h^{-1}$, the volumetric recirculation rate was kept constant during all the experiments. The MFCs were operated at a room temperature of 22 ± 2 °C.