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Electricity generation by a plant microbial fuel cell with an integrated oxygen reducing biocathode

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HIGHLIGHTS

- An oxygen reducing biocathode was successfully integrated in a PMFC.
- New two week record average power densities of 240 mW/m^2 PGA.
- 127 mV higher cathode potential with a biocathode than with a chemical cathode.
- PMFC is completely sustainable technology with biocatalyst in the anode and cathode.

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ABSTRACT

In this study we show that a chemical ferricyanide cathode can be replaced by a biological oxygen reducing cathode in a plant microbial fuel cell (PMFC) with a new record power output. A biocathode was successfully integrated in a PMFC and operated for 151 days. Plants growth continued and the power density increased reaching a maximum power output of 679 mW/m^2 plant growth area (PGA) in a 10 min polarization. The two week record average power densities was 240 mW/m^2 PGA. The new records were reached due to the high redox potential of oxygen reduction which was effectively catalyzed by microorganisms in the cathode. This resulted in a 127 mV higher cathode potential of the PMFC with a biocathode than a PMFC with a ferricyanide cathode. We also found that substrate availability in the anode likely limits the current generation. This work is crucial for PMFC application as it shows that PMFC can be a completely sustainable biotechnology with an improved power output.

1. Introduction

The threat of climate change, the depletion of fossil fuels, environmental pollution and the growing energy demand increase the urgency for new sustainable and reliable energy sources [1]. Several solar, hydro, wind and bio-energy technologies are already implemented and common in day-to-day life. The market share of bioenergy, such as bioethanol, bioelectricity and biodiesel is increasing [2]. However, bioenergy is not always sustainable. Deforestation and competition with food production for arable land are two occurring disadvantages [3]. The plant microbial fuel cell (PMFC) is an emerging technology which can produce electricity via living plants. PMFC is sustainable because it is renewable, has a clean conversion without emissions and has no competition for arable land or nature [4]. In the PMFC, plants grow in the anode where rhizodeposits are the substrates oxidized by electrochemically active bacteria to generate electricity. Natural wetlands offer a new electricity source in which PMFC can be integrated without extensive excavation of the soil [5]. PMFCs can also be implemented in rice paddy fields combining food and electricity production and so circumventing the competition with food production [6,7]. In addition, PMFC can be integrated in green roofs, combining the advantageous of green roofs (e.g. insolation, biodiversity) and electricity generation [8]. Even though PMFC is based on photosynthesis, it is expected to deliver electricity 24 h per day and year-round in case of suitable conditions (e.g. temperature and plant growth) [9]. The theoretical maximum electricity output of a PMFC is 3.2 W/m^2 plant growth area (PGA) [10], currently a long term output of 0.155 W/m^2 PGA is reached [11].

For research purpose often ferricyanide is used in PMFC as final electron acceptor. Ferricyanide is unsustainable as it reacts to fer-

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rocyanide and is not able to react back to ferricyanide within the PMFC. The reduction of ferric- to ferrocyanide is fast resulting in a minimal resistance of the cathode [12]. Ferricyanide is therefore suitable to investigate the limitations of the anode. For sustainable electricity production, ferricyanide cannot be used as final electron acceptor. Oxygen is preferred because it has an high redox potential, is widely available and the product is plain water [13]. Graphite is often used as cathode material in a PMFC. However, the reduction of oxygen on graphite is slow [14] and limits the power output of the PMFC [9]. Electrocatalysts like platinum are able to catalyze the reduction of oxygen. The high costs and the potential poisoning compounds in the solution make platinum undesired to be applied in the PMFC [15]. The reduction of oxygen can also be catalyzed with mixed culture microorganisms [16]. Microorganisms are cheap, self-replenishing and can be used in combination with the graphite electrodes [17]. Mixed culture microorganisms are able to catalyze the reduction of oxygen by growing a biofilm on graphite electrodes and are able to reach a stable current density of 0.55 A/m^2 projected electrode surface area (non-porous electrode) at pH 7, 31 °C and a controlled cathode potential of 150 mV vs Ag/AgCl [18].

Oxygen reduction can also be indirectly catalyzed by microorganisms for example by ferrous iron oxidizing microorganisms (*Acidithiobacillus ferrooxidans*). On the electrode surface, ferric iron is chemically reduced to ferrous iron. The microorganisms in the catholyte oxidize the ferrous iron back to ferric iron to maintain the concentration of ferric iron in the cathode. Higher current densities (4.4 A/m^2 projected electrode surface area; porous electrode) are reached with ferric iron reduction. A bipolar membrane is required between the anode and the cathode to maintain the solubility of iron in the cathode (pH < 2.5). [19]

The capacity of catalyzing microorganisms in the cathode of the PMFC in the range 0.55–4.4 A/m^2 projected surface area exceeds the long term average current density of the best performing PMFC (0.38 A/m^2 PGA) [11]. Also the potential of oxygen reduction (+0.60 V vs Ag/AgCl (pH 7)) and ferric iron reduction (+0.56 V vs Ag/AgCl) are higher than the potential of ferricyanide reduction (+0.20 V vs Ag/AgCl at pH 7 with 20 mM phosphate buffer) [20].

Replacing the ferricyanide reduction by a biocathode in the PMFC is a crucial step in the development of the technology towards its application. A biocathode in PMFC will make PMFC a sustainable biotechnology without decreasing the current and power output compared to a ferricyanide cathode. Oxygen reducing biocathodes are already combined with a bioanode in sediment microbial fuel cells [21] and single chamber microbial fuel cells [22].

The objective of this study is to show that a ferricyanide cathode can be replaced by an oxygen reducing biocathode in a PMFC without decreasing the power output. This study combines a bioanode and biocathode by integrating an oxygen reducing biocathode in a PMFC. First, the PMFC with a chemical oxygen reducing cathode was started and studied. Afterwards, the cathode was inoculated with microorganisms and an oxygen reducing biocathode was developed. The biocathode included, besides the microorganisms which catalyzed the oxygen reduction, also photothrophic algae which increased the oxygen concentration in the cathode during illumination. An adaptive control strategy was applied and long term performances and limitations of the biocathode PMFC were revealed.

2. Material and methods

2.1. Experimental setup

For the experiment a flat porous plate PMFC was constructed using transparent plastic plates (Fig. 1). The PMFC had one anode compartment with a size of 190 × 30 × 190 mm (l × w × h) and a PGA of 27 cm^2 (160 × 17 mm). Two cathode compartments of each 190 × 10 × 190 mm were connected to both flat sides of the anode. The anode and cathode were separated by a BPM (fumasep FBM, FuMa-tech GmbH, St. Ingbert, Germany) to maintain the pH gradient between the anode and cathode [19]. The anode was made from three layers of graphite felt (190 × 30 × 50 mm) by stacking several layers of felt (190 × 10 × 50 mm) (10 mm Grade WDF, National Specialty Products Carbon and Graphite Felt, Taiwan) [23]. The three layers were physically separated with plastic rings (D = 10 mm) to create a top, middle and bottom anode section. Each section of the anode and both cathode were connected with a golden wire as current collector. In this experiment, the differences in current distribution between the three layers was not analyzed and the three layers were therefore electrically connected together during the entire experiment. Also the cathodes were made of graphite felt. Unlike the anode, the cathodes consisted only of one layer of graphite felt (3 mm, Grade WDF, National Specialty Products Carbon and Graphite Felt, Taiwan).

In the anode the salt water grass species *Spartina anglica* was planted. This grass species was also used in previous PMFC researches [11,23,24]. The plants were collected at the Dutch coast one week before the experiment was started at the same location as was used in earlier PMFC research (GPS coordinates N51°.67654 E004°.13656) [24]. In the PMFC, several stems of *S. anglica* were planted with a total weight of 55 g. Also 86 g of dead roots were added to the anode of the PMFC which can accelerate the start-up, due to the availability of hydrolysable organic matter.

2.2. Operation

On day 1 of the experiment the plants were planted in the anode. The plants were constantly kept waterlogged by pumping a nitrate-less, ammonium-rich plant growth medium from a storage tank into the anode (Gilson minipuls 3, Den Haag, The Netherlands, 1 rpm, up to 300 ml/day). The used medium showed the best performance [11]. The medium was constantly flushed with nitrogen and included micronutrients [24] and 5 g/L NaCl. The PMFC was operated in a climate chamber at a temperature of 20 °C and a humidity of 70% (Microclima 1750, Snijders Scientific, Tilburg, The Netherlands). The light and dark ratio was 14:10 h and the average PAR light intensity during illumination was 373 ± 125 μmole m^{-2}s^{-1} (82 ± 28 W/m^2) measured at the top, middle and bottom height of the leaves with a light meter (Li-250A, Li-cor, Lincoln, USA). The light intensity on the cathode was 37 ± 10 μmole m^{-2}s^{-1} (8 ± 2 W/m^2).

The PMFC was started with a mixed culture oxygen reducing biocathode and was inoculated with aerobic wastewater from the treatment plant in Bennekom, the Netherlands on day 26 and again on day 182. Aerobic wastewater contains among others bacteria, fungi, algae and protozoa [25]. On day 182 also catholyte from a running oxygen reducing biocathode at pH 7 was added [18]. The mixed culture biocathode was started at pH 7 (+/−0.5) by manually adjusting the pH with NaOH and HCl. The pH was only adjusted to pH 7 until the biocathode started up. The catholyte consisted of phosphate buffer (0.02 mol/l), macro- and micronutrients [26] and vitamins [19]. The catholyte was constantly recirculated via a one liter bottle through both cathodes (Watson-Marlow 505S, Rotterdam, The Netherlands, 30 rpm, 150 ml/min) and kept air saturated with pressurized air. From day 292 to day 323 the recirculation and aeration of the cathode was stopped to investigate the oxygenic photothrophic effect in the cathode. On day 323 the recirculation and aeration was started again.

The PMFC was controlled with an external resistance of 1000 Ω between the anode and cathode from day 1 until day 182. From day 182 until day 323 the cathodes were controlled with a potentiostat (Vertex, Ivium Technologies, Eindhoven, The Netherlands).