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Characterization of the internal resistance of a plant microbial fuel cell

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ABSTRACT

The objective of this research was to clarify the internal resistance of the PMFC. To characterize internal resistances of the PMFC current interrupt and polarization were used, and partial resistances were calculated. The internal resistance consisted mainly of anode resistance and membrane resistance which both decreased during current interrupt. The anode resistance was the result of mass transfer resistance in the electrochemically active biofilm. The membrane resistance was the result of accumulation of cations in the cathode. The polarization showed a distinct hysteresis which was explained by the increase of the internal resistance during polarization. The increase of this resistance makes it difficult to interpret the maximum power output of the PMFC.

1. Introduction

Increase of energy demand and depletion of fossil fuels result in a need for more renewable energy sources. Growing plants to produce renewable and sustainable bio-energy is an option because plant growth is based on photosynthesis which is renewable. The plant microbial fuel cell (PMFC) is a technology that has the potential to contribute to the need for a clean renewable energy source [1–3]. It is renewable because is driven by solar radiation (photosynthesis). The PMFC technology is clean because energy generation is based on bio-catalysts and therefore does not require the use of toxic catalysts and mediators. The advantage of the PMFC over conventional renewable energies based on plant growth is that it can be integrated with food production [4,5] and can be applied at locations unsuitable for food production like green roofs [3].

In the PMFC, the plant roots are integrated in the anode of a microbial fuel cell (MFC) [1], where roots provide electrochemically active bacteria with substrate via rhizodeposition (loss of (in)organic material by roots). Electrochemically active bacteria transfer electrons to anode electrode via oxidation of substrate which yields carbon dioxide, protons, and electrons [6]. Subsequently the electrons flow through an electrical circuit and power harvester to the cathode, where they are consumed by typically oxygen reduction. The produced carbon dioxide is converted again into substrate for electrochemically active bacteria by photosynthesis. In this manner, the PMFC produces in situ renewable electrical power in a clean manner.

Based on the highest reported values for photosynthesis, rhizodeposition and energy recovery in a MFC, the estimated maximum power production of the PMFC is 3.2 W m^{-2} (280,000 kWh ha^{-1} $year^{-1}$) [3]. Nevertheless, the reported power production of different PMFCs setups ranged from 0.22 to 0.0060 W m^{-2} of planted area [4,5,1,7,2] which is less than 10% of the maximum. The power output of the PMFC is a combination of the coulombic efficiency and voltage efficiency. The coulombic efficiency of the PMFC is affected by the presence of alternative electron acceptors [8] and microorganisms [9]. Helder et al. [10] showed that the power output increased in the absence of nitrate in the medium for the PMFC. Until now there is no clear insight in the voltage efficiency of the PMFC, although this is required to improve the power output. The voltage efficiency is determined by the potential losses during current generation and thus the internal resistance. Reported internal resistances of the PMFC are determined as the slope of the polarization curve and show a large variance between 21 Ωm^2 [5] and 0.5 Ωm^2 [1]. To increase the power production the internal resistance of the PMFC must be decreased. Until now there is no explanation for the high internal resistance of the PMFC compared to the internal resistance of the microbial fuel cells. In addition, the polarization behavior of the PMFC showed a typical very distinct hysteresis which is not reported for MFC.

The objective of this study was to clarify the internal resistance of the PMFC. In order to do so the current interrupt method and polarization technique were used. In order to calculate the partial resistances the cell, cathode, and anode potential were measured together with the pH, and conductivity in the anode of a PMFC.

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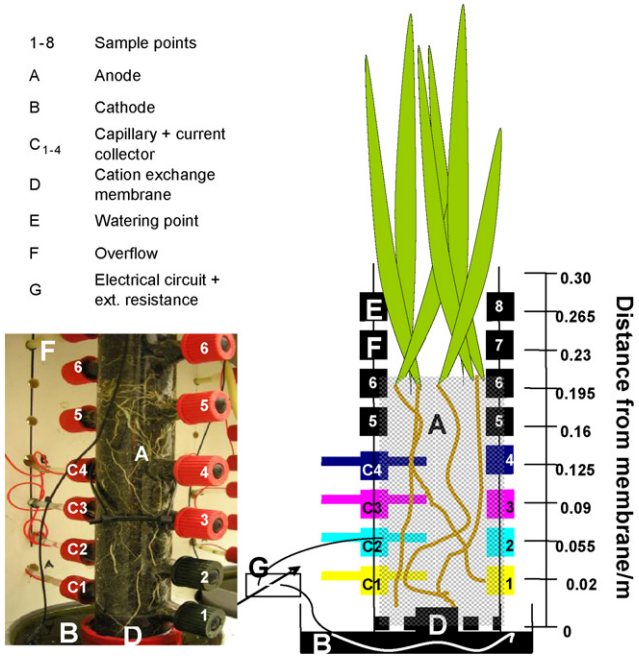

Fig. 1. Schematic presentation of the PMF setup.

To determine whether or not the internal resistance and polarization behavior was unique for the PMFC, a MFC setup without (plant)roots was also evaluated.

2. Experimental

2.1. Set-up

Fig. 1 shows a schematic representation of the experimental set-up. The anode compartment of the set-up consisted of glass cylinder with diameter of 0.035 m, height of 0.3 m, and two sample points opposite to each other at 0.02, 0.055, 0.09, 0.125, 0.16, 0.195, 0.23, 0.265 m from the bottom of the cylinder. At the bottom of the cylinder, a cation exchange membrane (fumasep®, FKB FuMA-Tech GmbH, St Ingbert, Germany) was fixed to separate the anode from the cathode compartment. The glass cylinder was filled with 165 g of graphite granules with a BET surface of 0.5 m^{-2} g to function as anode electrode. The cathode compartment consisted of a polyvinyl chloride (PVC) beaker with diameter of 0.11 m, and height of 0.04 m. This beaker included graphite felt to function as cathode electrode. The anode compartment was placed in the PVC beaker on top of the graphite felt. A gold wire glued to a teflon coated copper wire was used as current collector in both the anode and cathode. Current collectors were connected over a resistance of 900 Ω to close the electrical circuit.

Before the plant *Glyceria maxima* was planted, the set-up was operated as a MFC fed with 0.02 mol L^{-1} acetate. The medium used to grow electrochemically active bacteria on the graphite granules was ½ Hoagland buffered with 0.008 mol L^{-1} potassium phosphate buffer solution (pH 6.8).

Before graphite granules with the electrochemically active biofilm were used for PMFCs, they were mixed and rinsed with tap water to remove any residual substrate. In total, there were 6 PMFCs. In each PMFC, one stem of *G. maxima* (D'n Bart Waterplanten, the Netherlands) with a mass between 4.4 g and 7.8 g was planted. The medium used to feed the PMFCs was ½ Hoagland buffered with 0.008 mol L^{-1} potassium phosphate buffer solution as described by Timmers et al. [2] (pH 6.8, conductivity between 1.5 and 1.7 mS m^{-1}). The medium was fed through a sample point located 0.07 m above the graphite granules. The applied flow rate was 0.17 mL s^{-1} throughout the experimental period. The feeding frequency of the PMFC with buffered Hoagland medium was 5 min every 12 h.

Both, MFC and PMFC, setups were placed in a climate control cabinet (Microclima 1750 Snijders, Tilburg the Netherlands). In this manner, environmental conditions were fixed at illumination period of 14 h d^{-1}, average light density in the photo active region of 596 ± 161 μmol m^{-2} s^{-1}, temperature of 25 °C, and humidity of 75%.

2.2. Measurements

Cell potential (E_{cell}) was measured every 60 s online with data acquisition instrument (Fieldpoint module FP-AI-112) connected to a personal computer with Labview software via a Fieldpoint Ethernet Controller Module FP-2000 (National Instruments, Austin USA). Similarly, anode potentials and cathode potential were measured vs silver/silverchloride (Ag/AgCl) reference electrodes (3 mol L^{-1} KCl electrode, ProSense QiS, Oosterhout, the Netherlands, +205 mV vs. NHE). To determine the anode potential profile, the anode potentials were measured at 0.02, 0.055, 0.09, and 0.125 m from the membrane.

Samples were taken with a syringe (2 mL) through a septum. pH, conductivity and volatile fatty acids were measured in the samples. The pH was measured with a pH-electrode (Prosense Qis, Oosterhout, the Netherlands) together with a pH-meter (Metrohm 691 pH-meter Herisau, Switzerland). Conductivity was measured with a ProLine Plus conductivity meter (Prosense Qis, Oosterhout, the Netherlands). Volatile fatty acids concentration were measured as described by Timmers et al. [2].

2.2.1. Electrochemical characterization

The current interrupt technique, in which current generation is interrupted by opening the electrical circuit, gives an indication of the ohmic potential loss of the (P)MFC. To see the effect of the current interrupt method on the cell, anode, and cathode potential the current was interrupted by disconnecting the cathode from the resistance for about 4 h.

To acquire polarization curves, chronoamperometry was performed with an IviumStat potentiostat and IviumSoft software (IVIUM technologies B.V. Eindhoven, the Netherlands). The controlled cell potential was decreased stepwise from 0.4 V to 0.005 V (via 0.2 V, 0.1 V, and 0.05 V), and further raised again stepwise from 0.005 to 0.4 (via 0.05 V, 0.1 V, and 0.2 V). Each controlled cell potential was maintained for 5 or 60 min to study the effect of time on the power output. To measure the pH profile, pH-electrodes (Prosense Qis, Oosterhout, the Netherlands) were inserted at 0.02, 0.055, 0.09 and 0.125 m from the CEM in the PMFC. The pH electrodes were connected to a pH controller (Liquisis M CPM 253, Endress + Hauser, Reinach, Switzerland) which was connected to the Fieldpoint Ethernet Controller Module FP-2000 (National Instruments, Austin, USA).

2.3. Calculations

2.3.1. Profile gradients

Profile gradients of anode, pH and conductivity were defined as the slope of the linear trend line fitted to the profile. The anode potential gradient dE_{an}/dx was expressed in V m^{-1}, the pH gradient was expressed as dpH_{an}/dx in pH m^{-1}, and the conductivity gradient was expressed as $d\sigma_{an}/dx$ in S m^{-2}.