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SHORT COMMUNICATION

Green electricity production with living plants and bacteria in a fuel cell

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SUMMARY

The world needs sustainable, efficient, and renewable energy production. We present the plant microbial fuel cell (plant-MFC), a concept that exploits a bioenergy source *in situ*. In the plant-MFC, plants and bacteria were present to convert solar energy into green electricity. The principal idea is that plants produce rhizodeposits, mostly in the form of carbohydrates, and the bacteria convert these rhizodeposits into electrical energy via the fuel cell. Here, we demonstrated the proof of principle using Reed mannagrass. We achieved a maximal electrical power production of 67 mW m^{-2} anode surface. This system was characterized by: (1) nondestructive, *in situ* harvesting of bioenergy; (2) potential implementation in wetlands and poor soils without competition to food or conventional bioenergy production, which makes it an additional bioenergy supply; (3) an estimated potential electricity production of 21 GJ ha^{-1} $year^{-1}$ (5800 kWh ha^{-1} $year^{-1}$) in Europe; and (4) carbon neutral and combustion emission-free operation.

KEY WORDS: plant microbial fuel cell; solar energy; bioenergy; rhizodeposits; green electricity

1. INTRODUCTION

The current climate change threat by CO_2 emission from combustion of fossil fuels increases the urgency for alternative energy production based on reliable and renewable sources such as solar energy and biomass [1–3]. The bioenergy contained in plant biomass has solar origin and may encompass considerable shares in future sustainable renewable energy production [4]. Current systems for the production of bioenergy, such as green or bioelectricity, bioethanol, and biodiesel still have some drawbacks. They compete with food production for arable land and fertilizers, require an additional energy input, and are less 'sustainable' or 'green' than consumers demand

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[5–10]. In this work, we propose a plant microbial fuel cell (plant-MFC) concept, which lacks these disadvantages and promises high yields.

The plant-MFC aims to transform solar radiation into green electricity in a clean and efficient manner by integrating the roots of a living plant in the anode compartment of a microbial fuel cell. The plant-MFC is based on two proven processes, rhizodeposition of organic compounds by living plants and electricity generation from organic compounds in the microbial fuel cell.

The living plant is photosynthesizing in its leaves whereby solar energy is used to fix carbon dioxide in the form of carbohydrates. Depending on plant species, age, and environmental conditions up to 60% of the net fixed carbon can be transferred from its leaves to the roots [11]. The plant root system produces and releases different types of organic compounds into the soil, which include (1) *exudates*: sugars, organic acids, etc.; (2) *secretions*: polymeric carbohydrates and enzymes; (3) *lysates*: dead cell materials; and (4) *gases*: ethylene and CO_2 [12, 13]. The total of these release processes is called plant rhizodeposition and its products, rhizodeposits, are used in the plant-MFC as a renewable bioenergy substrate. The produced rhizodeposits can total up to 40% (or more) of the plant's photosynthetic productivity. Rhizodeposits play many roles in the rhizosphere. Carbonic acids have been implied in the mobilization of soil-bound cationic nutrients for uptake by the plants. Rhizodeposits contain carbon and a part of this carbon can be utilized by micro-organisms in the rhizosphere, which can lead to mutually beneficial interactions between plants and micro-organisms. Bacteria, for example, can positively interact with plant roots by forming protective biofilms or by producing antibiotics as biocontrols against potential pathogens [13]. Since the largest fraction of rhizodeposits are small molecules they are efficiently synthesized by the plant and efficiently metabolized by bacteria.

In the plant-MFC, the principal idea is that plant rhizodeposits will be utilized as substrates by the bacteria to generate electricity in the microbial fuel cell. The microbial fuel cell is an emerging technology which transforms biodegradable substrates from wastewater or (energy) crops into electricity [14–17]. The electrochemically active microbes (bacteria) in the MFC act as a kind of biocatalysts using a part of the chemical energy of the substrate for their own metabolism and simultaneously delivering electrons to the anode of the electrochemical fuel cell. The micro-organisms (bacteria) use the anode electrode as the preferred final electrode acceptor because the difference in free energy is larger than other available acceptors such as sulphate [16]. For the Coulombic efficiency, the percentage of electrons recovered from the substrate versus the theoretical maximum values were more often reported in the range of 20–60% [17]. Figure 1 presents a model of the plant-MFC proposed here. With this proposed

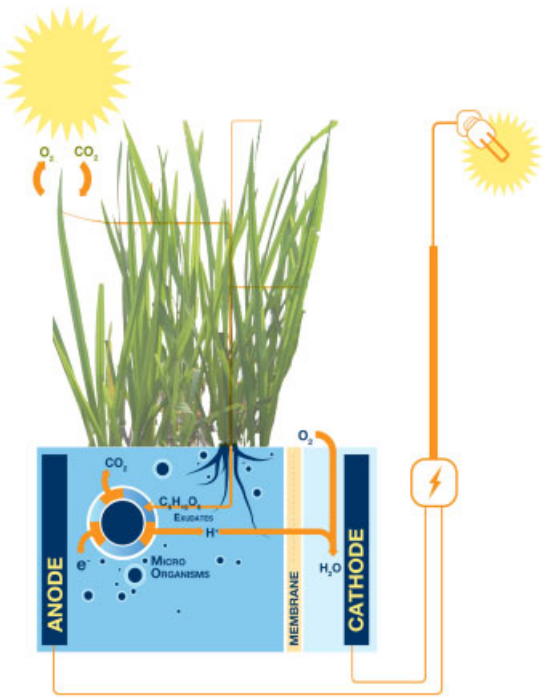

Figure 1. Model of a plant microbial fuel cell producing electricity and driving a light source. Carbon dioxide is fixed and released as rhizodeposits (e.g. root exudates) by the plants and are utilized by micro-organisms that return the carbon dioxide into the atmosphere. The micro-organisms use the anode as electron acceptor for gaining metabolic energy. These electrons flow due to the potential difference, from the anode through an electrical circuit with a load or a resistor to the cathode. Hence, electricity is generated which can be used, for example, driving a light source. To remain electroneutrality, protons are transported through the membrane into the cathode where oxygen is reduced with the protons and electrons to form water.

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system it is possible to produce green electricity by nondestructive harvesting of the rhizodeposits (mainly carbohydrates) of the plant. This has important environmental advantages such as no transport of harvested biomass, preservation of nutrients in the ecosystem, use of a renewable energy source, and no combustion or extra greenhouse gas emissions during production. Also from a social point of view, the plant-MFC has advantages. It can be implemented in natural environments such as wetlands with a minimal disturbance of the scenery and without being competitive with agricultural lands that are needed for food. Thus in the future, wetlands and also salted soils might worldwide be transformed into green power plants generating electricity in a carbon neutral way.

2. MATERIALS AND METHODS

2.1. Experimental set-up

The eight constructed plant microbial fuel cells were based on an anode compartment consisting of a glass tube (Schott, Duran) with a height of 30 cm and a diameter of 3.5 cm. The tube was wrapped with aluminium foil and the anode compartment was filled with the anode electrode: a graphite felt on the bottom (diameter 3.5 cm and 3 mm thick; FMI Composites Ltd.) plus above it graphite granules (diameter 1.5–5 mm; Le Carbone). The cathode electrode consisted of a graphite felt (8×8 cm and 3 mm thick; FMI Composites Ltd.) placed in a beaker glass which embodied the cathode compartment. To separate the compartments, a cation exchange membrane was fixed on the bottom of the anode glass tube (surface area of 8.5 cm^2; FuMA-Tech). The liquid volumes of the anode and cathode compartments were 150 and 300 ml, respectively.

The electrical circuit was formed by graphite rods, copper wire, and an external resistance of 10 00 Ω. The microbial fuel cells were placed in a cabinet with white reflective walls on the inside, except the front side which was open. Artificial illumination consisted of time-switch-controlled metal–halogen lamps (250 and 400 W Spacesaver) positioned above the set-up resulting in an illumination period of 14 h day^{-1}. The artificial illumination resulted in an average light intensity of 15 W m^{-2} at the plant level. The chosen ambient temperature was between 23 and 27°C. This is because both micro-organisms and the plant were expected to grow under these conditions. The micro-organism of the inoculum operated steady in this temperature range in an MFC running on acetate (data not shown) and the chosen plant *Glyceria maxima* habitats in the Netherlands where often these temperatures were reached in summer.

2.2. Plant microbial fuel cell operation

Reed mannagrass (*Glyceria maxima*), also named Reed sweetgrass, was obtained from a river bank in Renkum (the Netherlands). Reed mannagrass was chosen because it is one of the few local species that can grow in anaerobic riverbank sediments. These anaerobic conditions are necessary for a well-functioning anode compartment of an MFC. To our best knowledge, there is no quantitative data available about rhizodeposition of Reed mannagrass and other similar species. Therefore, it was not possible to determine *a priori* which species was the most promising. For the experiment, stems of reed mannagrass were isolated and securely freed from sediment residues. One or two smaller stem(s) of reed mannagrass (fresh weight 20–30 g) were placed in the anode compartment in each of the six microbial fuel cells. Two microbial fuel cells without a plant served as blanks. Several control plants were grown in potting soil (Vacq Belgium) and watered regularly with tap water.

For the start up of the plant-MFC it was operated without the plant. The anode compartments of the microbial fuel cells were, therefore, filled with graphite granules, inoculated with micro-organisms from another microbial fuel cell and fed with potassium acetate and the modified Hoagland nutrient solution [18] neutralized with NaOH to pH 7. After 33 days of start up, the granules were taken out and residues of KAc were removed by washing the granules with N_2 flushed (for 15 min) modified Hoagland nutrient solution (pH 7). Thereafter, the granules were

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mixed and placed with the plant in the anode compartment of the plant-MFC. The plant-MFCs were inoculated with electrochemically active micro-organisms from MFC running on acetate. Naturally occurring micro-organisms were already present on the roots of the plants at the time of placement into the plant-MFC. The plant-MFC therefore contains a whole range of micro-organisms, which was confirmed by microscopic analyses of samples. The plant-MFC was in operation now with modified Hoagland nutrient solution neutralized with NaOH to pH 7 in the anode compartment. The cathode compartment was during start-up and operation filled with demineralized water containing $2\,ml\,l^{-1}$ phosphate buffer (K_2HPO_4 $132.7\,g\,l^{-1}$; KH_2PO_4: $168.5\,g\,l^{-1}$). Water loss occurred in both the anode and the cathode compartments. In the anode compartment water loss was caused by water uptake by the roots and evaporation from the water surface. The anode compartment was refilled with demineralized water (until day 13), modified Hoagland nutrient solution with $4\,ml\,l^{-1}$ phosphate buffer (days 13–19 and day 24 until the end) or modified Hoagland nutrient solution with $4\,ml\,l^{-1}$ phosphate buffer without the components containing nitrogen (days 19–23). The nitrogen was temporarily left out to stimulate root exudate production [13]. From day 23, 40 ml of nutrient solution at a flow rate of $160\,ml\,h^{-1}$ was daily pumped (Minipuls, Gilson) into the anode compartment whereby excess overflow through an outlet. Water loss from the cathode compartment via evaporation was much less and the anode compartment was weekly replenished with demineralized water.

2.3. Analytical techniques

Cell voltage was measured off-line with a precision multimeter (True RMS Multimeter, Fluke 189) and online with an online data acquisition instrument (Fieldpoint modules & Personal Computer with Labview Software, National Instruments). A thermocouple was also connected to this instrument for the measurement of ambient temperature. Anode and cathode potentials were measured *versus* Ag/AgCl reference electrodes (3 M KCl, +205 mV *versus* standard hydrogen electrode, ProSense Qis) and a multimeter. Light intensity was measured with a light meter (Photodyne, 44XLA). Plants were photographed from the front side (Medium 5.0 digital camera) to registrate plant vitality. The plant-MFC internal resistance was determined with polarization curves by using a variable external resistance as described [15] and by electrochemical impedance spectrometry (EIS) [19]. EIS measurements were performed with a potentiostat equipped with a frequency response analyser (IVIUMstat, IVIUM, The Netherlands). Hereby a constant cell voltage was applied, which corresponded with the actual operative cell voltage with an external resistance of $1000\,\Omega$, with an amplitude of 10 mV for 20 frequencies in the range of 1000–0.0001 Hz. The ohmic resistance was thereby also estimated according to Bard and Faulkner [19] from the x-axis intercept of the Nyquist plot.

3. RESULTS AND DISCUSSION

3.1. Proof of principle

The proof of principle was performed using Reed mannagrass (*Glyceria maxima*), an abundant grass species in America, Europe, and Asia, with its roots placed in the bio-anode compartment of the microbial fuel cell. The cell voltage of 6 plant-MFC's (with one or two plants) and two blank MFCs (without a plant) was recorded during a period of 118 days. Figure 2 shows the results of the blanks and plant-MFCs number 1 and 2. An incubation period of 50 days proved to be necessary to obtain conditions favourable for electricity generation. The cell voltage of both plant-MFCs increased steadily from day 50 and reached maximum of 217 mV (plant-MFC 2, day 66) and 253 mV (plant-MFC 1, day 72), respectively. This corresponds to a current generation of, respectively, 0.217 and 0.253 mA. The maximal achieved electrical power production was 67 $mW\,m^{-2}$ anode surface. The anode potential was then typical for microbial fuel cells around −400 mV (*versus* Ag/AgCl). The cathode potential was then around −200 mV (*versus* Ag/AgCl) which

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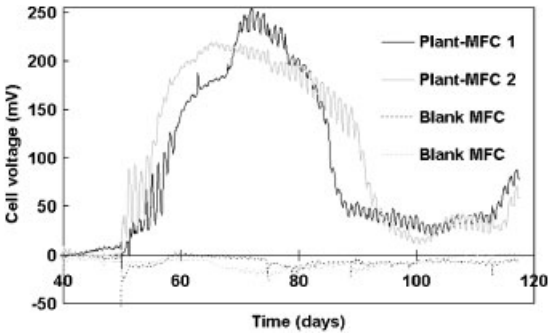

Figure 2. Plant-MFC proof of principle. Cell voltage (mV) of two plant-MFCs and two blank MFCs.

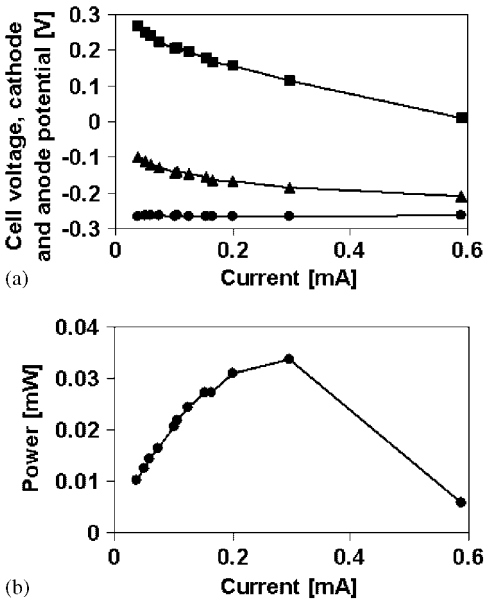

Figure 3. Polarization curve (a) with cell voltage (squares), cathode potential (triangles) and anode potential (circles); power curve (b) of plant-MFC no. 6 on day 90.

reflected the poor performance of an oxygen-reducing graphite electrode. Figure 3 presents the polarization (a) and power (b) curves of plant-MFC no. 6 (day 90). Since the anode potential remained constant during these measurements and the cathode potential dropped at higher currents it is clear that the cathode was rate limiting and thus needs improvement. From the EIS measurement (data not shown) and the polarization curve on, respectively, days 75 and 90 it was estimated that ohmic resistance was 30 Ω and total internal resistance was in the range of 450–600 Ω. This internal resistance of the plant-MFC was high compared with regular microbial fuel cells and indicates that the design can be improved to increase the electrical output by, e.g. combination with a biocathode [20]. For (plant-)MFCs, the high ohmic limitation is most likely due to the resistance of electrolytes, such as anolyte, catholyte, and cation exchange membrane [15].

The cell voltage showed oscillatory behaviour which was most pronounced between days 50 and 60 and was probably a reaction to the daily light cycle. The photosynthates produced during the day may have led to increased exudate production and substrate availability in the MFC thereby increasing the cell voltage. The simultaneous daily temperature fluctuations of 4°C probably affected the microbial activity as well, and thus the cell voltage. From day 60 on the electricity production continued at night, which means that the plant-MFC has the equivalent of a battery built into its system. After day 80 the current generation decreased to about 10–20% of the maximum value, followed by a small increase. From the start of the experiment the Reed mannagrass plants were vital and showed normal root and leaf growth. After the peak in current generation at day 68, the plant vitality slowly declined until the end of the experiment. This followed the normal decline of plant vitality at the end of the growing season and, possibly, an additional decline was caused by an invasion of aphids on day 40. The decline is not an effect of the conditions in the MFC bio-anode, as control plants in normal soil showed a similar decline in vitality. Eventually, all six plant-MFCs realized *in situ* electricity production for a period of more than 30 days (data not shown).

3.2. Future perspectives and applications

In this experiment, the total energy produced over the period from days 50 to 118 of plant-MFC no. 1 was 62 J, which was calculated from Ohm's law by integration of the actual cell voltage with the

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applied external resistance over time [15]. This was achieved by a single plant with a light intensity of a 15 W m^{-2} and a plant-MFC design that was not optimal. We estimate that the achievable electricity production of a plant-MFC is 21 GJ ha^{-1} $year^{-1}$ (5800 kWh ha^{-1} $year^{-1}$). This estimation is based on a solar radiation of 150 W m^{-2} in Europe [21], an average photosynthetic efficiency of 2.5% [18], a rhizodeposits yield of 40% [11], a rhizodeposits availability for micro-organisms of 30% [22], a microbial fuel cell energy recovery of 29% [23], and a growth season of 6 months. The proof of principle gives sufficient indication that improvement is possible by: (1) improved rhizodeposition by optimizing conditions and plant selection; (2) improved plant vitality management; (3) reducing the relative high internal resistance of the plant-MFC by, e.g. a biocathode; and (4) increasing of the light intensity from only 15 W m^{-2} in the proof of principle to, e.g. 150 W m^{-2}. If the plant-MFC employed in the proof of principle would have operated for a prolonged period of 6 months per year on the maximum achieved cell voltage and with a 10-fold light intensity of 150 W m^{-2} representative for Europe [21], it would have already produced 20 GJ ha^{-1} $year^{-1}$ (5600 kWh ha^{-1} $year^{-1}$).

In the future, plant-MFC technology may be integrated into hightech environments or into more natural environments such as salt marshes or other wetlands where the necessary anoxic anodic conditions exist. Applied in this way the plant-MFC does not compete with conventional bioenergy systems and food production in agriculture.

4. CONCLUSIONS

This work shows the proof of principle of a promising green power source: the plant-MFC. In the plant-MFC, the plant rhizodeposits were most likely utilized as substrates by the bacteria to generate electricity in the fuel cell. This technology may produce energy in an environmental-friendly way, not as a replacement of, but complementary to conventional bioenergy systems and without being competitive with agriculture. The here prospected gross plant-MFC output of 21 GJ ha^{-1} $year^{-1}$ (5800 kWh ha^{-1} $year^{-1}$) is similar to conventional green electricity production systems [24]. Full evaluation of its potential and environmental friendliness requires further implementation and development of the technology and a thorough life cycle analysis. Further research aimed at increasing the rhizodeposition by the plant, the efficiency of energy conversion in the MFC, up-scaling of the technology and further integration of plant and bio-anode should allow higher yields and a technology closer to practical implementation.

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