PROCEEDINGS

2nd INTERNATIONAL PLANTPOWER SYMPOSIUM

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November 22 and 23, 2012

Wageningen, the Netherlands

Sub-department of

ENVIRONMENTAL TECHNOLOGY

Colophon

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Preface

Our world is confronted with an energy crisis on a global scale. Our current energy supplies are polluting our environment and are not based on endless cycles. Clean technologies are needed that provide people and planet with safe, affordable and secure energy. PlantPower is a new additional source of electricity.

It was in 1911 when the British botanist Michael C. Potter showed that bacteria can cause electrical effects accompanied by decomposition of organic matter. Nowadays, 101 years later, this electrical effect evolved into the development of a multitude of bio-electrochemical systems providing all kinds of services like wastewater treatment, electricity generation or chemical recovery. The Plant Microbial Fuel Cell (Plant-MFC) offers *in-situ* electricity production with living plants and bacteria. This unique combination was just invented 6 years ago and is already scaled-up to 25 square meters. The last 4 years a multidisciplinary research team explored the Plant-MFC in an EU research project.

Exciting discoveries and great technological development took place over the last few years. New research questions came up and opportunities were identified to improve the system in the future. By bringing scientists, companies and entrepreneurs together we expect to bring PlantPower from the lab into the real world. The Plant-MFC is promising from a technical, environmental and economic perspective. The design criteria for the future are defined; but still development on several issues is needed.

Besides the fundamental research, scaling-up the technology is the next challenge. Especially wetlands offer the opportunity to produce electricity on a large scale. World-wide 800,000,000 ha wetland are present, however they are often under pressure due to our need of arable land for food, feed or chemicals. Here the Plant-MFC can be a solution since Plant-MFCs can be combined with nature and in that sense make nature preservation economically feasible. This 2nd international PlantPower symposium will show exiting results of the EU PlantPower consortium and other researchers.

Highlights of 4 years FP7 EU PlantPower Project

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Introduction & Objectives

PlantPower is electricity based on cooperation of living plants and microorganisms in a fuel cell [1]. Plants capture light energy during photosynthesis. In this process carbon dioxide and water is taken up and converted into chemical bonds of sugars. Part of this chemically stored energy is transferred via the roots and littered into the soil. This energy transported into the soil can be captured by the so-called electro-chemical active bacteria. These micro-organisms are capable to oxidize the organic matter and transfer energy rich electrons to an electrode. The energy carried by the electrons can be used as electrical energy, after which the electrons react at another electrode with oxygen to form water. This technology is called the Plant-Microbial Fuel Cell (Plant-MFC) (Figure I).

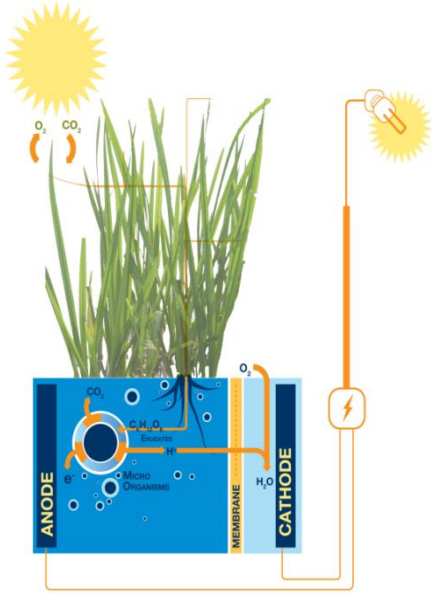

Figure I: Schematic of Plant-Microbial Fuel Cell

Materials & Methods

The EU FP7 PlantPower project explores new areas of science & technology to improve Plant-MFCs' power output up to 1.6 and 3.2 W/m^2 for wetlands and high-tech based systems [2]. To achieve this goal, all elements (plant, roots, root microbial community and fuel cell technology) forming the concept need to be improved in an integrated fashion. Research groups and companies with complementary backgrounds have joined forces in this PlantPower project.

Results & Discussion

Combined effort from all participants, universities, institutes and companies have led to scientific discoveries, technological developments, improved power outputs and the start-up of a spin-off company Plant-e.

Plant research showed that some plant species can be cultivated in Plant-MFCs and other species cannot or grow poorly [3]. It was shown that exudates as well as dead roots are important sources of fuel for the Plant-MFCs [4]. Via advanced anode-rhizosphere microbial analysis, microbial species have been identified and localized in the root/anode interfaces that are associated with high current production in the Plant-MFC [5]. These bacteria were applied to enhance start-up of Plant-MFCs. Materials for anodes and cathodes were improved by electrode modification including oxygen reducing biocathodes [6, 7]. The maximum and long term (2 weeks) power output of best performing Plant-MFCs reached 0.44 and 0.222 W/m^2.

This power density is comparable to conventional biomass-electricity chains. For wetlands a tubular based system was designed and being effective in reducing material while keeping the power density [8, 9]. The high-tech Plant-MFC is currently piloted at a 25m^2 'Green electricity roof' by Plant-e with support of several PlantPower participants. This pilot-set-up was assessed on environmental performance in an early life cycle assessment [10]. The studied showed the opportunities to reduce material use in new designs to improve the environmental impact. This combined with an increase in power output will bring the Plant-MFC closer to economic

applications. A PlantPower wetland can produce *in-situ* electricity without harvesting the plants, 24 hours per day at large scale. Four years FP7 EU PlantPower Project showed that the Plant-MFC is an emerging promising technology.

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Content

Program

Thursday 22nd November, 2012 Location: Impulse

8:30-9:00 Welcome and registration

9:00-9:30 Opening

Cees Buisman (Wageningen University, the Netherlands)
David Strik (Wageningen University, the Netherlands)

Theme I: Rhizodeposition

9:30-10:00 Keynote Filip Meysman (Royal Netherlands institute of Sea Research, the Netherlands)

10:00-10:20 coffee break

10:20-10:40 PlantPower Project results
René Kuijken (Wageningen University, the Netherlands)

10:40-11:00 PlantPower Project results
Stephan Blossfeld (Forschungszentrum Jülich, Germany)

Theme II: Electrobiocatalysis

11:00-11:30 keynote Miriam Rosenbaum (Institute of Microbiology, Germany)

11:30-11:50 PlantPower Project results
Frédéric Barrière (Université de Rennes, France)

11:50-12:10 PlantPower Project results
Tina Sieper (Helmholtz Zentrum München, Germany)

12:10-12:30 Urania Michaelidou (Wetsus, the Netherlands)

12:30-13:30 Lunch

Theme III: Bioelectrochemical technology

13:30-14:00 keynote Korneel Rabaey (University of Gent, Belgium)

14:00-14:20 Yvonne Mos (Wageningen University)
14:20-14:40 PlantPower Project Results
Jan Arends (University of Gent, Belgium)
14:40-15:00 PlantPower Project Results
Marjolein Helder (Wageningen University, the Netherlands)

15:00-15-20 Coffee break

15:20-15:40 Paolo Bombelli (University of Cambridge, United Kingdom)
15:40-16:00 Christopher Howe (University of Cambridge, United Kingdom)
16:00-16:20 Annemiek ter Heijne (Wageningen University, the Netherlands)
16:20-16:40 Abraham Esteve-Núñez (University of Alcala, Spain)

16:40-17:10 Closing Lecture
Dr. Bert Hamelers (Wetsus, the Netherlands)

17:10-18:00 Poster session

18:00-18:30 Reception

18:30-21:30 Diner

Friday November 23rd, 2012

9:00-9:20	Start at Impulse
9:45-10:15	Visit laboratories of Environmental Technology
10:30-11:00	Visit laboratories of Plant Research International
11:15-12:00	Visit Netherlands institute of Ecology (NIOO-KNAW) and Plant-e pilot green electricity roof
12:15-13:00	Lunch

Venue

Wageningen Campus
Impulse

Futurum, Building 115
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Bornse Weilanden 9
6708 WG, Wageningen

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NIOO-KNAW
Droevendaalsesteeg 10

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Abstracts

Theme I: Rhizodeposition

Keynote by Prof. Dr. Ir. Filip Meysman

Royal Netherlands Institute of Sea Research (NIOZ), Yerseke,
the Netherlands

Expertise

- Biogeochemical modelling of aquatic sediments
- Carbon cycling in marine sediments
- Darwin's last idea: Bioturbation and bio-irrigation
- Linking ecology and thermodynamics

CV

Studied Chemical Engineering at the K.U. Leuven (Belgium), specialization in waste water treatment technology. Afterward he did his second MSc, biology, at Ghent University (Belgium), specialization in marine ecology.

PhD- research on "Modelling the influence of ecological interactions on reactive transport processes in sediments", at Centre for Estuarine and Marine Ecology (NIOO-KNAW , The Netherlands), Dalhousie University (Halifax, Canada) and the Marine Biology Lab (Ghent University, Belgium).

Post-doc position in the Challenger Division for Seafloor Processes, Southampton Oceanographic Centre (UK) and later at the Centre for Estuarine and Marine Ecology (NIOO-KNAW, The Netherlands).

Since 2008: Associate professor, Earth System Sciences research Unit, Dept. Analytical and Environmental Chemsitry, Vrije Universiteit Brussel (Belgium).

2010-present: Senior Scientist at the Department of Ecosystem Studies, Centre for Estuarine and Marine Ecology (NIOO-KNAW, The Netherlands)

Microbial batteries in the seafloor: a novel form of electrogenic microbial metabolism

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Introduction & Objectives

Recently, an entirely novel type of microbial metabolism has been described from marine sediments, whereby filamentous bacteria are transporting electrons over centimeter-scale distances. By establishing such electrical circuitry, these micro-organisms are able to exploit spatially segregated pools of electron acceptors and donors, equipping them with a competitive advantage. This novel electrogenic metabolism was first demonstrated for sulphide oxidations in laboratory experiments, but until present, the process has only been demonstrated in laboratory incubations with artificially mixed sediments. Here we provide evidence that electrogenic sulphide oxidation also occurs in the natural environment.

Materials & Methods

High-resolution microsensor pore water profiling reveals that the reductive half reaction (i.e. the consumption of oxygen) occurred just below the sediment-water interface, while the oxidative half reaction (i.e. the removal of sulphide) takes place more than 10-20 mm deeper down in the sediment. To make such a separation of redox half-reactions possible, there must be a path by which electrons are transferred across this suboxic zone. Microscopic inspection of the sediment reveals that a network of centimeter-long filamentous bacteria of the Desulfobulbaceae family span the suboxic zone. Additional manipulation experiments show that these filamentous bacteria are necessary for the electron transport.

Results & Discussion

Our results show that electrogenic sulfide oxidation occurs naturally in the seafloor. We observed the geochemical fingerprint of electrogenic sulphide oxidation at three coastal sites in the North Sea. Our field observations reveal that the process occurs at sites with high rates of sulphide generation, and low rates of mechanical disturbance by infauna. Complementary laboratory experiments confirm that faunal reworking destroys the electrical connectivity between sediment horizons. Together, our results indicate that electrogenic sulfide oxidation can strongly affect the biogeochemical cycling in a wide range of marine sediments, including coastal eutrophic systems with seasonal hypoxia, intertidal salt marshes, and possibly hydrothermal vent environments. The sensitivity towards faunal reworking constrains the distribution in the present ocean floor, but suggests a more widespread prevalence in geological times, before the rise of animal life.

The link between root exudation and root morphology in tomato

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Introduction & Objectives

Where regular plant biomass can be converted to bio-energy by thermal conversion or gasification, plant root exudates can only be converted into electrical energy by the Plant Microbial Fuel Cell. However, root exudation is currently the limiting factor for energy production in this system. Genetic variation in root exudation can be utilized to improve root exudation. This genetic variation can also be used to improve phytoremediation, nutrient uptake in low input environments, avoidance of metal toxicity and general yield increase.

Besides genetic factors, also the environment determines the plant's exudation rate. Exposure of roots to elevated levels of aluminium is known to increase exudation of organic acids and to alter root growth [1, 2]. Root morphology also affects exudation, with exudation activity mainly taking place in the meristematic regions behind the root tip and at the region of cell elongation [3]. These different parts of the root also release different exudates [4]. In *Lupinus albus*, malate is mainly exuded from root apices whereas citrate exudation is restricted to proteoid cluster roots [5]. The environment in its turn, has a major role in shaping root morphology. It is because of this complex three-way interaction that the causal relation between root morphology and root exudation needs to be elucidated on order to optimally exploit genotypic and environmental effects on exudation.

The objective of this study was to 1) quantify genetic variation in exudation in a major greenhouse crop and 2) to locate the observed genetic variation (root or shoot).

Materials & Methods

Seeds were surface sterilized in 70% EtOH for two minutes, rinsed with sterile deionized (DI) water, incubated in 2.5% (w/v) household bleach for 45 minutes and rinsed with DI water six times again. Subsequently, seeds were incubated for 30 minutes in a mixture of 600 mg/L Penicillin, 250 mg/L Streptomycin, 100 mg/L cyclohexamide. Seeds were sown inside sterile glass culture tubes. When plants had 2 to 4 true leaves, they were transferred to a sterile plastic tube or container with a 3x diluted sterile nutrient solution (EC 2.0 dS m^{-1}, pH 5.0, [O_2] 10 ppm and a mineral composition of (mM) NH_4^+ 1.2, K^+ 7.2, Ca^{2+} 4.1, Mg^+ 1.8, NO_3^{2-} 12.4, SO_4^{2-} 3.3, PO_4^{2-} 1.1 and (µM) Fe^{3+} 25, Mn^{2+} 10, Zn^{2+} 5, B^{3+} 30, Cu^{2+} 0.75, Mo^{2+} 0.50). The sterile root environment was physically separated from the non-sterile above ground part of the plant by creating an interface with sterile dry cotton balls covered with Leucopore tape. Double strength sterile nutrient solution (EC 1.26) was applied through a sterile infusion system. In order to quantify exudation of organic acids, the nutrient solution in the rhizosphere was replaced by sterile DI water after the eighth leaf had appeared (t=0h). At this moment, a sample was taken and the measured levels of organic acids were subtracted from the concentrations measured 24 hours later (t=24h). Anions, including organic acids (acetate, malonate, maleate, malate, succinate, fumarate, α-ketoglutarate, oxalate and citrate) were quantified with a Dionex ICS2500 HPLC system. Anions were separated on an AS11-HC (4 x 250 mm) column at 30 °C, preceded by an AG11-HC guard column, and eluted with a 15 min linear gradient from 25 to 100 mM NaOH.

Results & Discussion

The study of root exudation is hampered by microbial breakdown of exudates in the root zone. Build-up and catabolism of organic acids in a sterile rhizosphere differs considerably from a non-sterile rhizosphere. In a sterile tomato rhizosphere, exudate quantities can

be determined that would have been underestimated or not detected at all in an non-sterile root environment (Kuijken et al., 2012, submitted).

In a diversity panel of nine wild and cultivated tomato genotypes with an aseptic root zone, significant differences were observed in citrate, oxalate (Figure II-A) and malate (Figure II-B) exudation. While wild species *S. habrochaites* exuded the most, the three commercially available genotypes, Moneymaker, Maxifort and M82, exuded the least (Figure 1AB). It seems that over the past decades modern highly productive tomato cultivars were selected for yield and, unintentionally, against high exudation.

To determine whether the genetic variation resides in the root or in the shoot, we grafted shoots of the commercial cultivar Moneymaker on top of the root systems of five different genotypes from the diversity panel. The observed higher malate exudation of *S. Arcanum* LA2157 and *S. habrochaites* LA1777 (Figure III) is in agreement with the high exudation observed in Figure 1B. For oxalate, the genetic differences were not significant. This, however, was probably due to high variation in observed exudation rates as the plants in this experiment got infected with an unknown bacterial strain.

Exudation of organic acids increases when the roots are exposed to an excess of aluminium. This phenomenon is considered to be a mechanism that provides tolerance to aluminium stress. Relative root growth (RRG) is often used as a measure for aluminium tolerance and is often related to exudation. RRG in the presence of aluminium might be used as a fast and inexpensive tool to screen plants for high exudation. In our experiments, however, high exuding tomato genotypes did not outperform low exuding genotypes in terms of RRG. Possibly there are two different mechanisms underlying aluminium induced exudation and exudation under optimal nutrient conditions. In future experiments root morphology and exudation mechanisms will be linked.

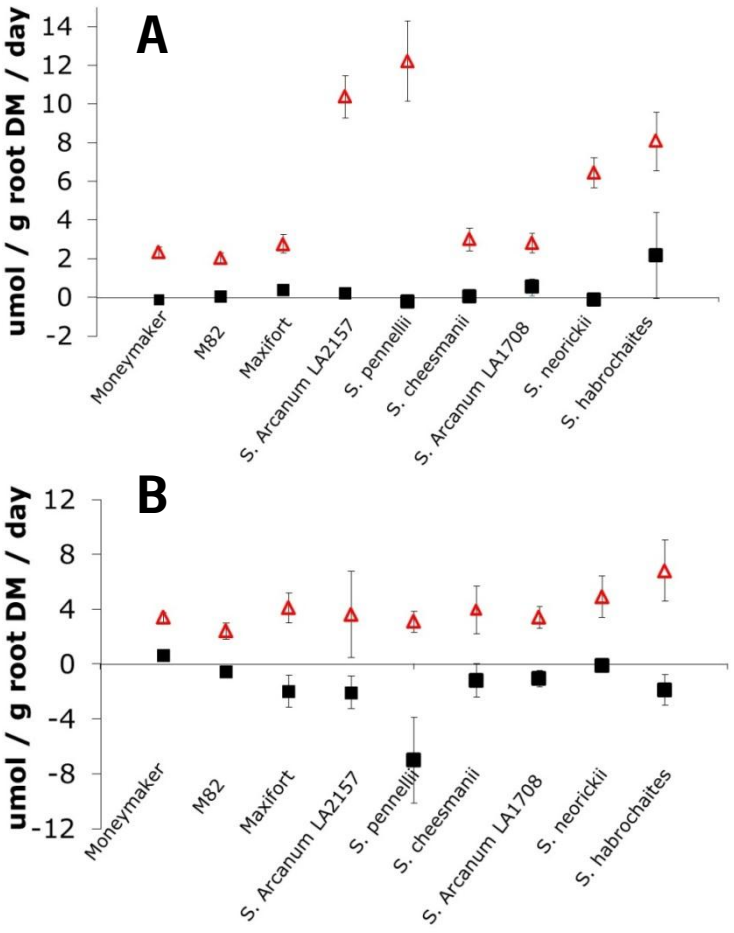

Figure II: Exudation of A) oxalate and B) malate from nine different genotypes. Triangles represent quantification of exudation in a sterile system. Squares represent quantification of exudation in a non-sterile system rhizosphere. Error bars represent the standard error of the mean (SEM).

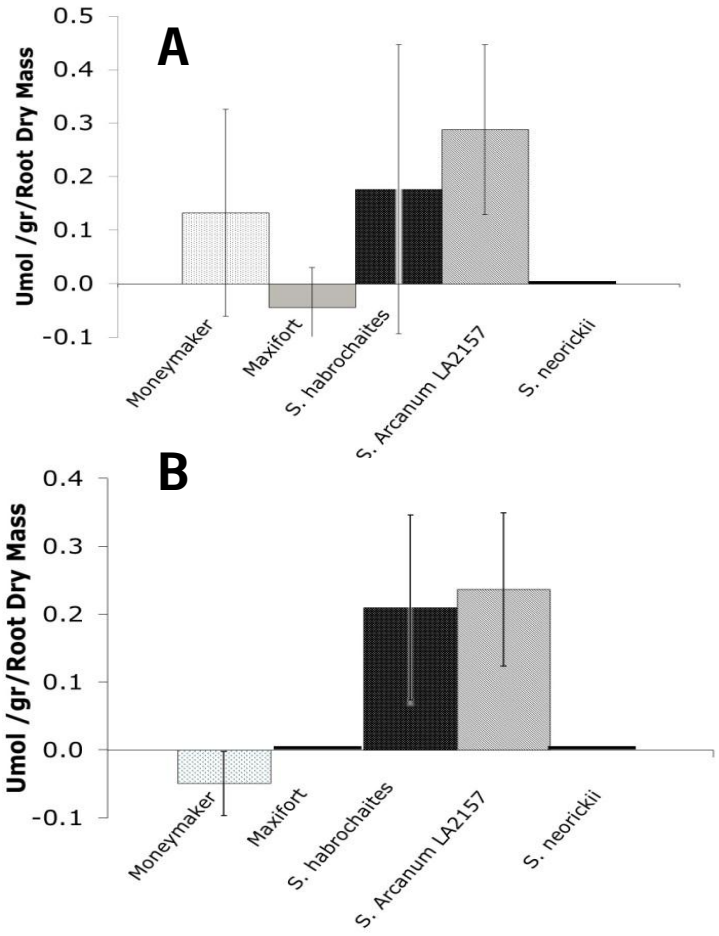

Figure III: Exudation of A) oxalate and B) malate from five different genotypes used as root stock and grafted with a shoot of cultivar Moneymaker. Error bars represent the SEM.

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Non-invasive mapping of pH, O_2 and CO_2 dynamics in the rhizosphere

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Introduction & Objectives

Live imaging methods have become extremely important for the exploration of biological processes. Especially non-invasive measurement techniques are key to unravel organismic interactions in close-to-natural setups, e.g. in the highly heterogeneous and difficult-to-probe environment of plant roots: the rhizosphere. The pH, O_2 and CO_2 concentration are main factors guiding rhizosphere reactions. Being able to monitor these parameters in high spatio-temporal resolution is of utmost importance for a subsequently relevant interpretation of the underlying processes, especially in the complex environment of non-sterile plant-soil relationships.

Materials & Methods

Successful elucidation of biogeochemical processes in the rhizosphere is strongly dependent on the available methods and technologies for assessing and monitoring the spatial and temporal dynamics of pH, O_2 and CO_2 without disturbing the original processes. Planar optode technology is the present state-of-the-art technology for this kind of research. It allows a detailed non-invasive quantitative imaging of the dynamics of protons, molecular oxygen and even carbon dioxide in the rhizosphere.

Results & Discussion

Preliminary studies with *Viminaria juncea* (a MFC non-tolerant plant) revealed high CO_2 contents of up to 70% close to the root surfaces, when growing in sand. In a recent study continuous and high-resolved measurements in the rhizosphere of *Oryza sativa* are performed. In particular: We applied pH, O_2- and recently developed CO_2 sensors to a rhizobox system in order to investigate roots of rice growing in

different waterlogged substrates, i.e. graphite, treated graphite and sand.

The comparison of the different anode substrates allows us to identify potential changes in the root associated processes, caused by the different substrates.

Theme II: Electrobiocatalysis

Keynote by Prof. Miriam Rosenbaum

Institute of Applied Microbiology, Aachen, Germany

Focus of her work

The interactions of microorganisms with electrodes, which function as synthetic (adjustable and controlled) electron donors or acceptors for microbial biochemical reactions.

CV

Studied Biochemistry at the University of Greifswald (Germany), specialization on microbiology and environmental chemistry.

PhD-research on “Development of microbial fuel cells for power generation from biomass", at the University of Greifswald (Germany).

Post-doc position at the Washington University in St. Louis, MO / USDA-ARS Peoria, IL, USA.

In 2009 Research Associate of the Department of Biological and Environmental Engineering, Cornell University, Ithaca, NY, USA.

2011-present: Juniorprofessor in the field of Microbiology of Defined Mixed Cultures at the Institute of Applied Microbiology, RWTH Aachen University, Germany.

Phototrophic Microorganisms for Bioelectrochemical Systems

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Introduction

From the very beginning of extended research into bioelectrochemical systems, photosynthetic microorganisms have been considered as possible microbial biocatalysts. Photomicrobial fuel cells can directly convert sunlight into electrical energy through microbial catalysis without the intermediary storage of sun energy in organics or biomass, thereby avoiding some of the most inefficient steps of dark microbial fuel cell concepts. However, even though photomicrobial BES have always been considered, still no clear path to application is laid out and while our understanding and potential utilization of dark BES is constantly expanding, the knowledge on photomicrobial BES seems to stagnate. This presentation attempts to analyse the reasons and perspectives.

State of the Art

Photomicrobial biocatalysts might be exploited in at least three different ways in BES: i) through the electrooxidation of photosynthetic hydrogen; ii) through non-hydrogen mediated current generation at an anode; and iii) through cathodic CO_2 reduction or *in-situ* photosynthetic oxygen supply. The utilization of photomicrobial hydrogen (i), to date is the most efficient way of photomicrobial current generation with current densities up to 1.5 mA/ cm^{-2}. However, specific growth conditions are required to sustain an anaerobic, hydrogen producing photosynthetic mode and the stability of the required electrocatalysts for hydrogen oxidation has not been evaluated for longterm operation. Non-hydrogen based current generation with photomicrobial biocatalysts (ii) has been observed for

several microbial pure and mixed cultures. In most cases, photosynthetic carbon fixation during a light period was followed by a respirative current generating dark period. Only in few cases, a direct, light-induced current response was detected. Direct and mediated electron transfer mechanisms have been proposed, however, could not conclusively be resolved so far. The cathodic production of photosynthetic oxygen (iii) could prevent oxygen supply difficulties caused by the low oxygen solubility as it has been shown for sediment BES. However, for BES reactor systems, the extra effort of cathode illumination might be technically challenging and open air cathodes might provide an even better oxygen supply. A very interesting concept is the cathodic photosynthetic carbon dioxide reduction. Initial mechanistic studies point to a direct electron transfer mechanism in this study, however, no further work on this concept has been published yet.

Perspective

The idea of using photomicrobial biocatalysts in BES is still a fascinating possibility that could have significant advantages over dark BES. However, a targeted, strong research program would be required to pace ground towards the mechanistic understanding of current generation with photomicrobial biocatalysts particularly under direct, light-induced conditions. For preliminary tests, we developed two new BES reactors designed specifically for mechanistic investigations of photomicrobial BES biocatalysts. These new systems currently undergo functional testing. A brief insight will be presented here.

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Plant-MFCs : Approaches to optimize the anodic compartment, the membrane and the cathodic compartment.

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Different strategies have been considered to optimize the different parts of a Plant Microbial Fuel Cell (Plant-MFC).

At the anodic compartment, we used the surface modification (by the reduction of aryl diazonium salts) to improve the performances of a bioanode. [1] Different aryls groups have been immobilized on graphite anodes, and the interaction with the biofilm has been studied. The immobilization of more complex chemical groups such porphyrins has also been carried out. [2]

Regarding the membrane we report the modification of a model ultrafiltration membrane made of polyethersulfone. [3]
At the cathode, we present ways to optimize the oxygen reduction reaction. In that context, three different approaches are considered: a molecular approach (by using metalloporphyrins), an enzymatic approach (by using laccase from *Trametes versicolor* and a redox mediator) and a microbial approach (by using a catalytic biofilm). [4]

Finally, the use of Plant-MFCs for powering micro electronic devices has been addressed.

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Assessment of the microbial community in the cathode compartment of a plant microbial fuel cell

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Introduction & Objectives

In plant microbial fuel cells (Plant-MFCs) living plants and microorganisms form an electrochemical unit are able to produce clean and sustainable electricity from solar energy. It is reasonable to assume that besides the bacteria in the anode compartment also the cathode compartment plays a crucial role for a stable high current producing Plant-MFC. In this study we aim to identify dominant bacterial species in the cathode compartment of the Plant-MFC.

Materials & Methods

DNA samples from the catholyte and a biofilm that formed at the cathode were prepared and graphite samples were fixed for fluorescent in situ hybridization (FISH). Bacterial 16S rDNA was amplified via PCR from all samples (650bp). With these amplicons 454-pyrosequencing was performed to identify the microbial key players in the cathode compartment. All sequences were assembled with 98% similarity by the Newbler software and the phylogenetic allocation of the 16S rDNA sequences was assessed by the ARB software. The obtained results allowed to select for specific 16S rRNA targeted oligonucleotide probes for FISH to verify the sequencing results and localize dominant bacterial species via confocal laser scanning microscopy (CLSM).

Results & Discussion

In previous experiments with samples from the anode *Clostridium sporosphaeroides* (on root samples) and *Geobacter sulfurreducens* (on graphite granules) were found to be associated with high current

Plant-MFCs. In the catholyte samples we found the genus *Brachymonas (β-Proteobacteria)* to be the most abundant in four out of six samples with the highest similarity to *Brachymonas denitrificans*. More striking was the abundance of a yet unknown member of the family *Sinobacteriaceae (γ-Proteobacteria)* in the biofilm samples from the cathode with a relative abundance of up to 30% of all sequences (see picture below). These sequences show highest similarity to *Steroidobacter denitrificans*, but the entire family seems to be highly divers and not many species are described so far. From CLSM-observations the biofilm on the graphite granules appears to be sustained with a thickness of up to 17µm. Observations of bacteria in the biofilms with FISH support the data obtained by 454-sequencing.

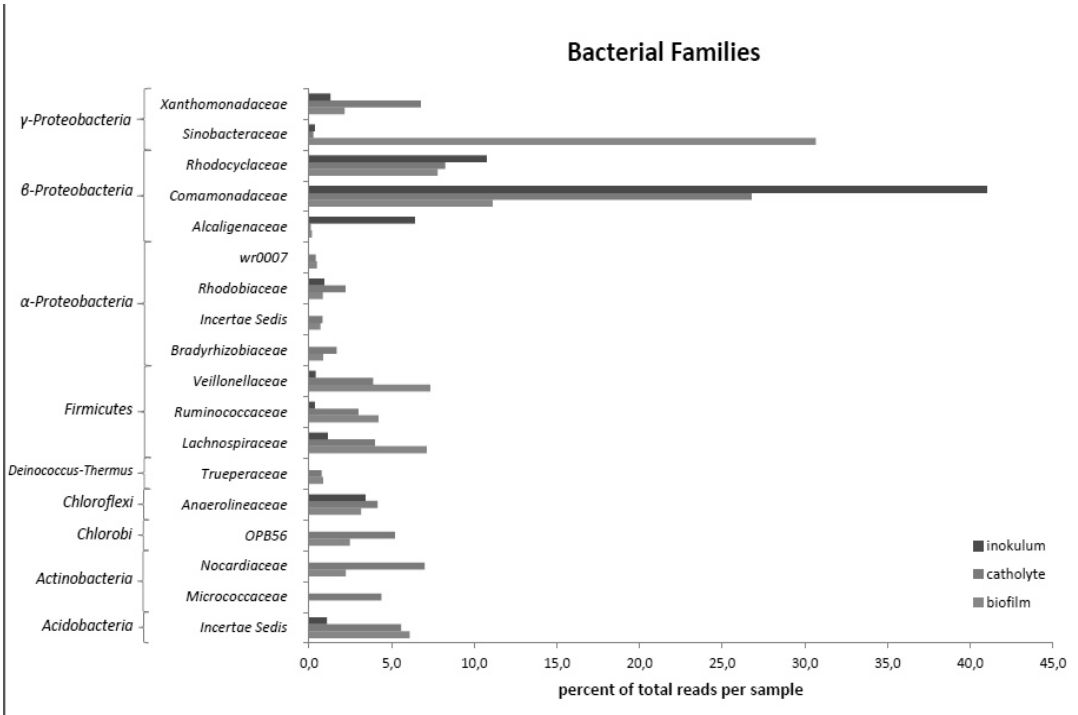

Figure IV: 454 sequencing reads in percent of total reads per sample phylogenetically allocated to different bacterial families by the ARB software package.

Reproducibility issues in mixed-culture microbial fuel cells

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Several studies have been conducted studying the parameters affecting microbial fuel cell (MFC) performance. Varied non-biological experimental parameters include but are not limited to: MFC unit design and volume, electrode surface area, material and coating, electrical connections, anolyte composition and conductivity, microorganism energy source, pH and temperature, startup conditions, applied potential (V) and type of cathodic reaction. Varied biological parameters refer to the microbial population in the anode; pure cultures versus defined mixed-cultures (consortia) or undefined mixed-cultures. The addition of this necessary biological factor in the anode, only adds to the complexity of an already complex system. In the case of undefined mixed-culture MFCs, where environmental samples or other mixed-cultures of unknown microbial composition are used as inoculum for startup, comparison and reproduction of results might not always be possible due to the experimental parameter variation. In this study, a number of MFC characteristics were investigated in order to determine reproducibility potential in mixed-culture MFCs. Three identical, but yet independent, flat-carbon electrode, acetate-fed MFC units were operated in a specially designed setup under the same environmental conditions with $Fe(CN)_6^{3-}$ in the catholyte. The MFC units were all inoculated with the same mixed-cultures and monitored over time combined with *in-situ* electrochemical testing of the bioanodes and *post-run* microbiological

analysis. Overall, the bioanodes showed a high degree of similarity in both electrochemical and microbiological characteristics. In addition, a new *Geobacter* strain, 98% similar to *Geobacter sulfurreducens* PCA, was detected as the major species in all bioanodes; both strains are electrochemically active and were also detected in other MFC studies.

Theme III: Bioelectrochemical technology

Keynote by Prof. Dr. Ir. Korneel Rabaey

Laboratory of Microbial Ecology and Technology (LabMET),
Ghent, Belgium

Focus of his work

- Innovative process development using microbial bioelectrochemical systems (BESs).
- Understanding microbial electrocatalysis as the key driver for a plethora of processes.
- Resource recovery from wastewater by implementing new technology.

Research interests

Bioelectrochemical systems (BESs), resource recovery, microbial electrocatalysis, electromigration.

CV

Studied Biochemical engineering at Ghent University (Belgium), specialization environmental technology.

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Bioelectrochemical production

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The past years, microbial bioelectrochemistry has not only lead to many new insights into microbial physiology, also the range of applications has steadily increased. The Plantpower symposium highlights the interactions between plants, or at least their exudates, and bioelectrochemical systems in the context of power production. Electrical power is but one outcome that can be achieved with this technology. In this presentation, I will overview alternative outcomes such as bioremediation and bioproduction, and then focus on how this could be used to drive production processes driven by organic conversions. These processes can involve the fixation of CO_2 or the conversion of substrate organics to products that have higher value or that can be extracted from the system.

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Understanding factors limiting current density in the P-MFCs: electron donor, pH and sulfate

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Introduction & Objectives

The Plant Microbial Fuel Cell (P-MFC) offers the possibility to produce bio-electricity using living plants and a microbial fuel cell (MFC). In a P-MFC, plants exude organic matter that is oxidized by microorganisms, releasing electrons to the anode. Energy from these electrons is extracted, next electrons flow to the cathode, where preferably oxygen is reduced. P-MFC performance is suggested to be limited by the organic matter flow from the plant towards the electrochemically active bacteria and/or proton accumulation in the electrochemically active biofilm (1). Besides these, a broad range of factors can govern the power density of P-MFCs.

Previous studies have reported that substrate availability and pH conditions can affect the performance of the P-MFC system (2,3). However, the effect of substrate availability and pH fluctuations in a P-MFC is poorly understood. Some MFC studies show that an increase of substrate concentration leads to a higher power and current density, but it can also decrease the Coulombic efficiency (4,2). Also, an increase of current density was reported when phosphate buffer (pH control) was used in bioanodes using acetate as electron donor (5). However, it is suggested that phosphate buffer negatively affects plant growth in a P-MFC (3).

The effect of sulfate on MFCs has been widely studied (6). Several researches have demonstrated that a slight increase of the sulfate concentration decreases the energy production up to 50% (7). Sulfate would be reduced to sulfide and accumulate, achieving toxic concentrations for the plants if not oxidized to elemental sulfur

(electrodeposited sulfur) as has been observed to occur (6). In contrast to previous studies, Helder *et al* (3) observed that in a P-MCF, the energy production increases when sulphate is slightly increased from 0 to 26 mg/L. Her results suggest that sulphide would stress the plant and decrease the oxygen loss from roots, which can reduce anodic internal currents (3).

In this research we aim to understand the limitations of anodic current in the P-MFC. Experiments with acetate, phosphate buffer and/or sulfate additions are performed to understand the performance of the P-MFC.

Materials & Methods

Five different performing flat plate mini P-MFC's (Pim de Jager, MSc thesis in preparation) were selected (P-MFC's 3, 7, 8, 9 and 10) and characterized by measuring polarisation curves and analysing the composition of the anolyte before the start of the experiments. P-MFC's were operated in a climate chamber (Microclima Jumo Imago, F3000, Snijders Scientific) at 20°C and 75% humidity with a light-dark regime of 16.5:7.5 h. Anode consisted of graphite granules (1-2 mm Le carbone). Plants of *Spartina anglica* were used in the P-MFC systems. To all media 5 g/L NaCl was added to mimic seawater.

P-MFC's 7, 8 and 10 are used to study the effect of acetate and phosphate buffer addition with a fixed sulfate concentration. P-MFC's 3 and 9 are used to study the effect of sulfate addition without acetate or phosphate addition.

P-MFC's 7, 8 and 10 will consecutively be fed by three different media; (1) 50% Hoagland solution with 0.1 M acetate in the form of sodium acetate, (2) 50% Hoagland solution plus 0.02 M phosphate buffer at the same pH as the receiving anode compartments and (3) 50% Hoagland solution with both 0.1 M acetate in the form of sodium acetate and 0.02 M phosphate buffer at the same pH as the receiving anode compartments. For all P-MFC's pH, redox potential, conductivity, volatile fatty acids composition and concentration, sulfide (S^{2-}), sulfate (SO_4^{2-}) is measured.

P-MFC's 3 and 9 will be fed with 50% Hoagland solution increasing sulfate concentrations from 0 to 150 mg/l, the latter can be lower or higher concentration depending of the results. For all P-

MFC's pH, redox potential, conductivity, volatile fatty acids composition and concentration, sulfide (S^{2-}), sulfate (SO_4^{2-}) is measured. At the end of the experiment the anodes will be analyse by SEM-EDX to determine if sulfur has been electrodeposited on the anode.

When the plant-MFC's have stabilized under the new conditions, polarisation curves will be measured and the anolyte will be analysed to compare the internal resistances and anode processes and composition to the standard operating behaviour.

Results & Discussion

The polarisation curves of P-MFC's 3, 7, 8 and 10 show maximum power outputs of 9.46 10^{-10}, 0.07, 0.08, and 0.1 W/m^2 respectively. In addition, P-MFC10 has a higher cell voltage and significantly lower concentrations of VFA and COD in the anolyte than P-MFC7 and 8. P-MFC10 is found to be the best performing plant-MFC in this experiment.

The first results after five days of feeding with medium 1 showed an increase in power density as well as the expected increase in COD, VFA and sulphide concentrations in the anolyte in both P-MFC7 and P-MFC8. In P-MFC10 however, the power density has decreased slightly. Data (not shown) shows that this plant-MFC had the highest power output before the start of the experiment and experienced an abundance of acetate faster than P-MFC7 and P-MFC 8 (within three instead of five days).

P-MFC's 3 and 9 are currently being operated and characterized with the 25 mg/L of sulfate. The P-MFC's were operated for 10 days without sulfate addition. When sulfate was added, electricity production decreased by two third of the initial production, which contrasts the increase of electricity reported by Helder *et al* (3) at the same sulfate concentrations. In this stage of operation, sulfide is not detected at the P-MFC's. In the following weeks, higher sulfate concentrations will be evaluated.
Final report of the experiments is expected December 2012.

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Benefits from the Plant-Sediment MFC

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Introduction & Objectives

A sediment microbial fuel cell uses the reduced organic matter in the anaerobic subsurface of a waterlogged system to produce an electrical current. This current is used in the overlying waterlayer to reduce a terminal electron acceptor, usually oxygen. In such a system, the catalyst on the electrodes is usually of a microbial nature. A plant-sediment microbial fuel cell is characterized by a continuous supply of organic matter to the anode electrode by means of rhizodeposition. A plant-sediment MFC faces several challenges such as 1) placement of the anode electrode/current collector at the site with the highest organic carbon concentration, i.e. the rhizosphere/plane and 2) A high internal resistance due to a relatively large distance between anode and cathode and usually a low conductivity of pore liquid. These two conditions create bottlenecks that need to be improved or circumvented in order increase the comparatively low power output from a plant-sediment MFC. In this work the first bottleneck is targeted while suggestions are done to address the second bottleneck. Moreover, an attempt is made to increase the value-creation of the plant-sediment MFC beyond electrical power. Therefore the impact of introducing an anode as alternative electron acceptor in a microbial niche is investigated. As a model CH_4 emissions of the rhizosphere of rice plants is used. Here, the plant-sediment MFC can possibly make an impact one of the largest anthropogenic sources of atmospheric CH4 release [1].

Materials & Methods

Anode electrode material and distribution screening tests were performed in duplicate microcosms of 350 ml with sand as the model sediment. Organic carbon was added in a controlled fashion as Na-

acetate. The anode current collector consisted of a carbon rod (5 mm, Morgan). The anode was inoculated with effluent from a running MFC. The cathode consisted of graphite felt (4 cm^2, 3.18 mm, Alfa Aesar) and a carbon rod current collector. An Ag/AgCl reference electrode was placed close to the cathode. Cell potential over an external resistance and electrode potentials were monitored every 5 min. using a data acquisition system (349704A, Agilent). Calculations are performed with hourly averages [2]. Studies on CH_4 emissions from rice agriculture were conducted in 4 microcosms (14 cm inner diameter, 35 cm high) filled with vermiculite and carbon granules [3]. The anode current collector consisted of graphite felt (10*10 cm) and a carbon rod. The cathode consisted of the same graphite felt (2*5*10 cm) and a carbon rod current collector. The rest of the setup was similar to the anode material study. Polarization curves were recorded twice a week [3]. Rice seedlings were planted in the microcosms and fed with ¼ Hoagland feed solution [4]. The microcosms were placed at 30 ± 4 °C at 12/12 light/dark regime. Greenhouse gas emissions were measured twice a week for 2 hours using the closed chamber method. CH_4 and CO_2 were analysed using a gaschromatrograph (Finnigin Trace GC Ultra, Thermo Fisher Scientific). CH_4 was determined using a FID while CO_2 was determined using a thermal conductivity detector (TCD). Pore liquid chemical oxygen demand (COD) was determined using commercial kits according to the manufacturer's instructions (Machery-Nagel, Germany).

Results & Discussion

The study on the size and amount of granular carbon to be used in a plant-sediment MFC showed that the same material but in differently sized granules, resulted in higher current densities for the smaller granules (0.25-0.5 mm) compared to the larger granules (1-5 mm) (Figure V a). Applying granular carbon (1-5 mm) at 2/3 ratio of the sediment volume gave the same current density compared to a 3/3 ratio (Figure V b). From a practical perspective, the larger granules were subsequently used in the study on greenhouse gas emissions from rice agriculture.

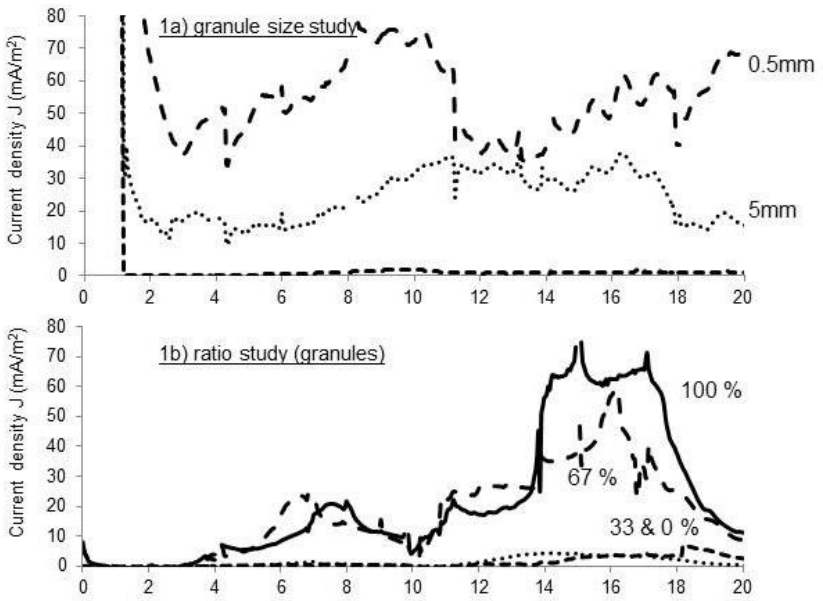

Figure V: Granule anode study. A) impact of granule size on current density. B) impact of application ratio on current density. 1-5 mm granules were used for study B.

Due to a low amount of current generation based on sole rhizodeposition, a model rhizodeposite was added to the rhizosphere. From the start of the addition of the organic carbon, current density started to increase (Figure VI, d. 40). Since no organic carbon nor CH_4 emissions were detected in the closed circuit period, an open circuit period was applied. At the end of this period (towards day 70), organic carbon was detected in the pore liquid and CH_4 emissions started to increase. Closing the circuit again with a 500 Ω resistor did not decrease the methane emissions. Decreasing the external resistance (100 Ω) and allowing more current to flow did not reduce the methane emissions (Figure VI). Current remained low during the last part of the experimental period (Figure VI). The reason for the low current can be found in the performance of the cathode electrode. Towards the end of the study a build-up of organic carbon (rice roots,

algae and dead leaves) was found on the cathode relating to the low activity of the oxygen reducing bacteria. The average cathode potential dropped from 0,47 ± 0,21 V vs NHE before and during the open circuit period (day 40-70) to -0,03 ± 0,21 V vs NHE from day 70 till the end of the experimental period. The large standard deviations are due to the circadian rhythm of the cathode potential.

From these results it can be seen that a large amount of anode material is needed to achieve a current density comparable to other, more connected materials such as felts [3]. However, applying granules has an advantage over felts when considering the use of agricultural practices. From the CH_4 emission study it can be seen that introducing an anode as alternative electron acceptor can extend the low-emission period of rice agriculture. This is comparable to applying for instance Fe (III) or sulphate to the rhizosphere [1].

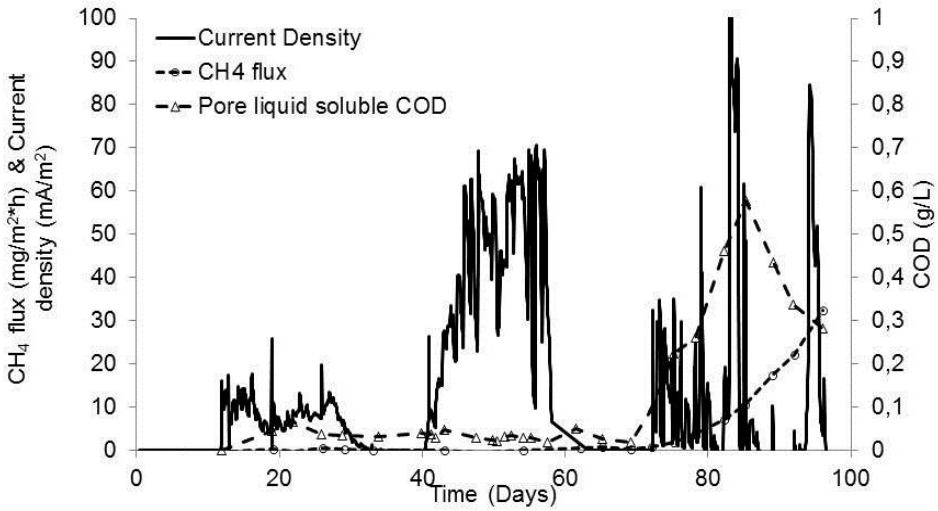

Figure VI: Relation between pore liquid organic carbon, current generation and CH4 emissions. A duplicate microcosm shows the same trend.

In order to improve the value creation of a plant- sediment MFC, it was shown that direct electrical power can be harvested by applying granular carbon electrodes. Next to that the anode shows the possibility to intervene in microbial metabolism in the rhizosphere of the rhizosphere.

A drawback of applying the standard sediment MFC paradigm is the deterioration of the cathode performance over time due to the accumulation of organic matter, leading to a loss in cathodic O_2 reducing capacity. This can possibly be circumvented by introducing a membrane or some other sort of separation between anode and cathode and between the cathode and the organic carbon accumulating in the overlying waterlayer. One possibility is to introduce oxygenated liquid in a tubular cathode in the rhizosphere. This separates the organic carbon from the cathode but also decreases the distance between the anode and cathode and thus positively impacting the internal resistance of the plant-sediment MFC.

Overall, the plant-sediment MFC can provide different benefits (electrical power generation, interaction in microbial processes) but the practical and importantly, the economical applicability needs to be further validated in terms of electrode use and configuration.

Acknowledgements

Evelyne Blondeel, Jonas Speeckaert, Jan Vermeulen & Prof. Pascal Boeckx are kindly acknowledged for their practical assistance and inspiring discussions.

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Design criteria for the Plant-Microbial Fuel Cell

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This abstract is based on and contains large parts of the summary of the PhD-thesis "Design criteria for the Plant-Microbial Fuel: Electricity generation with living plants – from lab to application" by Marjolein Helder.

Introduction & Objectives

To meet future electricity demand, alternative electricity generating technologies are needed. A new alternative electricity generation technology is the Plant-Microbial Fuel Cell (P-MFC), which uses living plants and bacteria to generate electricity (8). To further understand the underlying processes of the P-MFC and the factors that influence its power output, we determined design criteria for the P-MFC. The first focus of the design criteria was to improve the power output of the P-MFC. The higher the power output of the P-MFC, the larger contribution it could give to renewable electricity generation. The transition of a new electricity generation technology, however, is dependent on more than just power output. Therefore, we studied a number of additional factors that influence the applicability of the P-MFC.

Materials & Methods

Based on published work of the authors an overview was created on design criteria for the P-MFC. Additional design criteria assessed were sustainability (environmental performance, social acceptability and economic feasibility) and availability of energy when applying the P-MFC in practice.

Results & Discussion

Power output of the Plant-Microbial Fuel Cell

In 2008 the maximally achieved power output was 0.067 W m^{-2} [1], while 3.2 W m^{-2} was estimated to be theoretically possible [2]. Via selecting *Spartina anglica* as a plant, changing plant-growth medium, and changing the design of the P-MFC to a flat-plate system, power output was optimized to 0.44 W m^{-2} planting area.

Three plant species were tested (*Arundo donax*, *Spartina anglica* and *Arundinella anomala*). With two of those, *Spartina anglica* and *Arundinella anomala*, we were capable of producing bio-electricity and biomass concurrently in the P-MFC [3]. *Spartina anglica* outperformed *Arundinella anomala* considering maximum power output (0.22 W m^{-2} vs 0.021 W m^{-2}). Since *Spartina anglica* outperformed *Arundinella anomala* and *Spartina anglica* is a salt-tolerant species that can be found under various circumstances around the world, we focused on *Spartina anglica* for the rest of the design criteria.

With the below ground biomass we produced, maximum power density of the P-MFC was increased to 0.22 W m^{-2}, over 3 times as much as in the first experiment by Strik et al. in 2008 [1]. Power output could not be maintained over a longer period of time, however, and polarisation curves showed the anode to be limiting the power output [3]. The plant-growth medium used in the P-MFC contained a lot of nitrate. Removing the nitrate from the plant-growth medium and replacing it for ammonium led to a maximum power density of 0.21 W m^{-2}, and maintain a much higher power density over a resulted in a decrease in power output [4]. The effect of sulphur-cycling within the anode of the P-MFC is still not fully understood and should be researched further.

When taking the normal projected efflux of total carbon in the form of CO_2 from pastures of 0.09-0.12 kg C m^{-2} $year^{-1}$ [6], we could theoretically produce 30-40 mols of electrons per m^2 per year. This would lead to a current density of 0.092-0.122 A m^{-2}, which was regularly achieved or exceeded in different experiments. At a voltage of 0.5 V – a cautious estimate of 50% voltage efficiency for the MFC – a power density of 0.046-0.061 W m^{-2} would be achieved. This is

lower than the power density achieved before the start of this thesis project. Three explanations are possible for this difference in numbers:

- We overestimated our power output per m^2 due to overestimation of the biomass growth.
- Data from Kuzyakov underestimate the efflux of C from the soil, so in practice breakdown of organic matter is faster than projected and more electrons are released.
- Microbial activity and carbon turnover is enhanced in the P-MFC due to the availability a new electron-acceptor in the form of the anode.

The results with the new plant-growth medium were achieved in a new flat-plate design P-MFC. The flat-plate design resulted in a lower internal resistance for the P-MFC as compared to the previously used tubular P-MFC [5]. In total internal resistance can maximally be $0.094\Omega.m^2$ in order to reach 3.2 W m^{-2}. Internal resistance in our experiments ranges from 2-10 $\Omega.m^2$, so power density doesn't exceed 0.4 W m^2 and current density doesn't exceed 1.6 A m^{-2}. In the tubular system highest partial internal resistance was transport resistance, which was limited in the flat-plate system due to a smaller anode-cathode distance. The distance between anode and cathode is an important aspect to consider when designing a P-MFC.

Applicability of the Plant-Microbial Fuel Cell

After improving the power output of the P-MFC, we researched other design criteria for the P-MFC. We made a first attempt of putting the P-MFC under natural outdoor circumstances under harsh conditions on a Dutch roof to test the resilience of the system [7]. The P-MFCs produced electricity on the roof as long as the anode wasn't completely frozen. The plants died during winter and didn't recover in spring. Electricity production, however, recurred after frost periods. Anode-potential of both designs was quite stable, whereas the cathode-potential showed a diurnal cycle for part of the time due to the growth of algae on the cathode. To achieve 24 hours a day electricity production the cathode should be improved.

Another aspect that was assessed is the energy balance of the P-MFC. The energy balance of the P-MFC is dependent on its initial

energy input for construction, power output and its lifespan. The highest power density that was achieved and sustained over a longer period of time in this research is 0.2 W m^{-2} or 1.75 kWh m^{-2} $year^{-1}$ [5]. Based on electricity production solely, the payback time of the P-MFC – the time needed to net produce as much energy as was used to build the system – would be 136 years [8]. This exceeds the lifespan of the materials, so at this point in the development of the technology based on electricity production alone the P-MFC would not be renewable. Either the energy input needs to go down by reducing the amount of materials used or the power output of the system needs to go up. If we consider heat insulation of the green roof as a possible co-product of the P-MFC we can include the avoided heating in the energy balance of the P-MFC. Even at current power density payback time would go down to slightly over 30 years.

Sustainability was assessed based on environmental performance, social acceptability and economic feasibility. We assessed the environmental performance of the P-MFC and found that at current status of technology and materials the system is not competitive with existing electricity technologies for environmental performance [8]. The amount of materials needs to be reduced, especially activated carbon, and some materials should preferably be avoided altogether, like goldwire and Teflon coated copper wire. We assessed the environmental performance of the P-MFC via LCA methodology. LCA methodology is often used for environmental assessment of processes, products or technologies and assesses all impacts from cradle to grave. Typically LCA assessment is used for existing systems. The P-MFC is still under development and is difficult to assess via LCA methodology. Therefore, the approach of doing an LCA for the P-MFC at this point in time is an innovative way of applying LCA methodology.

Social acceptability is very dependent on the specific application of the technology. When applying the P-MFC on a green roof aesthetic value will be of particular interest for the user or owner of the building because it enhances the sustainable image of the company. Worldwide 52% of the companies has indicated that the company is willing to introduce sustainable solutions into the company and pay more for it than for non-sustainable solutions. When

looking at a decentralized application for developing countries social acceptability of the P-MFC will probably be high. Farmers are amongst the people with the lowest income around the world. Producing electricity with a product that they are familiar with, plants, will offer them an opportunity to increase profit. Moreover, applying the P-MFC as a decentralized system for electricity production will offer (part of) 1.2 billion people around the world that don't have access to electricity to develop economically and socially. Applying the P-MFC as large scale electricity generation technology will make an electricity plant look like a wetland. Again the aesthetic value is high and there is an opportunity of adding economic value to natural areas that currently only hold implicit value. It can be expected that the P-MFC will be socially acceptable.

Economic feasibility was assessed based on three cases: the Green Electricity Roof, decentralized electricity production in remote areas and large-scale electricity production in wetlands. Total costprice of the Green Electricity Roof at current state of technology would be over €600.- per m^2 including installation. When this system would be manufactured on large scale, though, one might assume that bulk prices can be used for calculating material price of the system. Moreover, installation would become much cheaper in the future. With solar panels, installation typically makes up 60% of the total price of the solar panel. When assuming this would be comparable for the P-MFC green electricity roof, total consumer price of the Green Electricity Roof come down as far as €30.-/m^2 installed. For large-scale wetland-electricity production technical adjustments are needed. For large-scale electricity production a tubular system could be produced like proposed by Timmers 2012 [9]. This tube could be implemented in existing wetlands or natural areas to generate electricity on a large scale. Due to an economy of scale, price of the system will drop dramatically, mainly because it can be assumed that less materials will be used and labour and maintenance costs will go down at the same time. A costprice of €1.13 per meter of tube with a circumference of 1 m might be possible. This would come down to a costprice of €0.35-5.65 per Watt installed. If technological constraints can be overcome for this system and the tubular configuration of the P-MFC can be scaled-up, this system

could compete with conventional fossil resource based electricity production.

Availability of electricity is dependent on source availability and storage. If we want to build a stand-alone system for decentralized electricity production that can deliver electricity at any wanted moment the P-MFC should be completely weather independent to avoid use of batteries, which is not (yet) the case. The P-MFC might, however, offer an opportunity for avoiding battery use. The system itself could maybe function as a battery due to high capacitance of the P-MFC. As was shown by Timmers et al. (2012) capacitance of the P-MFC, thus the capability of the system to internally store electrons, is high. This offers opportunities for alternately charging and emptying the system and letting it function as a battery by itself. This function should be further researched in order to fully understand the opportunities.

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Generation of current in vascular plant bio-photovoltaic systems based on rice (*Oryza sativa*) and an associated weed (*Echinochloa glabrescens)*

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Introduction & Objectives

Vascular plant biophotovoltaics (VP-BPV) is a nascent technology that uses higher plants to harvest solar energy and exploits the metabolic activity of heterotrophic microorganisms in the plant rhizosphere to generate electricity. VP-BPV, also known as Plant Microbial Fuel Cell (P-MFC) technology in the literature [1], was developed as an extension of microbial fuel-cells. In VP-BPV, photosynthesising vascular plants growing on top of a microbial fuel-cell feed heterotrophic microorganisms present in the plant rhizosphere, with concomitant transfer of electrons to an anode. The potential difference between the anode and cathode drives the movement of electrons through an external circuit to reduce an electron acceptor (e.g., O_2 or ferricyanide) at the cathode.

This 'carbon neutral and combustion emission-free' technology has a number of potential benefits. It could be used as a source of decentralized electricity in rural areas with minimum access to electricity infrastructure. Integrating electricity generation with the cultivation of food crops may provide a viable balance between food and energy production. VP-BPV systems could be combined with biofuel crop production to generate direct electrical power along with fuel from biomass.

The aim of this study was to evaluate and compare the performance of *Oryza sativa* (rice) and *Echinochloa glabrescens* (a rice paddy weed) in a novel VP-BPV configuration utilizing commercial compost and natural bacterial colonisation under greenhouse conditions. The VP-BPV configuration was operated without added nutrients or bacteria, to avoid interference with the natural formation of the rhizosphere environment. Also, a soft anodic material was utilized to minimise physical constraints on root formation.

The exoelectrogenic activities of the established rhizosphere communities were investigated by recording the daily voltage variation with a fixed external load over a period of 8 days. In addition, maximum power output variations were determined over a period of 30 days [2].

Materials & Methods

A VP-BPV device was constructed in a Magenta box (plant growth area = 36 cm^2). The cathodic compartment contained potassium ferricyanide solution and a stainless steel cathode was placed on one side in the Magenta box such that there was no free movement of the compartment within the device. A proton permeable membrane separated the cathodic chamber from the anodic compartment, which contained the plant material and a carbon fibre anode.

The anodic chamber, located beside the cathodic compartment in the Magenta box, contained a 3-dimensional nest of carbon fibre (Figure VII) with one end of the fibres protruding out of the Magenta box. Commercial compost was added around the carbon fabric to support plant growth, and tap water was added to maintain an anaerobic environment within the rhizosphere. The anode and cathode were connected to each other externally using a fixed external resistance.

The voltage across the fixed external load was recorded every 2 minutes using a multi-channel ADC-20 high resolution data logger (Pico Technology, St. Neots, UK) for three replicates of the two VP-BPV systems and one device for the two relevant negative controls (containing no vascular plants). The devices were kept in a greenhouse at a temperature of 21±2 ^oC, and maintained in an 18 hr light/6 hr dark cycle. The average light intensity was 14 Wm^{-2} during the light phase. Water (10 ml) was added to the plants every other

day to replace lost moisture and 100 mM potassium ferricyanide (2 ml) was added to the cathodic chamber every week to replenish the electron acceptor.

Polarisation curves were developed for the two VP-BPV systems and the negative control by measuring the cell voltage (V) under pseudo-steady state conditions with variable external loads (R_{ext}) from 1 MΩ to 270 Ω, and plotting V as a function of current density J (current per unit plant growth area (PGA)). Based on the polarisation curves, power curves were derived for each system by plotting the power density P (power per unit PGA) versus current density J. The power curves were further used to estimate the average maximum power output for each VP-BPV system and the negative control.

Figure VII: Three-dimensional mesh of carbon fibres used as anode in VP-BPV systems (2).

Results & Discussion

The voltage across a fixed external load was continuously recorded for eight days with established *O. sativa* plants (Figure VIII-a) and *E. glabrescens* plants (Figure VIII-b).

The VP-BPV systems were characterised by diurnal oscillations with clear variations between the trough and the peak values. No such trend was observed in the output of the negative control. Since temperature variations were absent throughout the experiments, these observations demonstrate a constant phase relationship between light fluctuation and the potential change recorded between the electrodes. However, the maximum and minimum voltage values did not directly coincide with the alternating phases of light and dark. This light-power output relationship may be the result of a series of events, beginning with synthesis of organic compounds in the leaves, and transport of these organic compounds through the plant vascular systems into the rhizosphere and subsequent absorption and consumption of the organic exudates by exoelectrogenic bacteria and culminating in the delivery of electrons to the anodic terminal. This indicates that power outputs in VP-BPVs are constrained by different processes, such as a lag-time in the delivery of root exudates to the rhizosphere and possibly microbial metabolism.

Power curves were developed for the two VP-BPV systems over a period about 30 days with established plants. The maximum power outputs of the *O. sativa* VP-BPV systems plotted versus time over a period of about 30 days showed that maximum power outputs increased from 0.403±0.075 GJ ha^{-1} y^{-1} on day 0 to 0.980±0.059 GJ ha^{-1} y^{-1} on day 32 of the experimental run. The presence of plant material (*O. sativa*) is necessary for obtaining this power output, as demonstrated by comparing these values with the negative control (0.027±0.009 GJ ha^{-1} y^{-1}).

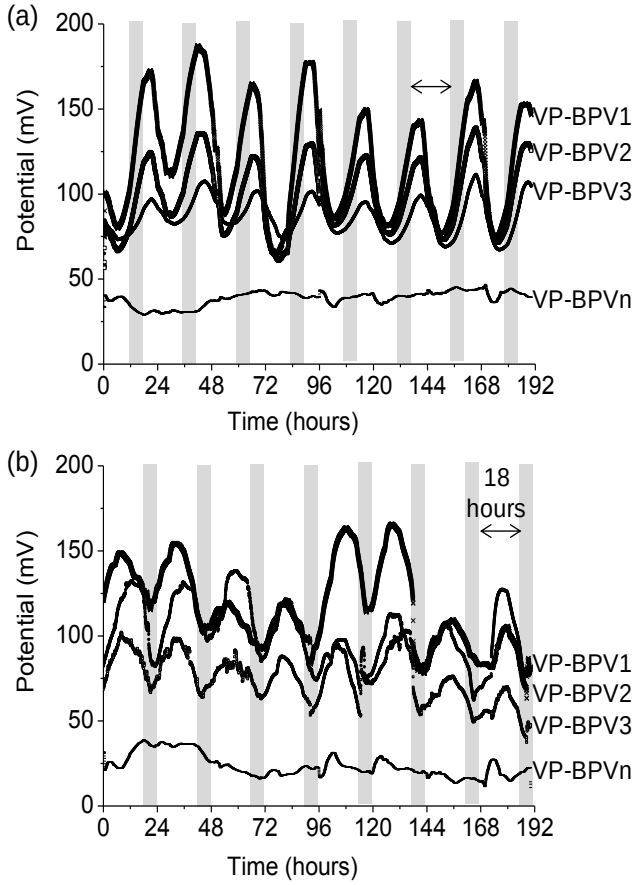

Figure VIII: Continuous records of voltage with a fixed external load for (a) *O. sativa* and (b) *E. glabrescens* as explained in the text. The grey background shows the dark phases (2).

On the other hand, the maximum power output for *E. glabrescens* did not increase significantly over time, beginning from 0.087±0.015 GJ ha^{-1} y^{-1} on day 0 and reaching 0.088±0.008 GJ ha^{-1} y^{-1} on day 31. Nevertheless, also for *E. glabrescens*, the presence of this vascular plant determined the power output (0.087±0.015 GJ ha^{-1} y^{-1}), as it was greater (ca. 3 times) than that of the negative control (0.027±0.009 GJ ha^{-1} y^{-1}).

This investigation successfully compares the VP-BPV performance of a plant performing C3 photosynthesis (*O. sativa*) with another

performing C4 photosynthesis (*E. glabrescens*). The maximum power output generated by *E. glabrescens* VP-BPV systems was almost 10 times lower than the maximum power output of *O. sativa* VP-BPV systems. As explained in the previous section, these variations in power output may be caused by differences in plant physiology and metabolism, and rhizosphere microbial populations.

Further work on the VP-BPV technology should focus on understanding and improving aspects of both the biology and device engineering. The biological aspects include exudate characteristics, exudate transport, presence of suitable microorganisms and microbe-exudate interactions. The engineering aspects that require understanding include the incorporation of electrodes into the rhizosphere landscape, anodic and cathodic reaction rates, and suitable electrode materials. This study shows that soft anodic material can be used in a VP-BPV system. In addition further optimization of the system may significantly enhance power output. Likely improvements include i) promoting root exudation, ii) introduction of exudate-specific bacteria, iii) inoculation of bacteria commonly found in natural rhizosphere of a plant and iv) watering the plants with solutions rich in organic nutrients. While understanding the 'underground' dynamic microbe-exudate interactions may be technically challenging, future investigation into these interactions may enable VP-BPV technology to become a sustainable means of electricity generation.

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Analysis of direct current generation by unicellular photosynthetic micro-organisms in biophotovoltaic devices.

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Introduction and Objectives

Solar radiation is a very attractive source of renewable and sustainable energy because it is the most abundant energy available on Earth, estimated at 4.3×10^{20} J per hour (1). Photosynthetic organisms have evolved to harness this energy directly and global energy conversion in such organisms is estimated to be ten times as much as current global energy consumption (4.0×10^{21} J per year) despite extremely low efficiencies of solar energy conversion to biomass (2). Circumventing carbohydrate synthesis through direct extraction of electrons from the photosynthetic electron transport chain (PETC) could potentially yield significant power outputs. To this end, we and others have developed a new type of electrochemical technology, which we have named biophotovoltaics (BPVs). BPVs are modified microbial fuel cells (MFCs) that generate power by harvesting electrons originating from the photochemical and respiratory activities of photosynthetic micro-organisms without the need for any chemical energy input (3). In order to optimise the efficiency of energy harvesting by biophotovoltaic devices, it will be necessary to acquire a detailed understanding of their behaviour. Here, we describe an analysis of parameters affecting the output of BPVs, the use of inhibitors to determine the source of electrons, an assessment of the capacity of biofilms to provide current in the absence of mediators, and a comparison of the behaviour of different anodic materials (4-6).

Materials and Methods

Initial quantification of parameters affecting power output was carried out in a BPV device containing three chambers using an indium tin oxide-coated polyethylene terephthalate (ITO) anode, containing cells of the cyanobacterium *Synechocystis* sp. PCC6803 and using ferricyanide as a redox mediator. DCMU 3-(3,4-dichlorophenyl)-1,1-dimethylurea, DBMIB (2,5-dibromo-3-methyl-6-isopropylbenzoquinone) and methyl viologen (1,10-dimethyl-4,4'-bipyridinium dichloride) were used to probe the source of electrons. Potential was measured across a range of different external resistances. For biofilm production, green algal (*Chlorella vulgaris, Dunaliella tertiolecta*) or cyanobacterial (*Synechocystis* sp. PCC6803, *Synechococcus* sp.WH5701) strains were grown directly on an indium tin oxide-coated polyethylene terephthalate anode. Assessment of anode function was carried out in a five-chamber BPV device using ITO, stainless steel (SS), glass coated with a conductive polymer (PANI), or carbon paper (CP) as anode.

Results and Discussion

Intact cyanobacterial or eukaryotic algal cells generated power in the dark, and an increased amount of power on illumination. Inhibitor studies indicated that light-dependent power output was due to electrons leaving the electron transfer chain from the reductive side of Photosystem I. Light-dependent power output was found to be proportional to the amount of photosynthetic cells present (as indicated by the amount of chlorophyll), and saturated at an unexpectedly low light intensity. The organisms used differed considerably in their ability to provide power output from biofilms in the absence of redox mediator, with *Synechococcus* sp.WH5701 showing the largest light-dependent power output. Power output from biofilms was self-sustained for several weeks and, as expected, depended on ambient light levels. Although power output was low, devices could be connected, and four BPVs connected in series (each with an anode area of 0.011 m^2) generated sufficient power to run a commercial digital clock. The comparison of performance of different anode materials showed surprisingly that the ratio between maximum dark and light power outputs varied according to the anodes used.

The results also showed, again surprisingly, that CP, a common anode used in many bio-electrochemical devices because of its large available surface area, may not be an optimal anodic material. Although ITO produced the highest light-dependent power outputs, stainless steel also performed well, and produced the fastest light-dependent response.

The fact that BPVs provide significant levels of power output in the dark is a particularly attractive feature for renewable energy generation when compared to conventional photovoltaic systems, which are light-dependent. This ability to produce power in the dark is particularly significant given the cost of power storage. The results have provided important insights into the requirements for power generation in BPVs. Although the overall power output (and efficiency of conversion of light energy into electrical power) of BPVs is low compared to conventional photovoltaic systems, the experiments described here will form the basis of future attempts to improve the performance of BPVs.

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Bioelectrochemical production of caproate and caprylate from acetate by mixed cultures

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Introduction & Objectives

The use of mixed cultures to convert waste biomass into medium chain fatty acids, precursors for renewable fuels or chemicals, is a promising route. To convert waste biomass into medium chain fatty acids, an external electron donor in the form of hydrogen or ethanol needs to be added. This study investigated whether the cathode of a bioelectrochemical system can be used as the electron donor for the conversion of acetate into medium chain fatty acids.

Materials & Methods

Two flat-plate electrochemical cells (0.56 L) were used. The anodes were made of a platinum-coated titanium mesh (projected surface area 0.025 m^2), and the cathodes were made of graphite felt (projected surface area 0.025 m^2). The anode and cathode were separated by a cation exchange membrane. One electrochemical cell was inoculated with enriched sludge consisting of mixed cultures, from a continuously operating anaerobic fixed film reactor that produced ethanol and C4-C8 fatty acids from acetate. The second electrochemical cell was not inoculated and served as a control.

Results & Discussion

In this study, we show for the first time that ethanol and medium chain fatty acids can be produced by mixed cultures, without the addition of an electron mediator or ethanol, in the cathode of a bioelectrochemical system (BES). At -0.9 V vs. NHE cathode potential, ethanol and the fatty acids butyrate, caproate, and caprylate were detected in the BES, with caproate as the predominant product (Figure IX). The control did not produce ethanol nor fatty acids and produced only a small fraction of hydrogen.

After 18 days of operation, the average cathodic electron efficiency, the

efficiency of capturing electrons from electric current and acetate in reduced organics, was 45%. This shows that indeed electrodes can be used for in-situ supply of electrons (or hydrogen). The largest part of the electrons was recovered in hydrogen (62%), caproate (26%) and butyrate (10%).

Most likely, the dominant mechanism of fatty acids production was via hydrogen. At -0.9 V vs. NHE cathode potential, both electrochemical hydrogen production and bioelectrochemical hydrogen production via hydrogen-producing microorganisms that can use the cathode as electron donor can take place.

Important elements to be addressed in future studies are (i) continuous production of medium chain fatty acids, (ii) choice of a suitable electron donor at the anode, and (iii) separation of the medium chain fatty acids from the catholyte.

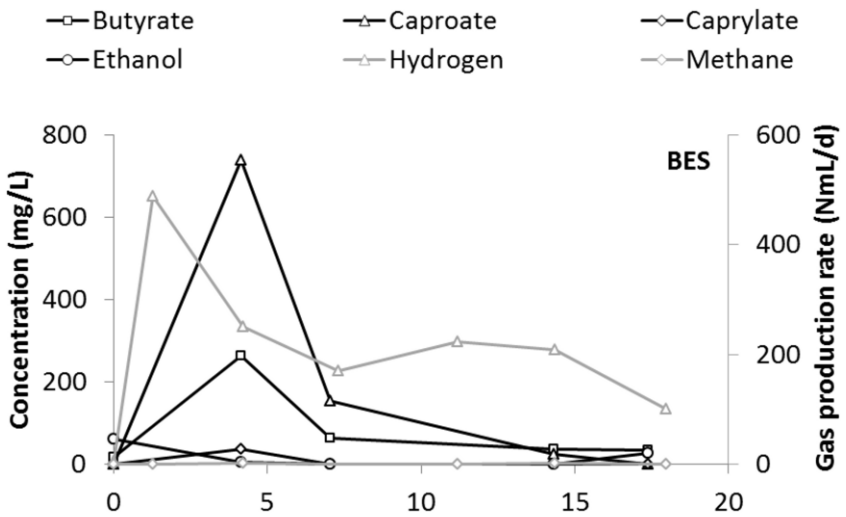

Figure IX: Concentration of reduced organics butyrate, caproate, caprylate, and ethanol, and production rates of hydrogen and methane with time at -0.9 V vs. NHE cathode potential (30ºC, pH 6) for the inoculated cell.

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Colloid formation for outperforming plant-sediment microbial fuel cells in soils with low conductivity

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Sediment microbial fuel cells (SMFCs) performance is usually limited due to soil features (type of structure, moisture and salt contents) in which they are allocated. In spite of the soil influence most of the efforts so far have been limited to hardware design in the bioelectrochemical device.
Our main objective was to outperform the SMFC by stimulating the *in situ* formation of silica
colloids in a low conductivity rice paddy soil. Our results have revealed how the presence of
silica colloid network, shown by Cryo-SEM analysis, reduces soil resistivity and consequently enhances the power production by a factor of 10. On top of that, our silica-supplemented soil showed a better utilization of electron donor, either artificially added acetate or natural rice root exudates, by electrogenic microbial populations. Sustainable manipulation of soil micromorphology using environmentally friendly reagents as silica offers a novel approach for outperfoming *in situ* microbial electrochemical applications on low conductivity soils, and should be considered as part of the SMFCs design in future applications.

Closing lecture by Dr. Ir. Bert Hamelers

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From Energy Production towards Resource Recovery, implications for the Plant MFC

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Introduction

Due to the growing world population and increasing level of wealth, the demand for energy and materials is strongly increasing. Bioelectrochemical systems (BESs) hold great promise for clean and sustainable production of energy and chemicals. BES systems can be fuelled with wastewater or plant rhizodeposits. In the past years, promising results have been obtained at lab-scale and the performance of BESs has been improved by several orders of magnitude. For further development of BES towards practical application, it is essential to have insight in the main factors that determine the total costs and benefits, and to have insight in BES performance. Analysis of internal resistances is a useful tool to determine the most limiting processes.

Results & Discussion

We compared the applicability of electricity producing Microbial Fuel Cells (MFCs) with hydrogen producing Microbial Electrolysis Cells (MECs). From analysis of the benefits (value of products and cleaning of wastewater) and costs (capital and operational costs), we determined the maximum internal resistance (in $m\Omega.m^2$) and current density that is required to make MFCs and MECs cost effective. The analysis of internal resistances shows that currently, the main limitations occur at the cathode of both systems (Figure X). Whereas the current densities of MFCs still need to be increased considerably

(i.e., internal resistance needs to be decreased), MECs are closer to application as their current densities can be increased by increasing the applied voltage. The higher value of the produced hydrogen in MECs compared to electricity in MFCs results in less stringent design criteria in terms of internal resistance. For the plant MFCs, the implication is that applicability is strongly dependent on additional values besides electricity production. Plant-MFC application at roofs create additional value via e.g. insulation, aesthetics and increase of roof life time. Sensor application of Plant-MFCs can be attractive due to low operational costs compared to battery powered sensors. Wetland Plant-MFCs application can be combined with nature preservation and support ecosystem services like: recovery of nutrients, CH_4 emission reduction, production of food and recreation.

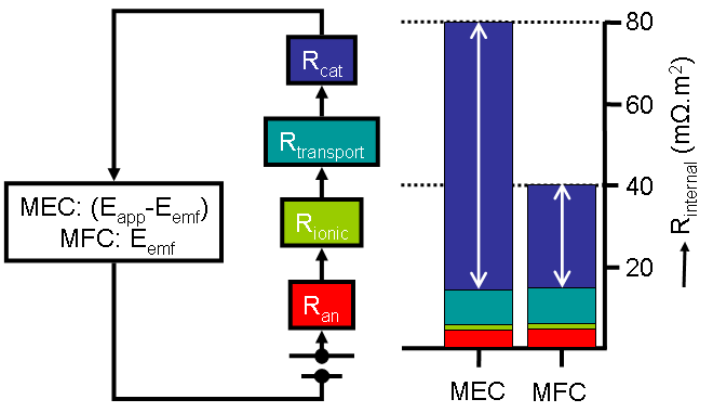

Figure X The internal resistance of BESs can be represented by an equivalent circuit. This internal resistance consists of the anode resistance, the resistance of the electrolyte, the resistance for ion transport through the membrane, and the cathode resistance. Together, these partial resistances make up the total internal resistance of the system. Cost analysis reveals that MECs can have a maximum internal resistance of 80 $m\Omega.m^2$, whereas MFCs can have a maximum internal resistance of 40 $m\Omega.m^2$. From this it can be calculated that, in an optimized system, the maximum allowed cathode resistance is 66 and 26 $m\Omega.m^2$ in an MEC and an MFC, respectively.

Posters

Effect of plants on pH and nutrient composition in the anode solution

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Introduction & Objectives

Up to now it remains still unclear, why some plant species survive the conditions of the anode of a plant-microbial fuel cell and others not. To test the hypothesis that the pH and the nutrient composition of the anode solution could be critical for plant survival, we cultivated six different plant species in sand or graphite filled pots. The investigated species were *Oryza sativa, Phalaris arundinacea, Spartina anglica* and *Arundinella anomala* (all survive MFC conditions) as well as *Lythrum salicaria* and *Viminaria juncea* (both do not survive MFC conditions).

Materials & Methods

The pots were kept waterlogged with nutrient solution. The loss of nutrient solution due to transpiration of the plants and evaporation of the pots was compensated by adding new solution each day. By this, we expected that the content of macro- and micronutrients will increase over time. However, we also expected that a substantial amount of the nutrients will be adsorbed to the substrate. In our experiments, we sampled an aliquot of the solution from each pot over a period of 5-10 days. The samples were analyzed for pH and in the case of *Oryza sativa* also for elemental composition.

Results & Discussion

The results demonstrate that except for *Phalaris arundinacea* the MFC tolerant species acidified the anode solution below pH 7, whereas the intolerant species did not acidify the anode solution. Elemental composition of the anode solution revealed that most macronutrients accumulate, but the key nutrients like iron or phosphorous did not accumulate. However, as soon as the pH of the solution dropped

below pH 6.5, large amounts of the nutrients were released again into the solution.

As a conclusion, the tolerance of plants towards MFC conditions is linked to the ability of the plants to modify the pH of the solution as well as a certain tolerance to high levels of macronutrients.

Effect of modified graphite material on P-MFC performance and plant growth

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Introduction & Objectives

In order to test if modified graphite granules will improve the performance of p-MFCs and if this modification will affect plant growth 10 tubular p-MFCs were installed and received either treated graphite materials or untreated graphite material.

Materials & Methods

The p-MFCs were planted with *Oryza sativa* and received additionally root material as well as granules from running p-MFCs prior to the start of the experiment. A chemical ferric cyanide cathode was used after 7 days of use of a biological cathode. The external resistance was set to 500 ohm. The cell potential of all p-MFCs was measured continuously over a period of more than three months.
The graphite modification aimed to test the effect of improving the hydrophilicity of granule surfaces. The treatment of modification consisted of an oxidation using nitric acid (120°C at reflux, overnight).

Results & Discussion

The data shows no clear effect of the treatment on cell potential. The variation of treated and untreated p-MFC was in a similar range. All p-MFCs showed a short start-up time and after changing the cathode from biological to chemical the cell potential raised quickly to 0.6 V in all p-MFCs. However, after one week the cell potential of all p-MFCs was below or close to 0.1 V again. Over time, the cell potential varied

strongly with no clear pattern, except for a clear day and night rhythm, which was detectable for all p-MFCs. The plant growth was not affected by the treatment. All plants showed a similar biomass production as well as a similar vegetative and generative stage. After three month the cell potential of all p-MFCs declined to very low values indicating a strong loss of functionality. The reasons for this are not clear so far, but might be due to limited rooting space or increased anode oxygenation by the roots.

Phenotyping of tomato roots under different environmental conditions

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Introduction & Objectives

Where new sequencing methods become rapidly available and high throughput genotyping became the standard during the last decade, phenotypic data seems to become the limiting factor in plant breeding. The study of genetic variation in root morphology and exudation has long been complicated by difficult and laborious phenotyping methods. Therefore, a phenotyping system was used to reveal the genetic variation within tomato for a broad range of root morphological traits and under different environmental conditions.

Materials & Methods

We investigated the influence of phosphorus limitation and microbial signaling (i.e. addition of active *Clostridium sporosphaeroides* cultures) on the following commercial tomato lines: *Solanum lycopersicum* var. Moneymaker, *S. lycopersicum* var Maxifort, and wild relatives: *S. arcanum*, *S. cheesmanii*, *S. chimeleskii*. The root traits were analyzed by taking daily photographs of the tomato roots, growing in an agar filled petri dish. The photographs were then analyzed via a specific software tool that allows the determination of the following root traits: total length of primary root, average lateral roots length, total root length, number of lateral roots, branching angle and convex hull area.

Results & Discussion

The different tomato genotypes responded differently to the treatments. In the control environment *S. cheesmanii* shows a higher total root length and lateral root number than *S. arcanum*. However, for *S. Cheesmanii* these values decrease when subjected to P stress. In the bacterial treatment the *S. Arcanum* showed a decline in total root length. Hence, the data indicates important genotype x environment interactions. Species specific adaptations obviously play a key role in root morphology.

Although the functional relation between root system architecture and exudation is widely described in literature, the causal relation has been under exposed. Currently we are studying the connection of root morphology data with information about exudation of the same species in order to elucidate the link between these root traits.

A new system for manipulation of anode temperature

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Introduction & Objectives

Preliminary experiments in climate chambers revealed that the cell potential of a Plant-Microbial Fuel Cell is strongly dependent on the anode temperature. An increase of the anode temperature by 5°C resulted in a significant increase of the cell potential and vice versa. However, in these preliminary experiments the entire chamber temperature was changed and not the anode temperature alone. By this a decoupling of anode temperature from the thermal energy input of the lighting system of the climate chamber was only possible during night times. Therefore, we developed a new system for manipulating the anode temperature independently from the chamber temperature.

Materials & Methods

The new system is designed for tubular MFCs but could also be adapted to flat plate systems. The system consists of tubing that is filled with glycol and connected to a cryostat device. The tubing was winded around the entire surface of the anode as well as the cathode. Thermal insulation was achieved by tightly wrapping isolation material around anode and cathode and all other tubing. This setup ensures a precise setting of the anode temperature with a deviation of less than 1°C from the set point. The vertical temperature gradient in the anode, caused by the energy input due to the illumination of the climate chamber, is also less than 1°C.

Results & Discussion

In a first trial we will investigate 6 independently manipulated MFCs. Over a period of several weeks, the anode temperature will be changed from low temperatures (i.e. 10°C) to high temperatures (i.e.

35°C) for different time intervals and during different times of the day. By this we aim to elucidate the correlation between anode temperature and cell potential and by this to evaluate the optimal temperature settings for an optimal performing Plant-Microbial Fuel Cell.

Effect of low P on total organic and inorganic carbon dynamics in the rhizosphere of rice: implications for Plant-Microbial Fuel Cells

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Introduction & Objectives

Phosphorous (P) is an essential micro-nutrient and crucial for plant survival. Thus, plants developed several strategies to tolerate low P contents in the soil. Especially the exudation of organic acids can improve the release of P from inorganic phases. This organic acid exudation under P deficiency can lead to a 10–1000-fold higher soil solution P concentrations. Thus, an interesting opportunity for the P-MFC concept is to promote a higher exudation of organic C from the plant roots by applying a low P content via the nutrient solution.

Materials & Methods

This study investigated the effect of low P on the content of total organic carbon (TOC) and in organic carbon (IC) of a low P tolerant and intolerant cultivar of *Oryza sativa* growing under non sterile and sterile waterlogged conditions.

Results & Discussion

The results indicated that the reduction of the P could be a possible tool to enhance the productivity of a plant-MFC. The intolerant cultivar responds with an increase in exudation of organic compounds during a low P treatment. The c flow per day of the low P intolerant cultivar increased from 0.1 to 1.71 mg carbon per plant dry weight and day. The tolerant cultivar responds also with an increased C flow per day, but only about 1/3 of the C flow of the low P intolerant cultivar. However, the low P tolerant cultivar formed nearly 40% more biomass than the intolerant cultivar.

A slower growth and (root) development is not a problem for the application in a plant-MFC as long as the ratio between increased exudation and reduction of root surface results in a higher C flow into the rhizosphere. This is the case for the low P intolerant rice cultivar.

Stability of anode (carbon) materials used in P-MFC's

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Introduction & Objectives

The Plant Microbial Fuel Cell (P-MFC) offers the possibility to produce bio-electricity without compromising the growing plant. The P-MFC is composed by the plant, an anode and a cathode. The plant and microorganisms living on its roots are in a close interaction. The plants exude organic matter that is oxidized by microorganisms, releasing and donating electrons to the anode. The composition and chemical interaction of the anode with its surrounding media might affect the P-MFC performance by several processes such as: nutrient release, leach of contaminants and shorten lifetime of the used materials. The processes mentioned above can also affect the total efficiency of P-MFC by limiting the plant growth or decreasing the activity of the microorganisms.

Three materials have been used in P-MFC's: 1-2 mm graphite granules (Ie Carbone, Wemmel Belgium), graphite felt (grade WDF) and activated carbon (1, 2). In general, these three carbon materials are expected to contain 98% carbon and less than 1% of ashes. However, it may be possible that they also contain impurities such as mica, iron oxides, granite and free silica and other traces elements such as cobalt, copper, antinomy and arsenic.

The objective of the current research is to study the composition and stability of electrode materials used in a P-MFC. The results from this research can give insights about: 1) long term stability of materials, 2) lifetime of technology, 3) environmental impact of effluent discharge.

Materials & Methods

To test the stability of the anode materials we proposed a modified toxicity leaching procedure (TCLP), which evaluates the hazardous of materials. A TCLP test assumes material disposition on landfill conditions; therefore, the test is performed using acetic acid at pH 5 and 20°C during 20 h (EPA 1994). For the leaching tests of the P-MFC materials we have selected oxalic acid at a concentration of 5 mM resembling plant exudates. Oxalic acid is one of the most abundant exudates from plants and is also one of the strongest organic acids (pKa = 1.3 and 4.2), providing extreme leaching conditions. The duration of the leaching test is extended to 6 months as a minimum to simulate the time that materials are exposed to leaching conditions during the P-MFC operation.

Serum bottles with 200 mL of oxalic acid 5 mM medium are agitated in a shaker at 20°C. Serum bottles are closed with a butyl rubber stopper and a crimped aluminium seal. Each test is run in triplicate for each material at three different pHs (2.5, 5, 7). These pH values were selected based on the observed pHs during the operation of the P-MFC (Sleutels 2011; Helder 2012). Three anode/cathode materials were used in the tests: (1) graphite granules (1-5 mm Le carbone) grained to 1-2 mm in the systems, (2) granular activated carbon (Norit PK 1-3) and (3) graphite felt (WDP grap felt). Materials were rinsed in demineralized water and dried at 30°C. The solid/liquid ratio of the materials was 50 g/L for graphite granules and activated carbon. The solid/liquid ration of graphite felt was 12.5 due to its low density value (0.11 g/cm^3). Bottles containing the materials were sterilized by autoclave before the start of the experiments.

The morphology of the materials was recorded using Scanning Electron Microscopy (SEM) and SEM Energy Dispersive X-ray Spectroscopy (EDX). EDX displayed the elemental composition of the materials at selected spots or areas selected under the microscope. Liquid samples from the bottles were filtered over 0.2 µm cellulose acetate membrane filter Spartan 30 (Whatman, Germany). Liquid sample composition was measured using ICP-OES (Varian). For each sample taken, pH and redox potential is controlled

in order to establish if leaching conditions are stable and/or if any microbiological activity is taken place despite of the sterilization pre-treatment.

At the end of the leaching tests (~6 months), materials are harvested by filtration of the solution contained in the bottles using paper filters (Schleicher & Schuell 589/1, pore size 12-25 µm). The paper filters are washed with demiwater and dried at 60-70°C. Dried material is characterized by SEM-EDX.

Results & Discussion

Anode materials were initially characterized using SEM-EDX analysis (Figure XI). The spectra by SEM-EDX was quantified in the entire sample but also in specific points. The average composition is displayed in Table 1, the number of spectra used for calculation is indicated between brackets.

The initial characterization of the anode materials indicated that graphite felt and graphite granules contain less than 1% of ashes. In the activated carbon anode, up to 7.8% of ashes containing a variety of impurities such as magnesium, aluminium, calcium but also minor elements as titanium and bromide was found.

The initial results from the leaching tests with the materials (after 20 h of leaching) already suggest that the anode materials have several impurities. In general, the impurities found in the three anode materials tested can be classified in two groups (A) containing Al, Ca, Fe, K, Mg at a concentration in the range of mg/L and (B) containing B, Ba, Cd, Cu, Li, Mn, Ni, Sr, Tl, Zn at a concentration in the range of µg/L (Table 2). In general, group A contains elements that, at these concentrations, probably will not affect the plants. Although the elements in group B are in the range of µg/L, these can produce a toxic effect in the plant if their concentrations in the solution rise during the time of the experiment.

The anode materials are currently being tested in long-term experiments. These preliminary results of this experiment suggest that the stability of the electrodes is questionable. We expect to bring more insights about the long term operation of a P-MFC and show how metal release can affect the performance of the system. The impurities released by these materials would impact the plants if the

system has no effluent discharge, due to the accumulation (concentration) of toxic elements. But also if the system has effluent discharge it would affect the receiving environment. Therefore the results will be linked to wetland conditions to discuss the impact of using carbon electrodes in wetland based P-MFCs.

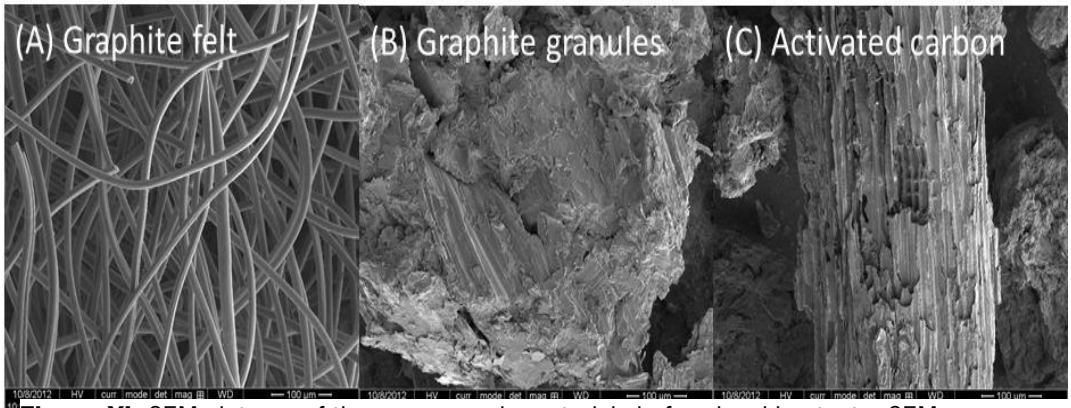

Figure XI: SEM pictures of three new anode materials before leaching tests. SEM photographs at magnification of 250 x.

Table 1: Average composition of new anode materials before leaching tests quantify by SEM-EDX.

Element in anode material (%)	C	O	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Br	Tot
Graphite felt (2 spectra)	99.97	-	-	0.06	-	-	-	-	-	-	-	-	-	100
Graphite granules (2 spectra)	99	1	-	-	-	-	-	-	–	-		-	-	100
Activated carbon (4 spectra)	92.2	3.76	0.34	0.42	0.27	0.18	0.16	0.06	0.33	2.52	0.09	0.65	0.3	100

Table 2: Impurities leached from anode materials into solution during the experiments at different pH values.

Impurities in group A (range mg/L)						Impurities in group B (range µg/L)									
	Al	Ca	Fe	K	Mg	B	Ba	Cd	Cu	Li	Mn	Ni	Sr	Tl	Zn
	mg/l	mg/l	mg/l	mg/l	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
(A) Graphite felt															
pH 2	0.03	1.12	0.08	4.1	0.45	48.22	26.5	0.3	5.9	0.1	1.8	1.1	9.0	3.8	52.7
pH 5	0.03	0.37	0.05	4.4	0.40	36.88	13.9	0.2	6.2	0.1	1.9	2.3	6.1	-	37.7
pH 7	0.06	0.70	0.03	10.0	0.41	34.76	6.5	0.1	6.3	0.2	2.4	3.7	6.9	1.3	33.2
(B) Graphite granules															
pH 2	0.05	1.60	4.54	63.6	0.40	51.79	41.7	0.6	5.3	2.5	3.8	11.7	17.1	-	81.5
pH 5	0.02	0.42	2.61	4.6	0.38	37.16	15.9	0.2	3.9	2.3	2.6	6.5	8.0	1.5	39.1
pH 7	0.01	0.51	-	5.6	0.37	31.86	5.0	0.2	2.9	2.3	1.3	-	7.2	4.3	11.2
(C) Activated carbon															
pH 2	4.71	1.28	0.02	40.5	-	4.62	6.0	0.7	2.2	1.8	0.9	0.4	16.4	2.0	6.1
pH 5	14.67	1.04	0.01	44.2	0.41	23.59	3.1	0.5	-	0.9	0.8	0.7	10.8	0.0	7.5
pH 7	15.34	0.98	-	44.5	0.36	23.00	3.1	0.5	-	0.9	1.1	-	10.4	0.0	7.2

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Scaling up Plant Microbial Fuel Cells and harvesting electricity for low power requiring applications

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Introduction & Objectives

In man's search for alternative sustainable energy sources, Plant Microbial Fuel Cell (PMFC) emerged as a promising technology which could supply renewable and sustainable energy (1). Based on photosynthesis, the principle of PMFC is that in the cell chamber where the plants grow, electricity is generated by electrochemically active bacteria (EAB) when the electron donating low molecular weight (LMW) organic compounds released by plants are consumed by these bacteria (2). Without the drawbacks of traditional fossil fuel industry such as environmental pollution and nature depletion, PMFC can produce safe clean and renewable energy with promising yield.

In this study, the objective is to scale-up a PMFC system and investigate the feasibility of harvesting the electricity for low energy requiring applications. Regarding electricity generation, the following specific research objectives are set:

1. Usable electricity.
   In this study, usable electricity is defined as electricity generated from PMFC which have sufficient power, voltage or current to run certain electricity appliances.
2. Stable performance
   It is not possible to power a long-term operation unless the power generation of PMFC is stable without significant fluctuations.

3. Maximum power output
   The purpose for a functioning PMFC systems is the generation of electricity which is sufficient to supply certain appliances. Logically, the ideal situation is to have maximum power output harvested, which indicates that the conditions under which maximum power output is reached should be investigated.

However, to meet the above requirements, apart from generating sufficient electricity and raising output voltage and current, another challenge in this study is the occurrence of cell reversal. Cell reversal can occur during stacked MFC operations. Unequal performances of individual cells can lead to different working voltages, so the total voltage can decrease when certain cells have bad performances. The reasons can be starvation of microorganism (3) and cell architecture (4), and this problem can be dealt with by maintaining a suitable condition for plants in terms of temperature, pH, humidity, illumination etc., while maximizing the contact between the reactants and electrodes in the operation.

The following research questions are expected to be answered in this study:

1. What is the average/maximum power output of the PMFC system regarding different cell connections?
2. Is the power generation long-term stable?
3. Is it feasible to supply electricity for low energy requiring applications by combining PMFC system with a capacitor and a DC/DC converter?

Materials & Methods

In this study, a PMFC system with a membrane surface area of 0.04m^2 is constructed with four anode chambers and five cathode chambers stacked together. This configuration is relatively bigger than former studies and allows changing ion transport direction which was proved to be significantly beneficial in increasing the power output (5).

Furthermore, as illustrated in the figure, three connections of the system are possible which can offer different voltage and current. By measuring the potential, power density and internal resistance of each connection, information about PMFC can be gained which can be used for increasing power output for future studies and practical operations.

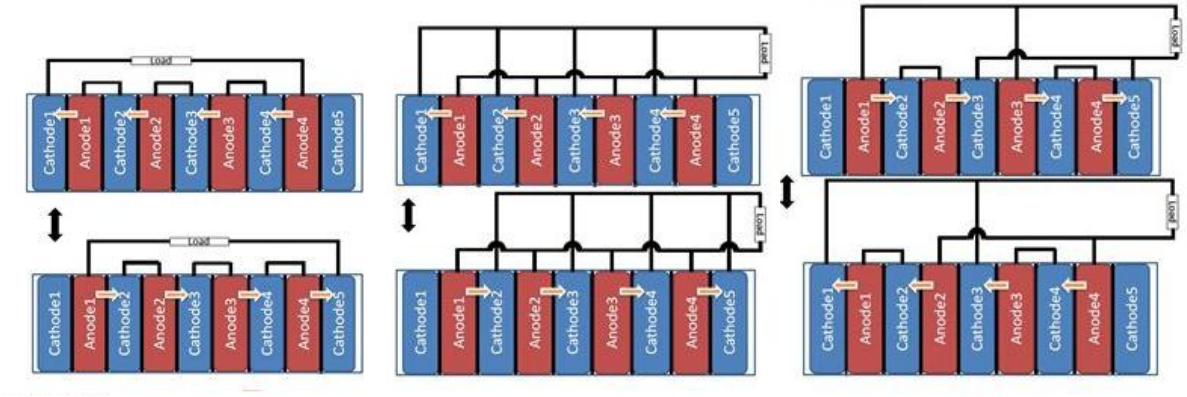
In terms of harvesting the electricity, the combination of PMFC and DC/DC converters is investigated to see the feasibility of increasing the output voltage into a usable range as well as storing and releasing electricity when it is needed.

The plant in this study is Spartina anglica which is a salt marsh species selected in former study (5). By using this plant, a relatively salty environment is possible which can increase the conductivity and reduce internal resistance. By using ferricyanide, the oxygen reduction kinetics can be improved resulting in increased power output (5).

Results & Discussion

The experiments are not completed yet so results are not available, but the hypothesis is that this scaled-up PMFC system with the mentioned configuration can increase the power output. By coupling the PMFC with DC/DC converters, electricity can be harvested and stored for low energy requiring application.

Connection A **Connection B** **Connection C**



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Immobilization of Porphyrins on Anode and Cathode of a Microbial Fuel Cell

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Porphyrins are a group of organic compounds widely distributed in nature. For example, the well-known O_2 carrier called heme is a prosthetic group that consists of an iron atom contained in the center of a porphyrin. Hemes are also a part of c-type cytochromes which are electron transferring proteins involved in electron transfer in Microbial Fuel Cells (MFCs). Recently, we described a method allowing porphyrins immobilization on carbon surfaces based on the electrochemical reduction of diazonium salts (1).

The immobilization of porphyrins may be used both on the anode and cathode sides for improving the performances of MFCs. Indeed, at the cathode the oxidant which is usually used is molecular oxygen because it is freely available and because it can be reduced to water. Nevertheless reduction of oxygen on a carbon cathode involves a significant over-potential that limits the cell voltage, and hence its power. In order to reduce this over-potential, metal porphyrins such as iron or manganese porphyrins can be use as an O_2 catalyst (2). At the anode side, the participation of artificial porphyrins in the microbial electron-transport chains has been reported. In that context we are studying the impact of immobilizing different porphyrins on a carbon surface on the performances of a bioanode.

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Maximizing power output of Plant Microbial Fuel Cell with sustainable bio cathodes

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Introduction & Objectives

The Plant Microbial Fuel Cell (PMFC) combines living plants with the microbial fuel cell. In the PMFC, the plant roots are allocated in the carbon anode electrode thereby providing the fuel to generate electricity. The PMFC concepts is attractive since it is a new source for renewable and sustainable green electricity [1]. There are several processes which determine the power output of PMFC: photosynthesis, rhizodeposition, and energy recovery in the Microbial Fuel Cell (MFC) [2].

Photosynthesis and amount of rhizodeposition are related to the type of the plants and many other factors. For PMFC, the applied plant should have the ability to survive at water logged "anaerobic"conditions in the anode[3]. Among studied plants, *Spartina anglica* has shown the best performance on average current and power densities[3]. Also, it has been proven that *Spartina anglica* can achieve long-term performance in a PMFC[4]. Therefore, *Spartina anglica* is an interesting model plant for PMFCstudies.

The amount of rhizodeposition and/or coulombic efficiency is affected by the plant growth medium used. Current production of a flate-plate PMFC using *Spartina anglica* increased from 186 mA/m^2 to 469 mA/m^2 (155 mW/m^2 planting area) in a nitrate-less medium [5]. This achievement is higher than others average current densities that range between 32 mA/m^2 and 214 mA/m^2 planting area[2].

To achieved the maximum power, the PMFC should have low internal resistance. Beside the likeable substrate limitation, high internal resistance has been a key factor that causes low power output in a PMFC[2, 4, 6]. Several researches succeeded to decrease

internal resistances. Timmers et al. was able to reduce anode and membrane resistance by modifying the cathode compartment into a bicathode system that changes ion transport directions [7]. The PMFC maximum power output increased almost 400%. Helder et al. designed a flat plate PMFC with lower internal resistances and reached a maximum power density of 0.44 W/m^2.

For study reason, the lab scale PMFC studies used non-sustainable ferricyanide reducing cathodes [1, 5, 7]. An option towards achievement of sustainable PMFCs is making use of oxygen reducing biocathodes. These biocathodes use widely available oxygen as final electron acceptor and bacteria that catalyse the reduction process at the cathode. Biocathodes must support microbial growth, have high electric conductivity, be cheap and inert [8]. Among other materials, graphite was proven to be a suitable biocathode material to be applied in practice[8, 9]. Recent studies show that biocathodes can reach current densities up to 4.5 A/m^2 (at pH 2.5; Fe^{2+}/Fe^{3+} as mediator; porous electrode)[10] or 0.313 A/m^2 (at pH 7.0; without mediator; flat plate electrode)[11]. These current densities are in the same order of magnitude of best performing PMFCs that reach current densities up to 1.6 A/m^2 [12].

The recent PMFC and biocathode developments make it possible to design a nove PMFC which has the potential to reach higher power output and make use of sustainable biocathodes. Here fore we developed a novel flat-plate bicathode PMFC which we will combined with several type of biocathodes. The objective of this research is to maximise the power output of PMFC with sustainable biocathodes. We will investigate the internal resistances, long term performance and ion transport.

Materials & Methods

This experiment will be conducted with four flat-plate bicathode PMFC with a similar anode. A bicathode PMFC consist of two cathode named cathode 1 and cathode 2 and one anode in between. Both cathode and anode are connected with an external resistance using a switch that enable each cathode is alternately operated by changing the switch. The operation method for this research will follow

Timmers [7]. To prevent pH changes in the PMFC, BPM membrane will be used for the all set ups [10].

In these four set up, a similar anode will be used as before [12]. In the anode, *Spartina anglica* will be used as a source of rhizedeposition because it has long performance ability [4]. Moreover, 25% volume of dead roots is added to the anode compartment to provide higher substrate availability that can increase power output and shorten start up time [12]. To ensure the plants have enough nutrients and produce high rhizodeposition that in the end will increase the power output, nitrate less growth medium will be prepared as used in Helder et al. [5].

For the cathode, three set ups are bio bicathode and one set up is using Pt-coated titanium as a reference. The first bio bicathode is using graphite felt in combination with ferric iron reduction and *Acidithiobacillus ferrooxidans* bacteria. This biocathode is chosen because it is sustainable and in a MFC it can generate power output 1.2 Wm^{-2} with very low cathode internal resistance (0.055 $\Omega.m^2$) [10]. The circulated catholyte for this set up will follow Ter Heijne et al., [10]. It is important to keep the pH level on this set up below 2.5 to prevent the precipitation of ferric iron hidroxide [13]. The last two biocathodes are using the similar materials, -graphite felt, oxygen, and mixed population of bacteria,- but at two different pHs. One is at pH 2 so as to compare with the first set up and another one is at pH 7 in which is the natural growth environment for *Spartina anglica* [5]. The circulated catholyte will be aerated as before [11].

For data collection, anode and cathode potential will be measured with Ag/AgCl reference electrode. Data will be logged every minute with fieldpoint and collected with Labview software. pH is controlled using pH controller. Sample from anode and cathode will be measured using ProLine Plus Qis instrument to determine the conductivity. All set ups are going to be placed in a climate chamber (Microclima 1750 Snijder) at 25 ^{0}C with 75% humidity and a day-night regime of 14:10 hours and average light intensity of 596$\pm$161 µmole m^{-2} s^{-1} will be used.

Hypotheses

To ensure the highest power output is achieved, it is important to use the best proven conditions, materials, and design. Early studies did improve the power output and reach long term [4]. We expect a higher power output due to combining the suitable growth medium [5], the flat plate PMFC [14], and the bicathode operation mode [7].

Applying ferric iron catholyte in the MFC can generate 0.86 Wm^{-2} of power output at 4.5 Am^{-2} current density [13]. While combining between ferric iron reduction and its oxidation by *Acidithiobacillus ferrooxidans* bacteria, the power output was increase to 1.2 Wm^{-2} at the same current density [10]. It means the *A. ferrooxidans* bacteria can increase the power output of MFC up to 40%.

A bicathode PMFC was able to decrease internal resistance up to 73 % (from 4.3 $\Omega.m^2$ to 1.2 $\Omega.m^2$) that resulted in increase in power output up to 398% [7]. In the latest research, Helder at al., [12] have found that a flat plate PMFC can generate 0.44 Wm^{-2} power output at current density of 1.6 Am^{-2}. In this research, the internal resistances were vary from 1.3 $\Omega.m^2$ to 4.2 $\Omega.m^2$.

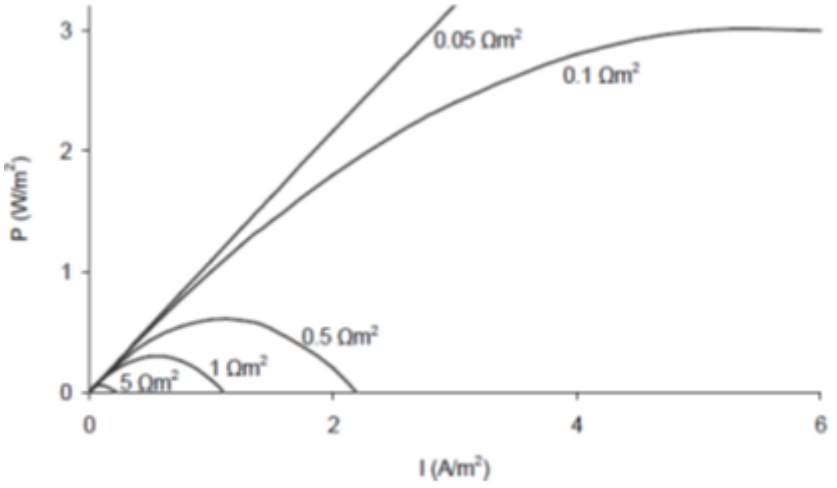

Figure XII: Relationship between internal resistances and power densities at several current densities [12]

Based on the achievements mentioned, we hypothesize that applying a bicathode system on a flat plate PMFC can maximize the power output. The internal resistance of the flat plate bicathode PMFC is predicted to decrease in a range 0.3 $\Omega.m^2$ – 1.1 $\Omega.m^2$. With this internal resistance, the maximum power output of 0.5 Wm^{-2} – 1 Wm^{-2} can be achieved (Figure XII). To maintain a long term maximum power output, additional substrate and/or buffer may be required, this to prevent exhaustion of electron donor and/or local acidification.

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Clarifying internal resistances of oxygen reducing cathodes towards PMFC application

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Introduction & Objective

Problem definition

A plant microbial fuel cell (PMFC) produces bioelectricity from solar radiation without harvesting the plants. PMFC is comparable to a microbial fuel cell (MFC), as electrochemically active bacteria are used for electricity production. The feasibility of an electricity producing technology depends among others on the costs required for the production of electricity. For both MFC and PMFC ((P)MFC), the measured cell voltage is dependent on the internal resistance of the cell as showed in equation 1. Equation 2 shows that also the electricity production depends on the internal resistance.

$$E_{cell} = OCV - IR_{int} \quad (1)$$
$$P_{cell} = VI = I(OCV - IR_{int}) \quad (2)$$

The measured cell voltage (E_{cell}) is the open cell voltage (OCV) minus the sum of all internal losses, IR_{int}, where I is the current and R_{int} the internal resistance. The electricity production of the cell (P_{cell}) is the voltage (V), in this case E_{cell}, multiplied by the current. In Figure XIII, the cell voltage losses (i.e. overpotential (η)) are visualized.

$\eta_{thermodynamic}$.: differences compared to standard cell voltage due to temperature, pressure and concentration
$\eta_{side\ reactions}$: unwanted side reaction
$\eta_{electrode\ kinetics}$: the rate of the reaction at the electrode
η_{ohmic}: resistance of electrode, electrolyte and membrane against the flow of electrons and ions
$\eta_{concentration}$: limited availability of substrates, accumulation of products and pH gradient
$\eta_{turnover}$: microbial metabolic rate

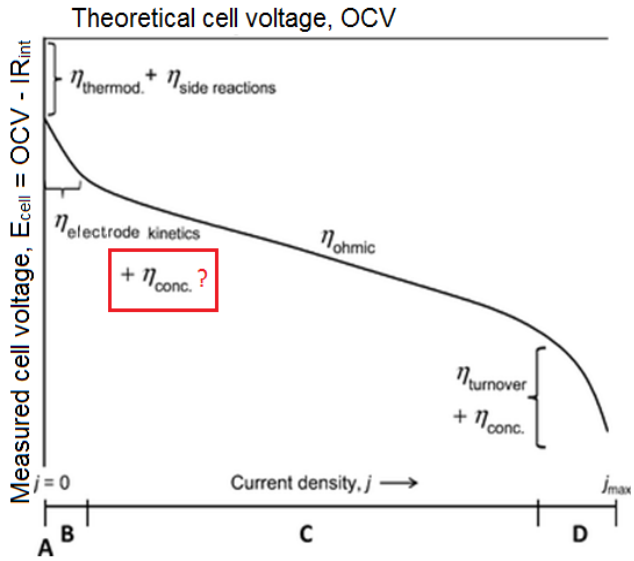

Figure XIII: Standard polarization of a (P)MFC with the dominant overpotentials at OCV (A), low (B), medium (C) and high (D) current densities. According to Popat et al. (2012), the concentration overpotential does not only occur at high current densities, but also at lower current densities. Figure adapted from Harnish and Schröder (1).

At OCV, the thermodynamic and side reactions overpotential mainly occur. At low current densities also the electrode overpotential decreases the performance. Increasing the current results in mostly an ohmic overpotential and at the maximum current density, mainly the concentration and turnover overpotential lower the performances. However, Popat et al. (2) showed concentration losses already at low current densities (<1 Am^{-2}) due to the accumulation of OH^- and locally higher pH at the cathode surface. The ohmic and concentration overpotential are operational losses. Electrode kinetics and turnover overpotential are mainly catalyst based losses (1).

The electricity production of a MFC is mainly limited because of the cathode resistances (3). Also in a PMFC, the first pilot project the cathode is limiting the electricity production (4) (data not shown). At the cathode oxygen is reduced (eq. 3 and/or 4).

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (3)$$

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \quad (4)$$

This reaction can limit the current production, because there is a lack of oxygen availability at the cathode and because the H^+ and/or OH^- are not optimal transferred to or away from the cathode surface(2). Possible improvements of the cathode are (5):

- the addition of a buffer (*ohmic and concentration overpotential*)
- changing the pH to increase the amount of available H^+ or OH^- (*concentration overpotential*)
- the addition of microorganisms to catalyze the oxygen reduction (*electrode kinetics and turnover overpotential*)
- an air diffusion biocathode to increase the oxygen concentration (*concentration overpotential*)

In this research the focus is on the first two mentioned improvements (i.e. the addition of a buffer and the change in pH). Low pH increases the amount of available protons and enhances the transportation of these protons from the anode to the cathode compartment (6). From the Nernst equation, a decrease of one pH level will theoretically result in 60 mV increase in cathode potential (7). A buffer can maintain the pH at a nearly constant level, therefore prevent a pH gradient to occur and prevent the accompanying voltage losses. Torres et al. (8) decreased the pH gradient with the addition of the buffer CO_2. CO_2 reacts with the hydroxide ions and creates carbonate or bicarbonate. Due to this reaction the pH level is maintained and the voltage efficiency increased. Buffers not only improve the proton transport away from the electrode (9) but also increase the ionic strength of the electrolytes by reducing the ionic resistance of the system (10). Jeremiasse et al. (7) compared different buffers at chancing pH levels. The buffers reduced the overpotential compared to the solutions without a buffer. Close to buffer pK_a, the smallest overpotential was reached. The current density affects the effect of a buffer. 100 mM phosphate buffer at pH 7.2 does clearly improves the cathode potential up to a current of 5 A/m^2. At a current density of

10 A/m^2 or more the buffer has hardly any effect. A higher buffer concentration is needed to improve the performance of a MFC with a higher current denisity (2).

Objective

It is clear from literature that buffer and pH and current density affect the power output of MFCs and can improve the power output of the PMFC. A buffer increases the current density at a pH close to the pK_a. At higher current densities more buffer is needed to reach the same effect, because more protons needs to be transported to the electrode to reduce oxygen. Low pH positively affects the current generation, due to a larger amount of available protons. Preferably a low pH and a buffer effective at that pH is required to increase the generated current.

The objective is to clarify the different internal resistances of the oxygen reducing cathode. The main goal of this research is to find out which areas of the polarization curve and as result which internal resistances are affected by a buffer and pH.

Materials & Methods

For the experiment, a MFC is constructed similar to the MFC used by Ter Heijne et al. (11). The cell consists of two plexiglas plates with flow channels separated by a cation exchange membrane. Each flow channel is connected to a flat plate graphite electrode. Catholyte and anolyte are pumped through the corresponding flow channel attached to the electrode. Each flow channel is 11 cm long by 2 cm wide. This surface (22 cm^2) is in contact with the electrode. Both the catholyte and anolyte consist of demineralized water with 1M KCl background electrolyte. The background electrolyte is added to minimize the solution voltage drop and to exclude migration and conductivity effects (Jeremiasse et al., 2009). In all experiments the anolyte is similar. The catholyte is continuously aerated and varies per experiment by adding different buffers and base/acid to change the pH.

In the first experiment, a blank is tested with catholyte including background electrolyte without a buffer. At each pH level from 2 to 12, a polarisation is done at a cathode potential from 400 mV to -400 mV vs Ag/AgCl (with steps of 100 mV). The OCV of an unbuffered cathode at pH 7 is normally around 0 mV vs Ag/AgCl (12). The experiment is also repeated at OCV to measure the maximum cathode potential for electricity production.

Afterwards, the experiment is repeated with a phosphate buffer added to the catholyte. Phosphate is the selected buffer because it is effective at three completely different pH ranges, it is common in nature and it showed good results on the overpotential in the study of Jeremiasse et al., (2009). The following three equilibriums occur in the catholyte when the pH is decreased:

$$HPO_4^{2-} \Leftrightarrow PO_4^{3-} + H^+ \quad (pKa = 12.8) \quad (5)$$
$$H_2PO_4^- \Leftrightarrow HPO_4^{2-} + H^+ \quad (pKa = 6.9) \quad (4)$$
$$H_3PO_4 \Leftrightarrow H_2PO_4^- + H^+ \quad (pKa = 2.1) \quad (3)$$

The experiment is again started at a high pH of 12 and gradually decreased to 2. The experiment is several times repeated with different carbonate concentration. The selected concentrations are 0 mM, 2 mM, 10 mM, 50 mM and 500 mM.

Follow-up experiments

Even though there are no results yet, it is already worth looking to the follow-up experiments. When different suitable buffers and pH ranges for a MFC are found, it does not automatically mean that they can be applied in a PMFC or together with catalysing microorganisms in an oxygen reducing biocathode. In the follow-up experiments, microorganisms will be added to the suitable combinations of buffer and pH. As a result can be seen if the microorganisms survive in this conditions, but also if they still have a catalysing effect. After microorganisms are added again polarisation curves are made to clarify the internal resistances which are related to the microorganisms. Plants often grow at a low pH, which makes the preferred low pH suitable for PMFC. However, the buffer and pH should not negatively affect the vitality and growth of the plants (13).

Acknowledgements

This research is financed in part by the BioSolar Cells open innovation consortium, supported by the Dutch Ministry of Economic Affairs, Agriculture and Innovation. Furthermore, this research is also in part financed by Alliander and Plant-e.

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