Design criteria for the Plant-Microbial Fuel Cell

Electricity generation with living plants – from lab to application

Marjolein Helder

Thesis committee

Thesis supervisor
Prof. dr. ir. C.J.N. Buisman
Professor of Biological Recovery and Reuse Technology
Wageningen University

Thesis co-supervisors
Dr. ir. H.V.M. Hamelers
Assistant professor at the sub-department of Environmental Technology

Dr. ir. D.P.B.T.B. Strik
Post-doc at the sub-department of Environmental Technology

Other members
Prof. dr. LE.M. Vet, Wageningen University
Dr. ir. B.M. Schober, Wageningen University
Prof. dr. ir. K. Rabaey, Ghent University, Belgium
Dr. F. Barriere, Université de Rennes 1, France

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Thesis

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Marjolein Helder
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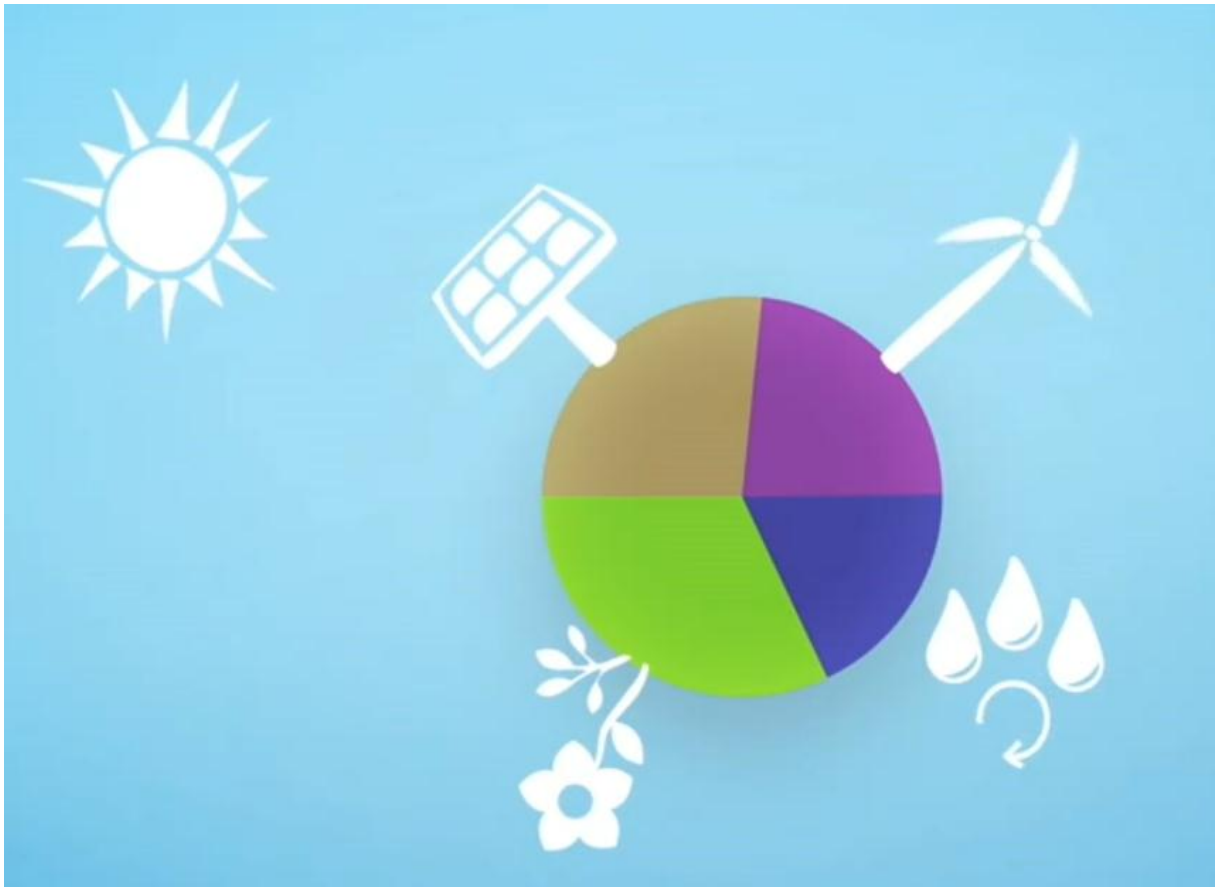
TABLE OF CONTENTS

1 INTRODUCTION

Paragraphs 1.1, 1.3 and parts of 1.4 based on:

Strik, D.P.B.T.B., Timmers, R.A., **Helder, M.**, Steinbusch, K.J.J., Hamelers, H.V.M., Buisman, C.J.N. – *Microbial solar cells: Applying photosynthetic and electrochemically active organisms* – 2011 – Trends in Biotechnology 29 (1), pp. 41-49



Due to a growing world population and increasing wealth energy demand is rising (1-5). Energy is a very important economic driver. It has been shown that energy is directly linked to economic welfare (Figure 1.1). Energy is needed for development (6) and energy conservation may even harm economic growth (3). In order to enable developing countries to actually develop their economy more energy will be needed especially there in the future.

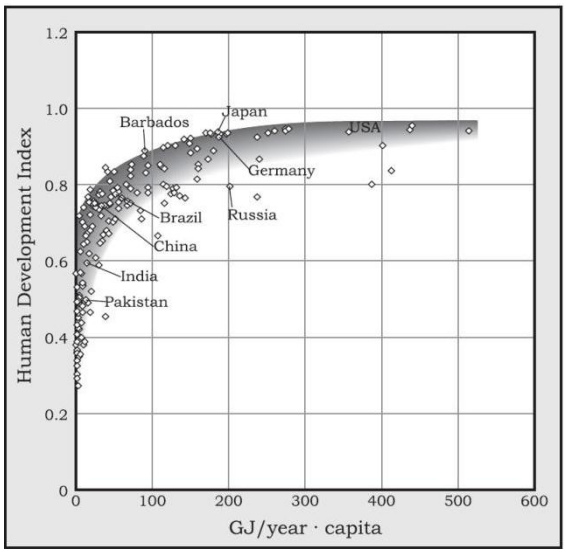


Figure 1.1: Human development index as a function of energy use per capita per year, in which higher human development index shows a higher energy use (6).

Apart from the general increase in energy demand, a specific and even faster increase in electricity demand can be seen over the last decades (7). It is expected that this increase in electricity demand will continue and might even go faster than before. This is mainly due to fast development of some previously underdeveloped regions in Asia and Africa (4, 7). Worldwide electricity generation is still mainly dependent on fossil resources (7). Over 67% of the electricity produced is originating from coal, oil or natural gas. Other sources are nuclear (13.4%), hydropower (16.2%) and others including wind, solar biofuels and waste (3.3%) (7). The share of fossil fuels in the total electricity generation has decreased over the last 50 years (7) and is expected to further decrease within the coming decades. The gap that arises from the increasing demand for electricity and the decreasing share of fossil fuels to produce them is expected to be met by natural gas and renewables in Europe (Figure 1.2).

There are three main problems with fossil fuels: 1) easily accessible fossil fuels are being depleted, 2) they are polluting (CO_2, NO_x emissions) and, 3) they are unevenly distributed over the world, leading to dependence of several countries on sometimes politically unstable regions (7). 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).

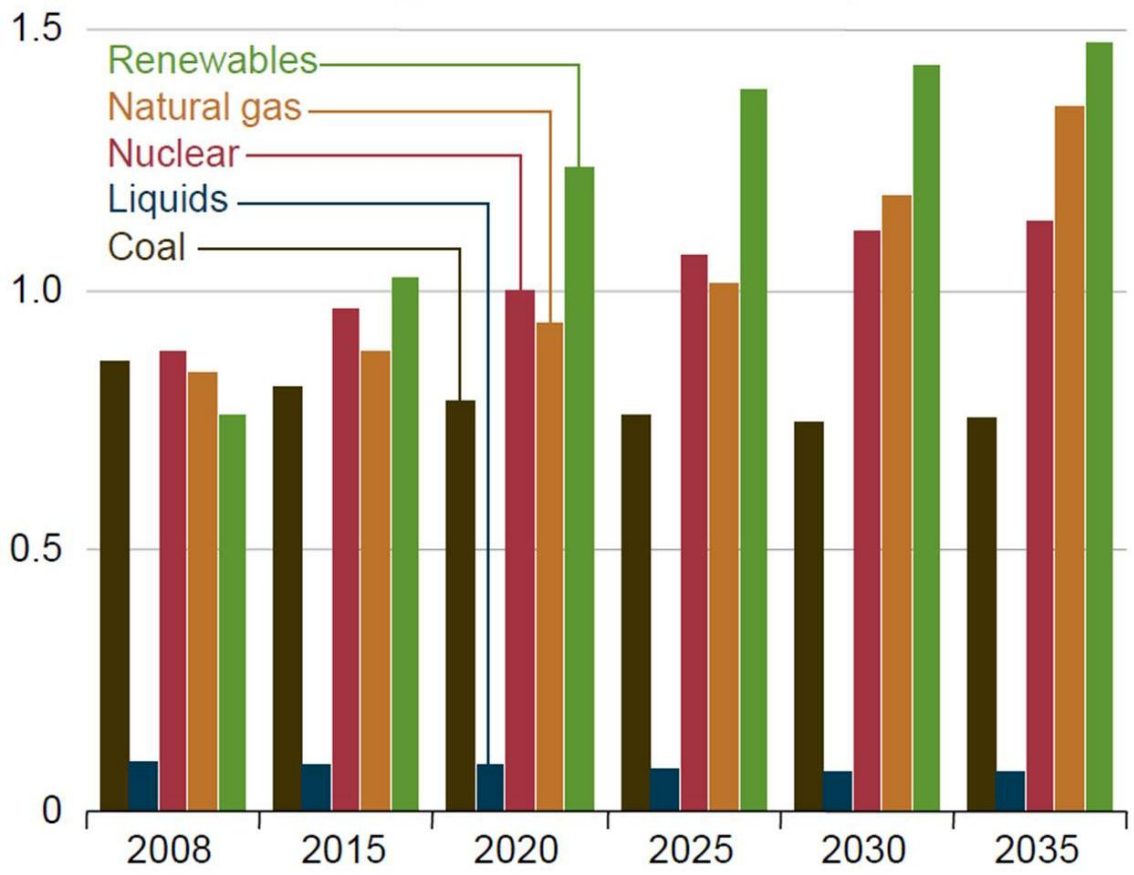


Figure 1.2: OECD Europe net electricity generation by fuel 2008-2035 as forecasted by the International Energy Agency (7).

1.1 The Plant-Microbial Fuel Cell (P-MFC)

The Plant-Microbial Fuel Cell (P-MFC) uses living plants and bacteria to generate electricity (8). The P-MFC makes use of naturally occurring processes around the roots of plants to directly generate electricity. The plant produces organic matter from sunlight and CO_2 via photosynthesis. Up to 70% of this organic matter ends up in the soil as dead root material, lysates, mucilage and exudates. This organic matter can be oxidized by bacteria living at and around the roots, releasing CO_2, protons and electrons. Electrons are donated by the bacteria to the anode of a microbial fuel cell. The anode is coupled, via an external load to a cathode. The protons that were released at the anode side travel through a membrane or spacer towards the cathode. At the cathode ideally oxygen is reduced together with protons and electrons to water. P-MFCs are a specific form of Microbial Solar Cells; systems in which Microbial Fuel Cells or Microbial Electrolysis Cells are solar powered. A schematic presentation of a Microbial Solar Cell and a Plant-Microbial Fuel Cell is shown in Figure 1.3.

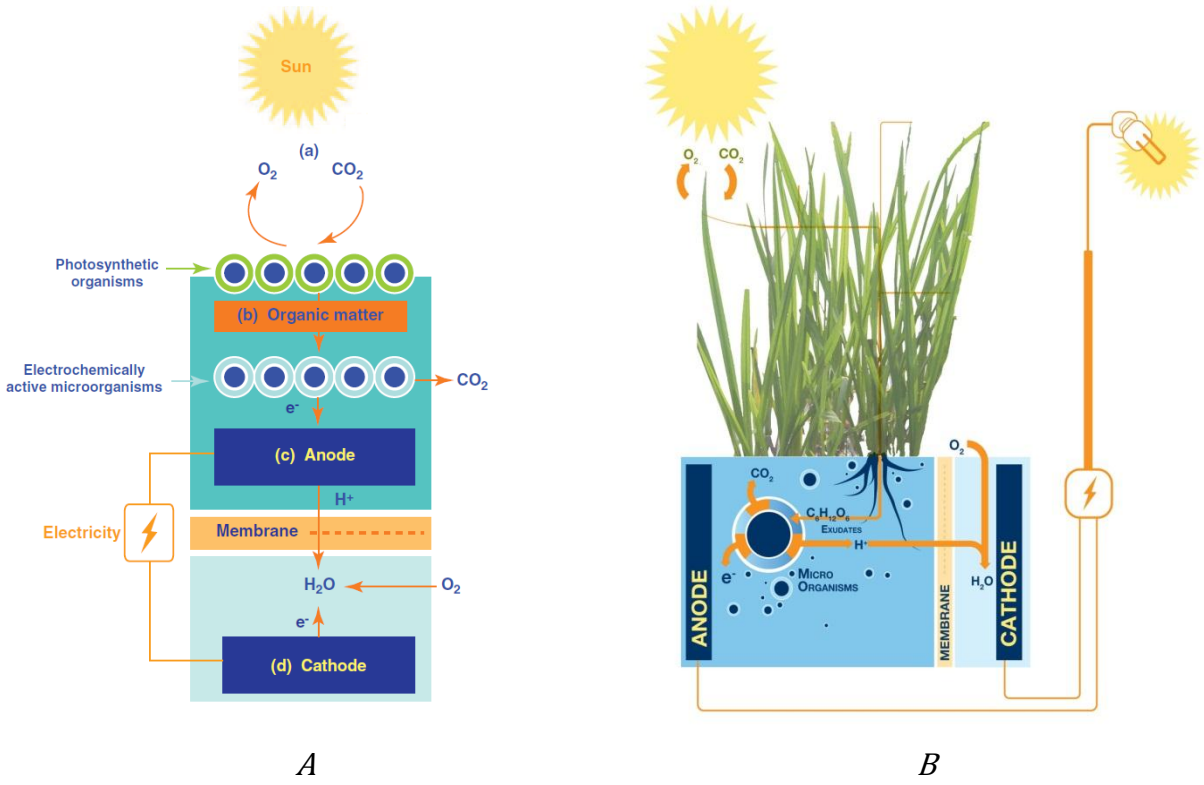


Figure 1.3: Schematic overview of a Microbial Solar Cell (MSC) (A) of which the Plant-Microbial Fuel Cell (P-MFC) (B) is a specific type. In the P-MFC the photosynthetic organisms are plants.

1.2 Objectives of this thesis

At the start of this thesis project it was estimated that the P-MFC can generate up to 3.2 W m^{-2} under Western European conditions. This is based on solar radiation of 150 W m^{-2}, photosynthetic efficiency of 5%, rhizodeposition of 70%, and 60% energy recovery in the MFC. Results from previous experiments have shown, however, that this power output is far off from being reached. Strik et al. reached a maximum power output of 0.067 W m^{-2} in 2008 (8) and Timmers et al. reached 0.1 W m^{-2} in 2010 (9). To further understand the underlying processes of the P-MFC and the factors that influence its power output, the objective of this thesis is to **determine 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.

1.3 Improving the power output of the P-MFC

The maximum power output of the P-MFC was 0.067 W m^{-2} at the start of this research. Theoretically it could be optimized to 3.2 W m^{-2}. The P-MFC consists of different process-steps that determine final power output. To improve the power output it is important to understand the different steps in the P-MFC. In the following paragraphs the different steps part of the P-MFC and their underlying processes are discussed in detail.

1.3.1 The plant

In the P-MFC typically plants that can grow with their roots under waterlogged conditions are used, to avoid oxygen intrusion from the air into the anode. If oxygen would be available at the anode, electrons would directly be used for oxygen reduction and would be lost for electricity production. Many grassy species, amongst others, are able to survive under waterlogged conditions. Biomass production from sunlight occurs via photosynthesis. In general photosynthesis rate can range from 2.5 to 5% (10). Photosynthesis is mainly dependent on CO_2-concentration and the PAR light intensity at crop level. The PAR light intensity is around 150 W m^{-2} in Western Europe, but can be 10 times as high around the equator. Different plants are discussed in Chapter 2 of this thesis.

1.3.2 The roots

In the P-MFC underground biomass is used for electricity production. The part of the biomass allocated to the roots will be used for growth and respiration of the roots as well as exudation. The organic matter originating from the plant that will be used by the bacteria for electricity production is both rhizodeposits and dead cell material. This organic matter is assumed to include all components of plant cells (11-13). Rhizodeposits consist of exudates, lysates, mucilage and secretions (11). In annual plants 30-60% of net fixed carbon is transferred to the roots. Perennial plants, however, can transfer 70-80% of the net fixed carbon to the roots (11, 12), of which 8-65% is released as rhizodeposition. On average is assumed that about 50% of the carbon fixed by the plant ends up in the soil either as roots or as exudates (12). Rhizodeposition is not uniformly occurring over the different parts of the roots (14). Literature suggests that specifically root-tips are involved in actively excreting exudates (12, 15, 16). Due to fast turnover of rhizodeposits it is very difficult to estimate the share of each of the processes attributing to the soil organic matter, let alone unravel the spatial distribution of the rhizodeposition. It is estimated that of all microbial respiration 50% is due to turnover of rhizodeposits and 50% due to direct root respiration (13, 17). In total it is estimated that 0.15-0.22 kg m^{-2} C is allocated below ground in normal pastures (12, 13). For *Spartina anglica* specifically, however, we find in literature dry belowground biomass production of 0.78-3.11 kg m^{-2} (18, 19).

Apart from carbon, plant roots excrete other compounds which can play a role in the functioning of the P-MFC: protons and oxygen. Protons are excreted to enable uptake of other compounds, generally nutrients (20). Some plants, including *Spartina anglica*, are able to survive under waterlogged conditions thanks to the forming of aerenchyma, oxygen

channels transporting oxygen from the air to the waterlogged roots (21-23). Oxygen, either via the air or via aerenchyma, is unwanted in the anode of the P-MFC since it limits the number of electrons that can be harvested via the electrical circuit. This is discussed in more detail in Chapter 3 of this thesis.

1.3.3 Microbial conversions

Microbial activity around the roots of a plant is more than 10 times higher than in the rest of the soil (15). At the root-soil interface organic matter is released by the plant (either actively or passively) and directly oxidized by the bacteria present (12, 14, 15, 24). In the P-MFC bacteria break down the organic matter and release electrons to the anode of the MFC. The complex mix of substrates available from the plant makes it difficult to assess what is precisely oxidized by the bacteria in the P-MFC. In this thesis we take acetate as a model-substrate for calculations. The oxidation of acetate by bacteria is as follows:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$$

After releasing the electrons, the electrons are optimally used for electricity production by donating the electrons to the anode of the P-MFC. This happens because bacteria can gain energy by donating electrons to another compound. Electron acceptors other than the anode can be present as well, though. These, so-called, alternative electron-acceptors can interfere with electricity production when it is energetically more attractive for the bacteria to donate the electrons to the alternative electron-acceptor instead of the anode (25). Some alternative electron-acceptors that can be present in the anode of the P-MFC are oxygen, carbon dioxide, nitrate and sulphate. Oxygen comes into the anode via two ways: 1) intrusion from the air, this is typically only the top two centimetres; 2) actively transported into the soil via aerenchyma (18, 21, 22, 26, 27). Nitrate and sulphate are normally present in plant-growth media for plant nutrition. Plant-growth media are discussed in Chapter 3.

1.3.4 The Microbial Fuel Cell (MFC)

The electrons that are released by the bacteria are harvested in a Microbial Fuel Cell. At the anode the organic matter is oxidized. By coupling this anode to a cathode with a higher potential energy can be generated. Anode and cathode are typically of carbon or graphite material. The cathode-reaction would preferably be oxygen reduction to water because oxygen is available, cheap and has a high standard potential. It is reduced according to:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

The total voltage that can be generated from the P-MFC can be calculated from the Nernst potential of the anode and cathode. The Nernst potential of the anode is described by (28):

$$E_{an} = E_{an}^0 - \frac{RT}{8F} ln\left(\frac{[CH_3COO^-]}{[H^+]^9[HCO_3^-]^2}\right)$$

In which: E_{an}=anode potential (V), E_{an}^{0}=standard anode potential at 298 K, all concentrations 1M (V), R=universal gas constant (8.314 J mol^{-1} K^{-1}), T=temperature (K), 8=number of electrons involved in the reaction (-), F=Faraday's constant (9.65*10^4 C mol^{-1}), $[CH_3COO^-]$=acetate concentration (mol L^{-1}), $[H^+]$=proton concentration (mol L^{-1}) and $[HCO_3^-]$=bicarbonate concentration (mol L^{-1}).

Since the concentration and composition of organic substrate in the P-MFC is largely unknown, the exact Nernst potential of the anode is difficult to determine. In this thesis we used the open cell potential of the anode – cell potential of the anode at open circuit – asE_{an}^{0}. This is typically around -0.289 V vs. standard hydrogen electrode (29) or -0.486 vs. AG/AgCl reference electrode.

The Nernst potential of the cathode in case oxygen is used can be determined by:

$$E_{cat,O_2} = E_{cat}^{0} - \frac{RT}{4F} ln\left(\frac{1}{pO_2[H^+]^4}\right)$$

In which: E_{cat}=cathode potential (V), E_{cat}^{0}=standard cathode potential at 298 K and atmospheric pressure (V) R=universal gas constant (8.314 J mol^{-1} K^{-1}), T=temperature (K), 4=number of electrons involved in the reaction (-), F=Faraday's constant (9.65*10^4 C mol^{-1}), pO_2=partial oxygen pressure (Pa), $[H^+]$=proton concentration (mol L^{-1}).

The standard cathode potential with oxygen reduction is typically +0.805 V vs. standard hydrogen electrode (29) or 0.608 V vs. Ag/AgCl reference electrode.

Optimally the P-MFC with oxygen reduction at the cathode would have a maximum cell voltage of 1.1 V according to (28):

$$E_{cell} = E_{cat} - E_{an}$$

In which: E_{cell}=cell voltage, E_{cat}=cathode potential, E_{an}=anode potential.

The oxygen concentration at the cathode is, however, subject to limitations in oxygen diffusion into the electrode. The electrode needs to be wet in order to transport protons and maximum oxygen concentration in water is low (~8 g L^{-1}). To avoid limitations at the cathode and be able to study the anode without effects of the cathode, we used another cathode-reaction in most of the experiments performed fort his thesis. Ferric iron, in the form of ferric cyanide, is reduced at the cathode of the P-MFC according to (30):

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$$

Nernst potential of the cathode in case of ferric cyanide use is:

$$E_{cat,Fe} = E_{cat}^{0} - \frac{RT}{1F} ln\left(\frac{[Fe^{3+}]}{[Fe^{2+}]}\right)$$

In which: E_{cat}=cathode potential (V), E_{cat}^{0}=standard cathode potential (V) R=universal gas constant (8.314 J mol^{-1} K^{-1}), T=temperature (K), 1=number of electrons involved in the reaction (-), F=Faraday's constant (9.65*10^{4} C mol^{-1}), [Fe^{3+}]=ferric iron concentration, [Fe^{2+}]=ferrous iron concentration

The standard potential of ferric to ferrous iron is +0.361 V vs. standard hydrogen electrode (30) or +0.164 vs. Ag/AgCl reference electrode. This makes the maximum voltage that can be obtained from the P-MFC lower compared to an oxygen reduction cathode. In practice, however, many other factors influence the final cell voltage that can be obtained from the P-MFC.

The total amount of electricity that can be obtained from the P-MFC is determined by two factors: voltage and current. The product of the voltage and current leads to the power output of the system, according to:

$$P = E_{cell} \times I$$

In which: P=power (W), E_{cell}=cell voltage (V), I=current (A).

The voltage is determined by the conversions at both electrodes minus the losses that occur in the system. These losses are caused by several factors leading to increased internal resistance in the system and lead to a lower voltage than theoretically could be obtained. This is discussed in further detail in Chapter 4. Factors that can influence the internal resistance of the P-MFC are, for example, the design of the P-MFC (chapter 4) and the presence of alternative electron-acceptors (chapter 3).

The current is determined by the number of electrons that ends up in the electrode to produce electricity. The percentage of electrons that is actually converted into electricity of all electrons that were present in the substrate is called the coulombic efficiency of the system (31). Again, for the P-MFC the coulombic efficiency is difficult to determine since the composition and concentration of the organic substrate is unknown. Presence of alternative electron acceptors is an important factor that influences coulombic efficiency (chapter 3).

1.4 Possibilities for applying the P-MFC as new electricity generation technology

To actually apply the P-MFC as energy technology in the market, not only power output is important. To avoid problems that have arisen with fossil fuels (depletion of easily accessible sources, pollution, uneven distribution), electricity production with the P-MFC should meet three criteria: it should be 1) renewable, 2) sustainable (PPP) and 3) available. Hereafter these three criteria are introduced and further broken down into specific aspects that were researched in this thesis to assess whether the P-MFC can be applied as electricity generation technology in the future. Several renewable energy sources have been developed. Mostly used are solar power, wind turbines and hydropower, of which

hydropower is the largest. Solar and wind power together make up less than 4% of the electricity production, whereas hydropower generates around 16% of the electricity needed (7). For each of the criteria, we shortly analyse the alternative electricity generation technologies that are already available as a first study of design factors that can influence the applicability of the P-MFC in the following paragraphs.

1.4.1 Renewability

Fossil fuels are exhausted in only a fraction of the time needed to create them and can therefore not be considered renewable (6). Wind power, solar power and hydropower are usually regarded as renewable because they make use of energy sources that are renewed and therefore won't be depleted. The P-MFC makes use of solar power as well and can in that respect be considered renewable as well. A second aspect that we will assess is the energy balance of the technology. It should be critically reviewed whether the overall energy balance of the energy technology is positive. If more energy has to be put in the technology to construct it than is generated with it, energy balance is negative and the technology cannot be considered renewable. We use the concept of payback time (PBT) to assess the renewability of the P-MFC. When energy input needed for construction of the technology can be paid back by electricity generation of the same technology within the lifetime of the materials, the technology can be considered renewable. It has long been under debate whether energy input for solar panels and wind power was actually renewable due to their long PBT (32). Nowadays, lifetime of both wind and solar power generally exceeds energy-PBT (33, 34) and thus these technologies can be considered renewable. Energy PBT of the P-MFC will depend on its power output and the energy input for the materials needed and was researched in this thesis. Renewability in this thesis is purely based on energy. Renewability of materials will be considered as part of the environmental performance of the system.

1.4.2 Sustainability

Sustainability as a concept has several definitions (35). Most commonly it's accepted that sustainability encompasses three different aspects: People, planet, profit. Or, in other words, social acceptability, environmental performance and economic feasibility.

1.4.2.1 Environmental performance

Alternative electricity generation technologies are sometimes debated for their environmental performance, even though they are renewable. Solar panels contain scarce metals and windturbines need the rare earth metal neodymium for construction (36). Especially mining of these metals causes a lot of environmental pollution, thus the environmental performance of wind and solar power can be debated. Hydropower is generally considered environmental friendly based on the materials used, but debate is on-going about the loss of natural areas due to submergence upstream of the dam (37). Environmental performance of the P-MFC is dependent on the materials used and was assessed in Chapter 6 of this thesis.

1.4.2.2 Social acceptability

Social acceptability of a technology is very difficult to assess, since it is very dependent on specific application of a technology and its context. We identified some social aspects that are debated concerning present renewable electricity generation technologies. Both solar panels and windturbines have difficulties to be accepted due to their low aesthetic value (38). P-MFCs could be fully integrated in a landscape and will therefore probably not meet this kind of opposition. Hydropower is sometimes debated for the fact that villages in remote areas are submerged, as is often the case in Brazil. We address the social acceptability of the P-MFC in Chapter 7.

1.4.2.3 Economic feasibility

Like social acceptability, economic feasibility is dependent on specific application and context. Solar and wind power are still being subsidized within Europe (39). On the long run, though, a technology should be capable of being economically feasible without subsidies. To assess the economic feasibility of the P-MFC we worked out three business cases in this thesis, for three specific applications: the green electricity roof, decentralized electricity production in developing countries and large-scale electricity production. Here, we shortly introduce these applications. In Chapter 7 we address the economic feasibility of the applications.

The Green Electricity Roof is typically suitable for developed countries and urbanised areas. It makes effective use of a space – roof-top – that is otherwise not used productively. The Green Electricity Roof has the advantages of a normal green roof – high aesthetic value, water retention, insulation of the roof – and adds electricity production to these advantages. Typically this application can be used even at a low power output of the P-MFC because of the added advantages of the green roof and the green image that arises from the product.

Decentralized electricity production in developing countries is interesting because of the low voltage applications that could be powered with a P-MFC. Nowadays remote, developing areas can be powered with stand-alone solar panel systems, which typically need a polluting battery. Moreover, 1.4 billion people didn't have electricity in 2009, mainly in remote areas (7). Applying the P-MFC in developing regions therefore offers the opportunity of economic growth in the poorest areas of the world.

Large-scale electricity production with the P-MFC in wetlands or natural areas could be a third application of the P-MFC as a renewable and sustainable electricity technology. It could offer additional economic value to natural areas that currently only hold implicit economic value. Therefore these areas are under pressure to be developed into urbanised areas and agricultural land. Producing electricity from these areas could add explicit economic value. Exact numbers of the global wetland area are not available since there is a large inconsistency in information between different countries and measurement methods (40). Estimations range from 560 000 000 ha to 1 279 211 000 ha. Assuming that the power output of the P-MFC could be 3.2 W m^{-2} or 28 kWh m^{-2} $year^{-1}$, 5.6%-13% of the global

wetland area would be needed to meet the global electricity demand. These wetlands should be located close to areas where the electricity is needed.

1.4.3 Availability

Availability of electricity is affected by two different factors: source availability and storage. An electricity generation technology or source can be limited geographically or be weather dependent, time dependent or otherwise limited in availability. Solar panel performance depends on light intensity. This makes them both weather dependent and daylight dependent. If the electricity production from a source is weather dependent but peaks in demand coincide with peaks in production, no problems arise. In practice, however, this is not the case with solar power. Peak demand for electricity in the Netherlands occurs after sundown e.g. (Figure 1.4).

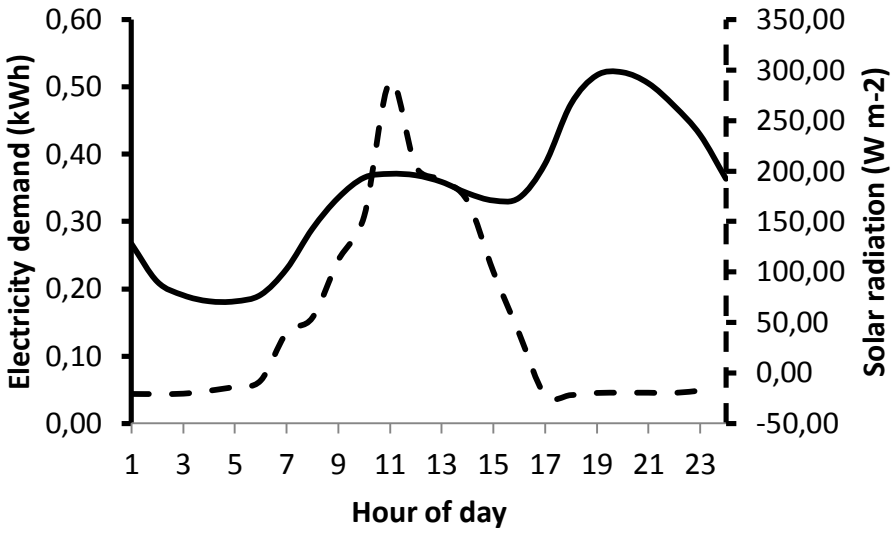


Figure 1.4: Electricity demand (kWh) of a Dutch household during the day in autumn (41) compared to average solar radiation during a day in September 2009 (W m^{-2})(42).

Wind power is weather dependent and geographically limited in application because open fields without too many buildings is needed. Hydropower is geographically limited to the course of the river and might in some cases be season dependent for its flow. The P-MFC is in theory not daylight dependent and can thus generate electricity day and night. In addition it is expected that the P-MFC might produce electricity year-round, so weather independent. This was further researched in Chapter 5 of this thesis.

When electricity can be stored, the problems of source availability can be overcome. Hydropower can store electricity directly via reversing the waterflow direction. Electricity from solar and wind power can only be stored indirectly, for example via the electricity grid. This is only possible at a well-developed electricity grid that can directly use electricity to increase the waterlevel of a hydropower system for example when demand is lower than supply. Another option for storage would be to use batteries. These, however, have an impact on the environmental performance of the total system. Storage of electricity is

possible within the technology itself would therefore have big advantages over external or indirect storage. Within the P-MFC electricity might be stored in the system itself since the system has a high capacitance (43). We further address this issue in Chapter 7 of this thesis.

1.5 Thesis outline

We shortly introduced the P-MFC technology and some of the aspects that influence the design criteria for the P-MFC. In this thesis we researched design criteria for the P-MFC to 1) increase power output of the P-MFC and 2) assessing additional factors influencing its applicability. Roughly the first set of criteria was researched in chapters 2 through 4; handling the different aspects of the technology. With the technical insights acquired in chapters 2 through 4, the additional criteria were researched in chapters 5 through 7.

In Chapter 2: Concurrent bio-electricity and biomass production in three Plant-Microbial Fuel Cells using *Spartina anglica*, *Arundinella anomala* and *Arundo donax* we discuss three different plant species and the power output of the different species. We calculate the amount of electricity generated as fraction of the total plant biomass that is produced. We conclude that we can generate bio-electricity and biomass concurrently but that most energy produced by the plant via photosynthesis is captured as biomass and not as electricity.

In **Chapter 3: New plant-growth medium for increased power output of the Plant-Microbial Fuel Cell** we try to improve the power output of the P-MFC by testing different plant-growth media. A common plant-growth medium, Hoagland medium, has been used in research until now. This medium, however, is not adapted for use in the P-MFC. The medium contains a lot of nitrate that can be used as an alternative electron acceptor by the bacteria in the MFC. If used as an alternative electron acceptor in the P-MFC, electrons are used for denitrification instead of electricity production, thus lowering the power output of the P-MFC. The Hoagland medium contains sulphate as well, which could function as another alternative electron acceptor. Sulphate can be reduced to sulphide taking up electrons. Other than with nitrate to nitrogen gas, sulphide can be used as an oxidator, releasing electrons. We find that a plant-growth medium with ammonium-bicarbonate instead of nitrate is a good alternative plant-growth medium for the P-MFC that increases power output. The new plant-growth medium was tested in a new design P-MFC: the flat-plate P-MFC.

In **Chapter 4: The flat-plate Plant-Microbial Fuel Cell: the effect of a new design on internal resistances** we discuss the effect of the new flat-plate design on the internal resistances of the P-MFC. Internal resistance is reduced per membrane area and anode volume compared to the previously used tubular design. This is mainly caused by a lower transport resistance in the flat-plate design compared to the tubular design.

Another new design is described in **Chapter 5: Resilience of roof-top Plant-Microbial Fuel Cells during Dutch winter.** Two types of vertical tubular designs are placed on a roof-top to

test the resilience of the P-MFC under outdoor conditions. This is the first time a P-MFC is placed outdoors as a first step towards applying the technology in a green roof set-up. The P-MFCs show electricity production as long as temperatures are above 0^{o}C. During frost-periods electricity production stops, but voltage returns after thawing of the P-MFCs. We see a diurnal cycle in electricity production developing, probably due to oxygen limitation at the cathode. The anode performs stable day and night.

In Chapter 6: Electricity production with living plants on a green roof: Environmental performance of the Plant-Microbial Fuel Cell we assess the environmental performance of the P-MFC. Normally technologies that have already been introduced into the market are assessed for environmental performance in an LCA to compare them to other systems. In case of the P-MFC technology is still under development and not commercially applied yet. The approach of the LCA is therefore different from usual. This LCA mainly focuses on the aspects and materials of the system that can be improved rather than comparing the P-MFC to other technologies. The environmental performance of the P-MFC is determined by the materials used in the system and the maintenance that might be needed.

Finally, in **Chapter 7: General discussion and concluding remarks** all results presented in the thesis are summarized. Based on those results an outlook is presented for possible application of the P-MFC technology. To make the P-MFC sustainable it should be environmentally friendly, socially acceptable and economically feasible. Whether the P-MFC is socially acceptable is determined by many factors. The most important one is probably the used land surface and the aesthetical value of the energy landscape. The P-MFC can possibly be combined with other applications of biomass on the same surface area, so no competition with food or feed production needs to occur. This adds to the social acceptance of the P-MFC. The economic feasibility of the P-MFC will be determined both by the power output and the costs of the materials used in the system. When an innovative technology enters the market it can be more expensive than comparable products for a while; early adopters will start buying the product at a higher costprice. On the longer run the technology will need to be economically attractive compared to the alternatives in order to acquire a place in the market. Electricity technologies like solar panels and wind power are still being subsidized in order to generate market pull for these technologies. On the longer run, though, market pull needs to arise because a technology is economically attractive by itself, so without subsidies. Three business cases are worked out in the final chapter in order to estimate the economic feasibility of different applications. These three applications are 1) the green electricity roof, 2) decentralized electricity production in developing countries and 3) large-scale electricity production with the P-MFC. These are applications for increasing markets and suitable for different stages of technology development.

A complete overview of this thesis and the aspects discussed in per chapter are summarized in the following table.

Objective	Aspect	Thesis chapter
Increase power output	Plant	2. Concurrent bio-electricity and biomass production
	Roots	2. Concurrent bio-electricity and biomass production 3. Improved medium for the P-MFC
	Bacteria	3. Improved medium for the P-MFC
	MFC	4. Internal resistances of the flat-plate design P-MFC 5. Roof-top P-MFCs
Assess additional design criteria for application	Renewability	
	Source	2. Concurrent bio-electricity and biomass production
	Energy balance	2. Concurrent bio-energy and biomass production 3. Improved medium for the P-MFC 4. Internal resistances of the flat-plate design P-MFC
	Sustainability	
	Environmental	6. Early life-cycle assessment of the P-MFC
	Social	7. General discussion and concluding remarks
	Economic	7. General discussion and concluding remarks
	Availability	
	Source	5. Roof-top P-MFCs
	Storage	5. Roof-top P-MFCs 7. General discussion and concluding remarks

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2 CONCURRENT BIO-ELECTRICITY AND BIOMASS PRODUCTION IN THREE PLANT-MICROBIAL FUEL CELLS USING *SPARTINA ANGLICA, ARUNDINELLA ANOMALA* AND *ARUNDO DONAX*

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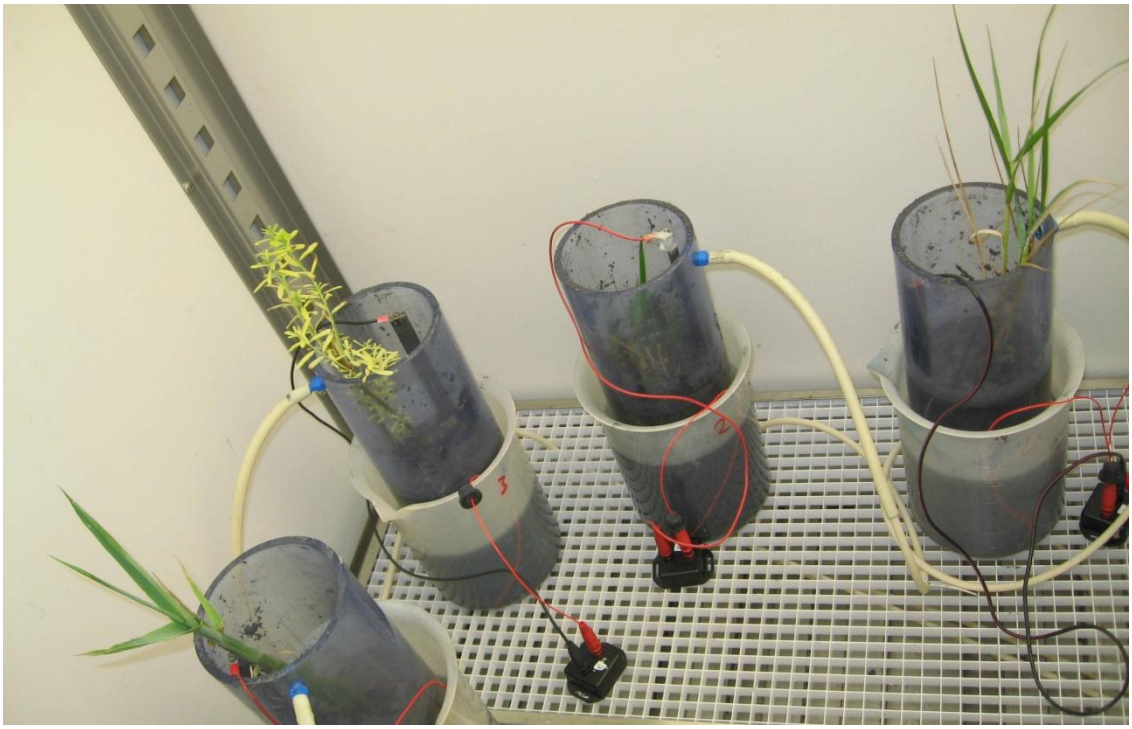

Abstract

In a Plant Microbial Fuel Cell (P-MFC) three plants were tested for concurrent biomass and bio-electricity production and maximization of power output. *Spartina anglica* and *Arundinella anomala* concurrently produced biomass and bio-electricity for six months consecutively. Average power production of the P-MFC with *S. anglica* during 13 weeks was 16% of the theoretical maximum power and 8% during 7 weeks for *A. anomala*. The P-MFC with *Arundo donax* did not produce electricity with a stable output, due to break down of the system. The highest obtained power density in a P-MFC was 222 mW/m^2 membrane surface area with *S. anglica*, over twice as high as the highest reported power density in a P-MFC. High biomass yields were obtained in all P-MFC's, with a high root:shoot ratio, probably caused nutrient availability and anaerobia in the soil. Power output maximization via adjusting load on the system lead to unstable performance of the P-MFC.

2.1 Introduction

The Plant-Microbial Fuel Cell (P-MFC) is a system that produces bio-electricity from plant derived organic matter without harvesting the plant. Rhizodeposits are excreted by the plant-roots and subsequently converted into electrons, protons and CO_2 by electrochemically active micro-organisms that are present around the roots. These micro-organisms have been found to be able to deliver these electrons to a solid surface, like a graphite electrode, under anaerobic conditions. This electrode (anode) is coupled to a second electrode (cathode) with a membrane in between. At the cathode, electrons are used to reduce oxygen or another compound along with protons which are transported through the membrane to the cathode compartment. The plant, growing in the anode compartment, is put under root submerged conditions to make an anaerobic environment in the anode possible. The P-MFC was first tested by Strik et al. (2008a) and has been claimed to produce non-destructive, sustainable bio-electricity (Strik et al., 2008a). This claim arises from the fact that for bio-energy production in a P-MFC, only rhizodeposits have to be harvested and not the biomass. This avoids transportation of the biomass and depletion of nutrients in the ecosystem.

For our research three different plant species were used: *Spartina anglica*, *Arundinella anomala* and *Arundo donax.* These plants are all three marsh species, which are able to survive and grow under waterlogged conditions as imposed in the P-MFC (Holmer et al., 2002; Wijte et al., 2005). *S. anglica* is a salt marsh species that has been tested in earlier studies and has shown to be able to survive and produce electricity in the P-MFC (Timmers et al., 2010). It was selected in the research of Timmers et al. for four reasons: (I) no competition with food production, (II) high biomass production, (III) worldwide occurrence on mudflats and (IV) salinity tolerance which offers the opportunity of operating the system at high ionic strength (Timmers et al., 2010). To compare with *S. anglica* another grassy marsh species was chosen: *Arundinella anomala. A. anomala* is a fresh marsh species and has therefore not the advantage of the low internal resistance that is ascribed to the high ionic strength of the solutions. It is therefore interesting to see whether a fresh water species is able to produce electricity in a P-MFC. *A. anomala* is a marsh species that grows in the Chinese Yangtze River and the Three Gorges Reservoir. It has been shown to be tolerant to flooding (New and Xie, 2008). *A. donax* grows in marshes, like *S. anglica* and *A. anomala*. But it is different from *S. anglica* and *A. anomala*. It has a C3 photosynthetic pathway in contrast to *S. anglica* and *A. anomala*, which have a C4 photosynthetic pathway. In general a C3 photosynthetic pathway is less efficient than a C4 photosynthetic pathway. *A. donax* however, has, in spite of its C3 photosynthesis, a higher photosynthesis rate than some C4 species. In other words, it is very efficient in using the sun's energy to produce biomass. Therefore it is an interesting plant for this research since a lot of biomass growth can be expected. In addition, *A. donax* is an energy-crop, used for bio-energy production because of its fast growth and high dry matter content (Angelini et al., 2008; DiTomaso, 1996). *A. donax* was used in this research to see if extra energy can be harvested from this energy-crop via

de P-MFC apart from burning for bio-electricity production. In earlier studies *Glyceria maxima* (Strik et al., 2008a) and *S. anglica* (Timmers et al., 2010) were tested in a P-MFC.

Strik et al. (2008a) achieved a maximum power output of 67 mW/m^2 membrane surface area. During the research of Strik et al. plant vitality was monitored and found to decrease after 68 days. As a possible explanation for this decrease in plant vitality, natural decline after the growth season of the plant is suggested (Strik et al., 2008a). Based on the results of Strik et al. we hypothesized for this research that plant growth is not limited by the P-MFC. Secondly, since Strik et al. used a fixed resistance while producing electricity with a P-MFC, we tested a maximization strategy for the P-MFC's by adjusting external resistance to internal resistance of the system in order to maximize power output. For the first hypothesis, we tested whether it is possible to produce bio-electricity in the P-MFC while concurrently producing biomass for other applications, without interfering with plant vitality. This would validate the claim that bio-electricity production in a P-MFC is non-destructive. In this research plant growth was monitored for the first time in P-MFC research. In addition we tried to maximize the power output of the system by adjusting external resistance.

2.2 Methods

2.2.1 Experimental set-up

We used a cylindrical P-MFC. The anode consisted of a Plexiglas cylinder (Ø 9.9 cm) with a cation exchange membrane (Fumatec, Frankfurt, Germany) glued to the bottom. We filled the cylinder with graphite grains (<1 mm, Le Carbone, UK). The plant-roots and graphite grains were cleaned with demiwater (water demineralized with Ministil P-12, Christ AG, Aesch, Switzerland) and afterwards the plant was planted in the graphite grains. The plants that we used were *S. anglica*, *A. anomala* and *A. donax. S. anglica* consisted of 2 stems of total 54 cm tall and a total fresh weight of above and below ground biomass of 25 g. *A. anomala* had 10 short stems of total 64 cm and total fresh weight of 59 g. *A. donax* had 1 stem of 31 cm and total above and below ground biomass of 85 g. *S. anglica* was offshoot of the one used by Timmers et al. (2010). It was grown in a greenhouse for approximately 2 months. *A. anomala* and *A. donax* were provided by Forschungszentrum Jülich GmbH (Jülich, Germany). We filled the anode compartment with modified Hoagland solution (Taiz and Zeiger, 2006) as described by Timmers et al. (2010) up to the overflow point (at 19 cm from membrane). On top of the graphite grains sand was put to the level of the overflow point to prevent algae growth on the graphite grains. When the sand showed to be insufficient for preventing algae growth, plastic granules were put on top of the sand. The anode cylinder was placed in the cathode compartment (Ø 12 cm), which consisted of a beaker in which a graphite felt (Grade WDF, 2.8 mm, National Specialty Products Carbon and Graphite Felt, Taiwan) was put on the bottom.

As a current collector for the anode, a graphite rod was placed in the graphite grains of the anode with a wire attached to it. For the cathode, a gold wire was woven through the graphite felt with an electrical wire attached to it. Anode and cathode wires were connected with a resistance (1000 Ω) in between. Ag/AgCl-reference electrodes (3 M KCl, +205 mV versus standard hydrogen electrode, ProSense Qis) were placed in syringes with a capillary attached to it, filled with KCl (3 M). The capillary was placed in anode and cathode to measure anode and cathode potential against the reference electrode. The anolyte consisted of modified Hoagland solution (Taiz and Zeiger, 2006) with phosphate buffer (K_2HPO_4 and KH_2PO_4, 20 mM, pH 7) (Strik et al., 2008b). The used iron complex in the Modified Hoagland solution was diethylenetraiminepentaacetic acid ferric sodium complex (Dissolvine D-Fe-11, or DTPA-Fe) (AKZO NOBEL Functional Chemicals bv, Herkenbosch, the Netherlands). In case of the *S. anglica* 20 g/l NaCl was added to provide a salt environment. The catholyte consisted of phosphate buffer (K_2HPO_4 and KH_2PO_4, 20 mM, pH 7). The set-ups were placed in a climate chamber (Microclima 1750 Snijders) that was controlled at 25 ^oC with 75% humidity, average light intensity of 596 ± 161 µmol m^{-2} s^{-1}, measured at the top of the reactors by a light intensity meter (Photodyne 44XLA), and an illumination period of 14 h per day.

2.2.2 Analytical techniques

In the first 10 weeks we measured anode and cathode potential manually with a multimeter (True RMS multimeter, fluke 189) against an Ag/AgCl-reference electrode. Starting in week 10, the anode and cathode potential were measured with Fieldpoint (Module S, National Instruments) against an Ag/AgCl-reference electrode. Cell voltage of the P-MFCs was measured with Fieldpoint from the beginning of the experiment. Data were collected with LABVIEW (National Instruments Software). Maximum power was determined via polarization curves, which were performed either manually or with a potentiostat (Iviumstat, The Netherlands). Manually, external resistance was adapted every 10 min from OCV (open cell voltage) to subsequently 1000 Ω, 500 Ω, 250 Ω, 100 Ω, 1Ω and then back to 100 Ω, 250 Ω, 500 Ω, 1000 Ω, OCV. With the potentiostat, cell potential was controlled from OCV to 1 mV and back to OCV in nine steps of 10 min. Plant growth was measured by counting the number of stems and leaves and measuring their length from top of the sand bed to tip (Holmer et al., 2002; Papazoglou, 2007; Spencer et al., 2006). Stem and leaf length were summed up for total length. For *S. anglica* both stems and leaves were measured since relatively much biomass growth is seen as leaf elongation when compared to the other two plants. For *A. anomala* and *A. donax* only stem length was measured. Fresh weight of the plants was determined directly after dismantling of the P-MFC's. Dry weight was determined after air drying until constant weight was reached. Numbers for plant growth are given in kg m^{-2} surface area, calculated to a growth season of 6 months. Where numbers from literature are used, these numbers are recalculated to kg m^{-2} at a growth season of 6 months as well.

Average weekly power output was calculated via:

$$P = (\bar{E}^2)/R/membrane\ area$$

Equation 2.1: Average power output, in which P = average power density in W/m2 membrane surface area during a week, E = mean cell potential calculated per week, R = external resistance which was constant at 1000Ω. The used period is the moment from the change of cathode solution to ferric cyanide until the maximization strategy was started.

Power output and current densities are all normalized to m2 membrane surface area, which is equal to the planting surface of the plant. Calculations for total electricity production were performed with:

$$Total\ electricity\ production\ (J/m^2) = \sum P \times t$$

Equation 2.2: Calculation of total electricity production in Joules for the duration of the experiment in which P = average power density in W/m2 during a week and t = one week (604,800 s).

Light intensity was calculated via:

$$Radiation\ (W/m^2 surface\ area) = radiation\ (\mu mol/m^2/s) \times f_{con}$$

Equation 2.3: Conversion of µmol m^{-2} s^{-1} to W m^2 for calculation of photosynthetic efficiency, in which $f_{con} = 0.25$, which is the conversion factor from µmol m^{-2} s^{-1} to W m^2.

Membrane potential is determined as the difference between the reference electrode in the anode and the reference electrode in the cathode and is represented by E_{a-c}.

2.2.3 Experimental procedure

Plants were directly planted in the P-MFC with their root-system in the graphite grains. The plants were fed daily with Hoagland-solution via a pump. The amount and time of feeding was gradually increased with the growth of the plants. After initial start-up of the plants, the catholyte was changed for potassium ferric cyanide ($K3(FeCn)_6$, 50 mM with phosphate buffer 20 mM, pH 7) (Strik et al., 2008b).

A maximization strategy was performed to find out whether it was possible to maximize power production of the plant-MFC. With a polarization curve the maximum power point was determined. This is the point where external resistance as imposed on the system equals internal resistance of the system itself. After making a polarization curve, external resistance was adjusted to the internal resistance that was derived from this curve. After a week a new polarization curve was made and external resistance was adjusted again. After two weeks the strategy was abandoned because of total collapse of current.

2.3 Results

Biomass was produced in all three P-MFC's (Figure 2.1). Electricity was produced with the P-MFC with *A. anomala* and *S. anglica* (Figure 2.2). For *A. anomala* and *S. anglica* a day-night cycle independent current production was observed for 12 and 7 weeks consecutively. Thus, in two of the three P-MFC's both biomass and bio-electricity was produced. However, in the case of *A. donax* no stable current production has been achieved.

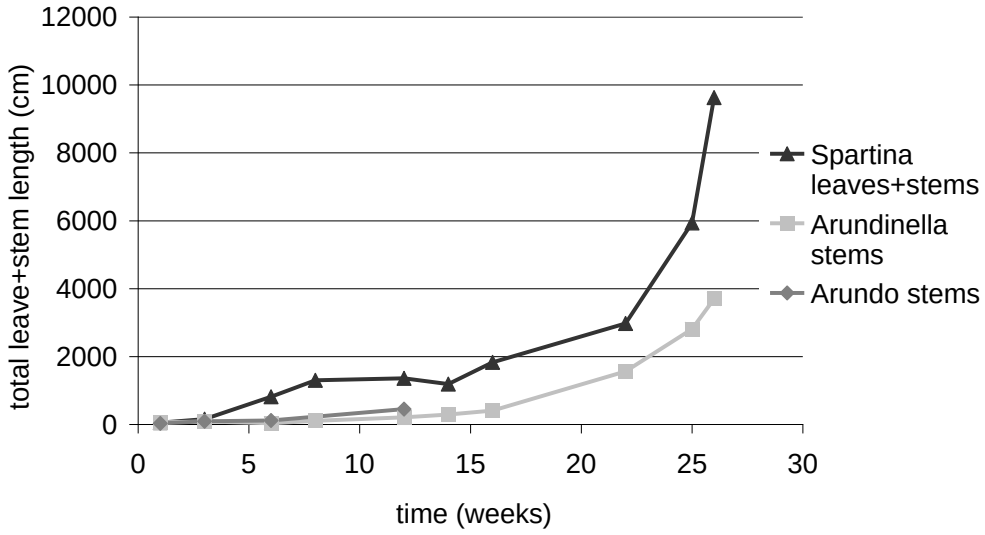

Figure 2.1: Plant growth of Spartina anglica, Arundinella anomala and Arundo donax in a P-MFC during 182 days of the experiment.

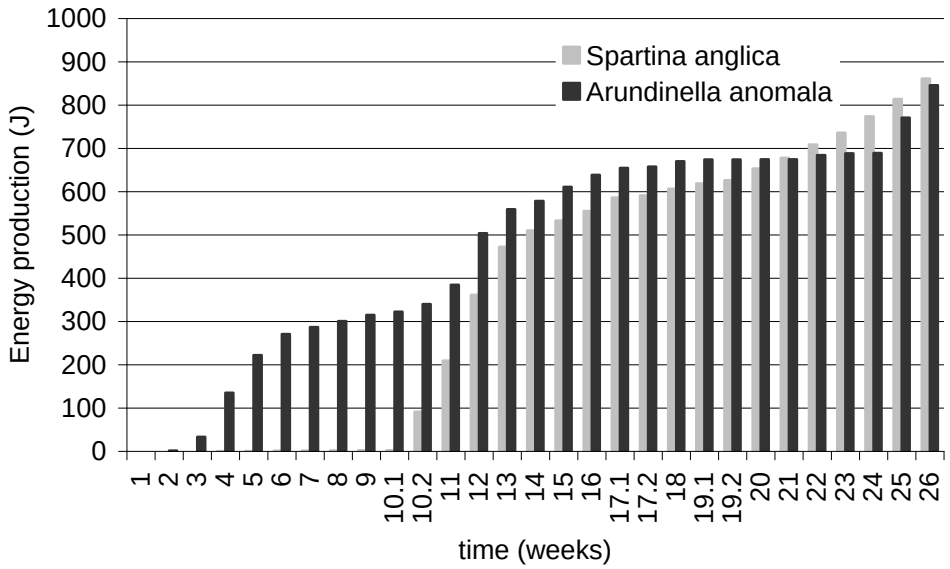

Figure 2.2: Electricity production of Spartina anglica and Arundinella anomala in a P-MFC during 26 weeks of experiment. Some weeks are split in two parts, indicated with .1 and .2, because of changing conditions. 10.2 = change of catholyte Arundinella anomala from buffer to ferric cyanide. 17.2 = change of external resistance at start of maximization strategy. 19.2 = change of external resistance at end of maximization strategy.

2.3.1 Biomass was produced in all three P-MFC's

All three plants increased in size and weight during the experiment. In Figure 2.1 it can be seen that above ground biomass increased with time. Even though there is a slight dip in S. growth on day 93, observations showed that there was no visible die back or decline of the *Spartina* plant.

A. anomala has grown from 64 to 3697 cm total stem length in 6 months' time. This is shown in Figure 2.1. Its biomass increased from 59 to 550 g, which is 71 kg/m^2 fresh weight, with a root:shoot ratio of 2.0. Dry end weight was 33 kg/m^2, with a root:shoot ratio of 3.1. Observation of the root system after finalizing the experiment showed that the root system had up to 2nd order branching in the largest part of the root system and the roots were thin and greyish.

S. anglica increased both in size and weight in 6 months' time. Growth monitoring of the plant has shown that total stem and leaf length increased from 54 to 9627 cm, a growth of 9573 cm in 6 months' time. (Figure 2.1) Its weight increased from 25 to 490 g fresh weight, which is 64 kg/m^2 of fresh weight at the end. Root:shoot ratio based on end fresh weight was 1.4. Dry end weight was 21 kg/m^2 with a root:shoot ratio 2.5. Observation of the root system after finishing the experiment showed that the plant had branching of more than 2nd order and had a yellowish colour. Greyish spots on the roots were caused by the graphite grains in which it had grown.

A. donax increased in size from 31 to 449 cm and in weight from 85 to 467 g (61 kg/m^2) in 10 weeks' time. Root:shoot ratio of *A. donax* based on fresh weight was 1.4. The experiment with *A. donax* was stopped after 10 weeks because of break-down of the system due to root growth of the plant. The root system showed a relatively even vertical distribution.

2.3.2 Bio-electricity was produced in P-MFC's with *Arundinella anomala* and *Spartina anglica*

In two of three P-MFC's bio-electricity was produced (Figure 2.2). In the P-MFC with *S. anglica* the highest power density was obtained: 222 mW/m^2. In the P-MFC with *A. anomala*, the highest obtained power density was 22 mW/m^2. *A. donax* did not reach a stable electricity production, due to break down of the system. Average power output for the P-MFC's with *A. anomala* and *S. anglica* was 21 and 10 mW/m^2.

2.3.3 Arundinella anomala

The P-MFC with *A. anomala* was the first that started producing electricity. From day 1 it showed an increasing cell voltage, stabilizing around 50 mV at an external resistance of 1000 Ω, thus producing 6.5 mA/m^2. In week 6 a polarization curve showed that the cathode reaction was limiting for power production. This can be seen from the fact that anode potential was stable during polarization curve and cathode potential decreased (see Figure 2.3).

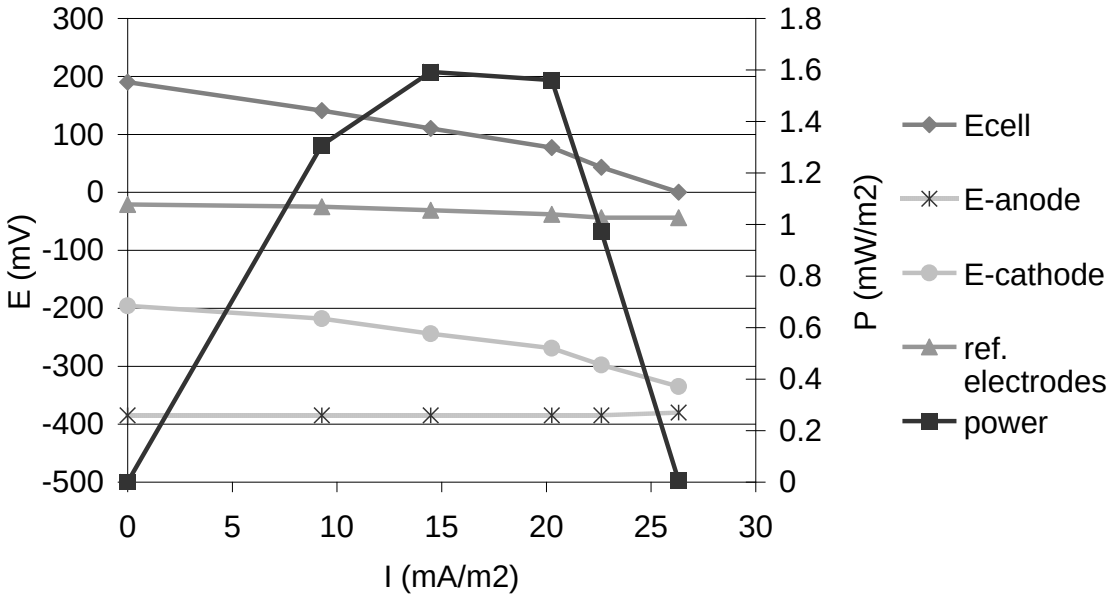

Figure 2.3: Polarization curve Arundinella anomala showing a stable anode potential and decreasing cathode potential, indicating that the reaction at the cathode is the limiting factor in power production.

After making the polarization curve the catholyte was replaced for potassium ferric cyanide (50 mM), to reduce overpotential at the cathode and provide an alternative electron acceptor. After replacement of the catholyte the current increased to 31 mA/m^2. Slowly electricity production decreased to 12 mA/m^2, concurrent with depletion of ferric cyanide in the cathode. Replacement of the catholyte in week 12 increased current again to 31 mA/m^2. After this replacement of the catholyte however, anode potential started increasing. The increasing anode potential at a stable cathode potential led to a decrease in cell potential and consequently decreased current. Current density dropped to 14 mA/m^2. In week 11 anode potential dropped again, stabilizing around -100 mV, while in week 1–11 it had been stable around -400 mV. Average power output between week 4 and 17 was 10 mW/m^2. This period was chosen because a fixed external resistance of 1000 Ω was used with a ferric cyanide cathode. In week 18 the maximization strategy was started (see 2.3.4) After the maximization strategy external resistance was put back on 1000 Ω. It took until week 22 for the cell potential to start rising again, as a result of dropping anode potential. The P-MFC kept producing electricity until the end of the experiment at week 26. After the maximization strategy average power density was 5 mW/m^2. During operation of the P-MFC a maximum power density of 22 mW/m^2 was achieved in a polarization curve in week 18. Total electricity produced in 26 weeks in this P-MFC was 846 J (Figure 2.2).

2.3.4 Spartina anglica

The P-MFC with *Spartina anglica* started producing current at the end of week 3, gradually increasing until week 10 to about 2.6 mA/m^2 (at 1000Ω external resistance). A polarization

curve that was made in week 10 showed that the reaction at the cathode was limiting for generating power in the P-MFC, like with *A. anomala* (Figure 2.3). After the polarization curve was made, the catholyte was replaced for ferric cyanide (50 mM). Current density increased to 39 mA/m^2 at an external resistance of 1000Ω. A polarization curve in week 17 showed a maximum power point of 222 mW/m^2. This is more than twice as high as the highest reported value in a P-MFC (Timmers et al., 2010). On average a power density of 21 mW/m^2 was achieved between week 10 and 17. After the optimization strategy (week 17–19) it took the P-MFC about two days to recover its former cell potential. However, the average power output after optimization strategy (6 mW/m^2) shows that the PMFC did not fully recover. The P-MFC with *S. anglica* kept on producing electricity until the experiment was terminated. Total electricity produced in 6 months' time was 861 J (Figure 2.2).

2.3.5 Maximization strategy for P-MFC's with *Arundinella anomala* and *Spartina anglica*

In week 17 a maximization strategy was started with the PMFC's with *S. anglica* and *A. anomala* to maximize power production of the P-MFC. With a polarization curve the maximum power point was determined. This is the point where external resistance equals internal resistance. External resistance of both P-MFC's was adjusted to internal resistance (*S. anglica*: 270 Ω, *A. anomala*: 100 Ω) to maximize power density of both P-MFC's. After a week, a new polarization curve was made, showing that maximum power output for both P-MFC's had dropped. Nonetheless, external resistance was adjusted again (*S. anglica*: 58 Ω, *A. anomala*: 69 Ω) to achieve maximum power. As a result of the adjusted resistance, cell potential collapsed, leaving us without power output after which external resistance was put back to 1000 Ω and the maximization strategy was abandoned.

2.4 Discussion

2.4.1 High biomass production and exceptional root:shoot ratio's in P-MFCs

Biomass yields for all three plants exceed the numbers found in literature for growth under natural conditions or in other experiments. For *A. anomala* is 1.1 kg/m^2 (Luo, 2009) total dry biomass is reported under natural conditions in China in literature, where we obtained 33 kg/m^2 in this experiment. In experiments performed at Forschungszentrum Jülich with *A. anomala* above ground fresh biomass production at a light intensity of 102 µE/m^2 and 21 °C in 60 days was 1.9 kg/m^2 (Luo, 2009). Extrapolating this result to 6 months, a biomass production of 5.8 kg/m^2 could have been expected. The below ground fresh biomass production that was achieved in Jülich (0.37 kg/m^2 in 60 days) extrapolated to six months growth gives 1.1 kg/m^2 (Luo, 2009). We achieved 72 kg/m^2 of fresh weight. In literature a yield of above ground biomass of *S. anglica* of 0.48–1.85 kg/m^2 is indicated (Gray et al., 1991; Swales et al., 2004) and 0.78–3.11 kg/m^2 of below ground dry biomass (Swales et al., 2004). In this research we obtained 6 kg/m^2 above ground dry biomass and 15 kg/m^2 below ground dry biomass. For *A. donax* 3.8–7.9 kg/m^2 (Angelini et al., 2008) of above ground fresh biomass is reported in literature. We achieved 23 kg/m^2. All numbers obtained in this

research are substantially higher than other reported values. In case of the results of Forschungszentrum Jülich the difference for *A. anomala* might be explained by the difference in light intensity. However the difference with numbers under natural conditions obtained from literature cannot be explained from radiation in the climate chamber. Radiation in the climate chamber is between 108.75 W/m^2 and 189.25 W/m^2 (Equation 2.3) for 14 h a day, corresponding to 1.5 to 2.6 kWh/m^2/day. Average radiation in The Netherlands is 2.7 kWh/m^2/day (KNMI, 2000). So, radiation in the climate chamber is lower than under natural conditions in The Netherlands. Therefore, other conditions in the climate chamber seem to have been beneficial for the plants in the P-MFC's. There are several possible explanations for this. One is that plants were fed with a nutrient solution which is developed specifically for plant growth and both water and nutrients were abundantly provided to the plants. A second possible explanation is that the plant receives light both from the top and from all sides since no other plants are growing around it. However, it could be hypothesized that the MFC actually favours plant growth. Further research should be done to explain the high biomass production. The second aspect of plant growth to be discussed is the difference in root system between *S. anglica* and *A. anomala*. With *A. anomala* was seen that most roots had up to 2nd order branching and roots were finer than with *S. anglica*. These are all indications of root growth in an anoxic or hypoxic environment (Blok, 2001). It seems that *A. anomala* wasn't able to nullify the waterlogged anaerobic conditions via aerenchyma. However, another possibility is that *A. anomala* suffered from nutrient deficiency caused by adsorption or absorption of the nutrients to the graphite grains. The large difference in growth conditions of the *S. anglica* and *A. anomala* root system might be explained from two things: (1) biofilm forming at the surface, (2) difference in ion-concentration. Due to the biofilm, the top of the root system might have been sealed off from the air, preventing oxygen diffusion into the soil and thus creating an anoxic environment. Due to difference in ion-concentration between *S. anglica* and *A. anomala* might have caused a lower nutrient availability for the fresh-marsh plant *A. anomala*. Even though A*. anomala* did not show a healthy root system it cannot be concluded based on this research that the plant is not suitable for growth in a P-MFC. Further research into the reasons for limited branching and fine root growth should be done to assess the suitability of *A. anomala* for P-MFC systems. *A. donax* grew very well in the plant-MFC but its ability to form a root system with a relatively even distribution in depth (Monti and Zatta, 2009) wasn't hindered by the P-MFC. For further research it is important to take rooting depth and root distribution of a plant into account when selecting for a P-MFC in order to avoid breakdown of the system. The third result to be discussed in this research is the root:shoot ratios. In literature, a root:shoot ratio of 0.3 (Gray et al., 1991) (based on dry weight) for *S. anglica* is reported and 1.55 (Quinn et al., 2007) (based on fresh weight) for *A. donax*. Jülich results indicate a root:shoot ratio of 0.2 (Luo, 2009) (based on fresh weight) for *A. anomala*. We obtained root:shoot ratios of 2.5 (*S. anglica*, based on dry weight), 3.1 (*A. anomala*, based on dry weight) and 1.6 (*A. donax*, based on fresh weight). This comparison shows that root:shoot ratio of *A. donax* is not exceptional, but root:shoot ratios of *S. anglica* and *A.*

anomala are. This might be explained from different factors. Again anoxic or hypoxic root conditions might be a possible explanation. Due to the low oxygen content in the system, nutrient uptake via the roots might be limited, inducing a faster root growth to supply the shoots with abundant nutrients. It has been reported that anaerobic or hypoxic conditions can lead to a shift in root:shoot ratio (Holmer et al., 2002; Nakano, 2007). Another explanation could be that nutrients were limited due to adsorption or absorption of the nutrients in the feeding solution to the graphite grains. In search of abundant nutrients, the plant might produce more roots to be able to supply the shoots. A third possible explanation for the difference between the P-MFC and the results obtained in Jülich can be a difference in root activity. A higher respiration rate, induced by higher oxygen concentrations in the soil in the Jülich experiment, would overcome the need for a high root biomass growth for supplying the shoots with nutrients.

2.4.2 Bio-electricity production in P-MFC's with *Arundinella anomala* and *Spartina anglica*

We achieved a maximum power density of 222 mW/m^2, which is more than twice as high as the highest reported yield up till now in a P-MFC (Timmers et al., 2010). Compared to the system of Timmers et al. (2010), who reached a maximum power density of 90 mW/m^2 there are some differences in the used system, which might explain these different results. These are (I) the use of smaller graphite grains (<1 mm in this research, 1–2 mm Timmers et al.) and (II) a larger anode volume (1463 ml 50% porosity for in this research, 270 ml 50% porosity Timmers et al.). Smaller graphite grains have a higher effective surface area, which might increase contact between micro-organisms and graphite, thus inducing lower internal resistance and higher power density. The second noticeable result is found when comparing the electricity production of the P-MFC's with *A. anomala* and *S. anglica*. It can be concluded that both P-MFC's produced approximately the same amount of electrical energy. However, their maximum power production was very different. For *S. anglica* this was 222 mW/m^2 and for *A. anomala* it was 22 mW/m^2. This can be explained from the fact that membrane potential of *A. anomala* is influenced by current density in the P-MFC, in contrast of the membrane potential of *S. anglica*. The membrane potential is the internal resistance that is caused by transport of ions through the membrane. There was a clear difference between the membrane potential between *S. anglica* and *A. anomala*, both in size and dependency on the current density. The average membrane potential of *S. anglica* was small (9 mV) and did not differ significantly from zero (F-test, 5% confidence interval). The membrane potential of *A. anomala* on the other hand was larger on average (-118 mV) and was a clear linear function of the current density. Linear regression gave as a result E_{mem} = -380 * I - 29, in which E_{mem} is the membrane potential in mV and I the current in mA/m2. The F-test showed that the slope differed significantly from zero at 5% confidence level. The higher the current density in the case of *A. Anomala* the more negative the membrane potential becomes, indicating that it costs more energy to transport ions through the membrane(Sleutels et al., 2009). Bigger energy loss across the membrane leads to a lower power density. The difference in membrane potential of both P-MFC's might be explained

from the fact that *S. anglica* is a halophyte and was grown under salt conditions, in contrast to *A. anomala* which is a fresh water species. The salt conditions provided ions abundantly in the P-MFC with *S. anglica*, thus facilitating transport across the membrane.

2.4.3 No successful maximization strategy

The method of obtaining maximum power densities via polarization curves is widely used in MFC research (Logan et al., 2006). However, it should be noted that these maximum power densities are snapshots. They are achieved in short term tests. In this research we did not succeed in maximizing power output of the P-MFC's following the maximum power densities achieved in polarization curves. There are two possible explanations for this: (I) inaccurate optimization and (II) capacitance of the system. The inaccurate optimization of the external resistance can be explained from the fact that a polarization curve is done stepwise, making it difficult to exactly determine the maximum power point. When, based on the steps in the curve, the external resistance is set at a value that is lower than internal resistance, electrons will flow faster than they are produced. This will cause a depletion of electrons in the system and subsequently a decreasing current and cell potential. Another possibility is that the maximum power density that is derived from the polarization curve is partly induced by capacitance of the system. The capacitance of the system is its ability to store electrons. These electrons might be released during the polarization curve, thus indicating a maximum power density that is higher than can be achieved when operating a system continuously.

2.4.4 Concurrent biomass and bio-electricity production in P-MFC's with *Arundinella anomala* and *Spartina anglica*

In the P-MFC's with *A. anomala* and *S. anglica* bio-electricity and biomass was concurrently produced. Grassy species seem to have the ability to grow and facilitate electricity production in a P-MFC, since *Glyceria maxima* (Strik et al., 2008a), *S. anglica* (Timmers et al., 2010) and *A. anomala* were all capable of facilitating electricity production in a P-MFC. The biomass production in both P-MFC's can be measured in terms of producible methane via digestion and subsequently electricity production. According to Pabón Pereira (2009) 0.21 l CH_4/gCOD (chemical oxygen demand) is produced by digestion of *S. anglica* at a total solids concentration of 0.32 g/g fresh matter of which 89% VS (volatile solids) and a COD of 1.42 gO_2/gVS (Pabón Pereira, 2009). Correcting for the dry matter content of the above ground biomass found in this experiment (0.23 g/g fresh matter), this would lead to 10 l CH_4 that can be produced from the biomass of *S. anglica*. This is equivalent to 391 kJ of energy. In a combined heat and power installation with an electrical efficiency of about 25% (van den Broek et al., 1996), this would lead to a production of 98 kJ of electricity for *S. anglica* with the above ground biomass. When we assume that *A. anomala* is comparable to *S. anglica* in digestibility and we correct for the dry matter content of the above ground biomass (0.33 g/g fresh matter), 141 kJ of electricity could have been produced with the above ground biomass of *A. anomala*. When we compare this to the electricity that is produced via the P-MFC, we can conclude that of all harvestable energy, we were able to produce 0.88%

directly in the P-MFC in case of *S. Anglica* and 0.60% in case of *A. Anomala*. When we look ahead to the long term performance of the system we can conclude that a lot of biomass is left below ground when above ground biomass would be harvested or growth season would be over. One of our future challenges will therefore be to harvest energy from below ground biomass. When looking into the electrical efficiency compared to the theoretical maximum, a different view can be formed. Based on radiation in the climate chamber (108.75–189.25 W/m^2), an average photosynthetic efficiency of 2.5%, rhizodeposits yield of 40%, rhizodeposits availability for micro-organisms of 30% and a microbial fuel cell energy recovery of 29% (Ter Heijne et al., 2007) and a 6 months growth season (Strik et al., 2008a) an estimated conservative net energy output of 129 mW/m^2 could have been achieved in this research. We obtained on average 21 or 10 mW/m^2 for *S. Anglica* and *A. Anomala* respectively, being 16% and 8% of the theoretical maximum. These numbers are based on average power output of the P-MFC's. However, the average power output is ten times lower than the maximum power output we obtained in a polarization curve for *S. anglica.* If we were able to optimize power output of the P-MFC to the maximum value obtained, we would even exceed the estimation of the net energy output, concluding that this estimation might be too cautious.

2.5 Conclusions

Biomass and bio-electricity can be produced concurrently in PMFC's. It can therefore be concluded that it is possible to produce non-destructive bio-energy with a P-MFC. Grassy species seem to have the ability to grow and facilitate electricity production in a P-MFC. Maximum power output of the P-MFC was more than tripled in 2008 to 222 mW/m^2 in this research. We did not succeed in maximizing power output. Based on maximum power densities compared to average power densities a successful optimization strategy could lead to a 10-fold increased power output of the system.

2.6 Acknowledgements

We would like to thank Xiao Qi Ye and Fang Li Luo for providing us with information and experimental data on Arundinella anomala. The research leading to these results has received funding from the European Community's Seventh Framework Programme FP7/2007-2013 under Grant Agreement No. 226532. In addition this research was funded by SenterNovem, the Dutch governmental agency for sustainability and innovation from the Ministry of Economic Affairs (Grant No. EOSLT06020) and supported by NUON.

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2.8 Supporting information

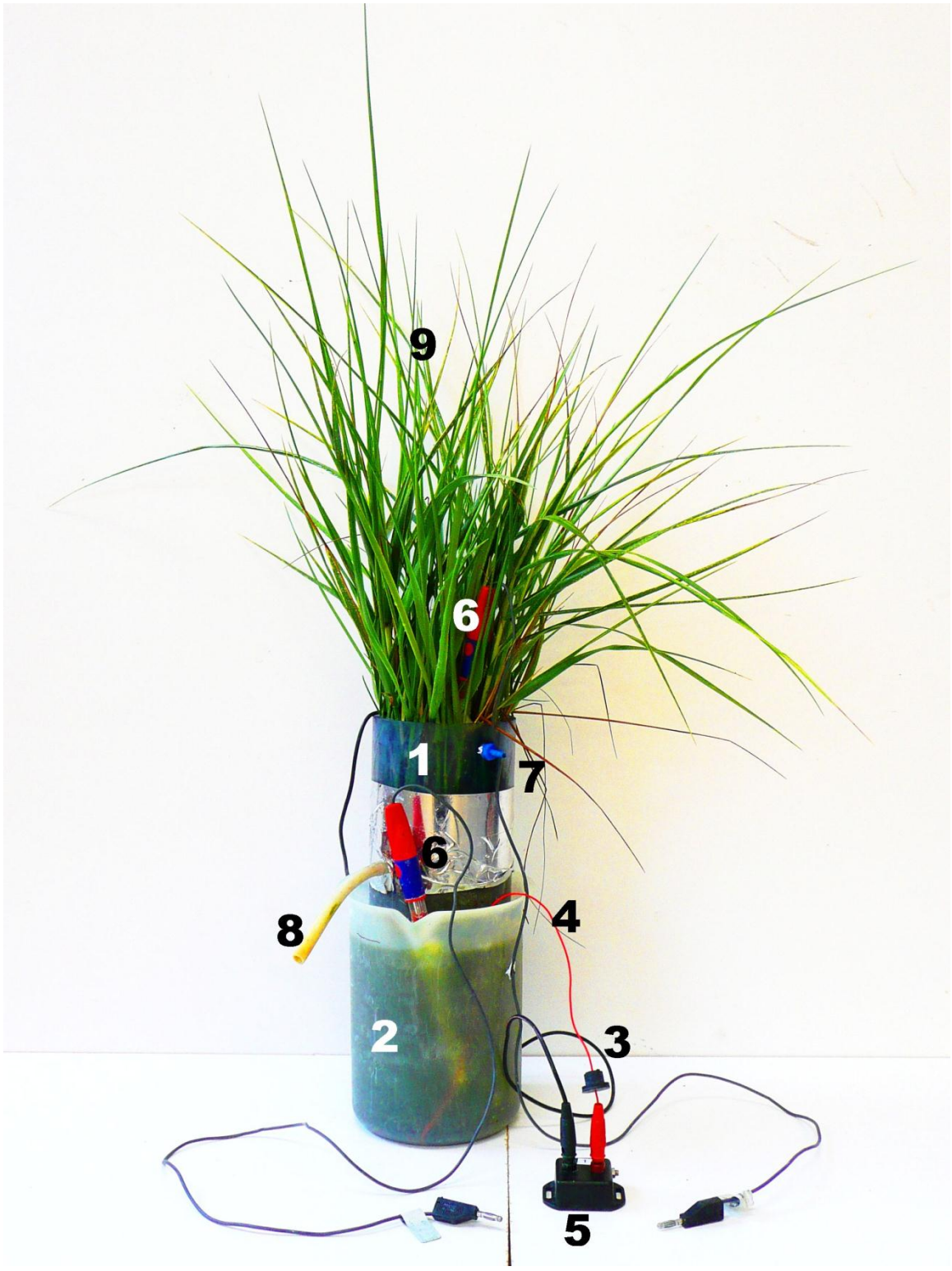
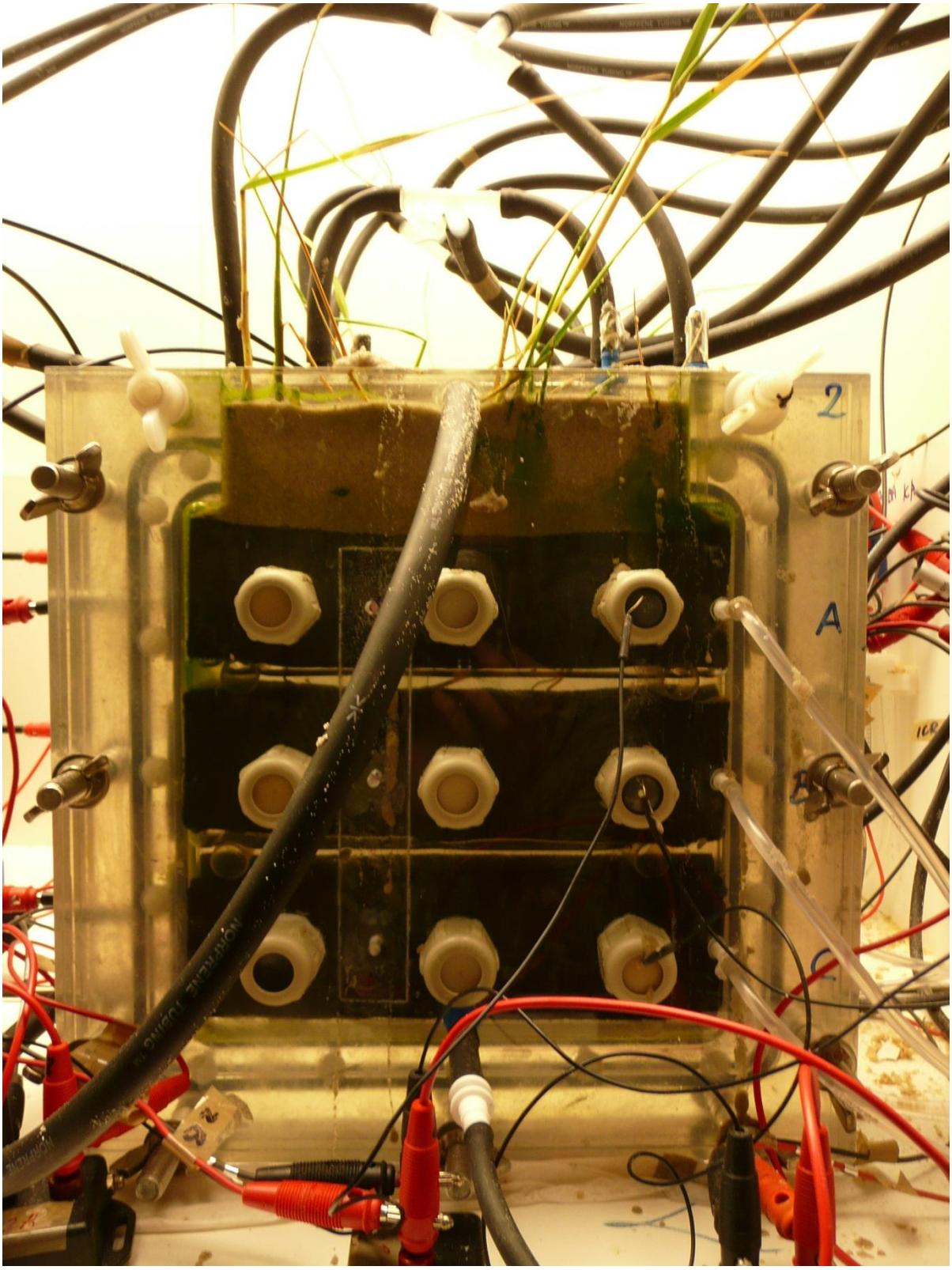


Figure 2.4: Experimental set-up, in which 1= anode compartment, 2=cathode compartment, 3=anode wire, 4= cathode wire, 5=external resistance, 6=reference electrode, 7=water and plant-growth medium filling point, 8=anode overflow, 9=Spartina anglica

Figure 2.5: Root system of Arundinella anomala at the end of the experiment

Figure 2.6: Root system of Spartina anglica at the end of the experiment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3 NEW PLANT-GROWTH MEDIUM FOR INCREASED POWER OUTPUT OF THE PLANT-MICROBIAL FUEL CELL

Chapter published as:

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Abstract

In a Plant-Microbial Fuel Cell anode-conditions must be created that are favourable for plant growth and electricity production. One of the major aspects in this is the composition of the plant-growth medium. Hoagland medium has been used until now, with added phosphate buffer to reduce potential losses over the membrane because of differences in pH between anode and cathode. We developed a new, improved plant-growth medium that improves current production, while the plant keeps growing. This medium is a nitrate-less, ammonium-rich medium that contains all macro- and micro-nutrients necessary for plant growth, with a balanced amount of bicarbonate buffer. Sulphate presence in the plant-growth medium helps to keep a low anode-potential. With the new plant-growth medium the maximum current production of the Plant-Microbial Fuel Cell increased from 186 mA/m^2 to 469 mA/m^2.

3.1 Introduction

The Plant-Microbial Fuel Cell (P-MFC) offers the possibility to produce bio-electricity while the plant is growing concurrently (Helder et al., 2010). Concurrent bio-electricity and biomass production enables us to produce bio-electricity that is non-destructive and can be combined with other applications for biomass (Strik et al., 2008). Average current densities between 32 mA/m^2 and 214 mA/m^2 planting area have been obtained and average power densities between 4 mW/m^2 and 50 mW/m^2 planting area have been obtained (Strik et al., 2011). The estimation of the theoretical potential is 3.2 W/m^2 planting area (Strik et al., 2011). The potential compares favourably to electricity production via anaerobic digestion of biomass, which generates net up to 220 mW/m^2 planting area (Strik et al., 2011).

A plant produces organic matter via photosynthesis, part of which is excreted at the roots into the soil. These so-called rhizodeposits are oxidized by microorganisms. In this oxidation-process electrons are released by the microorganisms and donated to the anode of a Microbial Fuel Cell (MFC) (Strik et al., 2008). To improve current and power densities of the P-MFC, three factors could be engineered: photosynthesis rate, amount of rhizodeposition, and energy recovery in the MFC (Strik et al., 2011). A factor that likely influences both the amount of rhizodeposition by the plant and the energy recovery in the MFC is the plant-growth medium, because it influences the conditions, as explained later, for both microorganisms and plant.

Current P-MFC research is performed with Hoagland medium with added phosphate-buffer (De Schamphelaire et al., 2008; Helder et al., 2010; Strik et al., 2008; Timmers et al., 2010). Hoagland medium is a plant-growth medium which consists of a balanced solution of macro- and micronutrients needed for plant-growth without nutrient deficiencies. The buffer is used to control pH in the anode for the bacteria (Rozendal et al., 2008). Hoagland and buffer concentrations are varied between different experiments (Helder et al., 2010; Strik et al., 2008; Timmers et al., 2010). Since the P-MFC has plants and bacteria in the anode, medium should enable both plant and bacterial growth. It has not been researched yet to what extent the Hoagland medium favours electrochemically active bacteria and what the effect of phosphate-buffer is on plant-growth.

The Hoagland medium contains different nutrients, like nitrate and sulphate, that could serve as an alternative electron-acceptor instead of the anode in the P-MFC. It might therefore be reducing the energy recovery from the system (Strik et al., 2011). Nitrate is added to meet the plant's nitrogen demand. Nitrate can be reduced by bacteria to nitrogen-gas according to (Clauwaert et al., 2007):

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O$$

The electrons needed for this conversion can directly be acquired by bacteria from the organic matter or from the electrode (Figure 3.1a,b).

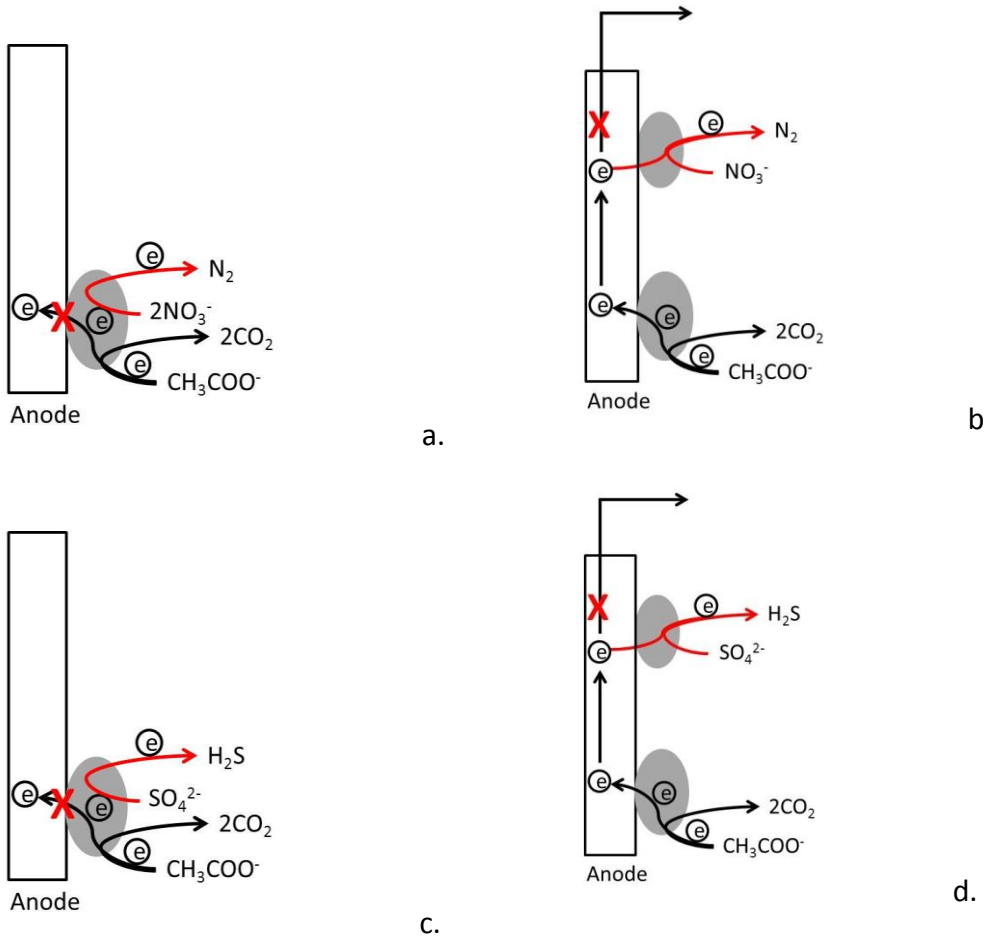

Figure 3.1: Two pathways of nitrate reduction (a, b) and sulphate reduction (c, d) at the anode of a Plant-Microbial Fuel Cell. In pathway 1 (a, c) electrons released in the oxidation of organic matter are directly used by the same organism for nitrate or sulphate reduction. In pathway 2 (b, d) electrons released in the oxidation of organic matter and donated to the anode are taken from the anode by another organism for nitrate or sulphate reduction.

The conversion of nitrate to nitrogen-gas is energetically favorable to bacteria when using organic matter as electron donor (ΔG_r^0=-1178 kJ, calculated from Haas and Shock (1999)). Both electrons and energy are lost in this conversion as they no longer can be used for electricity production at the anode. It has been described that denitrification can be effectively performed at the cathode of an MFC (Clauwaert et al., 2007; Morris et al., 2009). In a P-MFC, however, nitrate is added to the anode of the fuel cell. It has been reported that nitrate did not affect cell voltage or produced current of a MFC when present in the anode but did lower coulombic efficiency (Morris and Jin, 2009). Because substrate was abundantly present in the anode, still sufficient substrate was available to the bacteria to donate electrons to the anode after denitrification took place. Thus cell voltage was not affected. Electrons used in denitrification, however, cannot be used for electricity production, thus coulombic efficiency was lowered.

Since substrate concentration in P-MFCs is dependent on rhizodeposition from the plants, P-MFCs typically operate under substrate limiting conditions (Timmers et al., 2010). Denitrification in the anode of a P-MFC, therefore, leads directly to lower availability of substrate for electricity production at the anode. The potential of the anode might therefore be determined by both organic matter oxidation and denitrification. Such mixed potential in the anode (Harnisch and Schröder, 2010) will be higher than the potential of organic matter oxidation alone. The overall efficiency of the (P-)MFC is the product of the coulombic efficiency and the voltage efficiency. When using a chemical cathode and a fixed external load voltage efficiency is predominantly determined by the anode potential. It is therefore expected, that nitrate in the anode of a P-MFC will have an effect on both cell voltage and coulombic efficiency.

Sulphate could act as an alternative electron acceptor as well. Sulphate can be reduced to hydrogen-sulphide according to (Morris and Jin, 2009) (Figure 3.1c,d):

$$SO_4^{2-} + 8e^- + 10H^+ \rightarrow H_2S + 4H_2O$$

Compared to denitrification, this reaction is energetically less favourable to bacteria when using organic matter as electron donor (ΔG_r^0=-223 kJ, calculated from Haas and Shock (1999)) so less energy is available to the bacteria. Sulphate is added in a much lower concentration than nitrate. Sulphate is therefore beforehand expected to have a smaller influence on cell voltage or coulombic efficiency of the P-MFC, as compared to nitrate.

In this paper we describe the testing of a new plant-growth medium for the P-MFC that increases power output of the system, while plants keep growing. Phosphate-buffer removal from the medium was researched to test the effect on plant-growth. Nitrate and sulphate were removed, subsequently, to reduce the amount of available alternative electron acceptors in the system.

3.2 Methods

3.2.1 Set-up and operation

Four flat-plate P-MFCs (Figure 3.2) were operated for 370 days in a climate chamber (Microclima 1750 Snijders) at 20 ^{o}C and 75% humidity with a light–dark regime of 14:10 h and a light intensity of 596 ± 161 µmol m^{-2} s^{-1}, measured at the top of the reactors by a light intensity meter (Photodyne 44XLA). Anode-volume was 0.648 l (LxDxH = 16x2x16 cm). Anode consisted of three sections of graphite felt (Grade WDF, 6 mm, National Specialty Products Carbon and Graphite Felt, Taiwan) of 5 cm height (top, middle and bottom), which were physically and electronically separated by plastic half-rings. As current collectors, gold wires were woven through the graphite felt.

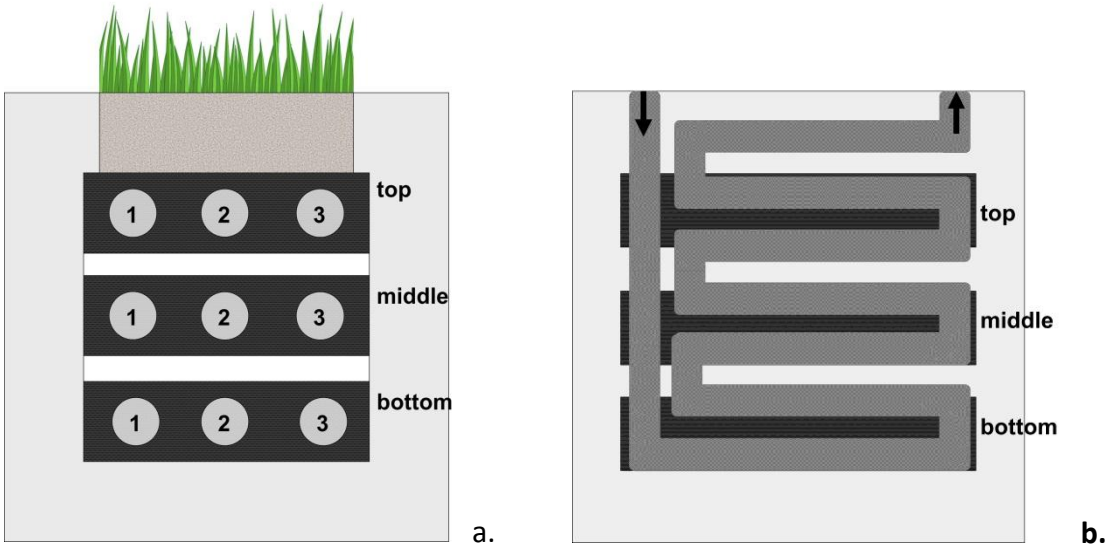

Figure 3.2: Anode (a) and cathode (b) schematic overview of a flat-plate Plant-Microbial Fuel Cell. In anode and cathode top, middle and bottom sections are indicated; in anode sample-points are indicated with numbers 1, 2 and 3; and in cathode the flow-through channel is shown. Anode and cathode were assembled with top, middle and bottom sections of anode and cathode against each other, separated by a membrane.

Three plants of *Spartina anglica* were used per P-MFC with a combined weight of 16.7 g per P-MFC averagely (sd 3.7). Plants were continuously supplied with a plant-growth medium from the bottom. During the experiment four different plant-growth media were supplied (Table 3.1): modified Hoagland 50% (Timmers et al., 2010) (1); nitrate-less, ammonium-chloride-rich medium (2); nitrate-less, ammonium-bicarbonate-rich medium (3); nitrate-less, sulphate-less, ammonium-bicarbonate-rich medium (4). To all media 10 g/l NaCl was added to increase conductivity. In P-MFC 1 and 2 buffer was added to the Hoagland-medium (20 mM, $K_2HPO_4^-$ /KH_2PO_4, pH 6.75). At the start of the experiment plant-growth medium was applied by continuous pumping (Minipuls 2, Gilson, Villiers le Bel, France) at a flow of 0.2 µl/s, which was gradually increased to meet plants' water and nutrient demand to 4.3 µl/s at the end of the experiment. The plant-growth media were continuously flushed with nitrogen gas to eliminate oxygen.

The different sections of anode and cathode were operated as one anode and one cathode during day 1–116 by connecting the wires of the different sections to start the P-MFC's as one system. External load on the system was 300 X. On day 116 the wires were disconnected and three separate anode–cathode couples were established per P-MFC, each anode connected to its cathode over an external load of 900 Ω. Cathode was a flow-through cathode in which catholyte was pumped through a flow-channel (total volume of channels and overflow bottles 1 l) at a continuous flow-speed of 1.5 ml/s (Watson Marlow 520U/R, Watson-Marlow Bredel Pumps, Falmouth, Cornwall, UK). From day 1 to 70 catholyte consisted of demi-water (demineralized with Ministil P-12, Christ AG, Aesch, Switzerland) with 10 g/l NaCl in case of P-MFC 3 and 4. In P-MFC 1 and 2 phosphate buffer and 10 g/l NaCl

Table 3.1: Concentrations of macronutrients in four plant-growth media used during different stages in the experiment: modified Hoagland 50% (1); nitrate-less, ammonium-chloride-rich medium (2); nitrate-less, ammonium-bicarbonate-rich medium (3); nitrate-less, sulphate-less, ammonium-bicarbonate-rich medium (4). Micronutrients as in modified Hoagland solution (Timmers et al., 2010).

	1 Day 1–116 Day 277–296	2 Day 116–190	3[a] Day 190–277 Day 296–328 Day 349–360 Day 366–370	4[a] Day 328–349 Day 360–366
Macronutrients (mg/l)				
KNO_3	303	–	–	–
NH_4Cl	–	124.81[b]	–	–
NH_4HCO_3	–	–	553.5	553.5
$Ca(NO_3)_2{\cdot}4H_2O$	472.32	–	–	–
$CaCl_2$	–	222	222	222
$NH_4H_2PO_4$	115.08	115.1	115.1	115.1
$MgSO_4{\cdot}7H_2O$	123.245	123.245	123.245	–
$Na_2SiO_3{\cdot}9H_2O$	142.1	142.1	142.1	142.1
KCl	–	223.68	223.68	223.68
P-buffer (mM)				
$KHPO_4/H_2PO_4$ (pH 6.75)	20[c]	–	–	–
Salt (g/l)				
NaCl	10	10	10	10

[a] The nutrient solution was adjusted to match all other nutrient concentrations in the original solution.
[b] To avoid rapid acidification of the anode due to proton-release by the plant, nitrogen added in the form of ammonium matched 33% of the original nitrogen that was added in the original Hoagland medium.
[c] Buffer was only added to P-MFC 1 and 2.

were added to the demi-water (20 mM, K_2HPO_4/KH_2PO_4, pH 6.75). At day 70 the catholyte was changed to ferric cyanide ($K_3(FeCN)_6$, 50 mM) with 10 g/l NaCl to increase and stabilize cathode potential. In P-MFC 1 and 2 buffer was added to the ferric cyanide (20 mM, $K_2HPO_4^-/KH_2PO_4$, pH 6.75). Ferric cyanide in the cathode was replenished whenever cathode-potential dropped below +200 mV (against Ag/AgCl reference electrode).

3.2.2 Measurements

Plant growth was measured with a tape-measure. Leaf-length of all leaves was added for total leaf-length of the plant. Anode and cathode potentials were measured with Ag/AgCl-reference electrodes (3 M KCl, +205 mV versus SHE, ProSense Qis). Cell voltage, anode potential, cathode potential and membrane potential were logged every minute with Fieldpoint (Module FP100, FP101, National Instruments) and collected with Labview (National Instruments Software). Anode and cathode were sampled regularly with a syringe. Anode was sampled at 9 sample-points, which were evenly distributed over the three anode-sections, so three sample- points in each anode-section. Samples of 1 ml each were measured for conductivity (ProLine Plus Qis, ProSense BV, Oosterhout, The Netherlands) and pH (691 pH-meter, Metrohm, Herisau, Switzerland).

Nitrate was measured via a cuvette test (Dr. Lange, Ion 500, LCK 339 and LCK 340, Dr. Lange BV, Tiel, The Netherlands). Sulphate was measured via ion chromatography (Dionex ICS-2100, Dionex Benelux BV with Chromeleon software).

3.2.3 Calculations

To be able to determine the source of occurring acidification in our system, two pathways of proton-release in our system had to be quantified. The two pathways can be proton-excretion by the plant for ammonium-uptake (Blossfeld et al., 2010) or oxidation of organic matter. Ammonium-uptake by the plant during 24 h was calculated via:

$$NH_4uptake = Q_{in} \times t \times C_{NH_4in} - V_{out} \times C_{NH_4out}$$

Equation 3.1: Ammonium-uptake by plant in 24 h, in which Q_{in} = inflow-speed of plant-growth medium in l/h, t = time in hours, C_{NH_4in} = concentration ammonium in the plant-growth medium in mmol/l, V_{out} = volume of medium overflow after 24 h, C_{NH_4out} = concentration ammonium in effluent in mmol/l.

Plants are able to take up ammonium by excreting a proton for every ammonium-molecule (Blossfeld et al., 2010). Proton-excretion caused by ammonium-uptake by the plant relates 1:1, so the amount of ammonium taken up equals the amount of protons excreted.

Electron production from organic matter oxidation was calculated via:

$$e^-production = \frac{E_{cell}/R_{ext}}{F} \times t$$

Equation 3.2: Electron production in mmol in 24 h, in which, E_{cell} = cell voltage in mV, R_{ext} = external resistance in Ω, F = Faraday constant ($9.64x10^4$ C/mol), t = 24 h.

According to:

$$CH_3COO^- + 2H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$$

Proton production relates to electron production as 9:8.

3.3 Results and discussion

3.3.1 Phosphate-buffer negatively influences plant growth

Plants in P-MFC 3 and 4 grew better than plants in P-MFC 1 and 2 (Figure 3.3). Plants in P-MFC 1 and 2 died after day 125 and measurements were stopped. Because P-MFC 1 and 2 were fed with plant-growth medium with phosphate-buffer and P-MFC 3 and 4 were fed with plant-growth medium without phosphate-buffer, it is expected that the plants in P-MFC 1 and 2 were hampered in growth by the buffer. The pH in the non-buffered system during the complete runtime of the experiment varied between 2.9 and 7.4, with an average of 5.7 (sd 0.9), which is considerably lower than pH in the buffered P-MFC's (av. 6.7 sd 0.1). Two explanations can be given for the difference in growth.

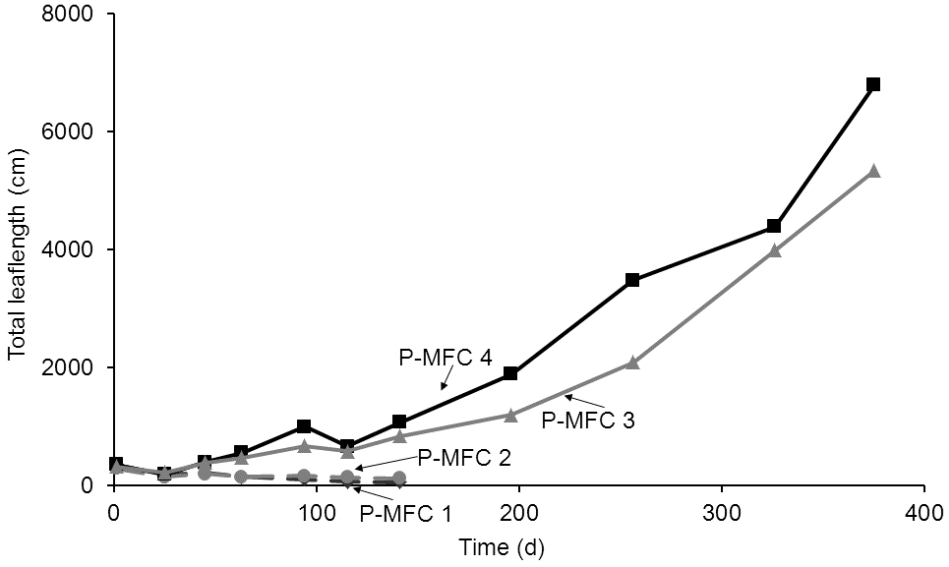

Figure 3.3: Plant-growth during 365 days of experiment in cm. P-MFC 1 and 2 were fed plant-growth medium with phosphate buffer, P-MFC 3 and 4 were fed plant-growth medium without phosphate buffer. Plant-growth measurement of P-MFC 1 and 2 was stopped after day 145 because of plant-death. Relative plant-growth was variable over the year.

First explanation for difference in growth is that plants in the buffered system were under alkalinity stress. Growth stunting and discolouring of leaves that was seen is consistent with symptoms for alkalinity stress in rice plants. In rice plants (which is a grassy species like *S. anglica*) alkalinity can lead to discoloration of the leaves, which starts at the tip with a patchy pattern of damage (International Rice Research Institute, 2009). This suits the damage

pattern as was observed in *S. anglica* plants in P-MFC 1 and 2 (data not shown). In earlier research (Helder et al., 2010) buffer concentration was the same as in this experiment and the damage pattern was not observed. Possible alkalinity stress in this experiment can be due to more thorough mixing compared to earlier experiments, thus exposing plants to higher pH-values. In this experiment plant-growth medium was continuously pumped into the anode, as opposed to earlier research in which batch-wise pumping was used (Helder et al., 2010; Timmers et al., 2010). Moreover, pumping speed in this experiment (hydraulic retention time approximately 8 h) was higher than in earlier research (Helder et al., 2010; Timmers et al., 2010). Because of these differences in pumping, the anode probably was better mixed in this experiment as compared to earlier research (Helder et al., 2010; Timmers et al., 2010). At low pumping speed or batch-wise pumping stratification in the anode could take place, allowing the plant to create zones around the roots with favorable conditions, which is not possible at continuous pumping at higher speed. Therefore, better mixing might lead to higher alkalinity-stress for the plants when compared to earlier experiments, even though buffer concentration was not higher. Moreover, in the tubular system with the membrane in the bottom of the tube, a pH-gradient was observed with increasing pH towards the membrane, while most roots were located in the top part of the anode (Timmers et al., 2010). Thus most roots were located in an environment with lower pH. In natural growth environments for *S. anglica*, neutral pH-values are found (Bouma et al., 2003; Koretsky et al., 2008; Otte et al., 1993), which conflicts with our hypothesis of possible alkalinitystress in this experiment. However, the environment in the P-MFC does not resemble natural circumstances, especially because under natural circumstances no pumping is applied, so locally different conditions can occur.

Second explanation for the difference in growth between the buffered and non-buffered P-MFCs is the new design of P-MFC that was used. Plants in P-MFC 1 and 2 hardly grew at all, while plant growth was reported in many recent publications which report the use of the same phosphate-buffer as in this experiment (8 mM (Strik et al., 2008; Timmers et al., 2010), 20 mM (Helder et al., 2010)). The total surface area on which the plants could grow is smaller than in the experiments of Timmers et al. (2010) since three plants were planted in the system, instead of one. It could be argued that space was too limited for plant growth. The use of three plants in one system might lead to auto-inhibition. Autoinhibition is the effect of intraspecific competition in dense populations (Bais et al., 2006). Competition between plants with the same genotype could lead to growth retardation per individual plant, but is very unlikely to result in death considering the fact that the studied plants were transplanted from the same batch before they were transplanted into the P-MFC (Bais et al., 2006).

3.3.2 pH decrease by exchange of NH4 for protons by plant roots

During the first 116 days (phase 1) pH in the phosphate-buffered anodes was between 6.5 and 7.0; pH in the non-buffered systems was between 4.9 and 6.5 (Figure 3.4). After removing nitrate from the medium and adding ammonium-chloride (phase 2), pH rapidly

dropped below 4.9 (Figure 3.4). This could be due to two different mechanisms. The first mechanism is the excretion of a proton for each molecule of ammonium that is taken up by the plant (Blossfeld et al., 2010).

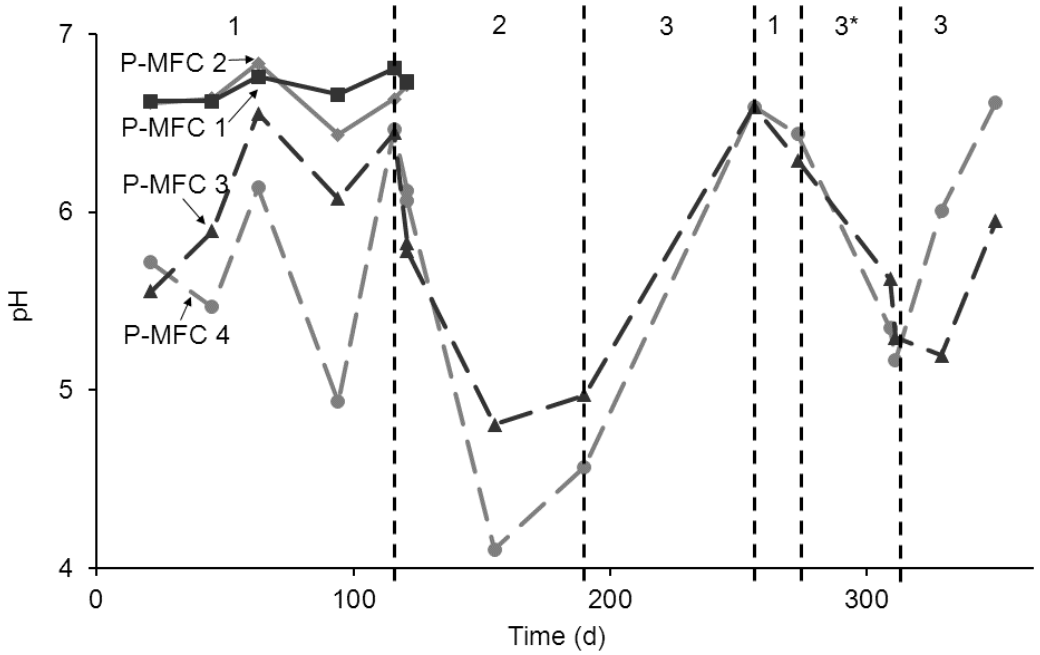

Figure 3.4 pH measurements during the 365 days of experiment with different plant-growth media. Changes in plant-growth medium are indicated with dotted lines. 1 = modified Hoagland medium 50%, 2 = nitrate-less, ammonium-chloride-rich medium, 3 = nitrate-less, ammonium-bicarbonate-rich medium

** The medium was changed, but without flushing the system with the new medium. Flushing with the new medium was done at the next dotted line.*

The second mechanism is the production of protons during oxidation of organic matter. Protons excreted from plant-roots for ammonium-uptake accounted for approximately 2 mmol in 24 h (Equation 3.1), protons produced from organic matter oxidation leading to electricity production accounted for 0.25 mmol (Equation 3.2). The total amount of protons coming from oxidation of organic matter is underestimated in this calculation because likely not all oxidized organic matter leads to electricity production. Proton production due to other oxidation reactions, however, is negligible compared to proton production due to oxidation for electricity production. Oxidation of organic matter, for example acetate, can occur according to:

$$CH_3COO^- + 2H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$$ or

$$CH_3COO^- + H^+ \rightarrow CH_4 + H_2O$$

In the second case no protons are produced but consumed. To neutralize pH ammonium was added in the form of NH_4HCO_3 at day 190 to make sure that proton production induced by

organic matter oxidation would likely the major process leading to acidification of the system. The pH increased after adding NH_4HCO_3 (Figure 3.4; phase 3).

3.3.3 Removal of nitrate from plant-growth medium leads to increased current and power production

P-MFC 1 and 2 hardly produced electricity, likely because plants in these P-MFCs did not grow so not enough organic matter was present for oxidation. P-MFC 3 and 4 did produce electricity (Figure 3.5) and will be discussed hereafter. When 50% modified Hoagland medium was fed hardly any electricity was produced in all P-MFCs (Figure 3.5, phase 1); max. 98 mA/m^2, average 8 mA/m^2 (Table 3.2). Average power density was below 1 mW/m^2 (Table 3.2). At day 115 up to 70 mg/l NO3-N at different sample points in the P-MFCs was measured, indicating that excess nitrate was added to the plant, which could serve as alternative electron acceptor. When a nitrate-less, ammonium-chloride-rich medium was fed current production increased in P-MFC 3 and 4, but not in P-MFC 1 and 2 (phase 2, Figure 3.5, data of P-MFC 1 and 2 not shown). In P-MFC 3 and 4 current production increased to 119 mA/m^2 average and 202 mA/m^2 maximum (Table 3.2). Average power density increased to 23 mW/m^2 (Table 3.2). Because of rapid acidification of the anode, the medium was changed to ammonium-bicarbonate-rich medium to buffer the protons excreted by the plant roots for uptake of ammonium. When an ammonium-bicarbonate-rich medium was fed, current production increased (Figure 3.5, phase 3) to 193 mA/m^2 on average and 384 mA/m^2 maximum (Table 3.2). Re-applying 50% Hoagland solution (containing nitrate) and subsequently re-applying ammonium-bicarbonate-rich medium confirmed that the increased current production was caused by the substitution of nitrate for ammonium (Figure 3.5, phases 1, 3* and 3, day 190 through day 272).

The lower current production with the nitrate-rich medium can be explained by nitrate being an alternative electron acceptor. The fact that presence of nitrate did not influence current production in a normal MFC (Morris and Jin, 2009) can be explained from substrate-limitation in the P-MFC. Because a P-MFC is operated under substrate-limiting conditions, competition between denitrifying and electrochemically active microorganisms will directly lead to a reduction in produced electricity, while this would not be the case when substrate would be abundantly available. Substrate limitation in the P-MFC makes it crucial to remove alternative electron acceptors from the plant-growth medium, because it directly influences current production. The increase of current production with ammonium-bicarbonate as compared to ammonium-chloride can be explained from the fact that pH-difference between anode and cathode was smaller with ammonium-bicarbonate than with ammonium-chloride.

The second period of applying Hoagland-medium shows over 700% higher current densities and almost 700% power densities compared to the first period (Table 3.2). The second period of applying medium 3 shows increase in average current density of 200% and an increase in power density of over 250% compared to the first period (Table 3.2).

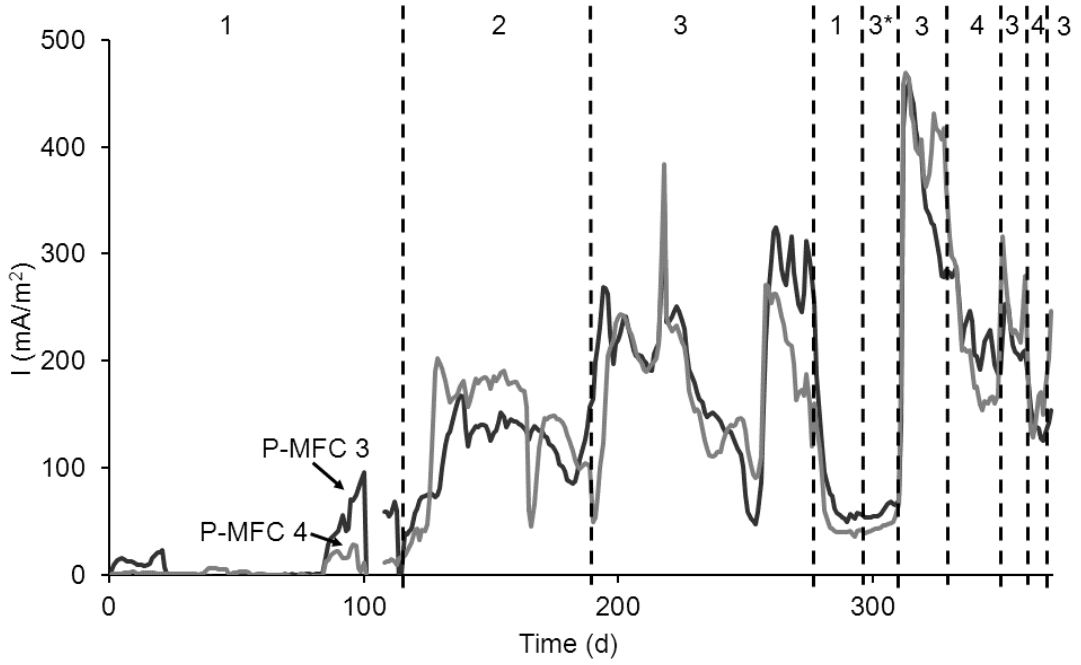

*Figure 3.5: Electricity production (mA/m²) in PMFC 3 and 4 during 365 days of experiment. Indicated with dotted lines are periods in which different plant-growth media were fed, in which 1 = modified Hoagland 50%, 2 = nitrate-less, ammonium-chloride rich medium , 3 = nitrate-less, ammonium-bicarbonate-rich medium, 4= nitrate-less, ammonium-bicarbonate-rich, sulphate-less medium. * The medium was changed, but without flushing the system with the new medium. Nitrate concentrations in the system on day 311 were up to 33.3 mg NO_3-N/L. Flushing with the new medium was done at the next dotted line.*

Table 3.2: Average and maximum current and power densities achieved in P-MFC 3 and 4 with different plant-growth media, in which: 1 = modified Hoagland 50%, 2 = nitrate-less, ammonium-chloride rich medium, 3 = nitrate-less, ammonium-bicarbonate-rich medium, 3= The medium was changed, but without flushing the system with the new medium. Nitrate concentrations in the system on day 311 were up to 33.3 mg NO_3-N/L, 4= nitrate-less, ammonium-bicarbonate-rich, sulphate-less medium.*

	1	2	3	1+3*	3	4
I_{max} (mA/m^2)	95	202	384	186	469	406
$I_{average}$ (mA/m^2)	8 sd 17	119 sd 50	193 sd 66	59 sd 30	384 sd 74	242 sd 63
P_{max} (mW/m^2)	26	56	164	51	211	165
$P_{average}$ (mW/m^2)	0.8 sd 3.3	23 sd 15	60 sd 34	5.5 sd 13	155 sd 47	72 sd 36

It seems that electricity production increases during the runtime of the experiment, independent of the used plant-growth medium. This can be explained from the fact that plants grew continuously so more roots were present at a later stage of the experiment. More roots would lead to more exudation and more root-turnover, which would increase the availability of organic matter present for oxidation and electricity production during the later stage of the experiment.

3.3.4 Removal of sulphate leads to lower current density

On average 25.9 mg/l (sd 15.3) of sulphate was measured in PMFC 3 and 4 on day 121 and day 140, indicating sulphate was fed in excess to the plants. On day 328 sulphate was removed from the plant-growth medium (Figure 3.5, phases 3 and 4). When sulphate was removed from the system electricity production dropped from 250 mA/m^2 to 200 mA/m^2 within a day in P-MFC 3 and from 400 mA/m^2 to 200 mA/m^2 in P-MFC 4 (Figure 3.5; phases 3 and 4). Average current density with medium 4 was 242 mA/m^2 compared to 384 mA/m^2 with medium 3 that was used just before. When sulphate was re-added to the plant-growth medium, electricity production increased again within a day to 300 mA/m^2 (Figure 3.5). The experiment was repeated on day 360 and the same effect was observed. The decrease in current production was accompanied by an increasing anode potential. Sulphate can be reduced in soils at low redox potentials (Connell and Patrick, 1968) to hydrogen-sulphide. Sulphate can therefore influence power output of a (P-)MFC by functioning as an alternative electron acceptor (Morris and Jin, 2009). Hydrogen-sulphide, however, can be re-oxidized to solid sulphur at the anode, releasing two of the electrons that were consumed in sulphate reduction (Rabaey et al., 2006). Part of the energy and electrons lost in sulphate reduction can be recovered (Figure 3.6). In this respect an increase of current production could be expected when removing sulphate from the plant-growth medium. Because of lower concentration of sulphate in the plant-growth medium compared to nitrate and possible re-oxidation of sulphide to sulphur a smaller effect of sulphate-removal was expected than was seen with nitrate-removal. Instead of the expected increase in current production, current production decreased after removing sulphate from the plant-growth medium, while anode potential increased. Two possible mechanisms can be responsible for the increase in anode-potential and decrease in current after removal of sulphate from the system.

The first mechanism is the effect of sulphide-presence on root-growth and root-permeability and consequently influence on rhizodeposition of the plant. It has been shown that presence of sulphide leads to stress for the plants and leads to immediate decrease of oxygen loss from the roots of rice plants (Armstrong and Armstrong, 2005). Since both rice and *S. anglica* are grassy species, a comparable effect could be occurring at the roots of *S. anglica*. So when sulphate is removed from the P-MFC, sulphide concentrations will decrease and oxygen loss from the roots will increase. Higher oxygen content in the P-MFC will lead to a higher mixed anode potential (Harnisch and Schröder, 2010). Plant-growth was observed all through the experiment, however, so apparent presence of sulphide has not prevented plant growth. The second mechanism has an effect on the mixed potential of the MFC. Possibly the

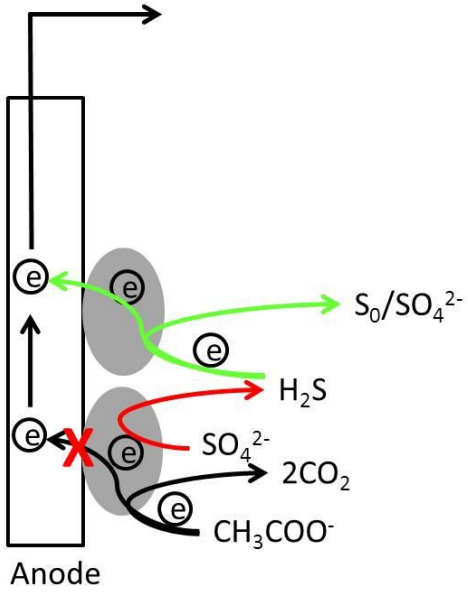

Figure 3.6: Re-oxidation of hydrogen-sulphide to solid sulphur at the anode of a Plant-Microbial Fuel Cell, regaining electrons for electricity production

oxidation reaction of sulphide to sulphur helps to maintain a low anode potential (Rabaey et al., 2006). When no more sulphate is reduced to sulphide, this reaction cannot occur, leading to an increase of anode potential in the P-MFC. Rabaey et al. (2006) have shown that anode potential increases with depletion of sulphide in case of an MFC.

3.4 Conclusions

Composition of plant-growth medium has influence on electricity production in a Plant-Microbial Fuel Cell. Use of P-buffer has a negative effect on plant-growth. Current density can be increased with 250% and power density can be increased with over 400% by replacing nitrate for ammonium-bicarbonate in the plant-growth medium. Removing sulphate from the plant-growth medium has no positive effect on current and power density. Changes in plant-growth medium offer new opportunities for engineering current and power output of the Plant-Microbial Fuel Cell by influencing the mixed potential in the anode, coulombic efficiency of the Microbial Fuel Cell and rhizodeposition from plants.

3.5 Acknowledgements

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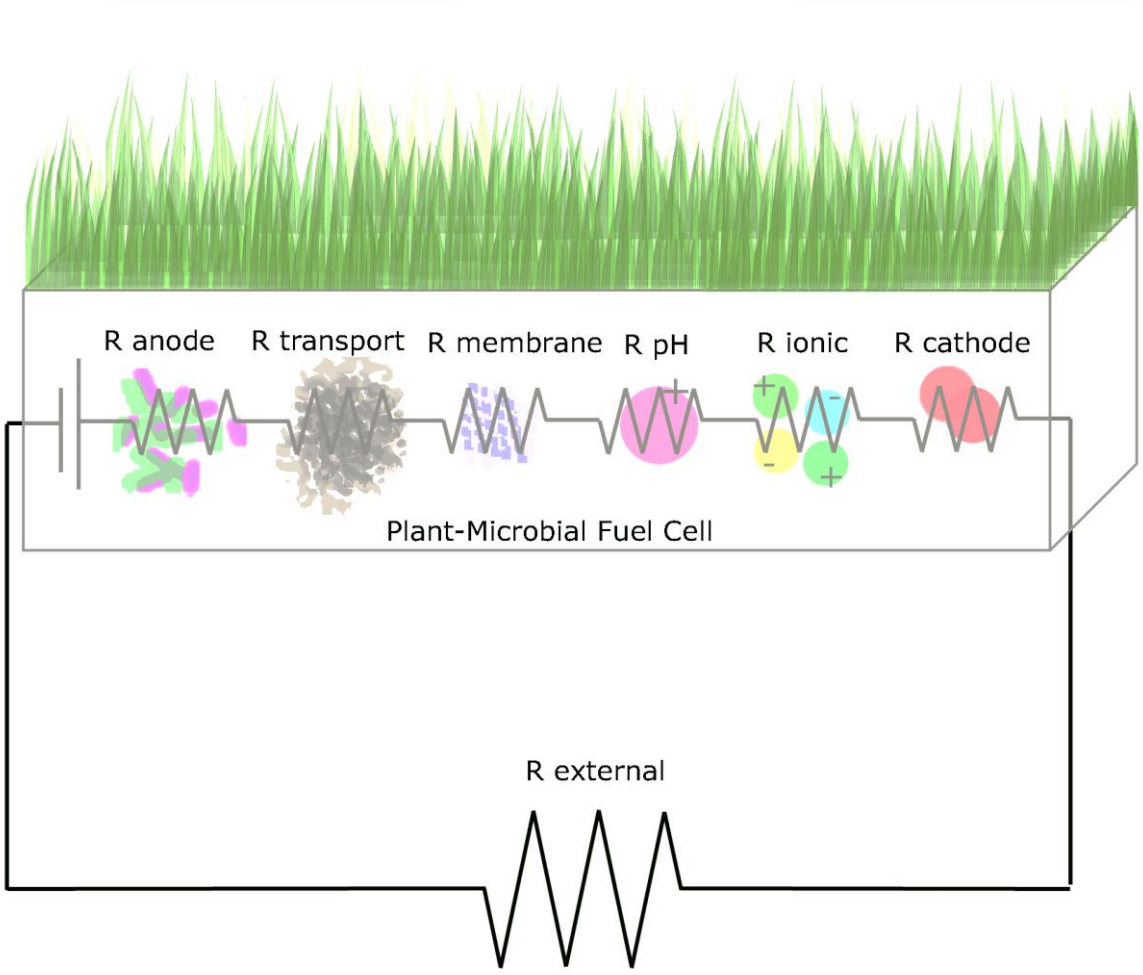
R anode
R transport
R membrane
R pH
R ionic
R cathode
Plant-Microbial Fuel Cell
R external

4 THE FLAT-PLATE PLANT-MICROBIAL FUEL CELL: THE EFFECT OF A NEW DESIGN ON INTERNAL RESISTANCES

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Abstract

Due to a growing world population and increasing welfare, energy demand worldwide is increasing. To meet the increasing energy demand in a sustainable way, new technologies are needed. The Plant-Microbial Fuel Cell (P-MFC) is a technology that could produce sustainable bio-electricity and help meeting the increasing energy demand. Power output of the P-MFC, however, needs to be increased to make it attractive as a renewable and sustainable energy source. To increase power output of the P-MFC internal resistances need to be reduced. With a flat-plate P-MFC design we tried to minimize internal resistances compared to the previously used tubular P-MFC design. With the flat-plate design current and power density per geometric planting area were increased (from 0.15 A/m^2 to 1.6 A/m^2 and from 0.22 W/m^2 to and 0.44 W/m^2) as were current and power output per volume (from 7.5 A/m^3 to 122 A/m^3 and from 1.3 W/m^3 to and 5.8 W/m^3). Internal resistances times volume were decreased, even though internal resistances times membrane surface area were not. Since the membrane in the flat-plate design is placed vertically, membrane surface area per geometric planting area is increased, which allows for lower internal resistances times volume while not decreasing internal resistances times membrane surface area. Anode was split into three different sections on different depths of the system, allowing calculating internal resistances on different depths. Most electricity was produced where internal resistances were lowest and where most roots were present; in the top section of the system. By measuring electricity production on different depths in the system, electricity production could be linked to root growth. This link offers opportunities for material-reduction in new designs. Concurrent reduction in material use and increase in power output brings the P-MFC a step closer to usable energy density and economic feasibility.

4.1 Introduction

With a growing world population and increasing welfare, energy demand worldwide is increasing (1). Currently used fossil fuels are unevenly distributed over the world, are being depleted, and are unsustainable (2, 3). Sustainable alternative energy sources that are available nowadays all have their drawbacks. They are weather dependent (wind, solar power), compete with food/feed production (some biofuels) (3, 4) or involve high investment costs (5). The Plant-Microbial Fuel Cell (P-MFC) is a technology that can potentially be used weather-independent, at any place in the world where plants can grow, without competition with food or feed production, and with relatively low investment costs (6-11). The technology is still in its infancy, however, and large improvements should be achieved to make this technology energetically and economically feasible. One of the main challenges with current state of technology is its power output. Even though theoretical power output is estimated at 3.2 W/m^2 geometric planting area (10), maximum power output has been improved only from 65 mW/m^2 in 2008 (12) to 220 mW/m^2 in 2010 (9) in systems with plants as sole organic matter source. Current biomass-electricity systems, like anaerobic digestion, produce the same amount of electricity per geometric planting area as the maximum that was achieved in P-MFCs, 220 mW/m^2 (10). So even at current power output, the P-MFC could compete with anaerobic digestion based on electricity production per geometric planting area. But maximum power outputs of the P-MFCs have been achieved in short term tests like polarization curves and were not sustained for longer periods of time. Over longer periods of time, average power output is limited to maximally 50 mW/m^2 geometric planting area (11). In some experiments a decrease in power output during runtime of an experiment was observed, due to an increase of membrane resistance and build-up of ion-transport resistances (11). In one recent publication, however, it is shown that average power output increases with runtime of the experiment. This latter experiment was done with a flat-plate P-MFC (13).

Power density of a P-MFC is determined by several aspects of the system: solar radiation, photosynthetic efficiency of the plant, organic matter allocation from plant to soil, and efficiency of the Microbial Fuel Cell (MFC) (10). Timmers et al. identified that the P-MFC has a high internal resistance, which limits the power density (14). In order to increase the power density, internal resistance should be decreased. When calculating the power density as a function of the internal resistance,

$$P = V_{\max} \times i - \left(i^2 \times R_i\right)$$

Equation 4.1: Power density (P) as function of maximum voltage (V_{max}=1.1 V), current density (i, A/m^2) and internal resistance (R_i, Ωm^2) in a P-MFC (15, 16). Derivation of equation can be found in supporting information.

it shows that current and power densities are very dependent on internal resistance of the system. From Equation 4.1 it can be calculated that the internal resistance needs to be

reduced to 0.094 Ω m^2 membrane surface area to be able to reach the theoretical power output of 3.2 W/m^2 membrane surface area (Figure 4.1).

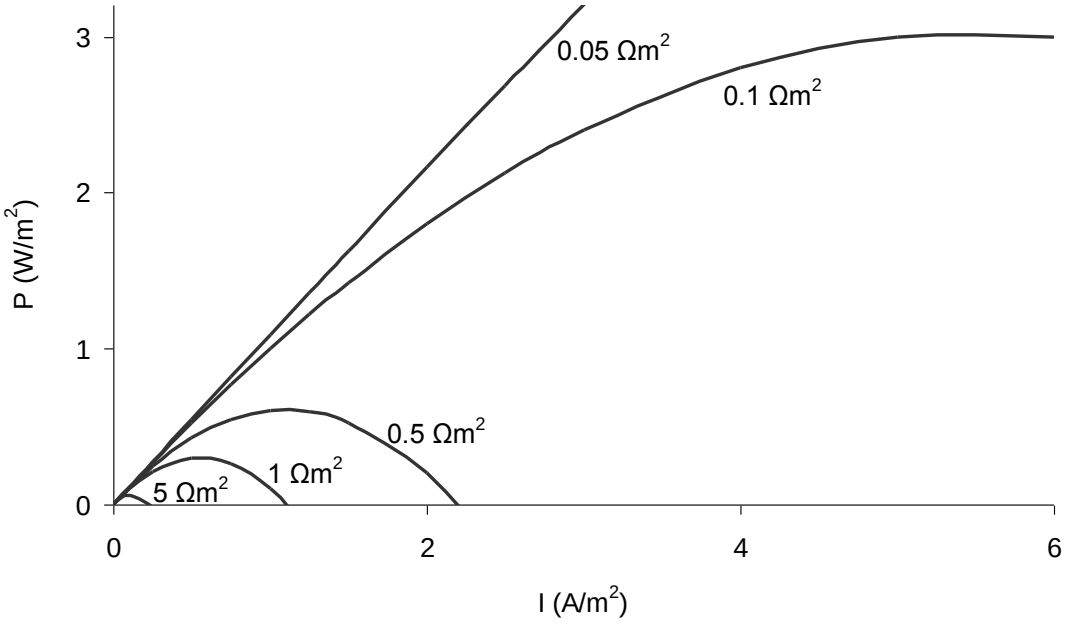

Figure 4.1: Power density as a function of current density at different internal resistances, which shows that internal resistance should be <0.094 Ωm² to achieve a power density of 3.2 W/m²

One of the factors influencing internal resistance is the average distance between anode and cathode. The design that was used by Strik et al.(12), Timmers et al. (11) and Helder et al. (9) is a tubular design. In this design anode is tubular shaped with a membrane at the bottom of the tube. Cathode is situated underneath the anode (Figure 4.2a). When electrons are homogeneously produced in the anode-compartment, average transport distance for a proton to travel from anode through the membrane to the cathode is relatively long. A long distance from anode to cathode leads to transport losses in the anode. Research by Timmers et al. (11) has shown that internal resistance of the P-MFC, especially transport resistance, is an important limiting factor in the power output of the system. In the flat-plate P-MFC (Figure 4.2b) anode and cathode are placed next to each other with a membrane vertically in between. This way distance from anode through cathode is smaller and transport resistance will be limited.

The flat-plate system has been described before, but internal resistances of this design were not characterized. In this paper we describe the different partial internal resistances in the flat-plate P-MFC after 320 days runtime of the experiment. Internal resistances were determined at different rooting depths in the P-MFC. To enable this, three separate anodes were used in the system, which were not electronically connected.

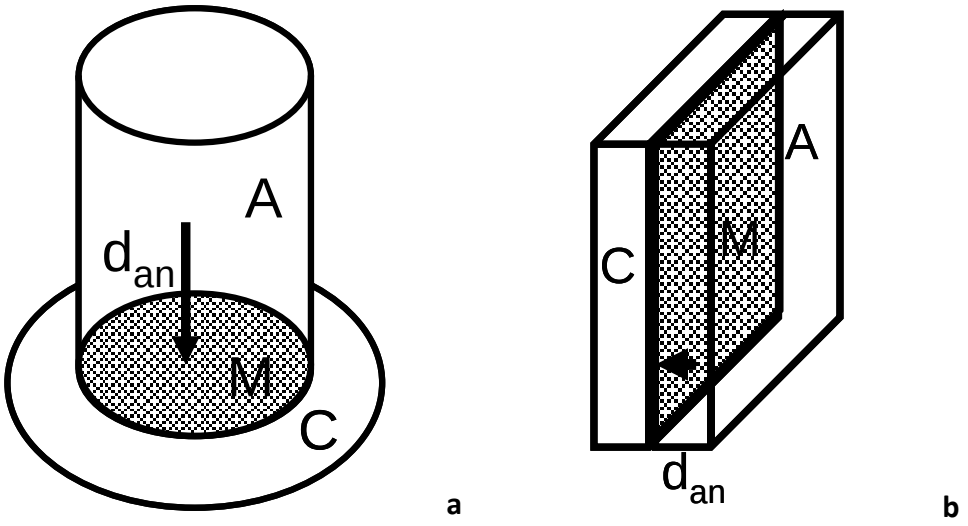

Figure 4.2: Tubular (2a) and flat-plate (2b) design of a Plant Microbial Fuel Cell, in which A=anode, C=cathode, M=membrane, d_{an}= average distance between anode and membrane. Distance between anode and membrane is shorter in flat-plate design than in tubular design.

4.2 Materials and methods

4.2.1 Set-up and operation

Two flat-plate P-MFCs were run for 703 days. The anode compartment had a total volume of 648 ml (18x18x2 cm). The anode consisted of three sections of graphite felt of 5 cm height (Grade WDF, 6 mm, National Specialty Products Carbon and Graphite Felt, Taiwan), which were physically separated (Figure 4.3a) A gold wire was woven through the graphite felt of each section to serve as current collector. Three plants of *Spartina anglica* (grown in a greenhouse from offshoot of Timmers et al. (2010)) were planted in each P-MFC. The anode compartment was separated from the cathode compartment by a cation exchange membrane (CEM) (Fumatec, Frankfurt, Germany).

The cathode consisted of three sections of graphite felt of 5 cm height, (Grade WDF, 2.8 mm, National Specialty Products Carbon and Graphite Felt, Taiwan), each corresponding with an anode section (Figure 4.3b). The cathode compartment consisted of two flow-through modules with the graphite felt in between. A gold wire was woven through the graphite felt of each section to serve as current collector. From day 70 ferric cyanide ($K_3Fe(CN)_6$, 50 mM) was used as catholyte to stabilize cathode-potential and be able to study anode-potential. Ferric cyanide was replenished whenever cathode-potential dropped below +200 mV (against Ag/AgCl reference electrode).

From day 1 through day 116 top, middle and bottom sections of the anode were electronically connected, thus behaving as one anode. During this period external load between anode and cathode was 300 Ω. From day 117 anode-sections were electronically

disconnected. The three anode-sections all were connected to their corresponding cathode over an external load of 900 Ω.

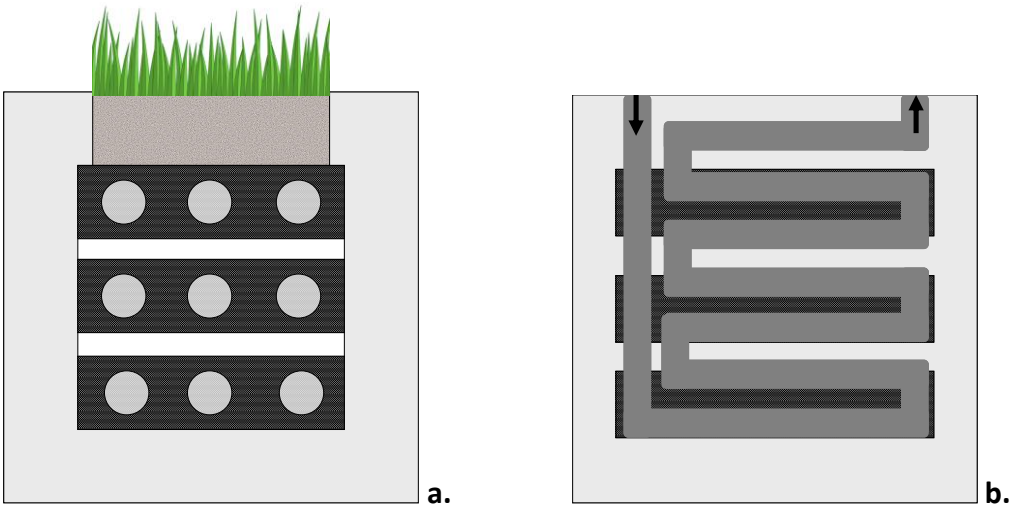

Figure 4.3: Anode (3a) and cathode (3b) schematic overview of a flat-plate Plant Microbial Fuel Cell. In anode and cathode top, middle and bottom sections are shown; in anode sample-points are shown; and in cathode the flow-through channel is shown.

Table 4.1: Concentrations of macronutrients, micronutrients, and added salts in demineralized water as composition of the plant-growth medium

	Concentration
Macronutrients	mg/L
NH_4HCO_3	553.5
$CaCl_2$	222
$NH_4H_2PO_4$	115.1
$MgSO_4.7H_2O$	123.245
$Na_2SiO_3.9H_2O$	142.1
KCl	223.68
Micronutrients	mg/L
KCl	1.864
H_3BO_3	0.773
$MnSO_4.H_2O$	0.169
$ZnSO_4.7H_2O$	0.288
$CuSO_4.5H_2O$	0.062
H_2MoO_4 (85% MoO_3)	0.04
$CoCl_2.6H_2O$	1
Na_2SeO_3	0.05
$C_{14}H_{18}N_3O_{10}FeHNa$	5
$NiSO_4.6H_2O$	0.03
Salt	g/L
NaCl	10

Different plant-growth media were used during the runtime of the experiment, as described in Helder et al. 2011 for P-MFC 3 and 4 (13). At determination of the internal resistances at day 320 a nitrate-less, ammonium-rich medium was used with composition as in Table 4.1.

Anode and cathode potential were measured with Ag/AgCl-reference electrodes (3 M KCl, + 205 mV versus SHE, ProSense Qis). Data was logged every 60 seconds with Fieldpoint (Module S, National Instruments) and collected with Labview (National Instruments Software). To test maximum power density polarization curves were made simultaneously for each section. These were made by disconnecting anode and cathode for 30 minutes to reach open cell voltage (OCV) and subsequently connecting anode and cathode over an external load of 900, 500, 250, 100, 10, 100, 250, 500 and 900 Ω, for 10 minutes each. At day 320 anode was sampled at 9 sample-points, which were evenly distributed over the three anode-sections, so three sample-points in each anode-section. Samples of 1 ml each were measured for conductivity (ProLine Plus Qis, ProSense BV, Oosterhout, The Netherlands) and pH (691 pH-meter, Metrohm, Herisau, Switzerland).

The set-ups were placed in a climate chamber (Microclima 1750 Snijders) with an average light intensity of 596 ± 161 µmole $m^{-2}s^{-1}$, measured at the top of the set-ups with a light intensity meter (Photodyne 44XLA). The climate chamber was controlled at 25˚C with 75% humidity and a day-night regime of 14:10 hours was used.

After 703 days the set-ups were taken apart and root-weight was measured for the three anode-sections per P-MFC.

4.2.2 Calculations

Internal resistance of the P-MFC can be split in several partial internal resistances as in (17):

$$R_{int} = R_{an} + R_{cat} + R_T$$

Equation 4.2: Internal resistance in a P-MFC (Ω.m²), in which R_{an} = anodic resistance (Ω.m²), R_{cat} = cathodic resistance (Ω.m²), R_T = transport resistance (Ω.m²).

Anodic resistance can be calculated from the over-potential of the anode according to(14):

$$R_{an} = \frac{(E_{an} - E_{an}^0)}{i}$$

Equation 4.3: Anodic resistance in a P-MFC (Ω.m²), in which E_{an}^0 = theoretical anode potential (V), E_{an} = measured anode potential at a certain external resistance (V), i = current density (A/m²).

Since the theoretical anode potential in the P-MFC is based on a mixed potential (18) and concentrations of different exudates are unknown, it is assumed that theoretical anode potential equals open cell potential ($E_{an,OCP}$).

Cathodic resistance can be calculated from the cathode over-potential according to(14):

$$R_{cat} = \frac{(E^0_{cat} - E_{cat})}{i}$$

Equation 4.4: Cathodic resistance in a P-MFC ($\Omega.m^2$), in which E^0_{cat} = theoretical cathode potential at 50 mM ferric cyanide solution (V), E_{cat} = measured cathode potential at a certain external resistance (V), i = current density (A/m^2).

Transport losses of the system were calculated as in Timmers et al. (2010)(11) and can be calculated as(11, 17):

$$E_T = E_{mem} - E_{\Delta pH} - E_{ionic}$$

Equation 4.5: Transport loss in a P-MFC (V), in which; E_{mem} = measured potential over the membrane (V), $E_{\Delta pH}$ = pH gradient loss (V), E_{ionic} = ionic loss (V).

When dividing this equation by current, transport resistance can be calculated. The potential over the membrane is measured as the difference between the reference electrode in the anode and the reference electrode in the cathode. The pH resistance is calculated as (11):

$$R_{\Delta pH} = \frac{\left(\frac{RT}{F}\ln(10^{(pH_{cath} - pH_{an})})\right)}{i}$$

Equation 4.6: pH resistance in an MFC, in which pH_{cath} = cathode pH, pH_{an} = anode pH, and i = current density per membrane area.

Equation for pH resistance is derived from the Nernst equation:

$$E_{OCP,an} = E^0_{an} - \frac{RT}{nF}\ln\frac{\left[CH_3COO^-\right]}{\left[H^+\right]^9\left[HCO_3^-\right]^2}$$

Equation 4.7: Nernst-equation, in which E^0_{an} is the standard potential (V), R is the universal gas constant (8.314 J mol-1 K-1), T is the temperature (K), n is the number of electrons involved in the reaction (-), F is Faraday's constant (96485 C mol-1), $\left[CH_3COO^-\right]$ is the acetate activity (mol L-1), $\left[H^+\right]$ is the proton activity (mol L-1), and $\left[HCO_3^-\right]$ is the bicarbonate activity (mol L-1).

This equation shows that one pH-unit difference will lead to a change in anode potential of 59 mV.

Ionic resistance is calculated as (11, 17):

$$R_{ionic} = \left(\frac{d_{an}}{\sigma_{an}}\right)$$

Equation 4.8: Ionic resistance in the anode of an MFC, in which d_{an}= average distance between point of proton production and membrane, and σ_{an}=conductivity of anolyte.

Power densities are expressed per geometric planting area because it gives insight in the possibility to use this technology for large scale electricity production.

4.3 Results and discussion

The plants in both P-MFCs kept growing throughout the experiment, allowing us to acquire data during 350 days on the performance of the P-MFCs with growing plants. During the experiment top anode of the P-MFC produced most electricity, the middle part less and the bottom part the least (Figure 4.4). This was consistent with the root-growth. Most roots were found in the top anode (43.8 and 15.1 g in P-MFC 1 and 2), less in the middle anode (1.0 and 3.2 g) and least in the bottom anode (<0.1 and 0.1 g). Electricity production seems linked to root growth, the more roots present in the anode, the more electricity is produced. This is consistent with the idea that the organic matter used for electricity production originates from the roots.

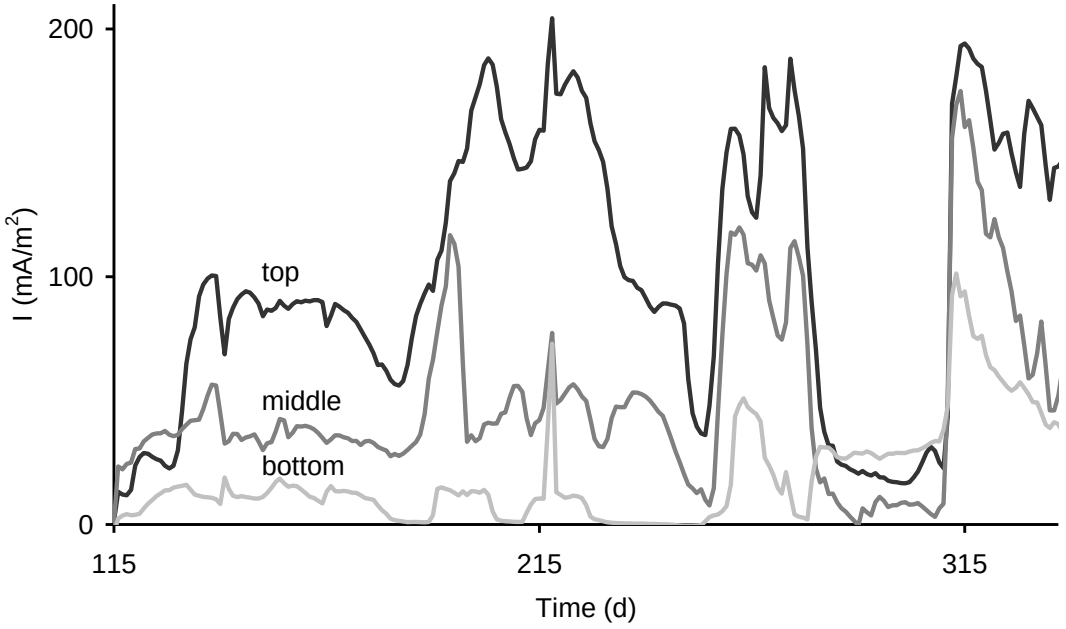

Figure 4.4: Electricity production (mA/m²) in top, middle and bottom sections of P-MFC 1 during day 115 through 337 in which top section produces most electricity. Fluctuations in power output over time are caused by changes in medium composition as described in Helder et al. 2011 [13].

4.3.1 Anodic resistance is the highest partial internal resistance in flat-plate P-MFC

Partial and total internal resistances were calculated for the three different levels in two P-MFCs (top, middle, bottom) on day 320 of the experiment (Figure 4.5). In both P-MFCs at all levels and both at low and high current density anodic resistance added substantially to the total internal resistance (Figure 4.5). It should be noted that we used ferric-cyanide as final electron acceptor in the cathode, thus cathode over-potential would not show in our calculations. Overpotential at the anode is the amount of energy that is lost in the oxidation

of organic matter and includes activation energy, microbial energy for maintenance and growth, ohmic losses and concentration losses (16, 19). Concentration losses are determined by the substrate availability at the anode-surface and accumulation of products at the anode-surface (16, 19). Substrate availability is determined by the substrate-input and its mass transfer. Substrate-input in the P-MFC is determined by root exudation and dead root turnover (10). It can therefore be expected that highest substrate-availability is where most roots are. Highest anodic resistance would therefore be expected where least roots are present.

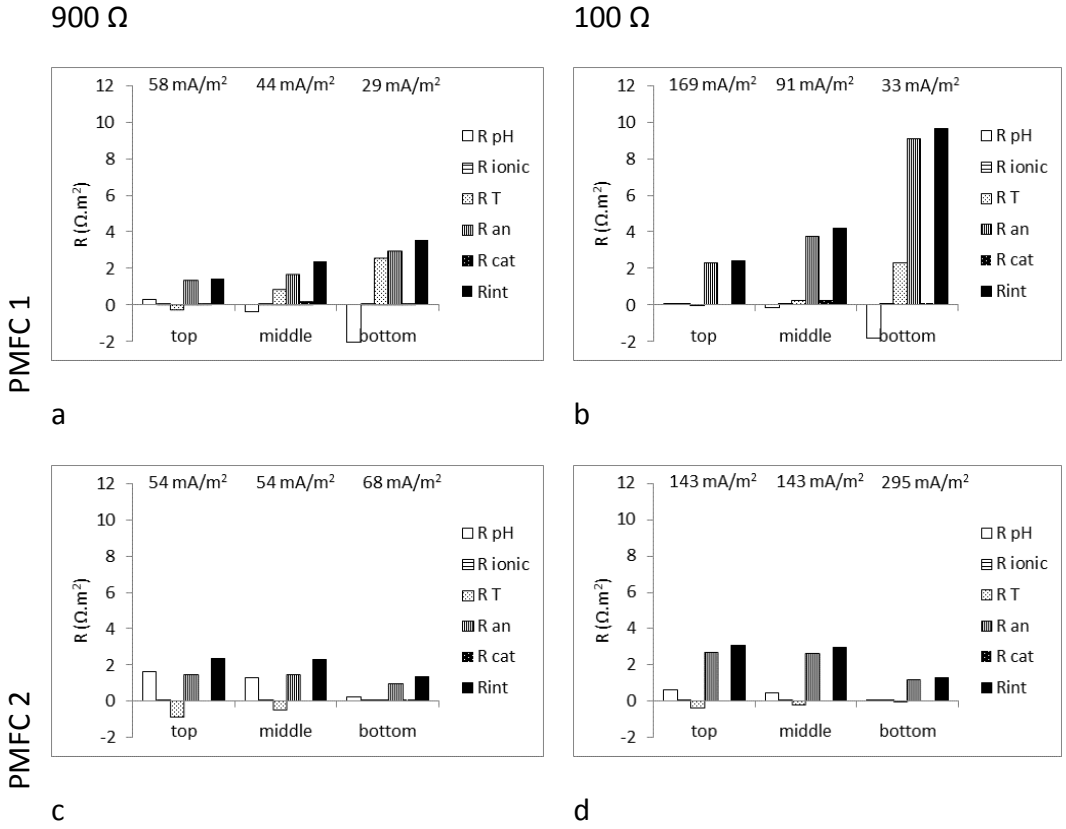

Figure 4.5: Partial and total internal resistances (Ω.m² membrane surface area) at three different depths (top, middle, bottom) in two P-MFCs on day 320 of experiment at 900 Ω and 100 Ω external resistance.

In case of P-MFC 1 this was true; most roots were found in the top part of the system, less in the middle part and least in the bottom part. Anodic resistance of the bottom part of P-MFC 1 (Figure 4.5a,b) increases with a lower external resistance, while current density does not increase for this level. This is likely due to the fact that hardly any roots were present (<0.1 g) and so substrate was not available to increase current density. If current density cannot be increased, but external resistance allows more current to flow, overpotential will increase. The same occurred in the middle part of P-MFC 1, albeit to a lesser extent, and even in the top part of P-MFC 1, where most roots were found, anode-resistance increased with a lower external resistance, indicating possible substrate-limitation.

P-MFC 2 shows a different pattern (Figure 4.5c,d). Top and middle parts of P-MFC 2 have shown for the largest part of the runtime of the experiment the same voltage and anode and cathode potentials. Likely an electrical connection between top and middle anode of P-MFC 2 existed, so that these two anodes have actually functioned as one. Top and middle level of P-MFC 2 show therefore the same partial and total internal resistance, even though more roots were present in the top part of P-MFC 2 than in the middle part of P-MFC 2. Since electrons could flow freely between the two anodes, substrate limitation at one of them will not directly lead to a higher anode resistance as long as at the other anode substrate is still available. Opposite to the situation in P-MFC 1, the bottom part of P-MFC 2 shows highest current and lowest internal resistance of the three levels in P-MFC 2. Like in P-MFC 1, the bottom part of P-MFC 2 hardly contained any roots. The bottom part of P-MFC 2, however, did contain at least one root-tip. Literature describes that so-called hotspots can occur in the rhizosphere (20, 21). A hotspot is a place in the root zone where microbial activity and exudation are enhanced compared to the rest of the rhizosphere (20). Intensity of turnover processes in these hotspots is at least one order of magnitude higher than in the bulk-soil (20). Even so, hotspots will likely have occurred in the top and middle anode as well. More research should be done to further explore the hotspot hypothesis and exclude artifacts.

The high anode resistance in our experiment is in contrast with earlier research with the tubular system, which showed a high membrane resistance, which was mainly caused by the transport resistance (11, 14) . In our experiment, however, membrane resistance stayed low during polarization (Figure 4.6), thus transport resistance did not increase. Experimental conditions of Timmers et al. differed on three important aspects from our experiment: 1) design, 2) plant-growth medium and 3) time-steps in the polarization curve.

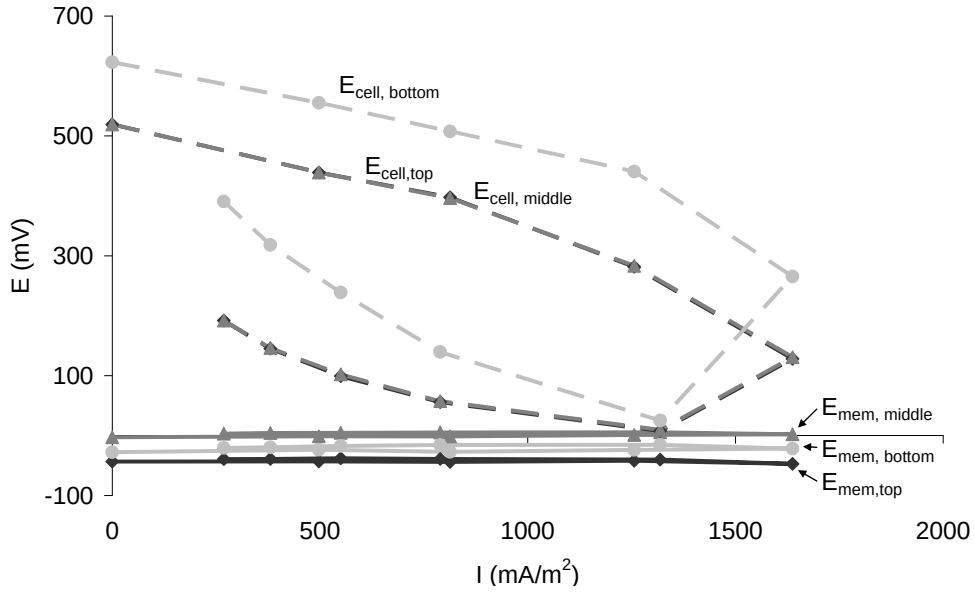

Figure 4.6: Membrane voltages (Emem) and cell voltages (Ecell) as a function of current density in top, middle and bottom sections of P-MFC 2 during polarization curve on day 320, in which membrane voltages stay low with increasing current, indicating a small membrane resistance.

4.3.2 Influence of design on internal resistance

It is likely that the design of the system (tubular versus flat-plate) has a large influence on the internal resistance. In our experiment plant-roots were mainly found in the top part of the system, which was consistent with previous experiments (9, 11, 12, 14). This means that in the tubular system the average distance for protons produced in the anode (or other cations like K^+ or Na^+) to travel to the cathode is larger than in the flat-plate system (Figure 4.2). A larger distance will lead to a higher ionic resistance (Equation 4.8) and with that to a higher membrane resistance. It was shown in previous research by Timmers et al. (11, 14) that membrane resistance was high and increased during polarization curves, which was not the case with the flat-plate system (Figure 4.6).

Internal resistance in the flat-plate P-MFC was, however, not lower than in the tubular P-MFC (Table 4.2). Current density was not higher in the flat-plate system P-MFC compared to the tubular P-MFC when normalized to membrane surface area (Table 4.2). The flat-plate design has, however, advantages over the tubular design. When calculating current and power per m^3 it shows that Timmers et al. produced 7.5 A/m^3 and 1.3 W/m^3 whereas we produced 122 A/m^3 and 5.8 W/m^3. Firstly, this leads to the conclusion that materials are more efficiently used in the flat-plate system than in the tubular system, leading to higher outputs on volume base. Secondly, when normalizing current and power density to geographic planting area 1.6 A/m^2 and 0.44 W/m^2 were achieved, which is higher than reported for a tubular P-MFC (0.15 A/m^2 and 0.22 W/m^2 (9, 11)) in a polarization curve with 10 minute time-steps. So with less material the flat-plate P-MFC harvests more electrons per plant than the tubular P-MFC and is therefore an important step towards optimizing the P-MFC.

4.3.3 Influence of difference in plant-growth medium on internal resistance

In the tubular system a large transport resistance was found, whereas transport resistance in the flat-plate system is low. It should be noted though, that the plant-growth medium can influence transport resistance as well. Conductivity was 0.15-0.17 $S.m^{-1}$ in the experiment of Timmers et al. and 1.1-1.3 $S.m^{-1}$ in our experiment. Higher conductivity in our experiment will lead to a lower ionic resistance compared to Timmers et al. This would mean, however, that according to Equation 4.5 transport resistance could be expected to be higher than in the case of Timmers et al. The use of buffer in the experiment of Timmers et al. and the lack of it in our experiment can have an influence on the pH-gradient over the membrane. It is shown in Figure 4.5 that pH-resistance in our case can be positive or negative, meaning the pH-gradient from cathode to anode can be either positive or negative (Equation 4.6). When cathode-pH is higher than anode-pH, pH-gradient is positive, protons produced in the anode will have to migrate from anode to cathode. Protons migrate from a low pH to a high pH, so transport is driven by pH-difference. A pH-resistance is present, however, due to the change in electromotive force (EMF), as described by the Nernst equation (Equation 4.7). When the gradient is negative, however, protons will migrate from cathode to anode and the resistance is reversed to a driving force to produce protons. Based on Equation 4.5, a

positive pH-resistance will reduce the transport resistance, but a negative pH-resistance will increase the transport resistance, which happens in the middle and bottom level of P-MFC 1 (Figure 4.5). Compared to the experiment of Timmers et al. transport resistance is lower in our experiment in all cases except bottom part of P-MFC 1. Thus, even though the difference in plant-growth medium between the experiments of Timmers et al. and ours could influence the internal resistance, it doesn't seem to explain the reduction of transport resistance in the flat-plate system compared to the tubular system.

Table 4.2: Total internal resistances in Ω.m2 membrane and Ω.m3 reactor volume of P-MFC 1 and 2 (flat-plate) and P-MFC (tubular) of Timmers et al. 2012 [14]. Numbers of Timmers et al. were estimated from figures.

	Time-step polarization curve (min)	Current density (mA/m^2)	Total internal resistance (Ωm^2)	Total internal resistance (Ωm^3)
P-MFC 1 top	10	58	1.4	0.03
P-MFC 1 top	10	169	2.4	0.05
P-MFC 2 top	10	54	2.4	0.05
P-MFC 2 top	10	143	3.1	0.06
P-MFC 1 middle	10	44	2.4	0.05
P-MFC 1 middle	10	91	4.2	0.08
P-MFC 2 middle	10	54	2.3	0.05
P-MFC 2 middle	10	143	3.0	0.06
P-MFC 1 bottom	10	29	3.5	0.07
P-MFC 1 bottom	10	33	9.7	0.19
P-MFC 2 bottom	10	68	1.4	0.03
P-MFC 2 bottom	10	295	1.3	0.03
Timmers et al. tubular	5	70	0.8	0.24
Timmers et al. tubular	5	1800	0.2	0.06
Timmers et al. Tubular	60	200	0.3	0.09
Timmers et al. Tubular	60	900	0.6	0.17

4.3.4 Influence of time-steps used in polarization curve on internal resistance

Timmers et al. have shown that the time-steps used to make a polarization curve have a large influence on the internal resistance (14). The longer the time-steps, the higher the internal resistance, due to an increasing anode resistance caused by proton build-up and an increasing membrane resistance caused by accumulation of cations in the anode (14). In order to properly compare our results with those of Timmers et al. and understand the mechanisms, it is therefore important to realize that time-steps in the experiment of Timmers et al. (2011) were 5 or 60 minutes (14). In Timmers et al. (2010) time-steps of polarization are not reported (11). In our experiment time-steps of 10 minutes were used. Compared to the 5 minute time-step results of Timmers et al., a higher internal resistance could be expected in the flat-plate system, but compared to the 60 minute time-step results,

our internal resistance was expected to be lower. Total internal resistance in the flat-plate P-MFC was higher than in the tubular system when normalized to membrane surface area, which cannot be explained from the difference in time-steps (Table 4.2). When we look to internal resistance when normalized to MFC-volume, however, the picture is different and the flat-plate P-MFC does indeed show a lower internal resistance than the tubular P-MFC in all cases except bottom anode of P-MFC 2 at low external resistance.

Table 4.3: Expected and measured power densities (P, W/m^2), based on calculated internal resistances (Ri, Ωm^2) and measured current densities (A/m^2)

R_i (Ωm^2)	i (A/m^2)	Expected P (W/m^2)	Measured P (W/m^2)	Δ P (W/m^2)
1.283	0.295	0.213	0.244	0.032
1.380	0.069	0.069	0.013	-0.056
1.444	0.058	0.059	0.010	-0.050
2.302	0.054	0.053	0.008	-0.045
2.354	0.054	0.053	0.008	-0.044
2.396	0.169	0.118	0.081	-0.037
2.404	0.044	0.043	0.005	-0.038
2.982	0.145	0.097	0.059	-0.038
3.060	0.142	0.095	0.057	-0.038
3.542	0.029	0.029	0.002	-0.027
4.169	0.091	0.066	0.023	-0.042
9.668	0.033	0.026	0.003	-0.023

4.3.5 Internal resistance in relation to power output of the flat-plate P-MFC

When comparing the obtained power and current densities of the flat-plate P-MFCs with the expected results based on Equation 4.1, it shows that only in a few cases measured value approximates theoretical value (Table 4.3). This has several reasons. Figure 4.1 was drawn based on theoretical potentials of anode and cathode and a total theoretical cell voltage of 1.1 V (22). This can only be obtained, however, when using oxygen as final electron acceptor in the cathode, whereas we used ferric-cyanide, which has a lower theoretical potential than oxygen. Even so, use of oxygen would not directly lead to higher power outputs, since oxygen-use in the cathode usually leads to high cathode over-potentials due to limited diffusion of oxygen into the electrode and thus oxygen-limitation at the electrode surface. On the anode-side the theoretical potential is probably being overestimated when assuming that it is -0.5 V (vs. Ag/AgCl), which is the theoretical potential of acetate oxidation under MFC-conditions (19). Since substrate in the P-MFC originates from the plant, it is a complex mixture of several different organic compounds with different theoretical potentials (10). Moreover, oxygen is being transported into the anode by the plant-roots, limiting the number of electrons available for electricity production, and, at low substrate concentrations leading to a mixed anode potential. This mixed anode potential will be higher than the assumed -0.5 V. Furthermore, the polarization curve shows that the internal resistance of the system is not linear. The theoretical internal resistance and resulting

current and power output based on Equation 4.1 is only valid when internal resistance of the system is linear (18). It is therefore not surprising that measured current and power densities don't match with the theoretical values.

4.4 Conclusions

The flat-plate P-MFC design resulted in a lower transport and membrane resistance than the previously used tubular P-MFC. It did, however, not result in a lower total internal resistance normalized to membrane surface area. Total internal resistance of the flat-plate P-MFC is at best comparable to total internal resistance of the tubular P-MFC, only differently distributed over several partial internal resistances. In the flat-plate P-MFC the anodic resistance is highest, when using a chemical cathode, due to substrate limitation or mass transfer limitation. To overcome the problem of substrate limitation, the plant should exudate more, exudates should be converted into electricity more efficiently or other rhizodeposits, like dead root material should be used. Possibly, when rhizosphere is fully mature, more dead root material is available, which will probably lead to higher substrate availability in the P-MFC. Higher exudation rates might be achieved by adapting the plant-growth medium to stimulate exudation (23). For future research it would be interesting to further reduce anode height, since the middle and bottom level anodes generally generated less electricity (Figure 4.4) than the top one and most roots were found in the top anode.

4.5 Acknowledgements

We would like to thank Ruud Timmers for his input on the flat-plate design and help with the practical work. We would like to thank the Plantpower consortium for thinking along with us on the design of the flat-plate system and the interpretation of the obtained results. The research leading to these results has received funding from the European Community's Seventh Framework Programme FP7/2007-2013 under grant agreement n° 226532.

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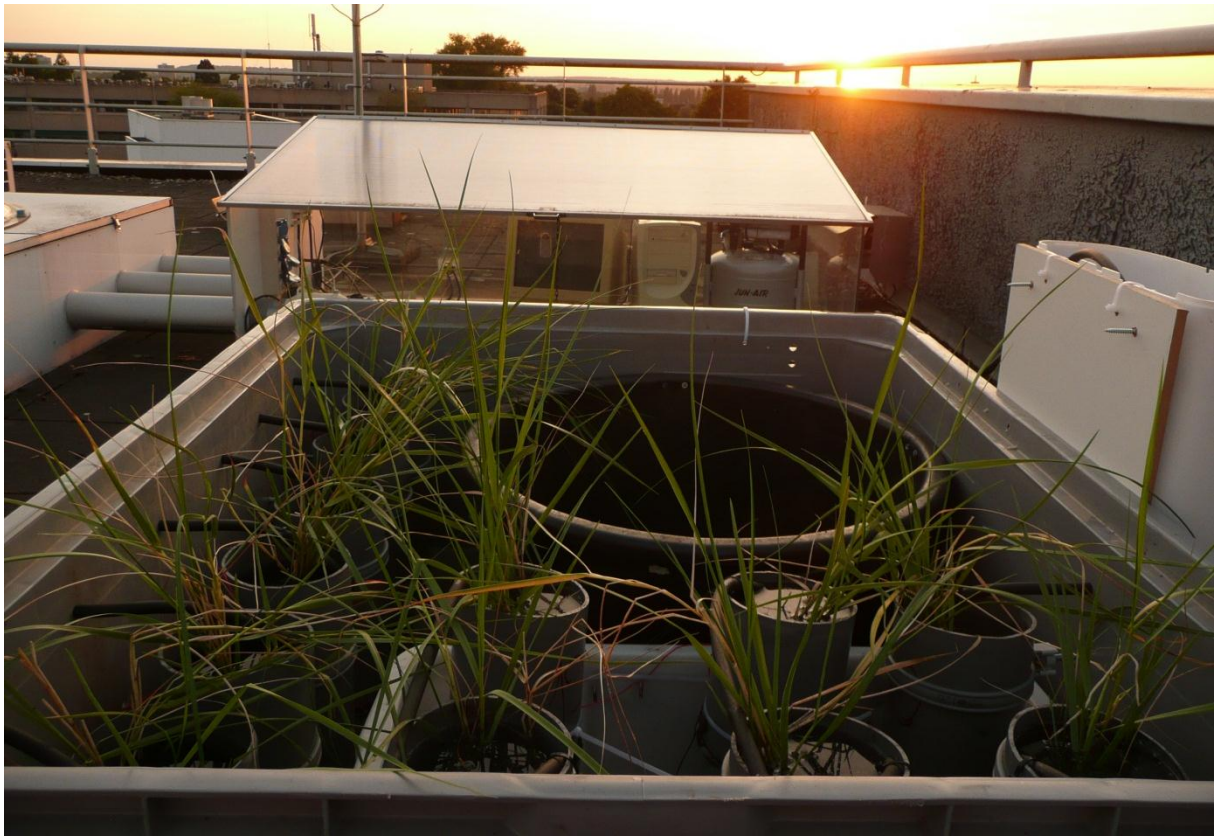

5 RESILIENCE OF ROOF-TOP PLANT-MICROBIAL FUEL CELLS DURING DUTCH WINTER

Chapter accepted as:

Helder, M., Strik, D.P.B.T.B., Timmers, R.A., Raes, S.M.T., Hamelers, H.V.M., Buisman, C.J.N. – *Resilience of roof-top Plant-Microbial Fuel Cells during Dutch winter* – 2012 – Biomass and bioenergy

Abstract

World population and welfare are increasing, leading to an increasing demand for energy, specifically electricity. New alternative energy sources should be found that are sustainable, reliable and stable at all weather conditions. The Plant-Microbial Fuel Cell (P-MFC) is in theory a technology that could produce sustainable electricity continuously. We operated two designs of the P-MFC under natural roof-top conditions in the Netherlands for 221 days, including winter, to test its resilience. Current and power densities are not stable under outdoor conditions. Highest obtained power density was 88 mW/m^2, which is lower than was achieved under lab-conditions (440 mW/m^2). Cathode-potential was in our case dependent on solar radiation, due to algae growth, making the power output dependent on a diurnal cycle. The anode-potential of the P-MFC is influenced by temperature, leading to a decrease in electricity production during low temperature periods and no electricity production during frost periods. Due to freezing of the roots, plants did not survive winter and therefore did not regrow in spring. In order to make a sustainable, stable and weather independent electricity production system of the P-MFC attention should be paid to improving cathode stability and cold insulation of anode and cathode. Only when power output of the Plant-Microbial Fuel Cell can be increased under outdoor conditions and plant-vitality can be sustained over winter, it can be a promising sustainable electricity technology for the future.

5.1 Introduction

World population and welfare are increasing [1], leading to an increasing demand for energy, specifically electricity [2-5]. Fossil fuels are rapidly being depleted and are mainly found in politically unstable areas of the world [4, 5]. These alternatives are renewables. Renewable energy sources are attractive because they can't be depleted, but most renewables have their negative side effects. Reliability, stability and sustainability of several renewable energy sources are not guaranteed. Solar and wind power are dependent on the weather and can therefore not be used continuously [7]. Moreover, sustainability of solar, wind and biomass power has been debated [7-9]. New alternative energy sources should be found that are sustainable and reliable. When alternative energy sources are stable at all weather conditions it would be possible to use them without the need to store the energy, further increasing their sustainability, and usable all over the world, making them available to anyone.

The Plant-Microbial Fuel Cell (P-MFC) is in theory a technology that could produce sustainable electricity continuously [6]. In a P-MFC plants provide organic matter to microbes at their roots in the form of rhizodeposits. Rhizodeposits consist of excretions, secretions, dead plant material and gases [6, 10]. So-called electrochemically active microbes around the plant-roots break down the organic matter and donate their electrons to the anode of a Microbial Fuel Cell, thus producing electricity. The technology is solar powered, via plant photosynthesis, but not dependent on direct sunlight, since organic matter excretion by the plant continues day and night, although a diurnal pattern sometimes can be observed [10]. The P-MFC has been first reported in 2008 [6, 11, 12]. Since then, several experiments with the system have been performed [13] but except from the experiment by Kaku et al. [12] no experiments were performed under natural outside conditions. The experiment of Kaku et al. was performed in a sediment-type system, in which organic matter is present in the sediment as well, apart from the plant [12]. No other experiments with a P-MFC without added organic matter were performed under outdoor conditions. To develop the P-MFC into a sustainable renewable energy technology, the technology should be operable stably under natural conditions, preferably weather independent.

We operated two designs of the P-MFC at natural rooftop conditions in the Netherlands for 221 days, including winter, to test the resilience of the P-MFC under outdoor conditions.

5.2 Materials and methods

Two designs for the P-MFC were placed on a roof-top in Wageningen, the Netherlands (51°97'N, 5°68'E) (Figure 5.1). Of each design six set-ups were built. Design 1 (P-MFC 1-6) consisted of a PVC cylinder (Ø 125 mm, height 300 mm), which functioned as the anode-compartment, filled with 2 l of graphite granules (diameter: 1; Le Carbone, UK). Current collectors were gold-wires attached to a copper wire and were located 2 cm above the

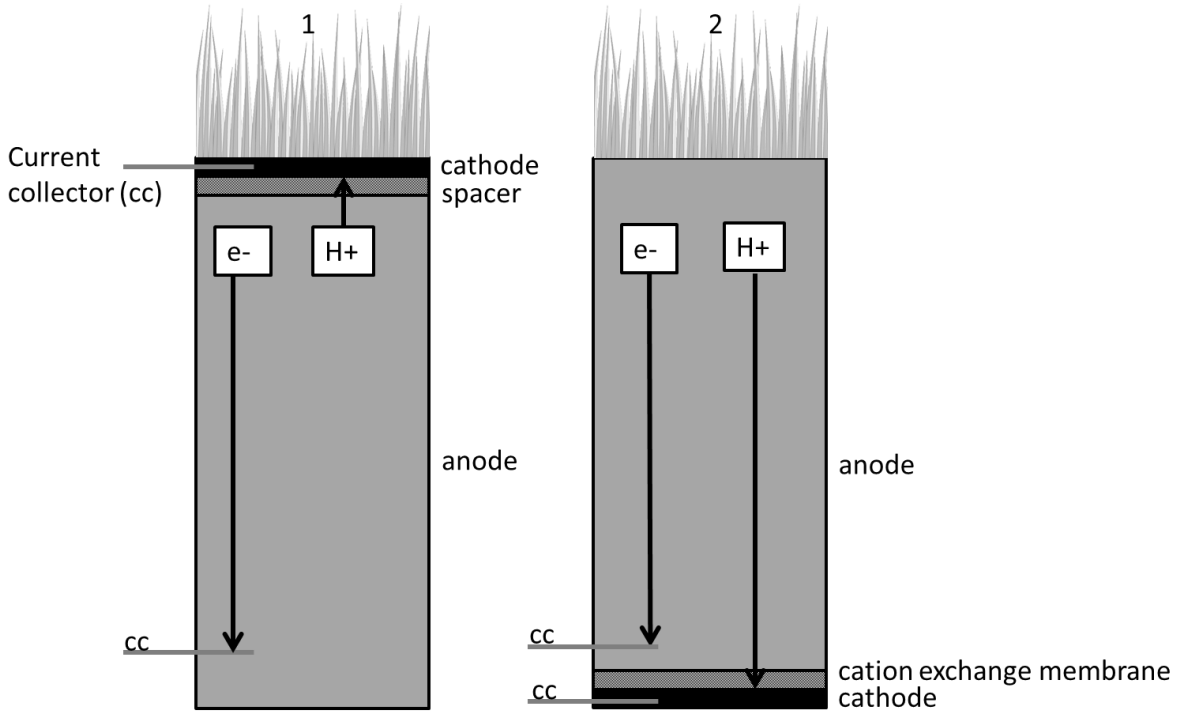

Figure 5.1: Schematic representation of Plant-Microbial Fuel Cells of design 1 (left) and design 2 (right) that were placed on a roof-top in Wageningen, the Netherlands.

bottom of the cylinder. An open plastic matrix was placed on top of the graphite granules to function as a spacer. The cathode-felt (Grade WDF, 6 mm, National Specialty Products Carbon and Graphite Felt, Taiwan) was placed on top of the spacer. Gold-wire with a copper wire attached to it was woven through the felt to function as current collector. Design 2 (P-MFC 7-12) consisted of the same cylinder as design 1 but with a membrane (heterogeneous cation exchange membrane, Zhejiang Qianqiu Group, Zheijang, China) at the bottom. The six cylinders were placed on a cathode that consisted of graphite felt of 17x17 cm. All cathodes were placed in a box that was filled with water. All cathodes were connected to their corresponding anode over an external load of 900Ω. Of P-MFC 1, 2, and 6 the external load was reduced to 500Ω at day 38. Each set-up contained one plant of *Spartina anglica*. Plants were off-shoot of the ones used by Timmers et al. [14]. Plant weight was between 61 and 242 grams and total added stem-length was 189-456 cm (overview of weights and lengths in Table 5.1). The plants were fed with one plant-feed cone each (Pokon voedingskegels, Veenendaal, The Netherlands) at the start of the experiment (composition in Table 5.2).

During the experiment plants were fed with rainwater during rainfall. Once (day 30) plants were manually fed with rainwater to avoid drought in the P-MFCs. At 5 cm under the top, holes were drilled in the cylinder to control water level and keep cathodes of design 1 open to air at all times. The experiment ran for 8 months, from August 2009 through March 2010.

Table 5.1: Plant weight and length of Spartina anglica plants in each P-MFC at the start of the experiment

P-MFC	Plant weight (g)	Plant stem and leaf-length (cm)
1	153	449
2	188	456
3	195	214
4	147	334
5	242	380
6	176	452
7	130	218
8	104	254
9	80	278
10	209	374
11	127	212
12	61	189

Table 5.2: Composition of plant-feed cones used for nutrition of plants at start of the experiment.

	Nutrient	% of total cone	Total weight (mg)
Macronutrients	NO_3	7.7	385
	NH_4	7.1	355
	P_2O_5	10	500
	K_2O	12	600
	MgO	2	100
Micronutrients	B	0.02	1
	Cu	0.05	2.5
	Fe	0.4	20
	Mn	0.06	3
	Mo	0.02	1
	Zn	0.015	0.75

Measurements of cell potential, anode potential and cathode potential were logged every minute with Fieldpoint (Module S, National Instruments) and corresponding LabView measurement software (National Instruments Software). Of all P-MFCs cell potential was measured every minute. Of P-MFC 1, 4, 7, and 10 anode potential and cathode potential were measured against Ag/AgCl reference electrodes (3M KCl, +205mV versus standard hydrogen electrode, ProSense Qis). Plastic tubes with a glass capillary attached to the end filled with 3M KCl were used as an extension of the reference electrode in order to place reference electrodes approximately halfway down the anode-cylinder. Capillaries attached to the cathode reference electrodes were placed on the cathode graphite felt. On day 28 and 60 polarisation curves were made of all P-MFCs. Cell-voltages, anode-potentials, cathode-potentials and membrane-potentials were measured with a multimeter and

Ag/AgCl reference electrodes manually. Polarisation curves were performed with time-steps of 10 minutes by starting at open cell voltage (OCV) subsequently connecting anode and cathode over a decreasing external resistance of 900Ω, 500Ω, 250Ω, 100Ω and 10Ω and then increasing external resistance with the same steps back to OCV.

In P-MFC 1 (design 1) and P-MFC 7 (design 2) anode and cathode temperature were measured with Pt 100 temperature sensors. Outdoor temperature was measured at the same site. When frost set in, freezing of the P-MFCs was observed by eye.

Solar radiation data were obtained from the Haarweg Weather station of Wageningen University, approximately 3 km from the experimental roof [15]. The coordinates of the weather station are 51° 58' NB; 5° 38' OL; which is about 7 metres above the sea level. Radiation of the climate chamber used in indoor experiments [16-18] was converted from mol/m^2/s into W/m^2 via E=hc/λ [19].

5.3 Results and discussion

Several different phenomena were observed during operation of this experiment. The experiment combined several novel influences on a novel and complex system. Moreover, no other experiments have been performed with a P-MFC on a roof before. The following section describes rather than explains the different observed phenomena and discusses possible explanations, where possible supported by literature. More research is needed to fund these explanations in the future.

5.3.1 Direct start-up of electricity production

Directly after build-up of the experiment in August, P-MFCs 1 through 6 started to produce electricity. P-MFCs 7 through 12 started up after 23 days (Figure 5.2) Under lab-conditions start-up times of up to 100 days are reported [14, 17]. There are four possible explanations for the shorter start-up time on the roof. The first explanation is that the plants we started with on the roof-top were taller and heavier than the plants that were used in the lab. Since electricity production is directly related to the amount of roots present in the anode of the P-MFC [20], more roots would lead to higher content of organic material. More organic material would have been available for electricity production from the start in that case, leading to a faster reduction of the anode and consequently a faster build-up of cell voltage. The second explanation is that light intensity in August on a roof is higher than in a climate chamber in a lab (~82W/m^2 in the climate chamber against ~122W/m^2 on the roof), which has caused higher activity of the plant and possibly higher exudation. The third explanation is that variable conditions on the roof, like wind, large temperature differences and changing light intensity, have stressed the plant, which can lead to more exudation [10]. A fourth explanation would be that roots of the plant probably have been damaged by building up the systems, leading to the presence of dead root material from the start of the experiment and thus availability of organic matter.

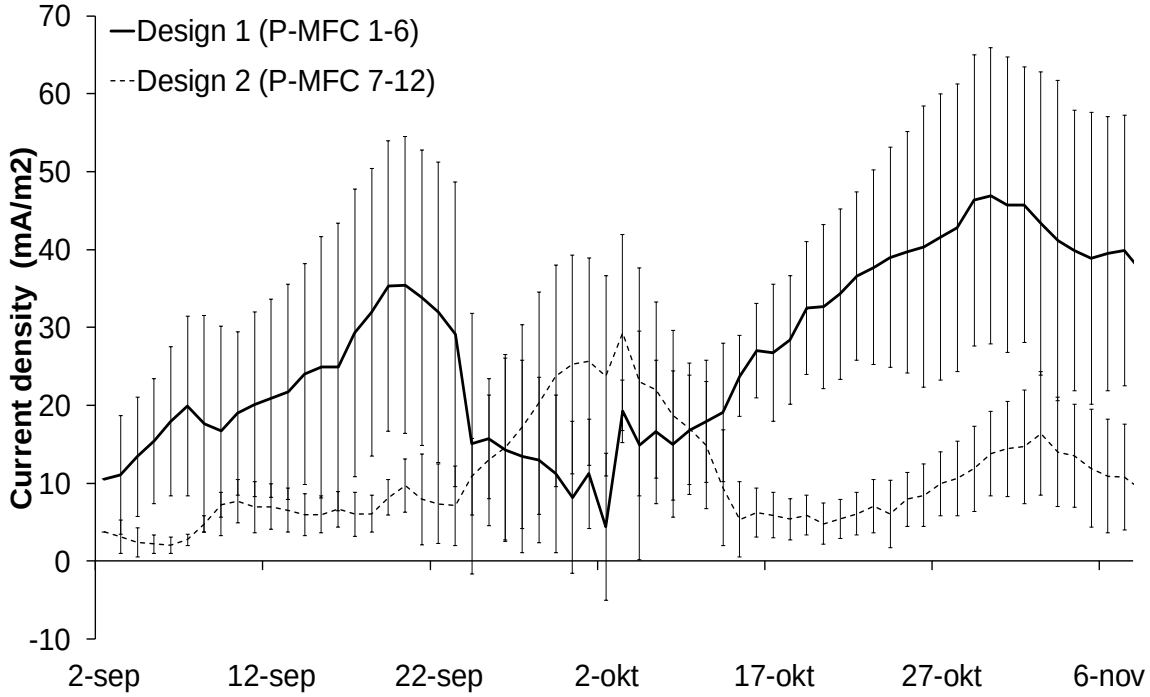

Figure 5.2: Average current density of two designs of Plant-Microbial Fuel Cells (6 per design) during first two months of experimental runtime, in which design 1 has a shorter start-up time than design 2, but both designs start-up within the first two months. Error bars represent standard deviation of average.

Until the first frost-period (day 188) cell voltage in P-MFCs 1, 2, and 7 through 12 a diurnal cycle was observed (data of P-MFC 1 as example in Figure 5.3). Anode- and cathode-potentials of P-MFC 1, 4, 7 and 10 were measured continuously. In P-MFCs 1, 4, 7 and 10 a day-night pattern was observed in the beginning, which was caused by a day-night fluctuation in cathode potential (data of P-MFC 1 in Figure 5.4).

During the day cathode-potentials were up to 400 mV and during night cathode-potentials dropped to -400 mV. Probably bio-cathodes had developed in the systems. In the same period algae growth was observed on the cathodes. Moreover, cathode potential was limiting maximum power output during all polarisation curves, an example of which is shown in Figure 5.5. A diurnal cycle, algae growth observation and a cathode limiting maximum power output are all indications of a bio-cathode [21]. Two aspects may have caused the fluctuation in cathode-potential: light and temperature. The drop in cathode-potential does directly correspond to sunset (Figure 5.4). This could be explained from the fact that algae-growth was observed on the cathodes. Algae produce oxygen during day and consume oxygen during night [21], thus inducing fluctuations in potential between day and night. The temperature in P-MFC 1 and 7 was measured and it was shown that the drop in cathode-potential lags behind the drop in temperature, so it is not likely that the day-night fluctuations are related to temperature.

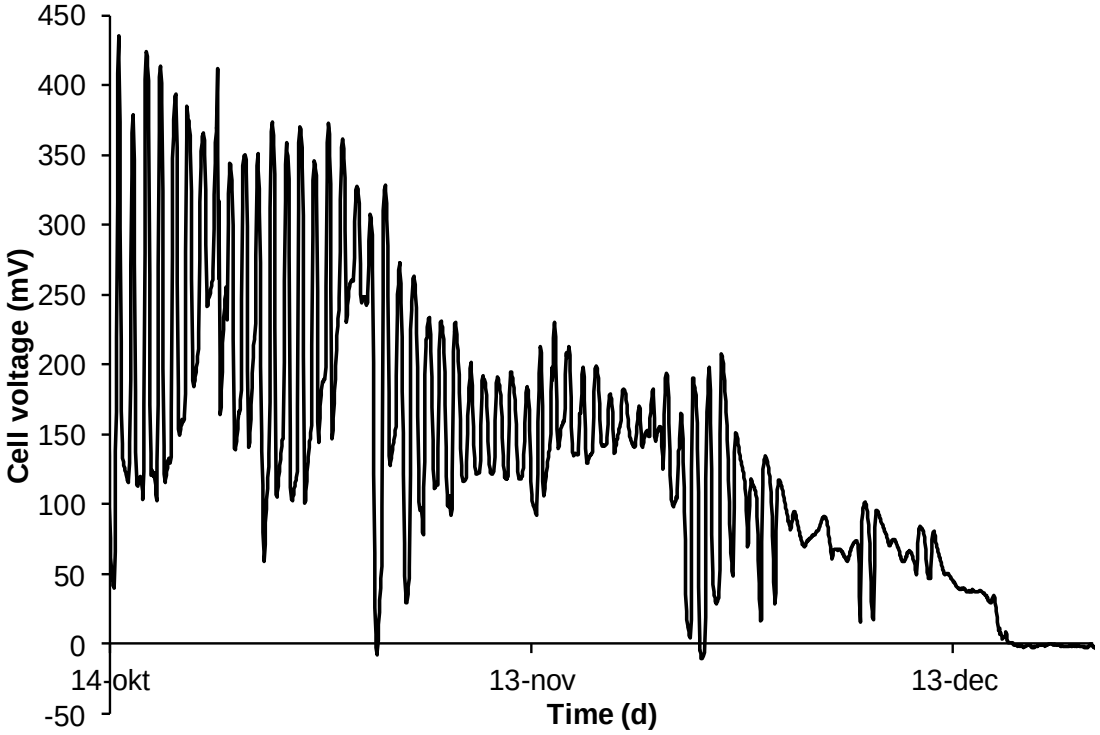

Figure 5.3: Diurnal cycle in cell voltage of P-MFC 1 as an example of diurnal cycles that were observed from start-up almost until first frost period on December 23. P-MFC 2 and P-MFCs 7-12 showed a similar pattern (data not shown).

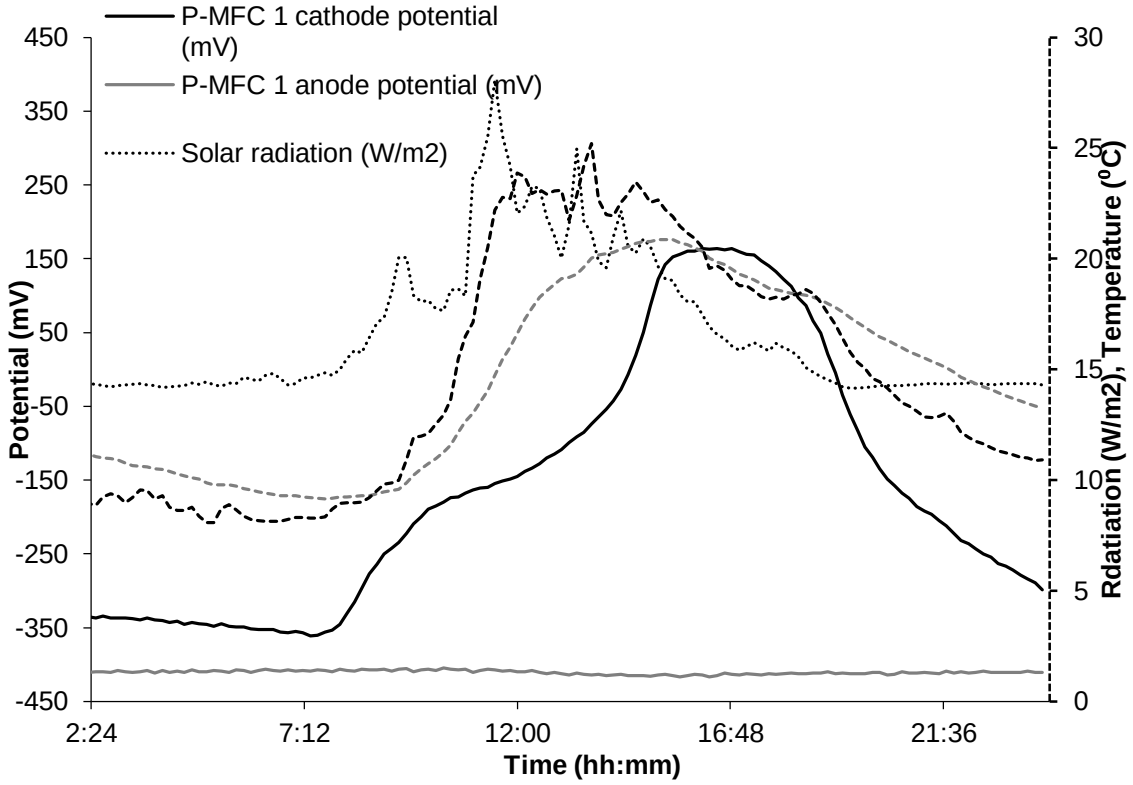

Figure 5.4: Development of anode and cathode potential of P-MFC 1 during 24 hours in relation to solar radiation and temperature, in which cathode potential shows a diurnal cycle.

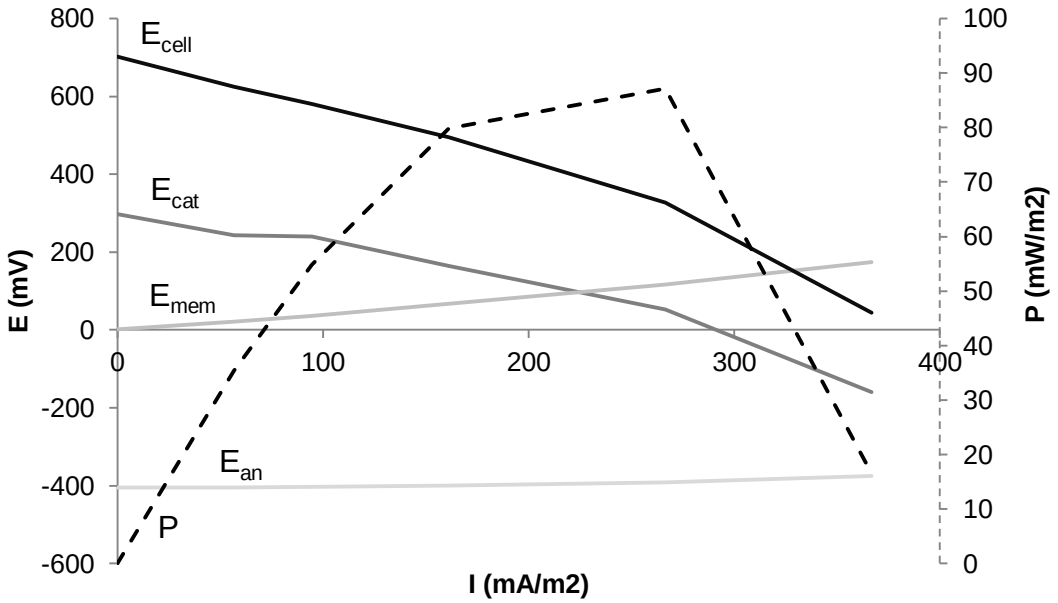

Figure 5.5: Polarisation curve of P-MFC 1 in which cathode is limiting maximum power output.

5.3.2 Electricity production returns after frost periods

Cell voltage dropped rapidly when winter set and temperatures dropped below zero (Figure 5.6). At frost-periods cell voltage became zero so electricity production stopped. It took some time, however, for the cell potential to drop to zero when frost set in. Even at temperatures below zero in the P-MFCs electricity production continued for a short while (Figure 5.6). Probably electron transfer is still taking place from reduced mediators towards the anode without active bacteria present. The fact that electricity production stops can be explained from the fact that after a while the water in the system is frozen and ions can no longer be transported [22, 23]. After frost-periods cell potentials re-established. They didn't return to their previous level, however (Figure 5.7). But directly after thawing of the P-MFCs cell potential returned. Even after a long period of frost with temperatures below -15°C cell potential returned directly after thawing.

5.3.3 Negative effect of lowering external resistance on power output

Of design 1, external resistance of three P-MFCs was lowered from 900Ω to 500Ω on 27 September (day 35). The other three P-MFCs of design 1 were still connected via 900 Ω external resistance. A zoomed-in picture of cell voltages of P-MFC 1-6, doesn't show large changes of cell voltages after external resistance in P-MFC 1, 2, 6 is changed from 900 Ω to 500 Ω (Figure 5.8). It can be concluded that changing external resistance does not lead to immediate change in cell voltage. On the long run lowering external resistance had a negative effect on cell voltage, however, as can be seen in Table 5.3.

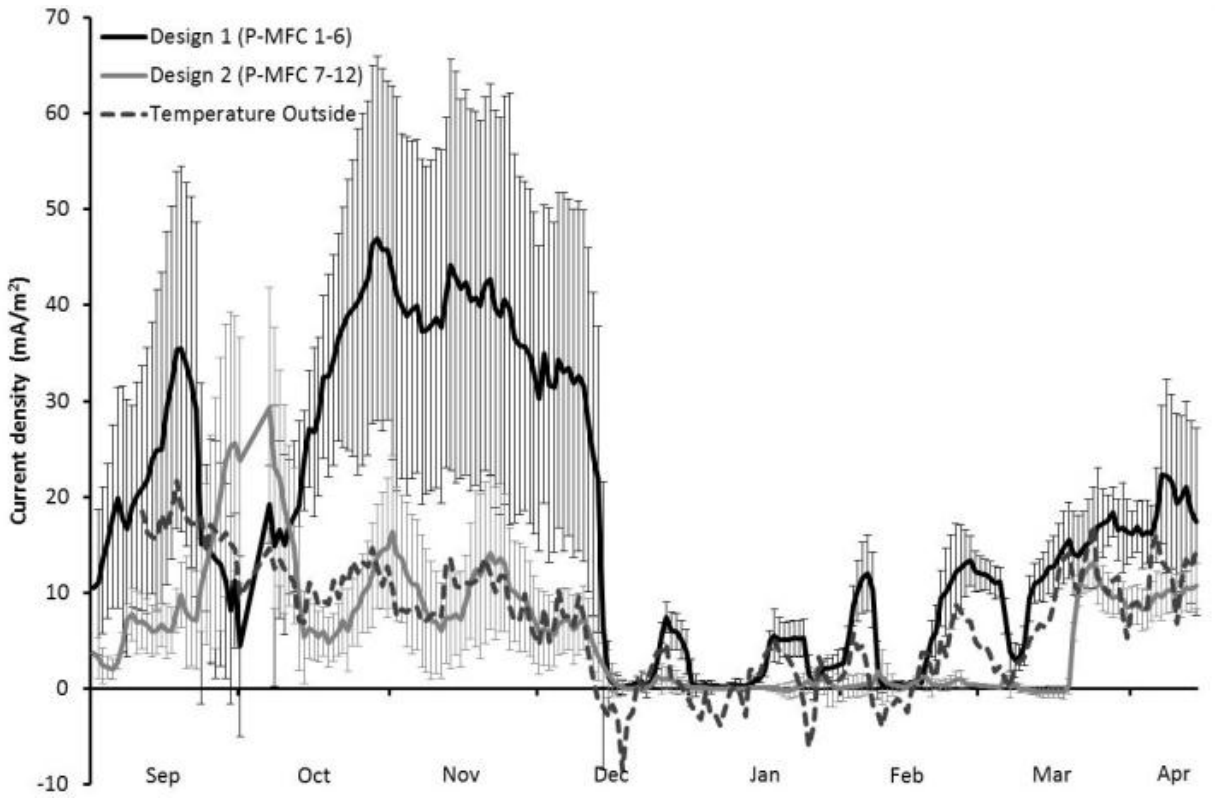

Figure 5.6: Average current densities (mA/m²), including standard deviation, of P-MFCs of design 1 (P-MFC 1-6) and design 2 (P-MFC 7-12) during complete runtime of the experiment in which design 1 shows consistently higher current densities than design 2.

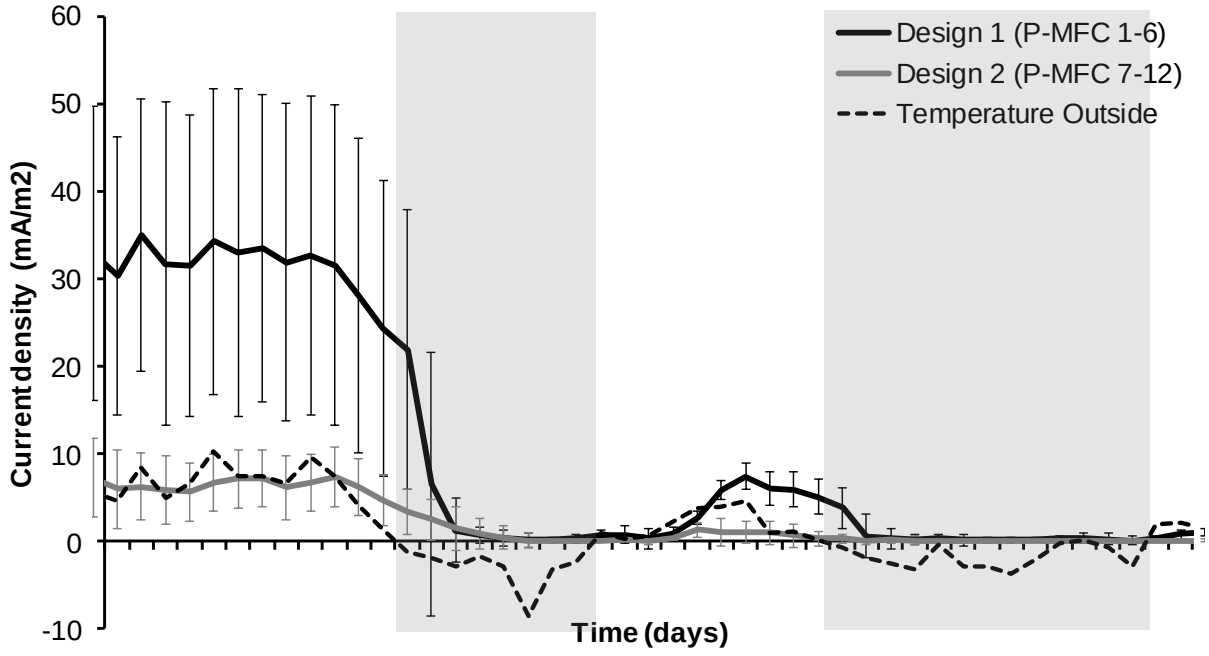

Figure 5.7: Average current densities over 6 P-MFCs of design 1 and 6 P-MFCs of design 2 at low temperatures. Grey areas represent frost periods. Current production continues shortly after frost sets in. Error bars represent standard deviation from average.

Table 5.3: Overview of current and power densities at 500 Ω and 900 Ω external resistance for P-MFC 1-6 (design 1)

PMFC	I (mA/m^2)	P (mW/m^2)
1,2,6 at 900 Ω	25.3 (sd 11.6)	9.4 (sd 6.7)
3,4,5 at 900 Ω	13.8 (sd 5.4)	3.3 (sd 2.5)
1,2,6 at 500 Ω	17.2 (sd 7.4)	4.1 (sd 4.0)
3,4,5 at 900 Ω	17.1 (sd 2.8)	5.9 (sd 1.9)
1,2,6 complete run	18.5 (sd 7.2)	4.9 (sd 4.0)
3,4,5 complete run	16.9 (sd 2.1)	5.7 (sd 1.6)

Table 5.3 shows that average current and power density of P-MFC 1, 2, 6 was higher at 900 Ω than at 500 Ω, while current and power density in the other three P-MFCs, 3, 4, 5 increased when comparing the two periods. Over the complete runtime of the experiment P-MFC 1, 2, 6 (at 500 Ω) had a higher current density than P-MFC 3, 4, 5 (at 900 Ω). A lower external resistance allows more current to flow, so current density is higher at lower external resistance. Power density of P-MFC 1, 2, 6, however, is lower than of P-MFC 3, 4, 5 over the complete runtime of the experiment due to a lower cell voltage. Lowering external resistance did not result in a higher power output. Probably the higher current resulted in higher internal resistance, leading to a lower power output. More research should be done in optimization of power output of the P-MFC.

5.3.4 Chilling and freezing stress symptoms in plants

Even though P-MFCs kept on producing electricity after winter, the plants did not survive winter and did not regrow in spring. Probably the plants suffered from severe cold stress and died consequently. This is supported by literature. *Spartina anglica* has shown to be cold tolerant down to 5°C [24] but below these temperatures no information is available. Chilling stress symptoms (<15°C) of plants involve chlorophyll inhibition and non-structural carbohydrate (sugar) storage. Freezing symptoms involve membrane disruption, chlorophyll inhibition and non-structural carbohydrates release [25]. Plants experience most cold-stress when below-ground temperature drop below zero. Freezing air-temperatures are less damaging to the plant and generally leads to survival of the roots and rhizomes and will lead to regrowth in spring. Observation of the P-MFCs showed that P-MFCs froze completely, including root system. This has probably severely damaged the root system, leading to plant death.

5.3.5 Chilling and freezing effects on P-MFCs,

In both sets of P-MFCs temperature was measured in anode and cathode of one P-MFC. This was done in P-MFC 1 and 7. It may be assumed that temperature in P-MFCs 2-6 was comparable to temperature in P-MFC 1 and temperature in P-MFCs 8-12 was comparable to temperature in P-MFC 7. Anode and anode-temperature in P-MFC 1 and P-MFC 7 is shown in Figure 9. A clear relationship between anode-potential and anode-temperature can be seen in both P-MFCs: the higher the temperature, the lower the anode-potential. Relationship is

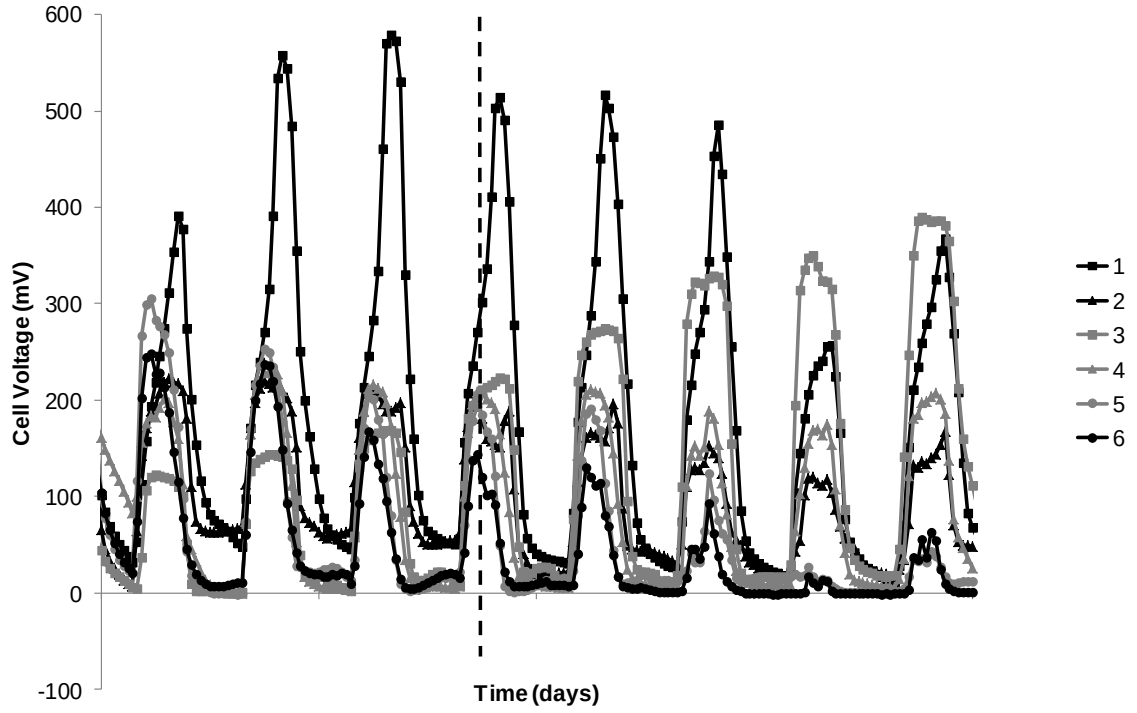

Figure 5.8: P-MFC 1-6 (design 1) before and after changing external resistance of P-MFC 1, 2, 6 to 500 Ω from 900 Ω and leaving P-MFC 3, 4, 5 at 900 Ω external resistance. Dashed line is moment of changing external resistance of P-MFC 1, 2 and 6. After changing external resistance no direct effect can be observed. After 3 days cell potential of P-MFC 6 drops.

more pronounced in the anode of P-MFC 1 (design 1) than in the anode of P-MFC 7 (design 2). Operation of P-MFCs at low temperatures has not been described before and even wastewater MFCs are not extensively described for low and even freezing temperatures. MFCs have been operated at different temperatures. Generally MFCs are operated around 30°C [26]. Lower current was reported at lower temperatures. It seems to increase coulombic efficiency in some cases, however, probably because of methanogen-inhibition [26-28]. Generally it is assumed that temperature dependency of power output of MFCs is caused by the temperature optimum of the biofilm [26, 29-32]. One study describes MFC operation at a temperature as low as 0°C, with 0 current [29]. The same paper describes that short exposure (30 min) of the biofilm to freezing temperatures does not damage the biofilm. However, longer exposure of the biofilm (24hrs) to freezing temperatures did damage the biofilm and led to a decrease in current production of 42-50% when put back at 35°C. In our case current production before first frost as compared to after the last frost is 33 mA/m2 versus 11 mA/m2, so a decrease of 67% occurs in P-MFC 1-6. A decrease of 9 mA/m2 to 5 mA/m2 was seen in P-MFC 7-12, which is a decrease of 45%. Differences between the two designs might be attributed to the more extreme temperatures that were measured in P-MFC 1-6 compared to P-MFC 7-12 (results not shown). Lower temperatures

and longer periods of freezing as experienced in P-MFC 1-6 might have done more damage to the biofilm than in P-MFC 7-12.

5.3.6 Design 1 outperforms design 2

Large differences in current and power density were observed between design 1 and design 2 (Figure 6). Average current density for design 1 is 4 times as high as average current density of design 2. Average power density in design 1 is 16 times as high as average power density in design 2. The presence of a CEM in design 2 and the lack of it in design 1 might lead to this difference. Data show, however, that membrane resistance of both designs is equally small. Of both designs two anode and cathode potential were measured in two P-MFCs. This shows that differences in cell voltage are caused by differences in anode potential rather than cathode potential (data not shown). Differences can possibly be explained from the longer transport distance for ions in design 2 as compared to design 1, leading to a higher transport resistance [33]. Most roots in both designs were found in the top half of the tube. Since most electricity is probably produced where most roots are present, most electrons and protons will be produced in the top half of the tube. Travel distance for protons and other cations from top half of the tube through the membrane/spacer to the cathode, to gain electro-neutrality after transport of an electron from anode through cathode, will be bigger in design 2 than in design 1. Transport resistance can therefore expected to be higher in design 2 than in design 1, leading to more losses. Consequently current density in design 1 will be higher than in design 2. Another possibility is the difference in oxygen intrusion between the two designs. Oxygen presence in the anode has two effects. The first is that it leads, at substrate-limiting conditions of the P-MFC, to a so-called mixed potential [34]. The anode-potential is in that case determined by the oxygen and organic matter present. The second effect is the effect of oxygen on the coulombic efficiency. When oxygen is present, some of the electrons released by the bacteria will be used for oxygen reduction. These electrons are no longer available for electricity production, thus coulombic efficiency will be lower. Design 1 has the cathode on top of the anode. The cathode consumes oxygen and limits therefore the amount of oxygen from the air available for intrusion into the anode. In design 2 this effect would not occur since the cathode is placed at the bottom of the tube. When oxygen is available to the top part of the anode, where most electrons are produced, more electrons will be lost to oxygen, leading to a mixed potential and a lower current density. Since oxygen intrusion from the air into the anode will be higher in design 2 than in design 1, losses in design 2 will be higher than in design 1 and current and power density in design 2 will be lower than in design 1.

Power output of both design 1 and 2 is low when compared to previously reported results (max. 88 mW/m^2 on the roof compared to 220 mW/m^2 in the lab [17]). One of the reasons for relatively bad performance of this system is that a biological oxygen cathode was used on the roof, whereas in most lab-experiments a chemical cathode in the form of ferric-cyanide is used [13]. A chemical cathode generally outperforms a biological or oxygen cathode [13].

When compared to lab-P-MFCs with a biological or oxygen cathode, results are alike [6, 16]. Still, power output is much lower than calculated theoretical maximum of 3.2 W/m^2, only 2.75% [13]. Current and power density could be much higher when cathode would function stable (Figure 5.4). When it would be possible to maintain cell voltage during the night, total current and power density could be expected to be twice as high. Another aspect that should be considered is that electricity was produced during winter-months, which had about 4 times lower solar radiation than the summer-months [15]. It can be expected that power output during summer will be higher, both because of higher radiation and higher temperatures. Higher temperature leads to a lower anode potential (Figure 5.9). A lower anode-potential leads to a higher cell voltage and therefore to a higher current and power density at stable external resistance.

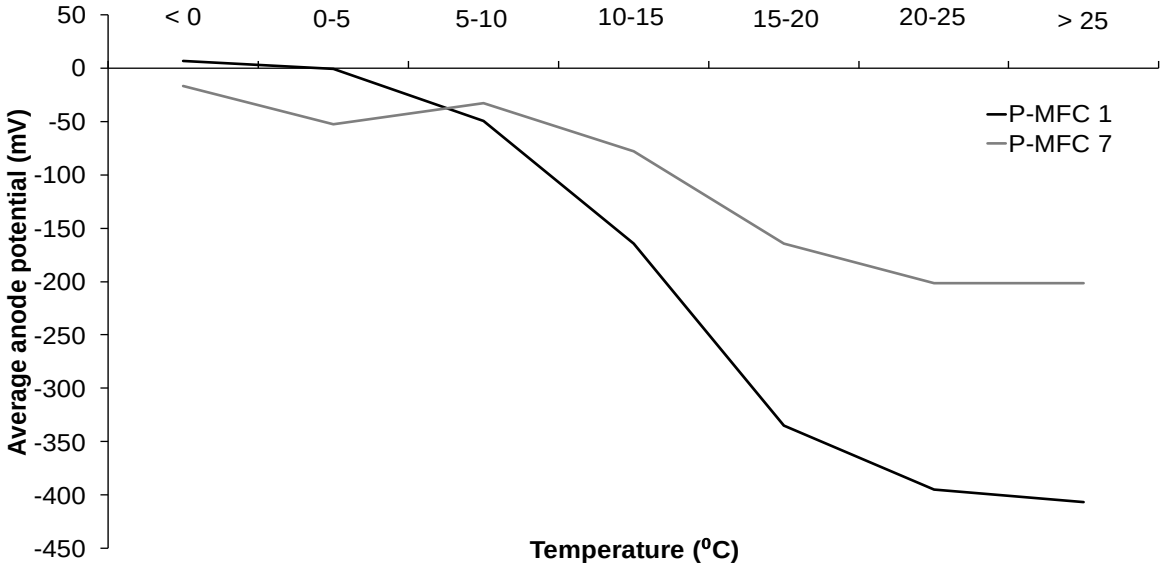

Figure 5.9: Average anode potential of P-MFC 1 and P-MFC 7 over all measurements (n=4695) in relation to temperature.

5.3.7 Total electricity production over 221 days

In total 12 P-MFCs with a combined surface area of 0.147 m2 generated 9.096 kJ over 221 days. Best performing P-MFC generated 2.254 kJ; worst performing P-MFC generated 0.187 kJ. Average power output over the complete runtime of the experiment was between 0.77 mW/m^2 and 9.29 mW/m^2 for all P-MFCs. During polarisation highest obtained power output was 88 mW/m^2. When extrapolating over a year, the best performing P-MFC could have generated 81 Wh/m^2. When optimised to its maximum power as obtained during polarisation, it could have generated 771 Wh/m^2. Previous research has shown, however, that maximum power points in polarisation curves are probably an overestimation of the maximum achievable power of the system [17]. Compared to existing sustainable energy systems as solar power and wind power, power density per geometric surface area of the P-MFC is still far lower [13].

5.4 Conclusion

The Plant-Microbial Fuel Cell is in theory a promising sustainable technology. Current and power densities are not stable, however, under outdoor conditions. Cathode potential was in our case likely dependent on solar radiation, due to algae growth, leading to a diurnal cycle in power output. The anode potential of the P-MFC is influenced by temperature, leading to a decrease in electricity production during low temperature periods and no electricity production during frost periods. Plants in our experiment did not survive winter, likely due to harsh temperatures around the roots. Even so, electricity production returned each time after frost periods. It can be concluded that the P-MFC is resilient when considering electricity production. The P-MFC will only be sustainable, however, when plants survive winter and electricity production can continue more than one season. In order to make a sustainable, stable and weather independent electricity production system of the P-MFC attention should be paid to improving cathode stability. Cold insulation of the anode as well as selection of cold-resilient species are possibilities for increasing plant survival over winter. Only when power output of the Plant-Microbial Fuel Cell can be increased under outdoor conditions it can be a promising sustainable electricity technology for the future.

5.5 Acknowledgements

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6 ELECTRICITY PRODUCTION WITH LIVING PLANTS ON A GREEN ROOF: ENVIRONMENTAL PERFORMANCE OF THE PLANT-MICROBIAL FUEL CELL

A unique early Life Cycle Assessment of an innovative bio-electricity generation technology, in which living plants generate electricity on a green roof.

Chapter published as:

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Abstract

Several renewable and (claimed) sustainable energy sources have been introduced into the market during the last centuries in an attempt to battle pollution from fossil fuels. Especially biomass energy technologies have been under debate for their sustainability. A new biomass energy technology was introduced in 2008: the Plant-Microbial Fuel Cell (P-MFC). In this system electricity can be generated with living plants and thus bio-electricity and biomass production can be combined on the same surface. A green roof producing electricity with a P-MFC could be an interesting combination. P-MFC technology is nearing implementation in the market and therefore we assessed the environmental performance of the system with an early stage Life Cycle Assessment (LCA). The environmental performance of the P-MFC is currently worse than of conventional electricity production technologies. This is mainly due to the limited power output of the P-MFC and the materials presently used in the P-MFC. Granular activated carbon (anode material), goldwires (current collectors) and Teflon coated copper wires (connecting anode and cathode) have the largest impact on the environmental performance. Use of these materials needs to be reduced or avoided and alternatives need to be sought. Increasing power output and deriving co-products from the P-MFC will increase environmental performance of the P-MFC. At this stage it is too early to compare the P-MFC with other (renewable) energy technologies since the P-MFC is still under development.

6.1 Introduction

In an attempt to battle pollution from fossil fuels, several renewable energy sources have been introduced into the market during the last and current century. These renewable energy sources can roughly be divided into solar, water (hydropower and marine power), wind, geothermal and biomass energy technologies. (1) Especially biomass energy technologies have been under debate for their sustainability. Often it is claimed that biomass production for energy and fuels competes with food and feed production directly.(2, 3) Other negative effects of biomass production have been identified, like an overall higher CO2 emissions due to land use change and indirect competition with food/feed production due to pushing out other land uses.(1) A new biomass energy technology was introduced in 2008: the Plant-Microbial Fuel Cell (P-MFC).(4-6) The system consists of a plant in a Microbial Fuel Cell (MFC) (Figure 6.1) and uses naturally occurring and known processes around the roots to produce electricity. The plant produces organic matter via photosynthesis under influence of sunlight. Up to 60% of this organic matter ends up in the soil as root material or exudates. (7) The exudates are oxidized by naturally occurring bacteria in a Microbial Fuel Cell (MFC). The bacteria release electrons and donate the electrons to the anode of the MFC. The anode is coupled to a cathode, at which oxygen together with electrons and protons is reduced to water. In this way electricity can be generated directly, without harvesting the plant. (4, 8, 9) P-MFCs are relatively new, but wastewater MFC's have already gained a lot of interest during the last decade. This has resulted in the first pilot-scale plants for industrial wastewater being built right now. (10, 11) Although considered as renewable and sustainable electricity generation technology, little is yet known about the environmental performance of MFC-technologies. Even though the MFC-technology is being used in pilot stage projects already, life cycle assessments (LCA) of the system are scarce. One paper describes the key aspects that should be addressed when doing an LCA of bioelectrochemical systems (10) and another actually performs an LCA of MFCs and MECs (Microbial Electrolysis Cells) and anaerobic treatment of wastewater. (12)

The P-MFC was later developed than wastewater MFCs and much less research has been performed into this specific type of MFCs. Nonetheless, a spin-off company, Plant-e, has already been established from the research into P-MFCs and a first pilot experiment was started (13). The pilot study is performed on the roof of the Dutch Institute for Ecology (NIOO) in Wageningen, the Netherlands, and is 15 m^2 large. It combines electricity production from P-MFCs with a green roof application. The pilot study on the NIOO-roof does not yet represent a commercially available product. It offers an opportunity, however, to evaluate the environmental performance of an early design of the P-MFC applied on a green roof. Strik et al. (2008), Kaku et al. (2008) and De Schamphelaire et al. (2008) have claimed that the P-MFC is a sustainable energy technology, that can combine electricity production with biomass production for other applications.(5, 6, 14) Now the P-MFC technology is nearing application in society, it is time to put the expectations of the environmental performance of the system to the test.

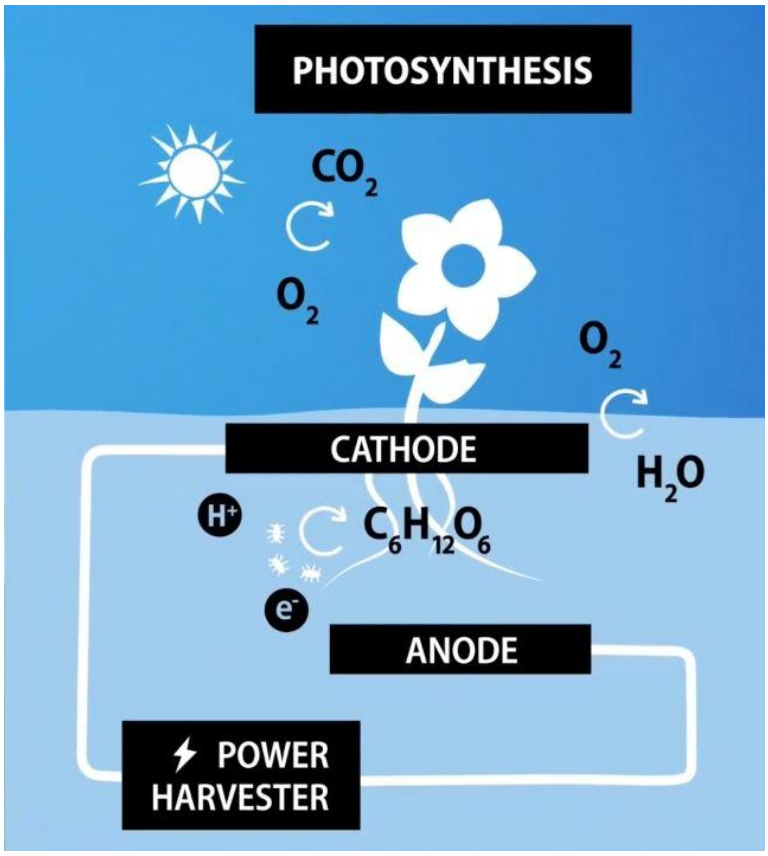


Figure 6.1: Schematic overview of Plant-Microbial Fuel Cell (13)

The environmental impact of the P-MFC during operation is expected to be small, but unknown yet is the indirect environmental impact for the construction of the P-MFC itself (i.e. the "hardware"). We performed a life cycle assessment (LCA) to determine the overall environmental performance, i.e. covering direct and indirect impact, of the P-MFC on a roof as a first indication of what aspects can be improved and whether the P-MFC has the opportunity to become a real sustainable electricity technology.

6.2 Methods and means

Life cycle assessment (LCA) is a powerful tool to assess the environmental performance of product and service systems. (15) LCA systematically quantifies a broad range of environmental impact categories. It starts at resource extraction, moves subsequently through production and consumption stages and ends at a product or service system. The coverage of the whole life cycle and range of impact categories facilitates identification of dominant environmental issues, and allows evaluation of trade-offs within and net-gains over the whole system resulting from process improvement measures. An LCA consists of four methodological phases: goal and scope definition, inventory analysis, impact assessment and interpretation. (16)

6.2.1 Goal definition

Scope definition basically sets the other LCA phases by specifying all their methodological details. The goal of this LCA was to assess the environmental performance of electricity production by a P-MFC installed on a flat-roofed building.

6.2.1.1 Functional unit

The functional unit for the assessment of the P-MFC can be chosen based on different uses for the system. Since the P-MFC on a green roof produces electricity, the functional unit could be kWh of electricity produced. The produced electricity, however, is dependent on the size of the installed system, so kWh per m^2 or per m^3 could be used as well. Because we wanted to test the environmental performance based on electricity production, the functional unit for this LCA was the production of 1 kWh electricity.

6.2.1.2 System description and boundaries

The pilot-experiment on the NIOO-roof comprised 61 P-MFC compartments that were connected with wires to a power extraction device. Each compartment consisted of grassy plants (Spartina anglica or Glyceria maxima), a polypropylene container, a cathode of carbon felt, a polypropylene spacer, an anode of granular activated carbon, goldwire as a current collector for both the anode and cathode, and Teflon-coated copper wires to connect anode and cathode.

The combination of electricity production with biomass production concurrently offers opportunities for the production of (potential) co-products, some of which were already identified in earlier research, like biomass for digestion or food production.(6, 8, 17) Combining the P-MFC with a green roof, however, offers additional co-products. It would combine the advantages of decentralized bio-electricity production with the advantages of a green roof. Generally accepted advantages of a green roof are 1) Stormwater run-off retention, 2) High aesthetical value, 3) Increasing biodiversity, 4) Air quality improvement, 5) Insulation of the building and 6) Urban Heat Island mitigation. (18, 19) The P-MFC green roof is expected to add new advantages without seriously compromising or improving the advantages of the green roof. The flow diagram in Figure 6.2 gives a schematic overview for electricity production and supply by the pilot P-MFC on the NIOO-roof, including its (potential) co-products. We only included energy-related (additional) co-products in our LCA, i.e. biomass for digestion (used for electricity production), and insulation of the building on which the P-MFC is installed (warming and cooling the building). The flows were quantified per kWh electricity supplied. Also the included and excluded processes, as indicated by the drawn system boundaries, relate to the reference scenario. Additional scenarios alternately include or exclude (production of the) co-products.

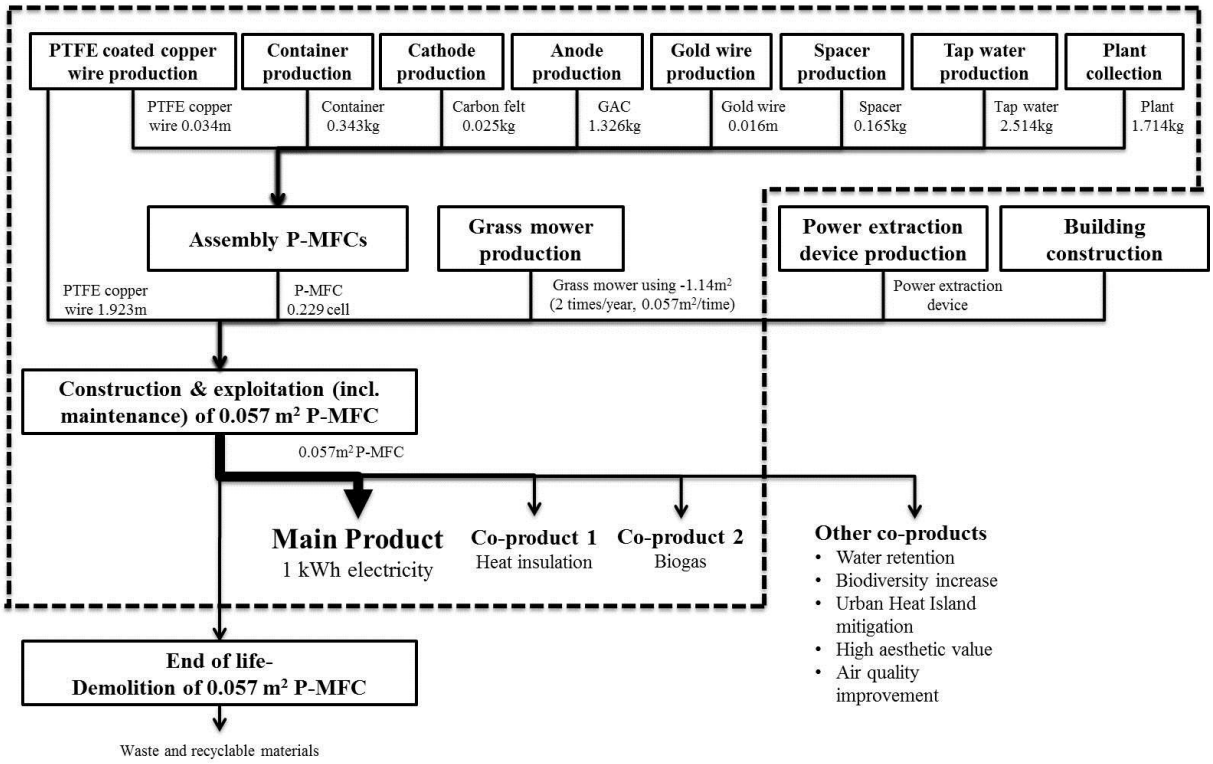


Figure 6.2: Flow chart of a P-MFC to produce and supply 1 kWh electricity to the grid of the building on the pilot on the NIOO-roof. The quantified flows relate to the reference scenario in this LCA with 1.75 kWh/m²/year electricity production. The dotted line generically indicates the system boundaries for all scenarios; inclusion of heat insulation and biogas differ between scenarios.

Maintenance, although difficult to estimate whether it will be necessary in the future, was included in the LCA in the form of mowing of the grass by a motor mower. Irrigation of the plants was excluded since rain-water in the Netherlands appears to be sufficient for keeping preferred waterlogged conditions in the system, based on precipitation and evaporation numbers from the Royal Dutch Meteorology Institute (KNMI) (20). The power extraction device was not included in the system boundaries due to its design not yet being decided on. Furthermore, the device is expected to have a fixed size, independent of how many P-MFC compartments are connected to it.

6.2.1.3 Reference system and scenarios

Main focus of this LCA is on what aspects of the P-MFC can be improved in the future, rather than comparing the system to other (bio-)electricity technologies. A reference system is needed though. We used the current electricity production in the Netherlands, as included in the EcoInvent database, as a reference system.

The environmental performance of a P-MFC depends on its lifespan, the presence of co-products and efficiency of electricity production. Since much of the P-MFC is unknown at this stage of development, we built scenario's to compare the different possibilities for the future. The baseline scenario (S1) is based on the currently achieved lab-scale power output

of 0.2 W/m^2 or 1.75 kWh/m^2/year, (21) and no use of co-products. In scenario 2, 3 and 4 the use of co-products is included; heat insulation of the green roof (S2), biogas production from harvested biomass of the roof (S3) and both heat insulation and biogas production (S4). Four more scenarios (S5-S8) were built based on the theoretical maximum power output of the P-MFC of 3.2 W/m^2 or 28 kWh/m^2/year. (17) In this case S5 is without co-products, S6 with heat insulation, S7 with biogas production and S8 with both heat insulation and biogas production.

The influence of the P-MFC lifespan is evaluated by identifying in all scenarios when environmental costs of the P-MFC become smaller than the environmental costs of the avoided conventional electricity production and supply. We assume a lifespan of 30 years possible, based on the fact that most materials used are, so far known, inert and have a long lifespan. This might not be true for all materials, however, but long-term research is needed to affirm a lifespan for the system.

6.2.2 Life Cycle Inventory

Environmental inputs and outputs for the cradle to electricity supply processes in the flow diagram in Figure 6.2 are quantified with the EcoInvent database (22) where possible, supplemented with information from literature and experts (Table 6.1). Where relevant, system expansion is used to credit the P-MFC for its co-products.

6.2.3 Impact assessment

Different impact categories were used for the impact assessment. Since we assessed electricity production, most importantly the Cumulative Energy Demand (CED) was quantified. CML 2 baseline 2000 was used to assess additional impact of the P-MFC. (23) Covered impact categories in CML 2 baseline 2000 were: Abiotic Depletion (AD), ACidification (AC), EutroPHication (EPH), Global Warming (Potential; GWP), Ozone Depletion (Potential; ODP), Human Toxicity (HT), Fresh Water Aquatic Ecotoxicity (FWAE), Marine Aquatic Ecotoxicity (MAE), Terrestrial Ecotoxicity (TE), PHothochemical Oxidation (PHO).

6.3 Results and discussion

Figure 6.3 compares the environmental performance of electricity supply by the P-MFC in the reference scenario (S1) with conventional electricity supply in the Netherlands. The results show that the contributions to all impact categories are far higher for the S1 P-MFC than for conventional electricity production and supply. As next sections will show, however, improvements of the P-MFC are possible.

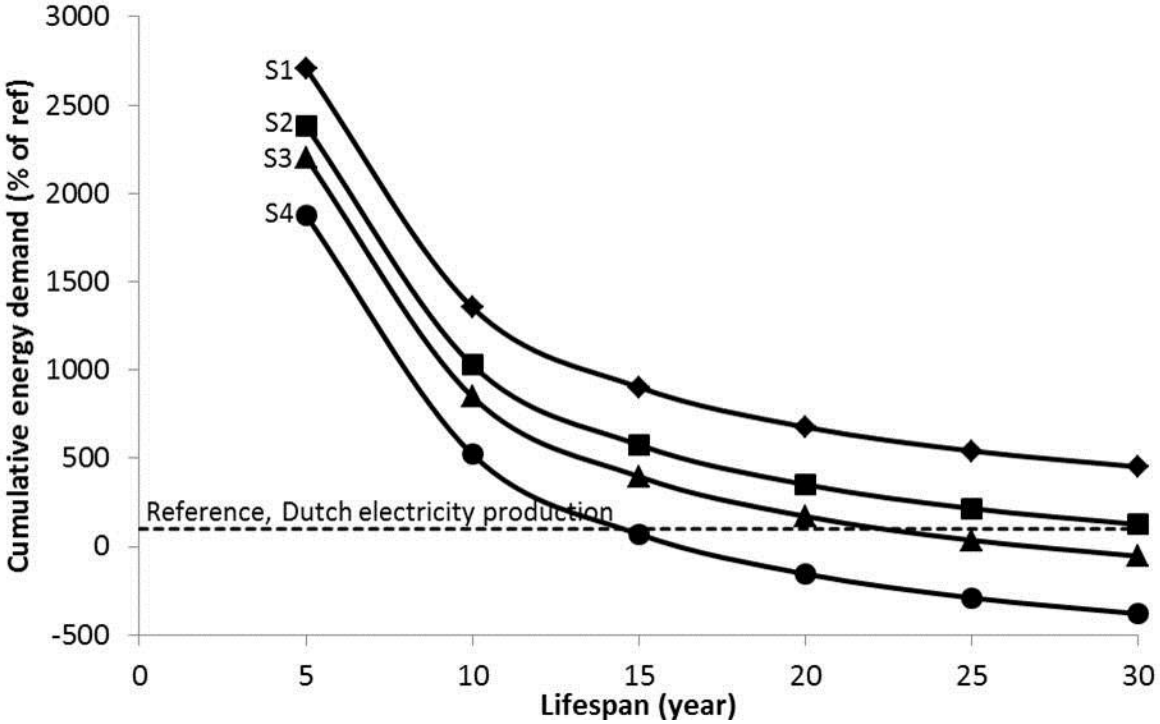
6.3.1 Main contributors to environmental performance

Figure 6.4 shows for all impact categories the relative contributions of the production of the construction parts of the P-MFC in the reference scenario (S1). Also the contribution of regularly mowing the plants is included, which shows to be hardly visible in any of the

Table 6.1: Overview of data sources to calculate, from cradle to functional unit, the environmental inputs and outputs per kWh electricity supplied (outflows relate to reference scenario = S1; outflows comes from given process and goes to next process)

	System parts or (co-)products ↳ Cradle to electricity supply processes	Outflow (in f.u.)	Data source	Comment
P-MFC construction	Spartina Anglica plants ↳ Road transport plants ↳ Harvesting plants	1.714 kg	EcoInvent (22)/188 km assumed	Transport, lorry >16t, fleet average/tkm/RER By hand and knife from nature, env. cost assumed zero
	Container, PolyPropylene (PP) ↳ Road transport container ↳ Injection moulding ↳ Cradle to PP granulate production	0.343 kg 0,047 tkm 0.345 kg 0.345 kg	 EcoInvent/138 km assumed EcoInvent EcoInvent	Transport, lorry >16t, fleet average/tkm/RER Injection moulding/kg/RER Polypropylene granules at plant/kg/RER
	Cathode, carbon felt ↳ Road transport cathode ↳ Sea transport cathode ↳ Road transport cathode ↳ Thermal treatment viscose felt ↳ Production added CO_2 flow ↳ Turning on kiln ↳ Transport viscose felt ↳ Viscose weaving ↳ Viscose fibre production	0.025 kg 0,002 tkm 0,012 tkm 0,001 tkm 8.468 MJ 0.105 kg 0.075 Wh 0,196 tkm 0.078 kg 0.078 kg	 Ecoinvent/99 km assumed EcoInvent/465 km assumed EcoInvent/49 km assumed EcoInvent/Meier (1997)(30): process EcoInvent/Mast carbon (2011)(31) EcoInvent/Meijer (1997): process EcoInvent/2,500 km assumed EcoInvent/Carter (1971) (32): Ø fibre EcoInvent	Transport, lorry >16t, fleet average/tkm/RER Transport, barge/RERU Transport, lorry >16t, fleet average/tkm/RER Natural gas, burned in industrial furnace>1000kW/RERU Carbon dioxide liquid, at plant/RERU Electricity, medium voltage, production NL, at grid/NLU Transport, lorry >16t, fleet average/tkm/RER Weaving, cotton/GLOU Viscose fibres, at plant/GLOU
	Spacer, PolyPropylene (PP) ↳ Road transport spacer ↳ Injection moulding ↳ Cradle to PP granulate production	0.165 kg 0,008 tkm 0.166 kg 0.166 kg	 EcoInvent/47 km assumed EcoInvent EcoInvent	Transport, lorry >16t, fleet average/tkm/RER Injection moulding/kg/RER Polypropylene granules at plant/kg/RER
	Anode, Granular Activated Carbon (GAC) ↳ Road transport of anode ↳ Combustion of inputs to yield GAC ↳ Extraction water input ↳ Production coal input ↳ Production coke input ↳ Production wood input	1.326 kg 0,060 tkm 2.214 kg 1.326 kg 0.438 kg 0.438 kg	 EcoInvent/45 km assumed Romero-Hernandez (2004) (33) EcoInvent EcoInvent EcoInvent EcoInvent	Transport, lorry >16t, fleet average/tkm/RER Weights of inputs for GAC, emissions of CO_2, SO_2, NO_x Water, unspecified natural origin/kg Hard coal supply mix, at regional storage/US U Hard coal coke, at plant/GLO U, 1 kg coke = 30.4 MJ Wood, feedstock
	Wire, copper coated with Teflon (PTFE) ↳ Road transport wire ↳ Coating PTFE on copper wire ↳ Copper wire drawing ↳ Copper production	0.008 kg 0,001 tkm 0.004 kg 0.003 kg	1.957m;4.3g/m EcoInvent/98 km assumed Own measurements EcoInvent	Transport, lorry >16t, fleet average/tkm/RER Weights of inputs for Teflon coated copper wire Wire drawing copper/RER U Copper, at regional storage/RER U No data available

	↳ Polymerisation of PTFE	0.003 kg	EcoInvent	Tetrafluorethylene at plant/RER U
	↳ Cradle to PTFE granulate production	0.001 kg		
		0.001 kg	EcoInvent	
	Gold wire	<0.000 kg	0.016m;0.96g/m	
	↳ Road transport of wire	<0,000 tkm	EcoInvent/126 km assumed	Transport, lorry >16t, fleet average/tkm/RER
	↳ Gold wire drawing	<0.000 kg	Own measurements	Proxy: Wire drawing copper/RER U
	↳ Production gold input	<0.000 kg	EcoInvent	Gold, at regional storage/RER U
	↳ Production silver input	<0.000 kg	EcoInvent	Silver, at regional storage/RER U
	↳ Production copper input	<0.000 kg	EcoInvent	Copper, at regional storage/RER U
	Avoided electricity production from biogas production from mowed plants	5.381 kWh	Ecoinvent	Electricity, production mix NL/NL U
	↳ Biogas combustion	5.381 kWh	Ecoinvent	Electricity, at cogen with biogas engine, allocation exergy/CH U. 32% of the biogas energy is yield and transferred into grid.
	↳ Biogas production			
	↳ Road transport harvested plants	2.530 m^3	EcoInvent/Pabón Pereira (2009) (34)	Biogas, from biowaste, at storage/CH U, 67% methane
		0,855 tkm	EcoInvent/28.5kg per f.u./ 30 km assumed	Transport, lorry >16t, fleet average/tkm/RER
	↳ Plant mowing by motor mowing	1.140 m^2	EcoInvent/2 times mowing per yr	Mowing, by motor mower/CH U
	Insulated heat			
	↳ Avoided electricity for air-conditioning	1.911 kWh	TheEngineeringToolBox (2011) (35)	Cooling capacity of air-conditioner: Min. 2.93kWh_{heat}/kWh_e
	↳ Heat insulated in summer	5.600 kWh	Liu & Minor (2005) (36)	Heat flux: 0.115/0.11/0.095 Jul/Aug/Sep
	↳ Avoided natural gas for heating	3.428 kWh	Ecoinvent/EERE (2011)(37)	Natural gas, burned in boiler modulating >100kW/RER U
	↳ Annual heat insulated in winter	2.742 kWh	Liu & Minor (2005)	Heating capacity of water boiler: Minimum 0.8 kWh_{heat}/kWh_{heat} from natural gas Heat flux: -0.045/-0.065/-0.050 Dec/Jan/Feb



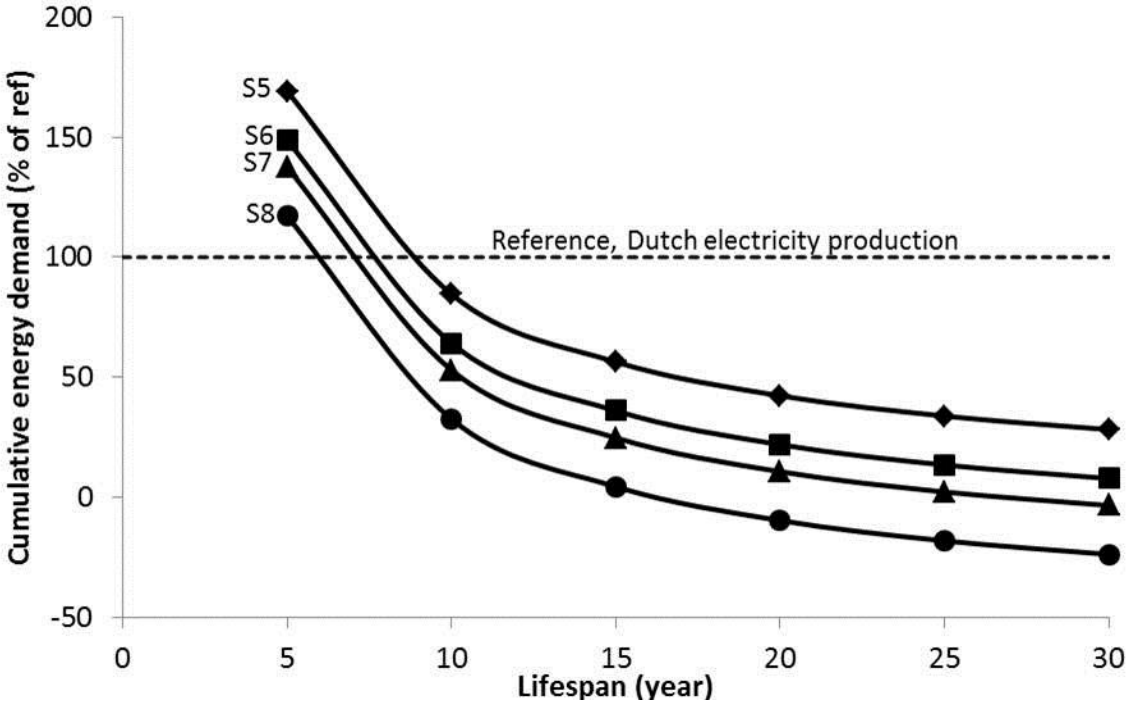


Figure 6.3: Cumulative energy demand of the P-MFC in different scenario's as percentage of the Cumulative energy demand of conventional electricity production. Both are calculated as a function of the life span of the P-MFC. In which, S1= power output of P-MFC of 1.75 kWh/m²/year, no co-products; S2=1.75 kWh/m²/year + heat insulation; S3=1.75 kWh/m²/year + biogas production, S4=1.75 kWh/m²/year + heat insulation + biogas; S5-S8 like S1-S4 but with 28 kWh/m²/year

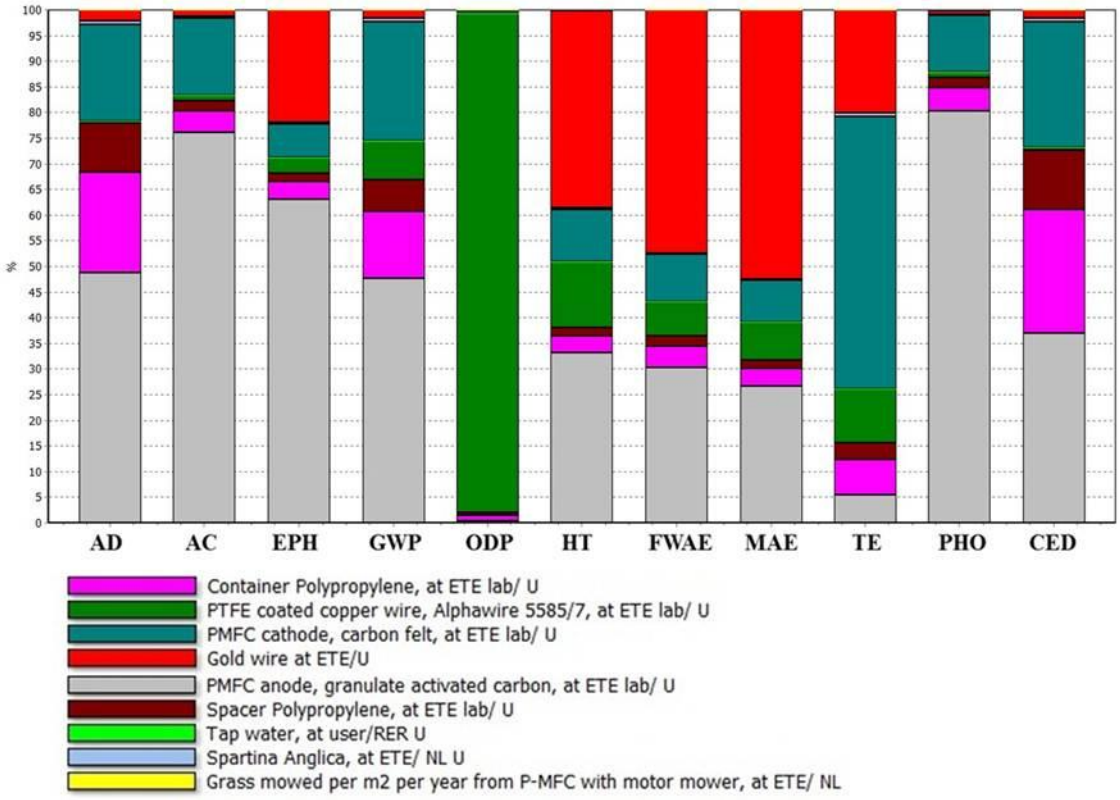


Figure 6.4: The contributions of the different parts of the P-MFC construction and grass mowing to the selected impact categories (calculated for 1 kWh electricity supply in the reference scenario), in which AD=Abiotic Depletion, AC=Acidification, EPH=EutroPHication, GWP=Global Warming Potential, ODP=Ozone DePletion, HT= Human Toxicity, FWAE=Fresh Water Aquatic Ecotoxicity, MAE=Marine Aquatic Ecotoxicity, TE=Terrestrial Ecotoxicity, PHO=PHothochemical Oxidation.

impact categories. The construction determines the environmental performance of the S1 P-MFC. There are four parts of the P-MFC construction whose production roughly explain the environmental performance of the S1 P-MFC: the anode of Granular Activated Carbon (GAC), the carbon felt cathode, the Teflon coated copper wire, and the gold wire.

The LCA shows room for improvement of the construction of the P-MFC when environment performance is added as a selection criterion for the materials used. The results indicate which materials are most important to focus at when it comes to improving environmental performance. Crude simplifications were used for some materials, e.g. as a current collector for both anode and cathode a piece of goldwire was selected for in the NIOO-pilot and as a consequence in the LCA. In practice, several current collectors can be used, like other metals or graphite rods or screws, graphite felt. (4, 5, 8, 24)

This LCA included the main materials, but excluded less important materials of the P-MFC construction. Glue, tie-wraps and clips used to attach different parts of the system to each other were for example not taken into account in the LCA. These materials may or may not be needed anymore in future design of the P-MFC, and their mass-share in the present construction is small. Their environmental contribution is also expected to be small.

As indicated before, also the power extraction device was not included in the LCA due to its design not yet being decided on. Any power extraction device is expected to contain small amounts of metals. When the future design of the P-MFC and the choice of power extraction device have been further defined, an update LCA needs to include these metals. Their mass-share in the total system may namely be small, but their contribution to overall impact can nonetheless be significant as similarly illustrated by the Teflon-coated copper wire and gold wire.

6.3.1.1 Granular activated carbon as anode material

Production of the GAC anode makes a large contribution to almost all impact categories, but clearly dominates in Abiotic Depletion (AD), ACidification (AC), EutroPHication (EPH), and PHotochemical Oxidation (PHO). The dominance in overall AC, EPH and PHO traces back to the emissions from input combustion (i.e. 10% wood, 10% coke, 30% coal and 50% water; see (Table 6.1). About 70% of the inputs is emitted as water vapour, carbon dioxide, sulphur dioxide and nitrogen (di)oxide, whereas 30% is converted into GAC. Contributions of anode production to the other impact categories mainly trace back to the production of the inputs. The fact that GAC is abundantly available as a resource, relatively cheap, compared to metal electrodes, and suitable for plants to grow in, make it to the main candidate for the anode in the P-MFC. Wastewater MFCs usually use carbon felt or fibre as anode material, but these have a negative impact on the environmental performance of the system as well (see 6.3.1.2 and (12)). Since the plant is growing with its roots into the GAC and electrons are produced close to the roots, (25) contact between root and GAC is considered important for total power output. (26) Reduction of use of GAC implicates that more roots will need to be located in less material. This can be achieved by either mixing the GAC with another material or integrate plant-roots more efficiently with the GAC. Since mixing of the GAC doesn't lead to good results due to loss of interconnection between the granules, (26) more efficient integration of the roots with the GAC is more promising. The recently described flat-plate P-MFC might be a good option to more efficient use of the GAC. (25) More research into the impact of different carbon materials is needed and would be beneficial for (P-)MFC research in general.

6.3.1.2 Carbon felt as cathode material

Production of the carbon felt cathode makes the largest contribution to Terrestrial Ecotoxicity (TE), and Cumulative Energy Demand (CED). The high use of electricity use in viscose fibre production and weaving almost completely explains the contribution to TE. The thermal treatment of the viscose felt is most important factor in contribution to CED. This is consistent with results from chemical fuel cell LCA, in which the carbon fibre has a considerable impact as well. (27) The emissions of the mass loss of viscose felt, roughly 70%, are not yet included in the calculations due to lack of data on emissions. This may create a considerable extra emission of carbon dioxide. In the study of Foley et al. (12) carbon fibre electrodes are indicated to impact the environmental performance of a wastewater MFC as well. Reducing the amount of carbon felt is difficult since little is used. A possibility would be

to use different sorts of carbon and graphite felt (4, 5, 9, 17, 21). These felts are produced in different ways and it is therefore difficult to say whether database values for the carbon felt used in this LCA approximate values for those other carbon and graphite felts. Results from other studies, however, indicate that this difference might be small. (12, 27) Other options for cathodes are air-cathodes and bio-cathodes. Air-cathodes generally contain a Teflon coating and should therefore from an environmental performance point of view probably be avoided (see 6.3.1.3). Moreover, gas-diffusion electrodes, like an air-cathode, are regularly used in chemical fuel cells and have the largest environmental impact of all fuel cell materials. (27) This high impact is mainly caused by the use of platinum catalysts in the gas diffusion electrodes. (27) Bio-cathodes – graphite/carbon electrodes with bacteria or algae growing on it - on the other hand could reduce the amount of graphite/carbon felt needed, since the bacteria are catalysing the oxygen-reduction process. These bio-cathodes are still under development, however, and may show not to perform stable under outdoor conditions as a diurnal cycle might occur. (28)

6.3.1.3 Teflon coated copper wire to connect anode and cathode

Ozone Depletion (OD) is completely dominated by the production of Teflon coated copperwire, and can be traced back to production of the monomer Tetrafluoroethylene in Teflon. In the pilot-experiment Teflon coated wires were used for their water resistance. Easiest way to avoid the Teflon coated wires is connecting all P-MFC compartments directly to each other instead of individually connecting them to a power extraction device. By connecting the compartments to each other about 98% of wire can be avoided (i.e. 0.03 instead of 2 metres per functional unit). This leads to a 95% reduction in overall ODP. Using a Teflon-coated air-cathode may introduce a new source of Teflon in the system and should therefore carefully be considered.

6.3.1.4 Goldwire as current collector

The length of goldwire is only 0.02 metres per functional unit (100 times less than the length of copper wire used). Gold wire production nonetheless is the largest contributor to Human Toxicity (HT), Fresh Water Aquatic Ecoxicity (FWAE), and Marine Aquatic Ecotoxicity (MAE). Goldwire consists for two-thirds of gold, one quarter of silver, and one twentieth of copper. It is the gold production that is responsible for the large contribution of this wire to HT, FWAE and MAE. Gold wire is use as a current collector because of its high electrical conductivity and chemical resistance. The LCA of a wastewater MFC performed by Foley et al. (12) is not as detailed on the materials as this one, but identifies stainless steel current collectors as one of the main materials impacting the environmental performance. Replacing the goldwire by stainless steel wire or mesh is therefore not expected to improve the environmental performance of the system. Other current collectors could be graphite materials like rods, paper or wires. Both technical and environmental performance of these materials needs to be tested.

6.3.2 P-MFC co-products and longer lifespan

The environmental gain was calculated for two co-products, i.e. heat insulation and biogas, and for electricity production at the theoretical maximum efficiency. Figure 6.3 exemplifies for Cumulative Energy Demand (CED) the environmental gain from both co-products versus lifespan for all scenarios. For each impact category, the lifespan was determined where the P-MFC starts to be better than conventional electricity production and supply. The results are summarised in Table 6.2. A lifespan of 30 years is assumed to be possible, but since no experiments of that timeframe have been performed it is difficult to estimate. Table 6.2 shows that there are four impact categories for which not any scenario, within a lifespan shorter than 30 years, are able to perform better than conventional electricity production and supply. This underlines a necessity for adjusting the P-MFC construction such that at minimum lower contributions are obtained for ACidification (AC), Ozone Depletion (ODP), and PHotochemical Oxidation (PHO).

Table 6.2: Different P-MFC scenarios for the efficiency in electricity production and co-products, and the timespan in years for each impact category where the environmental gains starts to exceed the environmental costs. Timespans >30 years are indicated with x.

Impact categories	Scenarios							
	S1	S2	S3	S4	S5	S6	S7	S8
Abiotic Depletion (AD)	x	x	23	15	9	8	8	6
ACidification (AC)	x	x	x	x	x	x	x	x
EutroPHication (EPH)	x	x	x	x	x	x	28	25
Global Warming Potential (GWP)	x	x	x	19	9	8	8	7
Ozone Depletion Potential (ODP)	x	x	x	x	x	x	x	x
Human Toxicity (HT)	x	x	x	x	x	29	27	24
Fresh Water Aquatic Ecotoxicity (FWAE)	x	x	x	x	29	26	24	22
Marine Aquatic Ecotoxicity (MAE)	x	x	x	x	28	24	21	19
Terrestrial Ecotoxicity (TE)	x	x	x	x	x	x	x	x
PHotochemical Oxidation (PHO)	x	x	x	x	x	x	x	x
Cumulative Energy Demand (CED)	x	x	23	15	9	8	7	6

6.3.2.1 Heat insulation

Numbers on the insulating effect of the green electricity roof as used in our study are indicatively based on literature and do not originate from measurements done at the pilot site. The insulating effect of the green roof, however, adds largely to the environmental performance of the P-MFC on a roof. Exact avoided electricity caused by the green electricity roof still needs to be measured, and this is important information that we hope to derive from the pilot P-MFC on the NIOO-roof.

6.3.2.2 Biogas production

The other advantage of using the above ground biomass for extra energy production via anaerobic digestion looks promising. Practical problems might be encountered, however,

when using mowing grass on a roof-top for biogas production in anaerobic digester. First, a facility needs to be available for (co-)digestion of the grassy material possible. Second, the logistical infrastructure needs to be available for (energy) efficient collection and transport of the grassy material. In case of the NIOO-pilot an anaerobic digester will be placed on-site. On-site digestion of the grass material is possible and probably even more interesting as it avoids the need for collection and transport infrastructure.

Regular moving the above ground biomass might make it necessary to add nutrients to the system, since nutrients leave the system as well. This was not included in the LCA, but adding nutrients may lead to an increase of the system's environmental impact and its CED. In the case where an anaerobic digester is available on-site, however, digestate can be used as a fertilizer and nutrient cycles can possibly be closed.

6.3.2.3 Other co-products

This LCA clearly shows that not electricity production is the unique selling point of the P-MFC, but the opportunity of combining its electricity production with other applications. Since co-products play such significant role in the environmental performance of the system, this encourages to further think about co-products that can be achieved besides electricity production by the P-MFC. Other expected advantages of the green roof were not assessed in this study since no reliable data is yet available on these advantages. The fact that the included co-products, show to make a large difference on the environmental performance of the system, makes it important to also quantify other benefits of the green roof with the P-MFC.

Application of the P-MFC on a green roof may offer interesting opportunities for implementation of the technology for decentralized electricity production on a roof. This could fit well in a concept for decentralized use of resources and decentralized treatment of waste streams and decentralized production of energy. A trend can be seen in developing decentralized concepts, examples of which are the zero-energy houses and the Cradle2Cradle philosophy. The P-MFC could be integrated in such a larger concept in which for example wastewater can be used in combination with a P-MFC in a helophyte filter or constructed wetland system for combined electricity production and wastewater treatment.

6.3.3 Surface-based functional unit versus kWh as functional unit

As earlier indicated, the chosen functional unit has an effect on the outcome of the LCA. We chose kWh as functional unit, because we considered the P-MFC primary as energy source. This has implications on the use of co-products, however, since their benefits are dependent on size (m^2) rather than kWh power output. With a higher power output of the P-MFC (3.2 W/m^2 instead of 0.2 W/m^2), the necessary size to reach one kWh is smaller and therefore the added benefits of insulating capacities of the green roof and the available biomass for digestion are smaller. The scenarios that include the co-products have a lower environmental impact than the scenarios without co-products; the electricity production

apparently increases slower than the gain from the co-products decreases. This underlines the importance of the co-products for the environmental performance of the P-MFC.

In addition to the previous, when considering the installation of a P-MFC, its dimensions will probably be based on the available surface rather than a fixed amount of electricity needed. For future development and assessment of the system it will therefore be important to focus on surface area. This LCA was focused on the green roof application of the P-MFC. As already identified in the introduction, however, the P-MFC is a platform technology that can possibly be integrated in all kinds of systems where biomass is growing under waterlogged conditions. Future applications could include electricity production in rice-paddy fields, large-scale electricity production in wetlands, and electricity production combined with wastewater treatment in helophyte filters.(6) Especially in the large-scale applications, assessment of the system per surface area is needed.

6.3.4 P-MFC as electricity generation technology

Conventional electricity supply in the Netherlands is based on fossil resources mainly, and represents proven technology. It therefore has the advantage of a so-called economy-of-scale. This LCA shows that the P-MFC can be improved considerable from an environmental point of view. If the P-MFC proves to be a competitive technology in the future, it may be assumed that it will similarly gain an economy-of-scale advantage during the coming decades. This will influence the environmental comparison between fossil based and P-MFC based electricity supply. Pehnt (2006) already described the limitations of mainstream LCA for developing energy technologies.(29) LCA is by nature a static assessment for a given point in time, at a specific place, without accounting for the fact that the technologies are still under development in a developing market, like renewable energy technologies. (29) Future developments, as we explored in previous sections, should be incorporated in an LCA to get an idea of the future environmental performance of a technology. (29)

When comparing the P-MFC to a wastewater MFC it can be assumed that energy input of the P-MFC will be lower, considering the fact that a lot of energy is lost in a wastewater MFC due to transport of organics into the system. (12) But due to a lower power output of the P-MFC compared to the MFC CED can either be higher or lower. When comparing the P-MFC to solar panels, which can equally be installed on a roof, it can be assumed that environmental impact from metals will be higher in solar panels (29), but due to the higher power output of solar panels overall environmental performance of solar panels per kWh can still be lower.

6.4 The Plant-Microbial Fuel Cell: a new sustainable energy technology?

Present bio-energy technologies are criticized for competing with food/feed production for the same surface area. The P-MFC offers opportunities to combine energy production with food production. (5, 6) The P-MFC is a waterlogged system, however, which limits the

number of food crops that can possibly be grown in the P-MFC. Moreover, the P-MFC should not reduce crop yield, otherwise competition with food production would still occur. When applying the P-MFC in developing countries, it might offer an opportunity for remote communities to acquire electricity, which could speed up economic development. Since the P-MFC can easily be assembled and is relatively low-tech, it could possibly be maintained by the communities itself. Again, location would be important and possible competition with other land-uses should be avoided.

On the roof the P-MFC technology possibly competes with other applications for the roof, i.e. a normal green roof or solar panels. A normal green roof would not produce electricity, but offers all other advantages the P-MFC offers too. Solar panels don't offer the advantages of a green roof, but produce more electricity than the P-MFC. For each location it should therefore carefully be assessed what would offer most economic, social and environmental benefits. Social and economic effects should be considered when evaluating the technology's overall sustainability.

The Life Cycle Assessment of the early phase Plant-Microbial Fuel Cell (P-MFC) clearly indicates that the environmental performance of the P-MFC is currently worse than of conventional electricity production technologies. A considerable improvement of the overall environmental performance of the P-MFC system can be obtained, however, through co-products as biogas from the mowed grassy material and insulating value of the P-MFC as a green roof. At current power density, not electricity production is the Plant-Microbial Fuel Cell's unique selling point, but the opportunity of combining electricity production with other applications.

6.5 Acknowledgements

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7 GENERAL DISCUSSION AND CONCLUDING REMARKS

After four years of research our understanding of the possibilities of the P-MFC has increased. Part of the black box was turned into grey. In this final chapter you'll find an overview of the current status of technology and the opportunities the P-MFC for turning into a commercially applied energy technology.

We set two objectives for this thesis: 1) to increase the power output of the P-MFC and 2) to assess its applicability as an electricity generation technology in the market.

7.1 Power output of the Plant-Microbial Fuel Cell

At the start of this thesis 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). We tried to improve power output by adjusting different parts and processes of the system. This was discussed in chapters 2 through 4 of this thesis. Power output was optimized to 0.44 W m^{-2} planting area.

7.1.1 Plant and roots: *Spartina anglica*

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. *Spartina anglica* outperformed *Arundinella anomala* considering maximum power output (0.22 W m^{-2} vs. 0.021 W m^{-2}), although total electricity produced over the complete runtime of the experiment was almost equal between the two species. We found that we were not able to optimize the power output to the maximum we achieved in a polarisation curve. On average we were able to produce 0.021 W m^{-2}. Both *Arundinella anomala* and *Spartina anglica* are grassy species. It is understandable that grassy species perform well in the P-MFC. Most grassy species can grow under submerged conditions (3) and have a high carbon allocation to the roots, up to 80% (4). 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 thesis.

Not much is known on the specific photosynthetic efficiency of *Spartina anglica*, but in general C4-photosynthetic plants have a photosynthetic efficiency up to 6% (5). Literature describes specific photosynthetic rates for *Spartina anglica* of 0.3-1.9% (6, 7). These data, however, were achieved during chilling treatments specifically and can be assumed to be lower than average photosynthetic rates (6, 7). Literature also describes below ground biomass of 0.8-3.1 kg C m^{-2} (8).

If we compare these numbers to our experimental data from Chapter 2, we can conclude that we calculated a total biomass of 21 kg m-2, of which 6 kg above ground and 15 kg below ground (9), about 10 times higher than reported in literature. Dry grass generally has a higher heating value of 12-14 MJ kg^{-1}. Now if we calculate the total radiation in the climate chamber (149 W m^{-2}, 14 hours of light day^{-1}, 172 days) we come to the conclusion that photosynthetic efficiency must have been around 24%, which is impossible. With the

knowledge acquired during this research, we re-assess the data and look again at the picture of the set-up from the relevant experiment. In Figure 7.1 we see the set-up.

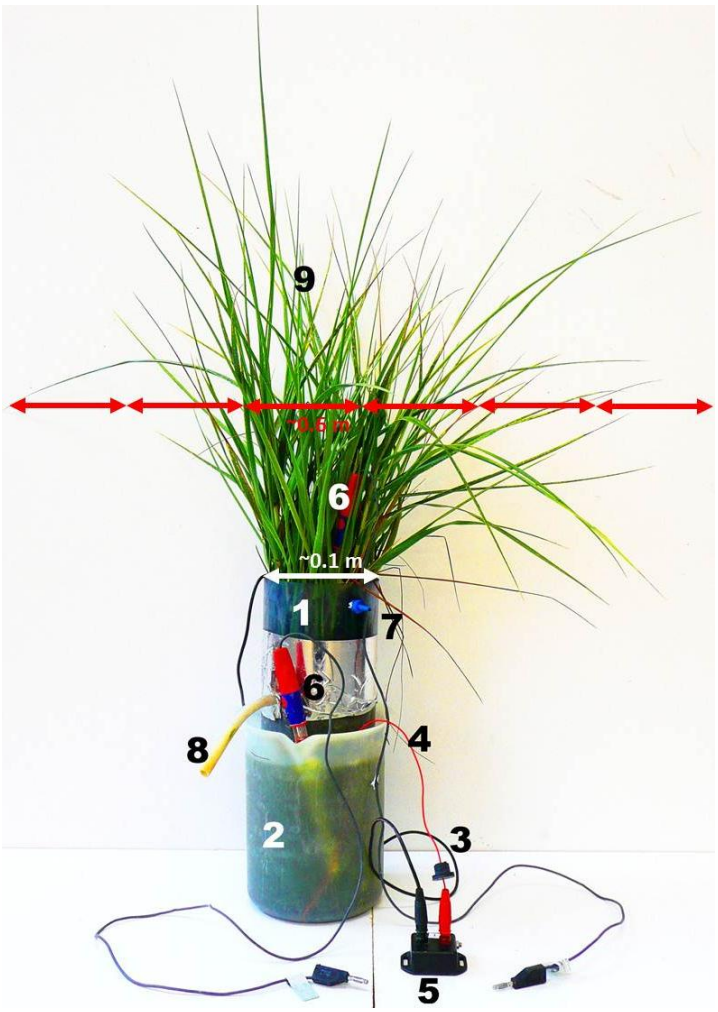

Figure 7.1: Experimental set-up from chapter 2, in which maximum width of above ground biomass is approximately 6 times width of anode.

The most obvious explanation would be that we overestimated biomass per surface area by extrapolating the biomass-weight from the surface area of the system (0.0077 m^2) to 1 m^2. Maximum width of the above ground biomass is about 6 times as large as the diameter of the anode. This would mean we have overestimated the above ground biomass with a factor 36, or assuming that most biomass is contained in approximately 3 times the anode width, we overestimated with a factor 9. The point is that it is impossible to approximate the actual biomass per m^2 we would have achieved under the same conditions. If we assume that we overestimated all biomass with a factor 9-36, photosynthetic efficiency would have been 0.7-2.6%; possible but rather low considering the growth conditions. It would otherwise mean that we would have acquired 0.8-3.3 kg m^{-2} below ground biomass, which is comparable to what is found in literature (8).

Below ground biomass, however, was contained in the projected surface area of the anode. Even if growth is overestimated, it could be possible that total biomass could be contained

per m^2 as calculated. Due to less above ground biomass growth and thus lower photosynthesis, we assume that it will take 9 times longer to build up the amount of biomass. Considering the efflux of carbon from the soil, which is projected at 0.09-0.12 kg m^{-2} $year^{-1}$, total time to build up 15 kg of below ground C per m^2 would be 4.6 years.

7.1.2 Microbial conversions

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, 9). Power output could not be maintained over a longer period of time and polarisation curves showed the anode to be limiting the power output. The plant-growth medium used in the P-MFC contained a lot of nitrate. Nitrate is an electron-acceptor and the presence of nitrate in the anode led to a loss of electrons for denitrification. 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}, so comparable to the earlier experiment (chapter 3). This time, however, power density was maintained over a longer period of time; 0.15 W m^{-2}. Removing sulphate from the plant-growth medium did not lead to higher power densities, even though it's an electron acceptor as well. Removal of sulphate from the plant-growth medium resulted in a decrease in power output. This is probably due to the fact that sulphate cycles via sulphide back to elemental sulphur, thus releasing electrons to the anode again. The anode potential showed to increase when removing sulphate from the plant-growth medium, which indicates that the cycling of sulphide to sulphur or even sulphate could play a role in keeping the anode at a low potential. The effect of sulphur-cycling within the anode of the P-MFC is still not fully understood, though, and should be researched further. This could be important specifically for application in sulphur-rich soils like peatlands (10).

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} $year^{-1}$ (4), 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 during this and other researches. 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.

The question rises why we seem to achieve current and power densities that are apparently not easy to reach based on existing knowledge. Various explanations are possible. Again, like with biomass growth, we might have overestimated current and power density per planted area. If the actual above ground biomass covers a larger surface area than project, it would be logical to divide the produced current and power over a larger area as well. The experiment in which 0.4 W m^{-2} was achieved was a different experiment than pointed out above, but something comparable might have happened when extrapolating biomass amount to m^2. Figure 7.2 shows, however, that overestimation in this case must have been a lot smaller, maximally in the order of 2-3 times overestimation. Even when we

overestimated our surface area with a factor 3, we could produce a power density of 0.13 W m^{-2}, at least twice as high as would be possible based on the C-efflux found by Kuzyakov. Other literature suggests, though, that C-efflux can be higher than estimated by Kuzyakov.

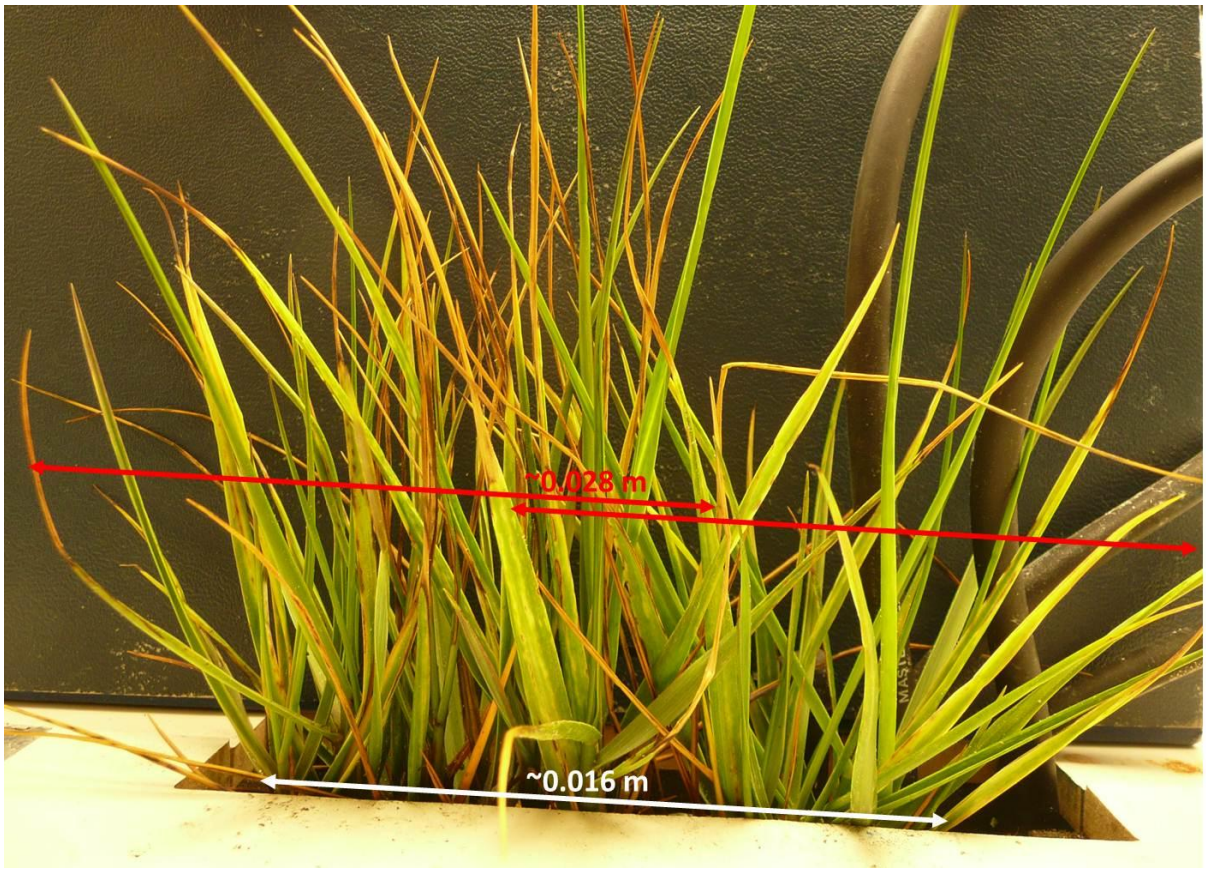

Figure 7.2: Experimental set-up from chapter 3 and 4, in which maximum width of above ground biomass is 1.5 times anode width.

Another explanation could be that actual microbial activity under natural conditions is higher than estimated by Kuzyakov et al., thus in practice carbon breakdown is faster than projected and more electrons are released. Or it could be that 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 (11).

7.1.3 Microbial Fuel Cell

The results with the new plant-growth medium were achieved in a flat-plate design P-MFC (chapter 4). The flat-plate design resulted in a lower internal resistance for the P-MFC as compared to the previously used tubular P-MFC. Still, we see a high anode internal resistance, caused by substrate limitation. Even though we have a high belowground biomass storage, we're not able to harvest it effectively as electricity. One reason might be due to the biodegradability of the *Spartina* roots. It was shown that of *Spartina anglica* biomass only 59% is readily anaerobically biodegradable (12). As with anaerobic digestion, hydrolysis of the biodegradable material might be a rate-limiting step (13). In total internal resistance can maximally be 0.094Ω.m^2 in order to reach 3.2 W m^{-2} as is seen in Figure 7.3.

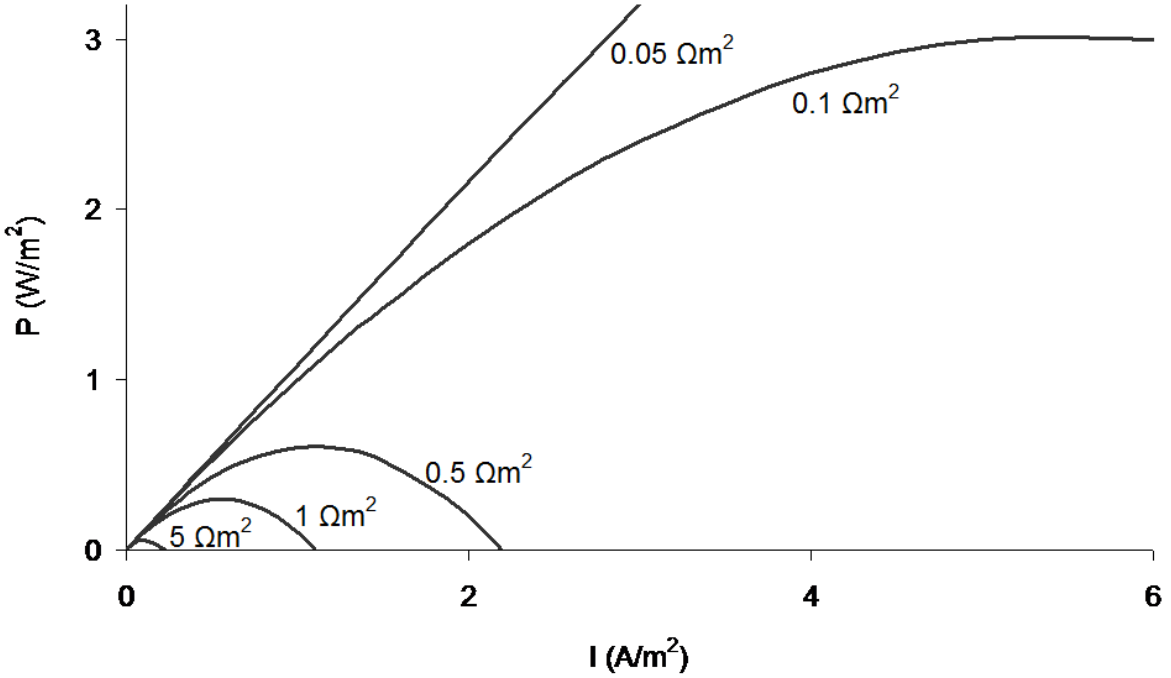

Figure 7.3: Power density as function of current density at different internal resistances, based on $P=P_{max}-I^2R_{int}$

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 set-up described in Chapter 2 and extensively researched by Timmers et al. (14) internal resistances showed to be higher than in the flat-plate system as developed in Chapter 3 and 4 of this thesis. 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.

7.2 Applicability of the Plant-Microbial Fuel Cell

In chapters 5 and 6 we assessed the applicability of the P-MFC. In chapter 5 we made a first attempt of putting the P-MFC under natural outdoor circumstances under harsh conditions on a Dutch roof. Even though the flat-plate system performs better than the tubular system, we chose to use tubular systems on the roof because it was easier to build. When moving towards application of the technology, practical considerations come into view. A tubular system with the anode on top and a tubular system with the cathode on top were built. The system with the cathode on top performed better than with the anode on top. This might be due to oxygen intrusion from the air into the anode. Both designs 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. No ferric cyanide was used as electron acceptor at the cathode, but used oxygen as electron acceptor. We found that 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. So another design-issue that needs to be addressed before the P-MFC can be applied is the cathode. Moreover, the plants didn't survive winter, which drastically limits the lifespan of the system. Long freezing of the system should therefore be avoided.

Apart from the technical design criteria, some additional design criteria were formulated in the introduction of this thesis. We will address them hereafter.

7.2.1 Renewability

The P-MFC is renewable in the sense that it uses solar power to produce electricity. The energy balance of the system was assessed in Chapter 6.

To build a P-MFC costs energy. If we assume that no energy is lost in maintenance of the system, 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} $year^{-1}$. Based on electricity production solely, the payback time of the P-MFC on the NIOO roof (Chapter 6) – the time needed to net produce as much energy as was used to build the system – would be 136 years (Figure 7.4). 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. In chapter 2, however, we showed it is possible to concurrently produce electricity and biomass (9). So if we could use the biomass effectively and include it in the energy balance of the P-MFC, energy balance could be positively affected. We described in chapter 5 and 6 the possibility of applying the P-MFC on a roof as a green roof system (Chapter 5 and 6). 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. At present it is important to effectively use the possible co-products from the P-MFC, apart from electricity production. For the green roof application, co-products that add positively to the energy balance of the system are available. In other applications, however, this might not be possible. In those cases the energy balance of the P-MFC needs to be positive based on electricity production alone. When power output of the P-MFC would be increased payback time would drop. At a power output of 0.9 W m^{-2} or 8 kWh m^{-2} $year^{-1}$, the P-MFC would have a positive energy balance within an estimated lifespan of 30 years based on electricity production alone at current material use.

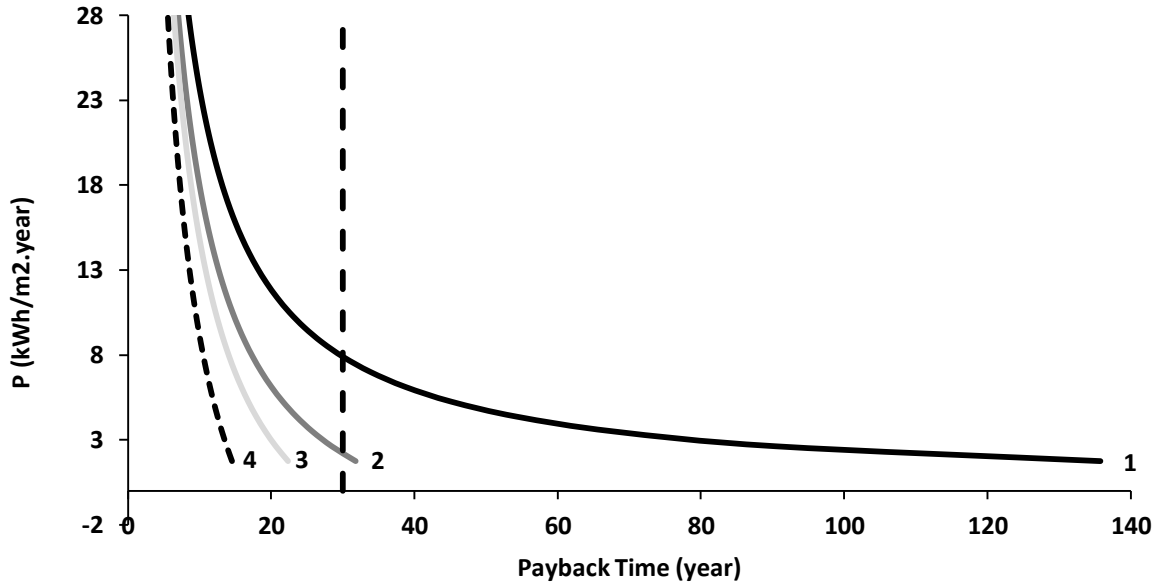

Figure 7.4 Payback time – when energy input in system equals energy output – of the P-MFC based on different power output of the P-MFC ranging from 1.75 kWh m^{-2} $year^{-1}$ to 28 kWh m^{-2} $year^{-1}$ (0.2W m^{-2} – 3.2 W m^{-2}) for four scenarios: 1) without co-products, 2) with heat insulation as a co-product, 3) with biogas production as a co-product, and 4) with both heat insulation and biogas production as co-products.

7.2.2 Sustainability

Sustainability was assessed based on environmental performance, social acceptability and economic feasibility.

7.2.2.1 Environmental performance

In chapter 6 we discussed 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. 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. For some of the materials it is difficult to actually assess their impact. The origin of the granular activated carbon plays a major role in its environmental performance. It can be coal or (waste) biomass based and this makes a difference in environmental impact. If using biomass for example, there are two ways of making electricity out of the source material: direct burning of the biomass or producing activated carbon and using it in a P-MFC to produce electricity. Again, it will fully depend on the lifetime of the P-MFC which of the two will be more beneficial.

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. Many uncertainties arise when trying to assess the amount of material that will be used in the future, the maintenance that needs to be done to the system and the overall lifetime of the system. Pehnt (2006) already described that forecasting with LCA is very difficult and a dynamic approach must be used for assessing innovative systems (15). This approach includes changes in the market and customer behaviour that arise from using the innovative technology.

Comparing a biological system, like the P-MFC, to a physical-chemical system, like a coal-fired power plant, is difficult. We used kWh as functional unit for the LCA. If a coal-fired power plant would be scaled down to 1 kWh, total impact of the system would be much larger, because relatively more material would be needed. The other way around, though, scaling-up the P-MFC does not guarantee a reduction of materials, since it is a biological system.

7.2.2.2 Social acceptability

Social acceptability, as discussed in the introduction, is very dependent on the specific application of the technology. In itself plants are aesthetically of high value and media attention during the course of this research has shown that there is a lot of interest from possible future consumers. 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 (16).

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.

Table 7.1: Material and labour prices for three P-MFC applications: 1) green electricity roof, 2) decentralized electricity production based on the modular green roof system, but with bulk prices and 3) large-scale centralized electricity production with a horizontal tubular system based on Timmers et al. (17) The tubular system is assumed to be 1m in diameter.

		Green Electricity Roof		**Bulk prices GER and decentralized production**		**Centralized production tubular system**	
System part	Material	€/m2	ref	€/m2	ref	€/m2	ref
module	polypropylene	€ 55.20	(19)	€ 3.90	(20)	€ 0.00	No module needed
anode	granular activated carbon	€ 42.15	(21)	€ 0.01	(22)	€ 0.12	
spacer	grindplaat/grasplaat	€ 11.50	(23)	€ 1.87	(20)	€ 0.29	Tubular membrane (24)
cathode	carbon felt	€ 170.00	(25)	€ 0.00	(26)	€ 0.00003	
current collector anode	graphite paper	€ 8.00	(27)	€ 0.00	(28)	€ 0.00003	Assume graphite paper
current collector cathode	gold wire	€ 40.00	(29)	€ 1.53	(30)	€ 0.00003	Assume graphite paper
wiring	Teflon coated copper wire	€ 2.00	(29)	€ 0.59	(31)	€ 0.00	Assume non needed
other materials	glue, clips, etc.	€ 1.00	(29)	€ 0.79		€ 0.041	10% of total
control hardware		€ 1.00	(17)	€ 0.79		€ 0.0041	10% of total
Total hardware		€ 330.85		€ 9.48		€ 0.4957	
Installation and maintenance	labour	€ 175.00	(29)	€ 14.23	60% of total costs (32)	€ 0.4055	45% of total costs (32)
Unforeseen + margin 25%		€ 126.46		€ 5.93		€ 0.4506	
Total		**€ 632.31**		**€ 29.64**		**€ 1.1266**	

7.2.2.3 Economic feasibility

We used three cases to assess economic feasibility of the P-MFC. These cases differ in size, scale and market. The Green Electricity Roof and decentralized electricity production are modular systems. The tubular system is a non-modular system. When approaching large-scale application, costprice of electricity will be the determining factor for economic feasibility. For small-scale applications additional benefits can play a role as well.

Green electricity roof

One of the possible applications of the P-MFC is the green electricity roof, as was already discussed in some of the previous chapters. The environmental performance of the P-MFC was assessed on the roof of the NIOO in Wageningen in Chapter 6. When we look into the same system for its economic performance, we can see that total costprice for the system per m2 is over €600.- including installation (Table 7.1). This is comparable to what was estimated by Timmers, 2012 (17). 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 (Table 7.1). Normal grass roofs typically, which are comparable to the Green Electricity Roof considering vegetation, cost between €80.- and €120.-/m^2 (18).

When considering the price per W installed or per kWh produced, assumptions need to be made for both power output per m^2 and lifespan of the system. We assume a power output of 0.2 W m^{-2}, which was stable achieved in the lab for a longer period of time, as lower limit for power output and the estimated maximum of 3.2 W m^{-2} as higher limit. Current costprice per Watt installed at a power output of 0.2 W m^{-2} is over €3000.-. If the power output would be 3.2 W m^{-2} and costprice would go down to €30.- m^{-2} costprice would be less then €10.- per Watt installed. Currently, PV solar panels cost between €3.10 and €5.80 per Watt installed after having dropped in price rapidly during the last few years (32).

Figure 7.5 shows initial investment costs and pay-back time for a roof of 100 m^2 for normal grass roofs, PV solar panels and the Green Electricity Roof in three scenarios: worst case, base case and best case. Worst case scenario is current state of technology and pricing (0.2 W/m^2 and €630.-/m^2). Best case is maximum power output and minimum costprice (3.2 W/m^2 and €30.-/m^2). Base case is 1.7 W/m^2 and €330.-/m^2. It is assumed that the Green Roof and Green Electricity Roof cover the full roof. It is assumed that solar panels are installed with a power output of 3500 kWh/year, which is the average electricity demand of a household. Pay-back time of the PV solar panels is calculated based on the avoided electricity costs, assuming an electricity price of €0.25 kWh^{-1}. Pay-back time of the Green Roof is calculated based on the avoided heating/cooling costs, approximately €91.- $year^{-1}$

(33). Pay-back time for the Green Electricity Roof is calculated based on the avoided heating/cooling costs as well as avoided electricity use.

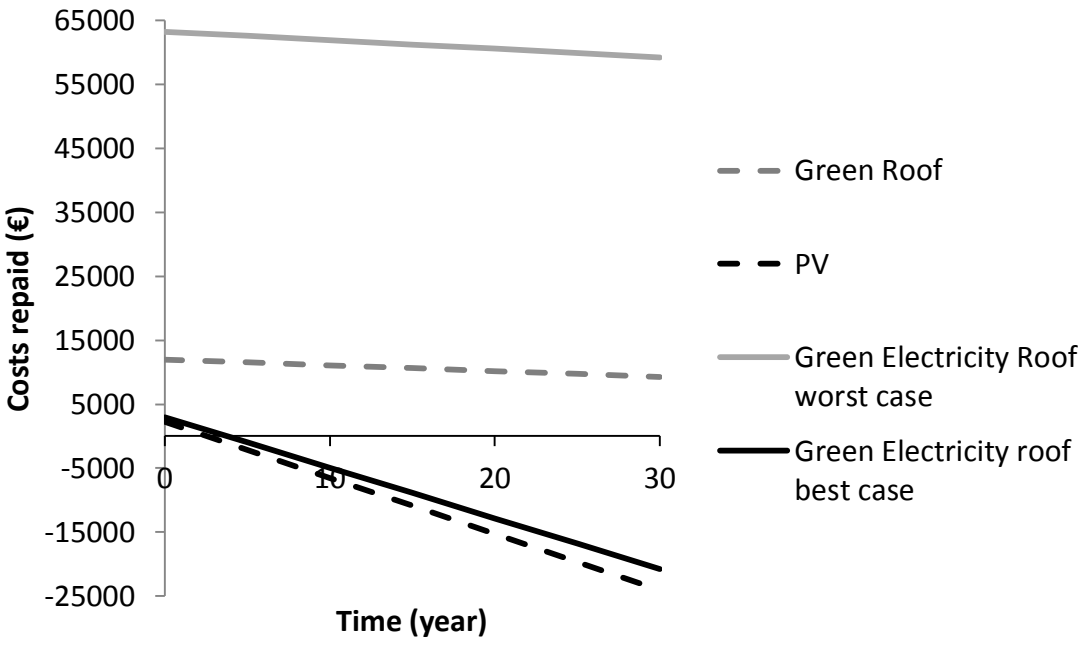

Figure 7.5 Investment-costs and pay-back time of normal green roofs, PV solar panels and the Green Electricity Roof in three scenario's. Worst case scenario is current state of technology and pricing (0.2 W/m² and €630.-/m²). Best case is maximum power output and minimum costprice (3.2 W/m² and €30.-/m²).

The worst case and base case scenario of the Green Electricity Roof are not able to compete either with the normal Green Roof or PV solar panels. Investment costs are high and won't pay-back within 30 years. Best case Green Electricity Roof scenario, however, outperforms the normal green roof and performs equally to PV solar panels. To be able to pay-back the system within 30 years, costprice for 100 m^2 should not exceed €2760.- without electricity production but can go up to almost €25,000.- at maximum power output of 28 kWh m^{-2} $year^{-1}$ (Figure 7.6).

Decentralized electricity production in developing countries

The economic performance of the P-MFC as a decentralized electricity system in developing and remote areas is different than that of the Green Electricity Roof. Heat-insulation of the building is no longer considered as a co-product since it can be assumed that buildings in developing countries won't be suitable for the weight of the Green Electricity Roof. There is a large need for electricity, though, since no electricity grid is available in these situations. Surface area is in these remote areas abundantly available so we assume that the P-MFC can be applied on the ground without competing with other applications or even in combination with food production. Nowadays these remote areas are generally powered by stand-alone solar PV systems with lead-acid batteries. Batteries are needed because PV solar systems only generate electricity during (sunny) days. The use of batteries leads to several problems.

The lead-acid batteries are environmentally unfriendly, are sometimes stolen and have a short lifespan of 2-5 years at most. This leads to high maintenance costs for the PV solar system.

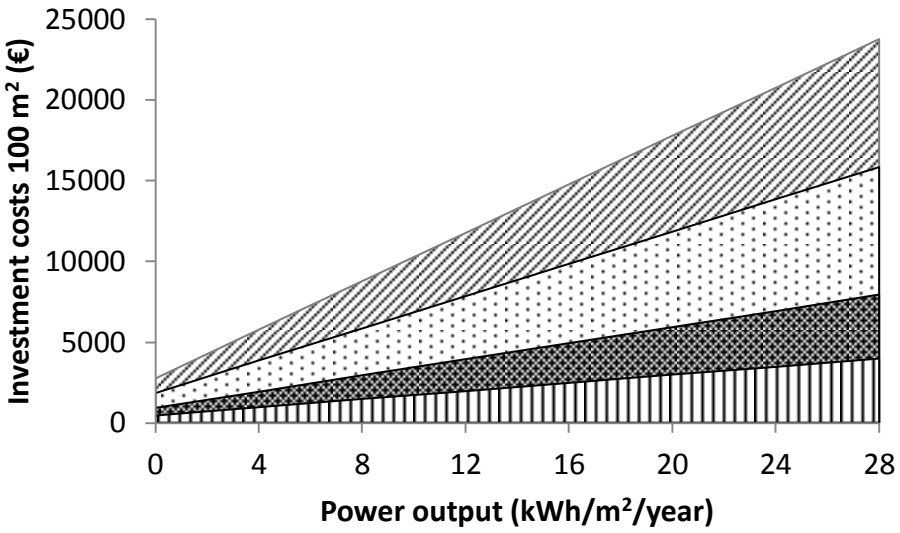

Figure 7.6: Investment costs for 100 m² of Green Electricity Roof at increasing power output. For a pay-back time of maximum 30, 20, 10 and 5 years investment costs should be in the shaded area of the graph. Highest line is 30 years, lowest 5 years.

Since the P-MFC can generate electricity day and night – provided that the cathode will be improved – the use of a battery can probably be avoided. Moreover, maintenance costs can be expected to be very low. Figure 7.7 shows two scenarios of a stand-alone PV solar system compared with two scenarios of a stand-alone P-MFC system. PV worst case is with a lifespan of the battery pack of 2 years, PV best case is with a lifespan of the battery pack of 5 years. P-MFC worst case is based on 0.2 W m^{-2} and optimized costs of €9.26 m^{-2}, P-MFC best case is 3.2 W m^{-2} and optimized costs of €9.26 m^{-2}. The reason that the worst case P-MFC scenario makes us of optimized costs is that it is assumed that the system will not be applied in applications other than the green roof as long as costprice doesn't drop.

The figure clearly shows that at longer lifespans the P-MFC worst case scenario outperforms the worst case PV solar system. The P-MFC best case scenario already outperforms the best case PV solar system from the beginning. So even at a low power output the P-MFC can be an interesting alternative energy system for developing and remote areas without electricity grid. It is important, however, to avoid the use of a battery; not only to avoid higher costs but for even more important for better environmental performance.

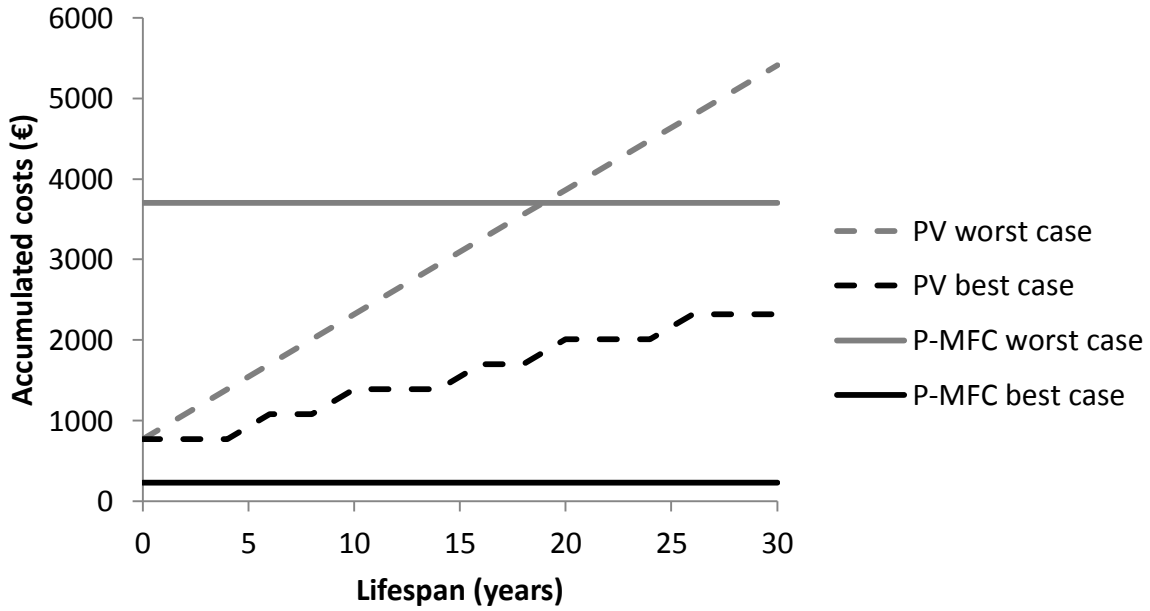

Figure 7.7: Accumulated costs over a 30 years lifespan of a stand-alone PV solar system and a stand-alone P-MFC system. PV worst case is with a lifespan of the battery pack of 2 years, PV best case is with a lifespan of the battery pack of 5 years. P-MFC worst case is based on 0.2 W m^{-2} and optimized costs of €9.26 m^{-2}, P-MFC best case is 3.2 W m^{-2} and optimized costs of €9.26 m^{-2}.

Large scale wetland-electricity production

For large-scale wetland-electricity production technical adjustments are needed. The currently small-scale systems and first up-scaled system on the NIOO roof are not suitable for hectare size (or bigger) surfaces. The system would be much too capital intensive. For large-scale electricity production a tubular system could be produced like proposed by Timmers 2012 (17). 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. When assuming bulk prices for the materials (Table 7.1) and 25% extra costs for installation and maintenance 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. Current electricity bulk prices in Europe are around €0.05 kWh^{-1}. At a 30 year lifespan and a power output of 1.75 kWh m^{-3} $year^{-1}$ (0.2 W m^{-2} as measured by Timmers 2012 (17)) costprice would be €0.02 kWh^{-1}. When power output would increase to 28 kWh m^{-3} $year^{-1}$ costprice with a 30 year lifespan of the system would be €0.001 kWh^{-1}. 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.

7.2.3 Availability

We assumed on forehand that the P-MFC could produce electricity day and night, which holds for lab-situations. Under natural conditions on the roof, however, the cathode showed a diurnal rhythm, leading to a daylight-dependent system for at least part of the runtime of the experiment. Anode, however, did not show any daylight dependence. The cathode performance should be improved to make electricity generation with the P-MFC daylight independent. We showed in the same chapter that we are able to produce electricity as long as the system is not frozen. In the Netherlands this would be approximately 11 months a year in total, in other regions it might be 12 months per year.

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. As seen in the business case for decentralized electricity production, there is a large economic benefit to avoiding the use of batteries. Apart from the economic feasibility, batteries are polluting (17) and should therefore be avoided altogether. 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.

When it comes to large-scale electricity generation with the P-MFC again the battery/storage function of the system can be interesting. Currently problems are arising within Europe due to peak electricity production during sunny days by solar panels. The electricity grid needs to be carefully balanced to avoid power failures and this gets increasingly difficult with an increasing number of weather dependent systems connected to the grid. In Europe this had not led to large problems yet, thanks to the number of options to shut down other power sources at peak performance of the solar panels for example. Other, non-European, electricity grids are less stable and developed which leads to problems when demand is higher than supply or the other way around. Recently a big power failure in India led to large problems (34). Even if the P-MFC can't function as a battery in itself, it provides stable electricity during the day, which is an asset for a balanced electricity grid.

7.3 Concluding remarks

Based on four years of research we can conclude that there is still a lot of work to be done. Technologically we still face numerous challenges. Comparing results from the research to literature has led to new questions about biomass growth and allocation, carbon flux into and out of the soil and consequently the theoretical amount of electricity that can be produced. Possible explanations for these different results are at best an estimated guess. We were not able to increase power output to 3.2 W m-2. That doesn't mean, however, that

we will not be able to come closer to that estimated maximum. Based on the biomass calculations we can conclude that we probably need at least 4.6 years to fully grow the underground biomass into the P-MFC of chapter 2, which is over 2 times as long as the longest experiment until now. We could prove nor disprove the possibility of achieving this theoretical power output. We have identified some technical challenges, however, that need to be overcome before applying the P-MFC in society: cathode-performance, substrate limitation at the anode, anode-cathode distance, scaling-up of the system and outdoor performance of the system.

The P-MFC as a platform technology has many possible applications. Leaving out specific (technical) restraints, one could come up with several applications of different size and scale that can be envisioned with the P-MFC. A few examples would be 1) the Green Electricity Roof; combining electricity production with the advantages of a green roof 2) producing electricity in rice-paddy fields; combining electricity production with food production 3) producing electricity in natural wetlands; combining nature conservation with producing electricity. Traditionally market is viewed as a place where supply meets demand. Demand creates supply, or when available technologies or products cannot meet demand, new technologies or products will be introduced. We already identified that on a global scale energy demand will rise and new technologies need to fulfil certain requirements. It should be renewable, sustainable and available. Even when a technology, like the P-MFC, meets those requirements, it doesn't directly mean that it stands a chance in being implemented in society. We will shortly address the challenge of introducing a new technology into the market.

Innovative technologies, like the P-MFC, face a range of challenges when moving towards commercial application. The P-MFC can be viewed as a radical and innovative technology since it produces electricity in a completely new way. There are several dimensions in innovation, ranging from incremental innovation (doing what we do better) to radical or disruptive innovation (new to the world). Whether the P-MFC can be viewed as a disruptive innovation can only be concluded on hindsight, but one can speculate on forehand. Disruptive innovations provide a set of functions which are likely to appeal to a different segment of the market than was the case with the old technologies. In case of the P-MFC this could be natural area preservation organisations turning into energy producers. Out of every 10 disruptive technologies, 9 fail to reach the market. A growing group of researches shows that factors contributing to new product success are not universal, but depend on a range of technological and market characteristics (35). It shows that specific managerial processes, structures and tools are appropriate for marketing new products. This is based on the fact that both technological and market maturity determine the marketing process.

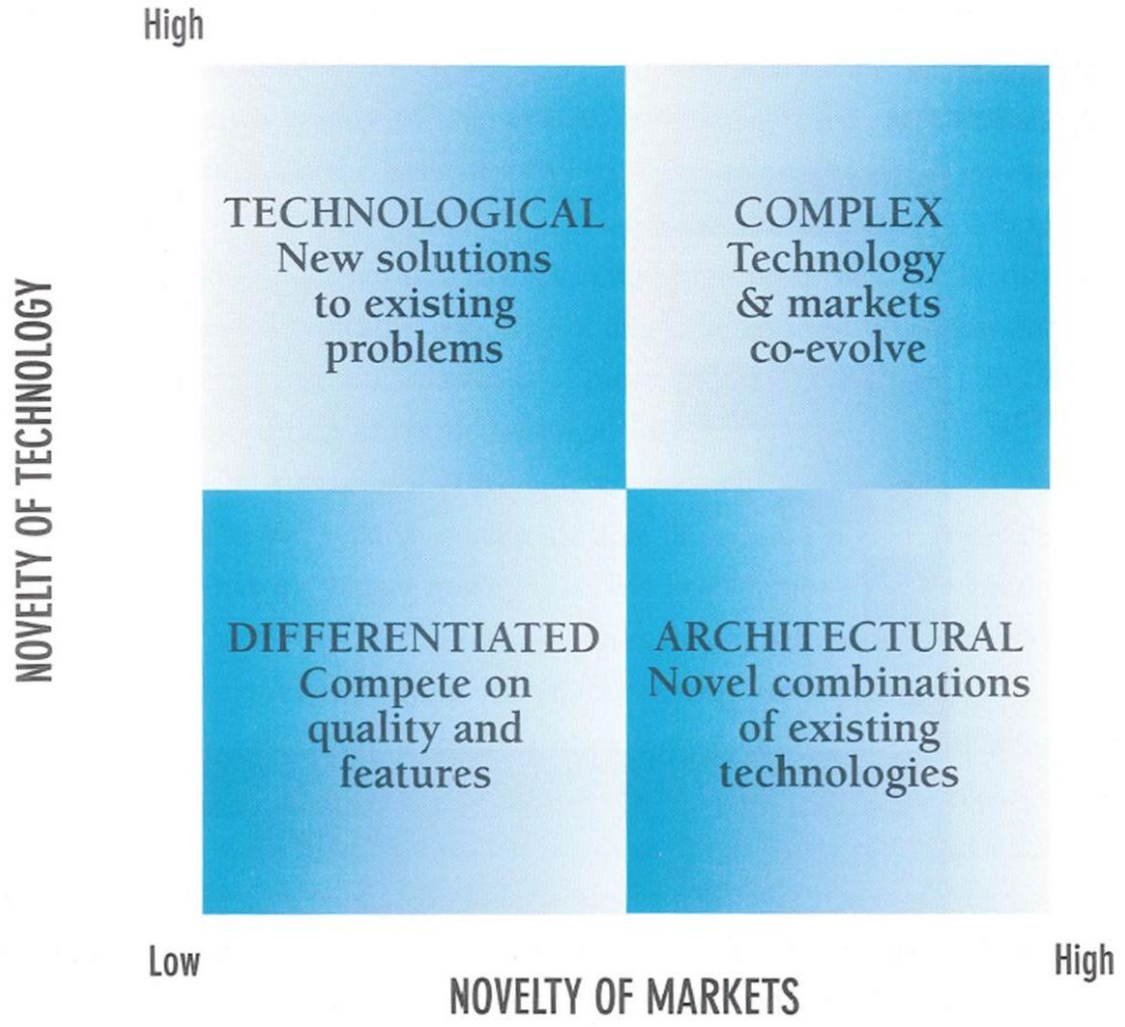

Figure 7.8: Relation between novelty of technology and novelty of markets (35). The P-MFC could be placed in the upper right quadrant

Since the P-MFC is a technology that has high novelty and could develop in novel markets, technology and markets will co-evolve (Figure 7.8).

We researched two sets of design criteria for the P-MFC: technical design criteria to improve the power output of the P-MFC and additional design criteria to assess possibilities for application of the P-MFC. Researching both sets of criteria has led to new questions. Based on what we know now we cannot forecast if the Plant-Microbial Fuel Cell will become a success as new renewable electricity technology, but it certainly asks for trying.

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SAMENVATTING

Door een groeiende wereldpopulatie en stijgende welvaart stijgt de wereldwijde energiebehoefte. De vraag naar specifiek elektriciteit stijgt nog harder. De huidige elektriciteitsvoorziening is vooral afhankelijk van fossiele brandstoffen. Er zijn drie problemen met fossiele brandstoffen: 1) de goed toegankelijke fossiele grondstoffen worden langzaam uitgeput, 2) ze zijn vervuilend (CO_2, NO_x emissies) en 3) ze zijn onevenredig verdeeld over de wereld waardoor er afhankelijkheid van verschillende landen van vaak politiek instabiele regio's ontstaat. Om in de toekomstige elektriciteitsbehoefte te voorzien zijn nieuwe elektriciteit producerende technologieën nodig. Een nieuwe elektriciteit producerende technologie is de Plant-Microbiële Brandstofcel (P-MBC, in het Engels P-MFC). De P-MBC maakt gebruik van levende planten en bacteriën om elektriciteit te genereren. De P-MBC maakt hierbij gebruik van natuurlijke processen die plaatsvinden rondom de plantwortels om rechtstreeks elektriciteit te produceren. De plant produceert organisch materiaal vanuit zonlicht en CO_2 via fotosynthese. Tot 70% van dit organisch materiaal komt in de bodem terecht als dood wortelmateriaal, afbraakproducten en exudaten. Dit organisch materiaal wordt door bacteriën rondom de wortels geoxideerd waarbij CO_2, protonen en elektronen vrijkomen. De elektronen worden door de bacteriën afgegeven aan een electrode (anode) van de P-MBC. De anode is via een externe weerstand gekoppeld aan een kathode. De elektronen die vrijgemaakt zijn aan de anode-kant worden via een draadje en de externe weerstand naar de kathode getransporteerd. De protonen die aan de anode zijn gevormd worden door een membraan of andersoortig scheidingsmateriaal van de anode naar de kathode getransporteerd. Aan de kathode wordt zuurstof, samen met de getransporteerde protonen en elektronen, gereduceerd tot water.

Om de processen die ten grondslag liggen aan de P-MBC en de factoren die zijn vermogen bepalen beter te begrijpen was het doel van dit proefschrift om **design criteria voor de P-MBC te bepalen**. De eerste focus van de design criteria was om het vermogen van de P-MBC te verhogen. Hoe hoger het vermogen, hoe groter de bijdrage aan duurzame elektriciteitsproductie. De ontwikkeling van een nieuwe elektriciteitstechnologie tot een volwaardig commercieel product behelst echter meer dan alleen het vermogen. Daarom hebben we nog een aantal andere factoren onderzocht die de toepassingsmogelijkheden van de P-MBC bepalen.

Vermogen van de Plant-Microbiële Brandstofcel

Toen dit onderzoek startte was het maximaal behaalde vermogen van de P-MBC 0,067 Wm^{-2} terwijl was berekend dat 3,2 W m^{-2} mogelijk zou moeten zijn. We hebben geprobeerd om het vermogen te verhogen door verschillende onderdelen van het systeem te variëren en verschillende processen te beïnvloeden. Dit is beschreven in hoofdstukken 2 t/m 4 van dit proefschrift. We waren in staat om het vermogen te verhogen naar 0,44 W m^{-2} beplant oppervlak.

Drie verschillende soorten planten zijn getest (*Arundo donax, Spartina anglica* en *Arundinella anomala*). Met twee van deze soorten, *Spartina anglica* en *Arundinella anomala*, waren we in staat om gelijktijdig bovengrondse biomassa en elektriciteit te produceren in de P-MBC. *Spartina anglica* leverde meer vermogen dan *Arundinella anomala* (0,22 W m^{-2} vs. 0,021 W m^{-2}). Omdat *Spartina anglica* meer vermogen leverde dan *Arundinella anomala* en *Spartina anglica* bovendien een zout-tolerante soort is die onder uiteenlopende omstandigheden over de hele wereld groeit, hebben we de rest van het proefschrift gefocust op *Spartina anglica*.

Met *Spartina anglica* waren we in staat om het vermogen te verhogen naar 0,22 W m^{-2}, ruim 3 keer zoveel als behaald was in het eerste experiment van Strik et al. in 2008 . We waren echter niet in staat om dit vermogen voor langere tijd te leveren en uit polarisatiecurves bleek dat de anode het vermogen beperkte. Het plantengroeimedium wat we gebruikten in de P-MBC bevatte veel nitraat. Door nitraat uit het medium te verwijderen en het te vervangen door ammonium, waren we in een nieuw experiment in staat om een maximaal vermogen van 0,21 W m^{-2} te behalen en een hoger vermogen over langere tijd te kunnen leveren; 0,15 W m^{-2}. Het verwijderen van sulfaat uit het plantengroei medium leidde niet tot een hoger vermogen, maar tot een lager vermogen. Het effect van de zwavel-cyclus die hier vermoedelijk een rol in speelt is nog niet volledig duidelijk en zou verder moeten worden onderzocht.

Wanneer we de cijfers nemen die door Kuzyakov in literatuur beschreven wordt voor de koolstof-efflux in de vorm van CO_2 van grasland (0,09-0,12 kg C m^{-2} $jaar^{-1}$), dan zouden we theoretisch 30-40 mol elektronen per m^2 per jaar produceren. Dit zou leiden tot een stroomdichtheid van 0,092-0,122 A m^{-2}, die we gedurende dit onderzoek regelmatig hebben overschreven. Bij een voltage van 0.5 – wat een voorzichtige schatting van 50% MFC-efficiëntie is – dan zouden we een vermogen van 0,046-0,061 W m^{-2}. Ook dit is lager dan tijdens dit onderzoek is bereikt. Er zijn drie mogelijke verklaringen voor het verschil:

- Wij hebben ons reëel behaalde vermogen overschat doordat we de groei van onze biomassa hebben overschat
- De data van Kuzyakov onderschatten de mogelijke efflux van koolstof uit de bodem. Dus in praktijk is de afbraak van organisch materiaal sneller dan verondersteld en meer elektronen worden vrijgemaakt.
- Microbiële activiteit en koolstofafbraak wordt versneld door de P-MBC doordat een nieuwe elektronenacceptor wordt aangeboden aan de bacteriën in de vorm van een electrode.

De resultaten met het nieuwe plantengroeimedium hebben we behaald in een vlakke-plaat ontwerp P-MBC (hoofdstuk 4). Het nieuwe ontwerp resulteerde in een lagere interne weerstand voor de P-MBC vergeleken met het hiervoor gebruikte buisvormig ontwerp. Om een maximaal vermogen van 3,2 W m^{-2} te kunnen behalen, mag de interne weerstand van de P-MBC maximaal 0.094 $\Omega.m^2$ zijn. Interne weerstand in onze experimenten varieert van 2-

10 $\Omega.m^2$, waardoor het vermogen niet hoger wordt dan 0,4 W m^{-2} en stroomdichtheid niet hoger wordt dan 1,6 A m^{-2}. In het buisvormig systeem de hoogste partiële interne weerstand was transportweerstand. Deze was beperkt in het vlakke plaat ontwerp dankzij een kleinere afstand tussen anode en kathode. De afstand tussen anode en kathode is een belangrijk aspect bij het ontwerpen van een P-MBC.

Toepasbaarheid van de Plant-Microbiële Brandstofcel

In hoofdstuk 5 en 6 hebben we de toepasbaarheid van de P-MBC onderzocht. In hoofdstuk 5 hebben we een eerste poging gedaan om het systeem onder natuurlijke buitenomstandigheden te laten functioneren bij extreme condities op een Nederlands dak. De P-MBCs produceerden elektriciteit op het dak zolang de anode niet volledig bevroren was. De planten overleefden de winter niet. Elektriciteitsproductie kwam na de vorstperiodes echter weer terug. De anode-potentiaal van de twee verschillende ontwerpen die we gebruikten was stabiel, maar het kathode-potentiaal vertoonde een dag-nacht cyclus doordat de kathode was overgroeid met algen. Om 24 uur per dag elektriciteitsproductie te garanderen zal dan ook de kathode moeten worden verbeterd.

De energiebalans van de P-MBC is onderzocht in hoofdstuk 6. De energiebalans is afhankelijk van de initiële energie-input benodigd voor de constructie, het geproduceerd vermogen en de levensduur van het systeem. Het hoogst behaalde vermogen dat over langere tijd geleverd kon worden in dit onderzoek was 0,2 W m^{-2} or 1,75 kWh m^{-2} $jaar^{-1}$. Gebaseerd op slechts de elektriciteitsproductie van het systeem, zou het systeem een terugverdientijd – de tijd benodigd om net zoveel energie te produceren als er initieel ingegaan is – van 136 jaar hebben. Dit is een overschrijding van de levensduur van de materialen. Op dit moment is de P-MBC technologie dus niet hernieuwbaar wanneer we naar de energiebalans kijken. Ofwel de energie-input moet naar beneden, ofwel het vermogen van het systeem moet omhoog om een energetisch hernieuwbaar systeem te krijgen. Wanneer we echter naar mogelijke bijproducten van het systeem kijken, zoals warmte-isolatie van het gebouw wanneer we het systeem toepassen als groen dak, dan kunnen we de vermeden warmte die benodigd is voor het gebouw meenemen in de energiebalans. In dat geval zou de P-MBC zelfs bij het huidig vermogen een terugverdientijd hebben van iets meer dan 30 jaar.

De duurzaamheid van de P-MBC is onderzocht gebaseerd op milieu-performance, maatschappelijke acceptatie en economische haalbaarheid. In hoofdstuk 6 hebben we de milieu-performance onderzocht en geconcludeerd dat bij de huidige stand van zaken de P-MBC nog niet kan concurreren met andere energiesystemen op het gebied van milieu-performance. Daartoe zal het materiaalgebruik omlaag moeten, specifiek het gebruik van actief kool, en sommige materialen zullen volledig vermeden moeten worden, zoals gouddraad en Teflon-gecoat koperdraad. Om tot deze conclusie te komen hebben we Life Cycle Assessment (LCA) methodologie gebruikt. Deze methodologie wordt veelvuldig gebruikt voor het beoordelen van de milieu-impact van een technologie of product van oorsprong tot afbraak. Normaal gesproken wordt LCA methodologie vooral toegepast op

bestaande systemen. De P-MBC is een systeem wat nog volop in ontwikkeling is en is daardoor moeilijk te beoordelen via LCA methodologie. We kunnen onze benadering dan ook beschouwen als een innovatieve manier om de methodologie te gebruiken.

Maatschappelijke acceptatie van een product of technologie is zeer afhankelijk van de specifieke toepassing ervan. Wanneer de P-MBC toegepast wordt op een groen dak, dan zal de esthetische waarde van het product belangrijk zijn voor de gebouw-beheerder of eigenaar omdat dit het duurzame imago van het bedrijf benadrukt. Wereldwijd heft 52% van de bedrijven aangegeven te willen investeren in duurzame oplossingen, zelfs wanneer deze duurder zijn dan niet-duurzame oplossingen. Wanneer we naar de decentrale toepassing van de P-MBC in ontwikkelingslanden kijken, dan kunnen we ervan uitgaan dat ook hier maatschappelijke acceptatie hoog zal zijn. Boeren in ontwikkelingslanden behoren tot de armste groep mensen ter wereld. Elektriciteit produceren terwijl ze tegelijkertijd met hun bekende gewassen voedsel verbouwen, biedt hen de mogelijkheid om hun inkomen te verhogen. Bovendien zal decentrale toepassing van de P-MBC in ontwikkelingslanden een mogelijke toegang tot elektriciteit kunnen zijn voor de 1,2 miljard mensen wereldwijd die nog geen toegang hebben tot elektriciteit. Dit kan hen helpen om zowel economisch als sociaal verder te ontwikkelen. Ook grootschalige elektriciteitsproductie kan in de toekomst een mogelijke toepassing zijn voor de P-MBC. Dit zou mogelijk betekenen dat de elektriciteitscentrale eruit zal zien als moerasachtig gebied. Wederom is de esthetische waarde van groot belang, maar ook kan de P-MBC op deze manier economische waarde toevoegen aan al bestaande groene gebieden. Deze gebieden krijgen daardoor naast hun impliciete waarde als natuurgebied ook expliciete economische waarde door elektriciteit te produceren. Het is dan ook te verwachten dat de P-MBC op vele wijzen toegepast maatschappelijk acceptabel zal zijn.

Economische haalbaarheid van de P-MBC technologie hebben we beoordeeld op basis van drie business cases: het groen elektriciteitsdak, decentrale elektriciteitsproductie in afgelegen gebieden en grootschalige elektriciteitsproductie in moerasachtige gebieden. Totale kostprijs van het groen elektriciteitsdak bij de huidige stand van de technologie zou meer dan €600,- per m^2 zijn, inclusief installatie. Wanneer echter het systeem op grote schaal geproduceerd zou kunnen worden, dan mag men ervan uitgaan dat bulkprijzen gerekend kunnen worden voor de verschillende onderdelen van het systeem. Bovendien zal de prijs voor installatie drastisch dalen. De prijs zal daarmee naar verwachting dalen tot ongeveer €30,- per m^2. Bij deze prijs zou het ook aantrekkelijk zijn voor decentrale toepassing in afgelegen gebieden. Voor grootschalige elektriciteitsproductie zijn technische aanpassingen van de P-MBC benodigd. Het systeem zou ontworpen kunnen worden als een horizontale buis, zoals voorgesteld is door Timmers in 2012. Deze buis zou in bestaande groene, natte gebieden geïmplementeerd kunnen worden om op grote schaal elektriciteit te produceren. Dankzij een verwachte “economy of scale” zal de kostprijs van het systeem drastisch dalen door beperking van het materiaal gebruik en lagere onderhoudskosten. Een kostprijs van €1,13 per strekkende metere buis met een omtrek van 1 m is wellicht haalbaar.

Dit zou betekenen dat het systeem €0,35-5,65 per geïnstalleerd vermogen (W) zal kosten. Wanneer technologische problemen voor dit systeem kunnen worden getackeld en het horizontale-buissysteem opgeschaald kan worden, dan zou het systeem kunnen concurreren met bestaande fossiele elektriciteitsproductie.

Beschikbaarheid van elektriciteit is afhankelijk van beschikbaarheid van de bron en de mogelijkheid voor opslag. Wanneer we een decentraal systeem voor elektriciteitsproductie zouden willen bouwen wat op ieder gewenst moment elektriciteit kan leveren, dan zal een systeem ontwikkeld moeten worden wat weersonafhankelijk is om het gebruik van batterijen te voorkomen. Dit is nog niet mogelijk met de P-MBC. De P-MBC biedt echter mogelijkheden om het gebruik van batterijen te voorkomen. Mogelijk kan het systeem zelf als batterij fungeren door de hoge capacitiviteit van het systeem. Timmers heeft al aangetoond dat de capacitiviteit van de P-MBC, met andere woorden: de mogelijkheid om elektronen intern op te slaan, hoog is. Dit biedt mogelijkheden voor opladen en gebruiken van de beschikbare elektronen wanneer deze nodig zijn. De mogelijkheid tot het gebruik van de P-MBC als batterij zal echter verder onderzocht moeten worden.

SUMMARY

Due to a growing world population and increasing wealth energy demand is rising. Apart from the general increase in energy demand, a specific and even faster increase in electricity demand can be seen over the last decades. Electricity generation is mainly dependent on fossil fuels. There are three main problems with fossil fuels: 1) easily accessible fossil fuels are being depleted, 2) they are polluting (CO_2, NO_x emissions) and, 3) they are unevenly distributed over the world, leading to dependence of several countries on sometimes politically unstable regions. 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). The P-MFC uses living plants and bacteria to generate electricity. The P-MFC makes use of naturally occurring processes around the roots of plants to directly generate electricity. The plant produces organic matter from sunlight and CO_2 via photosynthesis. Up to 70% of this organic matter ends up in the soil as dead root material, lysates, mucilage and exudates. This organic matter can be oxidized by bacteria living at and around the roots, releasing CO_2, protons and electrons. Electrons are donated by the bacteria to the anode of a microbial fuel cell. The anode is coupled, via an external load to a cathode. The electrons flow through a wire and external load from anode to cathode. The protons that were released at the anode side travel through a membrane or spacer towards the cathode. At the cathode ideally oxygen is reduced together with protons and electrons to water.

To further understand the underlying processes of the P-MFC and the factors that influence its power output, the objective of this thesis was to **determine 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 to a commercial 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.

Power output of the Plant-Microbial Fuel Cell

At the start of this thesis the maximally achieved power output was 0.067 W m^{-2}, while 3.2 W m^{-2} was estimated to be theoretically possible. We tried to improve power output by adjusting different parts and processes of the system. This was discussed in chapters 2 through 4 of this thesis. 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. *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 thesis.

With *Spartina anglica*, the 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. Power output could not be maintained over a longer period of time and polarisation curves showed the anode to be limiting the power output. 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 longer period of time; 0.15 W m^{-2}. Removing sulphate from the plant-growth medium did not lead to higher power densities. Removal of sulphate from the plant-growth medium resulted in a decrease in power output. 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} $year^{-1}$, 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 during this and other researches. 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 (chapter 4). The flat-plate design resulted in a lower internal resistance for the P-MFC as compared to the previously used tubular P-MFC. In total internal resistance can maximally be 0.094 Ω.m^2 in order to reach 3.2 W m^{-2}. Internal resistance in our experiments ranges from 2-10 Ω.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

In chapters 5 and 6 we assessed the applicability of the P-MFC. In chapter 5 we made a first attempt of putting the P-MFC under natural outdoor circumstances under harsh conditions on a Dutch roof. 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.

The energy balance of the system was assessed in Chapter 6. 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} $year^{-1}$. 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. 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. In chapter 6 we discussed 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. 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 Life Cycle Assessment (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. 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.

DANKWOORD

Het is af! En jongens wat heb ik een plezier gehad! Er was enige overredingskracht van Bert voor nodig om me ervan te overtuigen dat promoveren wel wat voor mij was, maar hij kreeg gelijk. Het afmaken ging niet vanzelf, maar ik heb gelukkig nooit het gevoel gehad dat ik er alleen voor stond. Cees, Bert en vooral David, bedankt voor het vertrouwen wat jullie in me gesteld hebben en het zelfvertrouwen wat jullie me hebben gegeven.

Op de vraag hoe het op mijn werk was, heb ik de afgelopen vier jaar steevast geantwoord dat ik de leukste baan van de wereld had. En dat was ook zo! Natuurlijk vond ik mijn werk inhoudelijk leuk, maar mijn collega's maakten elke dag weer tot een feestje. Koffiepauzes die geregeld langer dat een kwartier (en een uur) duurden vormden niet alleen een fijn sociaal moment op de dag, maar zorgden ook voor een stukje externe motivatie wanneer ik geen motivatie in mezelf kon vinden. En dat waren de "gewone" dagen. De "bijzondere" dagen, waarop iets extra's te doen was, waren nóg leuker. Ik heb vele warme herinneringen aan borrels, themaborrels, bandrepetities en –optredens, kerstdiners, vakgroepuitjes en –reizen en schaatsfestijnen. Slopend, al die avonden waarop ik het licht uitdeed (en het alarm liet afgaan), maar ik kon niet eerder naar huis: het was té gezellig! Collega's bedankt!

Mijn promotietraject kreeg extra kleur door de halfjaarlijkse bijeenkomsten met het Europese PlantPower team. Het is heerlijk om samen met anderen aan dezelfde materie te werken en daarover inhoudelijk te discussiëren. En het is net zo fijn om die inhoudelijke discussies af te sluiten in de kroeg. Eén van mijn stellingen – die over effectieve teams – is ingegeven door de samenwerking binnen het PlantPower team. Ik heb genoten van de effectieve en constructieve manier van samenwerken met jullie: jullie zouden goede rugbyers zijn, bedankt!

Naast het werk heb ik gelukkig ook nog wat tijd gevonden om te ontspannen. Niets is zo ontspannend als na een dag hard schrijven afgebeuld te worden op de rugbytraining en je laatste beetje frustratie te botvieren een tacklebag of rugbykerel. Uiteindelijke beloning was doorgaans een knuffel, een boel slechte grappen en een jug bier ☺. Maar ook muzikaal viel er genoeg te ontspannen. Lieve Vivae, bedankt voor de fijne zondagen en repetitieweekenden. Ik kom gauw weer meedoen! Beste SOS'ers, hoewel meedoen altijd nóg leuker is, is het een genot om naar jullie te luisteren. Mijn productiefste weekend tijdens mijn promotie was vermoedelijk het bigband-weekend. Met jullie muziek op de achtergrond heb ik in een paar uur een heel artikel geschreven (zie hoofdstuk 5)!

Lieve familie en vrienden. Mijn werk heft me regelmatig opgeslokt in de afgelopen vier jaar. Ik heb jullie bij tijd en wijlen verwaarloosd. Toch waren jullie er steeds weer voor me als ik even uit mijn bubbel stapte. In het bijzonder gedurende het laatste half jaar heb ik op "planeet proefschrift" geleefd. Het is heerlijk om bij terugkeer op aarde te ontdekken dat jullie er nog zijn. Dank jullie wel! De Vikingen (ODIN ODIN) hebben we ruim 10 jaar geleden een lijfspreuk toegedacht en het wordt tijd dat ik daar weer (wat meer) naar ga leven:

Weet gij een vriend

Die gij wel vertrouwt

Wilt gij van hem goed verwerven

Wees gemeenzaam van geest

Met gaven gul

Verzuim niet vaak een bezoek

(Hávamál, spreuk 34)

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It's done! Finished! And I had a lot of fun. It took some perseverance of Bert to convince me that doing a PhD was a job for me, but he was right. Finishing the manuscript was tough. But I never felt I had to do it alone. Cees, Bert and especially David, thank you for you trust in me and the self-confidence you gave me.

To the question "how's work" I've always answered in the past four years that I had the best job in the world. Because it was true! Off course I liked the contents of it, but my colleagues made every day into a small party. Coffee-breaks that generally lasted longer than 15 minutes (+ 1 hour), were a nice social moment in the day. Moreover, they provided necessary external motivation as well from time to time. And those were the "normal" days. On "special" days, there was something extra to do. I have warm memories of "borrels", theme-drinks, band rehearsals and concerts, Christmas dinners, departmenttrips and tours and ice-skating events. Those nights, when I turned off the lights (and set off the alarm), were tiresome, but I couldn't leave earlier: I had too much fun! Dear colleagues, thank you for the great time!

My PhD-time was extra fun thanks to the PlantPower meetings throughout Europe. It's great to be working on the same matter together with others and discuss about it. And it's equally nice to finish those discussions in the pub, enjoying a Belgian/German beer or French cidre. One of my propositions – the one about effective teams – was inspired by the collaboration within the PlantPower team. I loved the effective and constructive cooperation within the team: you would make great rugby-players, thank you!

After work there was some time left to relax. After a day of hard work, nothing is as relaxing as being pushed around at a rugby training and releasing every last bit of frustration in hitting a tacklebag or tough guy. Final reward was generally a hug, a bunch of bad jokes and a jug of beer ☺. Apart from sports, music was another good way to relax. Dear Vivae, thank you for the nice Sundays and rehearsal-weekends. I'll join you again for the next project! Dear Sound of Science, even though joining you is even more fun, listening to you is a pleasure. My most productive weekend during my PhD was probably the bigband-weekend. With your music in my ears I wrote a complete chapter of my thesis within a day (chapter 5)!

Dear friends and family. On occasion my work has fully captured me during the last four years. I have neglected you from time to time. But still you were there for me when I escaped from my bubble. Especially during the last half year I lived on "planet thesis". It's fantastic to find out at my return on planet earth, that you're still here! Thank you ☺. The Vikings (ODIN ODIN) assigned me a piece of wisdom already 10 years ago and it's about time I start living according to it (again):

If you find a friend

You fully trust

And wish for his good-will

Exchange thoughts

Exchange gifts

Go often to his house

(Hávamál, motto 34)

ABOUT THE AUTHOR

Marjolein Helder (1983) was born in Amsterdam and grew up in the Zaan-area north of Amsterdam. After finishing her VWO at the Bertrand Russell College in Krommenie, she started her studies in Environmental Sciences at Wageningen University in 2001. During seven years in Wageningen she finished both BSc and MSc in Environmental Sciences. She majored in Environmental Technology, specifically focused on bio-energy, and did a minor in management studies. After her MSc-graduation in 2008 she started her PhD-project about living plants that generate electricity, while combining it with working for Wageningen Business School. After a year of research and entrepreneurship courses, she established the spin-off company Plant-e, together with her colleague David Strik. With Plant-e, Marjolein and David acquired several subsidies and grants to further develop the technology and the products based on it. After her PhD-graduation, Marjolein will devote her time fully to Plant-e to further commercialize the technology to generate electricity with living plants. Outside working-hours she resides in several boards (KLV alumni association, Rugby Club Wageningen), she plays rugby and sings in a choir (Vivavoce) and a bigband (Sound of Science).

LIST OF PUBLICATIONS

Helder, M., Strik, D.P.B.T.B., Hamelers, H.V.M., Kuhn, A.J., Blok, C., Buisman, C.J.N. – Concurrent bio-electricity and biomass production in three Plant-Microbial Fuel Cells using Spartina anglica, Arundinella anomala and Arundo donax – 2010 – Bioresource Technology 101 (10) , pp. 3541-3547

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GRANTS AND NOMINATIONS

Valorisation Grant Phase 1 – Strik, D.P.B.T.B., Helder, M., - *Plant-e – Living plants generate electricity* – STW – 2011

Postcode Lottery Green Challenge – Helder, M., Strik, D.P.B.T.B, - *Plant-e – Living plants generate electricity* – Postcode Lottery and DOEN Foundation – Finalist 2011

Life-sciences pre-seed grant – Helder, M., Strik, D.P.B.T.B., - Plant-e – Living plants generate electricity – NGI/ZonMW – 2012

Communications award – Helder, M. – Nationale Haringpartij – nominee 2012

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Socio-Economic and Natural Sciences of the Environment

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The Netherlands Research School for the
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born on 30 March 1983 in Amsterdam, the Netherlands

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The SENSE Research School declares that **Ms. Marjolein Helder** has successfully fulfilled all requirements of the Educational PhD Programme of SENSE with a work load of 63 ECTS, including the following activities:

SENSE PhD Courses

- Environmental Research in Context
- Research Context Activity: Co-organizing Masterclass on "Sustainable Bio-energy and Innovation", Wageningen, February 2009
- Sustainable bio-energy and innovation

Other PhD Courses

- Entrepreneurial Boot Camp, School of Business, Wisconsin University, Madison, USA, and Dutch Agro-Food Network of Entrepreneurship, Wageningen University, Netherlands
- STW Valorisation workshop, Technologiestichting STW
- Interactief voor de groep
- Writing and presenting scientific papers

Management and Didactic Skills Training

- Board member of KLV alumni association, 2008-2012
- Supervising new and potential students, Information days for new students, 2008-2010
- Founding and running spin-off company Plant-e
- Supervision of 4 MSc theses, 2 BSc theses and 5 internships
- Editing course material, lecturing and supervising for the course Introduction Environmental Technology

Oral Presentations

- *The electricity producing green roof: the ultimate solution for climate mitigation in the city?* Climate proofing cities, 1 December 2009, Amsterdam
- *Year round electricity production with living plants in a Plant-Microbial Fuel Cell*. 1st International PlantPower symposium, 10 Feburary 2011, Gent, and 3rd International Microbial Fuel Cell conference, 3-5 June 2011, Leeuwarden
- *Resilience of a Plant-Microbial Fuel Cell during Dutch winter*. 3*rd* International Rhizosphere conference, 25-30 October 2011, Perth

SENSE Coordinator PhD Education and Research

Mr. Johan Feenstra

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