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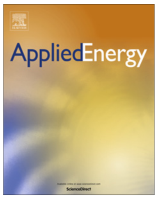
Applied Energy 185 (2017) 642–649

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy



Electricity from wetlands: Tubular plant microbial fuels with silicone gas-diffusion biocathodes

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HIGHLIGHTS

- Tubular PMFC with oxygen reducing biocathode was applied in salt marsh and peat soil.
- Oxygen was passively supplied in the cathode via a silicone gas diffusion layer.
- Long term power generation with both biological anode and cathode in peat soil.
- Maximum long term power generation of 21 mW m^{-2} plant growth area was achieved.
- Salt marsh biocathode only started with pure O_2 likely due to substrate crossover.

ARTICLE INFO

Article history:
Received 31 May 2016
Received in revised form 14 October 2016
Accepted 28 October 2016
Available online 10 November 2016

Keywords:
Plant microbial fuel cell
Oxygen reducing biocathode
Silicone gas diffusion layer
Spartina anglica salt marsh
Phragmites australis peat soil

ABSTRACT

Application of the plant microbial fuel cell (PMFC) in wetlands should be invisible without excavation of the soil. The preferred design is a tubular design with the anode directly between the plant roots and an oxygen reducing biocathode inside the tube. Oxygen should be passively supplied to the cathode via a gas diffusion layer. In this research silicone was successfully used as gas diffusion layer. The objective of this research is to start-up an oxygen reducing biocathode in situ in a tubular PMFC applied in a *Phragmites australis* peat soil and a *Spartina anglica* salt marsh. PMFCs with a biocathode were successfully started in the peat soil. Oxygen reduction is clearly catalysed, likely by microorganisms in the cathodes, as the overpotential decreased resulting in an increased current density and cathode potential. The maximum daily average power generation of the best peat soil PMFC was 22 mW m^{-2}. PMFCs with a biocathode in the salt marsh only started with pure oxygen diffusion reaching a maximum daily average power generation of 82 mW m^{-2}. Both wetland PMFCs were successfully started with natural occurring microorganism in the anode and cathode. Calculations show that the power density can be increased by improving the PMFC design limiting crossover of oxygen and substrate.

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1. Introduction

The plant microbial fuel cell (PMFC) is an emerging technology which generates sustainable electricity from living plants [1]. Rhizodeposits are oxidized by electrochemical active bacteria in the anode of the PMFC producing electrons. These electrons are transported to the cathode via an external circuit where energy is harvested. Oxygen is reduced to water at the cathode. The PMFC is a sustainable technology as it has no competition for arable land or nature, the substrate (i.e. rhizodeposits) is renewable and the product is plain water [1]. Currently, 0.24 W m^{-2} plant growth area (PGA) is generated continuously in the lab (two week average) [2]. PMFCs were demonstrated in rice paddy fields, green roofs and are commercially applied on 100 m^2 PGA to power public lighting [3–6]. The actual carbon sources of the PMFC are uncertain because rhizodeposition is difficult to reliably quantify as microorganisms rapidly decompose the organics [7]. Rhizodeposition consists of a large variety of carbon sources [8] that could be oxidized in the PMFC [9].

PMFC is preferably applied in wetlands because of the required anaerobic conditions [1]. Besides the enormous land covered by wetlands (8–10 million km^2 worldwide [10]) also the presence of alternative electron donors is beneficial for PMFC [11]. Additional electron donors likely result in a higher power output in the substrate limited PMFC [2]. Possible alternative electron donors present in wetlands are among others sulphide, organic fertilizer,

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http://dx.doi.org/10.1016/j.apenergy.2016.10.122
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stored ‘fossil’ organic matter (e.g. peat matter), biodegradable dissolved organic matter and dead biomass (e.g. phytoplankton, algae, seeds). Electricity is already generated by oxidizing these alternative electron donors in sediment in the so-called sediment microbial fuel cell (SMFC). SMFC have been applied in for example marine and river sediments [12–14]. Application of PMFC in wetlands will oxidize both the electron donors from rhizodeposits as the present alternative electron donors.

Oxygen is preferred as electron acceptor, because of the high redox potential (0.6 V vs Ag/AgCl at pH 7) and water as product [15]. However, the reduction of oxygen on graphite is slow and must be catalysed in order to increase the current densities in the PMFC [5,16]. One of the best and most common catalyst for oxygen reduction is platinum. However, the price of platinum makes it undesirable for application in a low density technology like the PMFC [17]. Oxygen reduction on graphite can also be catalysed by self-replenishing microorganisms. The first catalysis of oxygen reduction was performed by Bergel et al., who in situ grew a biofilm on a stainless steel cathode in seawater [18]. This breakthrough resulted in plenty of research focusing on biocathodes in microbial fuel cells [19]. Biocathodes have been among others applied in the rice rhizosphere [20] and are successfully integrated in PMFC [2]. Oxygen reduction is catalysed by microorganisms up to a current density of 0.9 A m^{-2} on graphite cathodes [21], which is higher than the maximum long term current density of a PMFC (0.4 A m^{-2} PGA) [2].

Application of PMFC in wetlands should be invisible without excavation of the soil to minimize the disturbance of the wetland. The preferred design is a tubular design with the anode on the outside directly between the plant roots and an oxygen reducing biocathode inside the tube [22] (Fig. 1). Oxygen should be passively supplied to the cathode, eliminating the need for energy intensive pumping of oxygen. Microbial fuel cells have been applied with passive oxygen diffusion through a polytetrafluoroethylene (PTFE) layer [23]. The production of PTFE has a negative impact on the environment, i.e. causes ozone depletion. Therefore PTFE should be avoided in microbial fuel cells [24]. An alternative for PTFE is silicone, which has a higher permeability for oxygen compared to other plastics and elastomers as PTFE [25].

The objective of this research is to start-up a tubular PMFC with a new design which can be directly installed in wetlands without the need for active pumping or aeration. Such a design was not developed before and should have an integrated oxygen reducing biocathode and passive oxygen diffusion. In this research we show for the first time that a silicone tube can be used as a gas diffusion layer within bioelectrochemical systems. The biocathode is started in situ using the locally present microorganisms and nutrients without extra inoculation of microorganisms in the cathode. The investigated tubular PMFC design with in situ start-up of the bioanode and biocathode can be used for real applications in wetlands. Three tubular PMFC with a biocathode were applied in a *Phragmites australis* dominated peat soil and three in a *Spartina anglica* dominated salt marsh. Both wetlands are widespread in the Netherlands and therefore used in this research [26]. The differences in biocathode start-up, short and long term biocathode performance, power output and limitations are analysed and described in this paper. Also possible improvements to the tubular design are suggested.

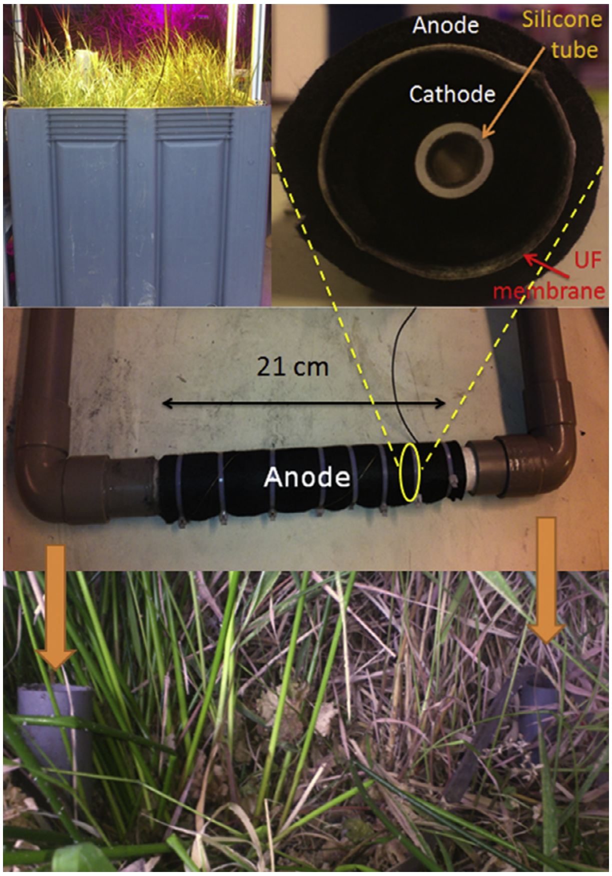

Fig. 1. Experimental setup. Top left: Wetland box in lab with *Spartina anglica* salt marsh. Top right: Cross section of the tube. Middle: Completed tubular PMFC before installation in the wetland. Bottom: Tube installed in *Phragmites australis* peat soil.

2. Materials and methods

2.1. Experimental setup

Three tubular PMFCs were installed at approximately 10 cm below the surface level in a *Phragmites australis* dominated peat soil and three tubular PMFCs in a *Spartina anglica* dominated salt marsh. The wetlands were installed polypropylene pallet boxes with an area of 1.2 m by 1.0 m and a depth of 1.0 m as explained in earlier research [27]. The tubes consisted from outside to inside of an anode, membrane, cathode and a silicone tube (ISS 6, Lapp Group, Stuttgart, Germany) (Fig. 1). The anode was made of 3 mm thick graphite felt with an area of 210 by 90 mm (CGT Carbon GmbH, Asbach, Germany) and a graphite stick current collector. The anode is wrapped round the outside of a 300 mm ultrafiltration membrane with an inner diameter of 24 mm (MEMOS Membranes Modules Systems GmbH, Pfullingen, Germany). 5 extra holes (±1 mm diameter) were made in the ultrafiltration membrane to enable exchange of microorganisms from the anode to the cathode. The holes resulted in a water flooded cathode which was required to transport the nutrients needed for the growth of the biocathode from the wetland to the cathode. The holes did not result in a short circuit of the PMFCs. This was tested prior to installation in the wetland by measuring the resistance between the cathode and anode. The graphite felt cathode had the same dimensions as the anode with a golden wire current collector and wrapped round a silicone tube and placed inside the ultrafiltration membrane (Fig. 1). The silicone tube had an inner diameter of 6 mm and a wall thickness of 0.9 mm. A silicone tube was selected because silicone is highly permeable for oxygen [25] and as such can provide oxygen in the cathode. PVC tubes were connected at both ends of the ultrafiltration membrane (Fig. 1). No anolyte or catholyte was added and electrolyte consisted thus purely of the water from the wetlands. Capillaries with 3 M KCl were placed in both the anode and cathode of each PMFC and connected to an Ag/AgCl reference electrode. All electrode potentials in this manuscript are therefore in mV vs Ag/AgCl (+210 mV vs NHE).

2.2. Operation

On day 1, the tubular PMFCs were installed in the wetlands. From the start of the experiment the PMFCs were controlled with a potentiostat at a cathode potential of 150 mV to start the biocathode (MCP, Bank Elektronik - Intelligent Controls GmbH, Pohlheim, Germany) [2,28].

The three PMFCs in each wetland were controlled with one reference electrode, the reference electrode of PMFC1. The distance of the cathodes of PMFC2 and PMFC3 to the reference electrode was approximately 50 cm. For the peat soil PMFCs the cathode control was from day 1 to day 82 (Table 1). Afterwards the peat soil PMFC2 was controlled by an external resistance between the anode and cathode. The external resistance was set at 4000 Ω on day 84, decreased to 2000 Ω on day 87, further decreased to 1000 Ω on day 114. From day 116 until the end of the experiment (day 160), the external resistance was 500 Ω for the peat soil PMFCs. The salt marsh PMFCs were cathode controlled at 150 mV from day 1 to day 82 and also from day 96 to day 136 (Table 1). The salt marsh PMFCs were controlled by an external resistance from day 84 to day 96 and from day 136 until the end of the experiment (day 160). The external resistance was 1000 Ω from day 84 to day 86, 2000 Ω from day 87 to day 93 and 16,000 Ω on day 94, day 95 and from day 136 to day 160. In each wetland, the three cathodes were electrically connected in parallel during controlled cathode potential operation. However, each PMFC was separately operated when the PMFCs were controlled by an external resistance. Pressurized air was pumped through the silicone tubes. This was changed to pure oxygen from day 41 to day 84 for all PMFCs. For the salt marsh PMFC, pure oxygen was also supplied to the silicone tube from day 89 until the end of the experiment.

The water level in the peat soil was kept at 5 cm below the surface level with a float valve connected to a tap water supply. In the salt marsh, a tidal effect was simulated by increasing and decreasing the water level from 5 cm above to 5 cm below the surface level twice every day by pumping the seawater in and out a rain barrel. The temperature in the lab was approximately 25 °C. Each wetland was illuminated by a 600 W LED grow lights during 14 h per day placed 1.5 m above the surface level.

2.3. Measurements

The electrode potentials and the cell voltage were measured and logged identically to previous PMFC research [11]. Polarization measurements were done multiple times to analyse the development of the biocathode, bioanode and the short term current and power generation. On day 20 and day 35 (day 38 for peat soil PMFC1), polarizations of all the PMFCs were performed by controlling the cathode potential and measuring the current in a three electrode set up (n-Stat, Ivium Technologies, Eindhoven, The Netherlands). The cathode potential was gradually decreased and afterwards increased starting and finishing at the cathode open circuit potential in steps of 600 s. On day 84 and day 88, polarization of all the PMFCs were performed by controlling the cell voltage in a two electrode setup. The cell voltage was gradually decreased from open cell (OCV) to 1 mV and afterwards gradually increased to open cell in steps of 600 mV. A polarization by controlling the cell voltage was also done on day 160 for the peat soil PMFCs. The results of the last second of each step are shown in the results. Deposition on the electrodes was analysed by an ICP (Vista MPX Simultaneous ICP-OES, Varian Inc., Palo Alto, USA). Samples were first washed with demineralized water, before they were dissolved in aqua regia.

2.4. Calculations

All results are reported per m^2 plant growth area. The PGA in this research is the projected surface area of the part of the tube with the electrodes (210 mm by 31 mm). The internal resistances (i.e. anode, cathode and membrane) were calculated as described [27] using the theoretical values of the electrode potentials based on the local pH.

The coulombic efficiency for oxygen reduction was calculated by dividing the current generation by the current equivalent of the oxygen flux through the silicone tube into the cathode (i.e. the current that could be generated by reducing the oxygen) into the cathode of the PMFC. The current equivalent of oxygen in the cathode was calculated according to the following formula based on Fick's law:

$$I_{eq} = AnFD\frac{\partial C}{\partial x}$$

In which, I_{eq} is the current equivalent (in A), A is the area through which the oxygen diffuses (in m^2), n is the number of electrons, F is the Faraday constant (96,485 A s mol^{-1}), D is the diffusion coefficient of oxygen in water ($1.97 \cdot 10^{-9}$ m^2 s^{-1}), ∂C is the difference in concentration (in mol m^{-3}) and ∂x it the distance (in m). Oxygen diffuses from the inside of the silicon tube through the entire cathode. The dissolved oxygen concentration in water (0.258 mol m^{-3} at 25 °C and 20.9% oxygen) is significantly lower than the oxygen concentration in air (8.708 mol m^{-3} at 25 °C and 20.9% oxygen). The oxygen diffusion through the silicone is neglected in the calculation because the oxygen concentration is higher and the oxygen diffusion coefficient of oxygen in silicone ($1.6 \cdot 10^{-9}$ m^2 s^{-1} [25]) is almost similar as oxygen in water. Oxygen diffuses over 0.0081 m, which is the thickness of the cathode compartment to the ultrafiltration membrane with an area of 0.0158 m^2 (Fig. 2). Oxygen reduction reduces four electrons per oxygen (O_2).

Table 1
Operation of the PMFCs during the experiment.

Peat soil PMFCs				Salt marsh PMFCs			
Days	Cathode control (mV)	Cell control (Ω)	O_2 supply	Days	Cathode control (mV)	Cell control (Ω)	O_2 supply
1–40	150		Air	1–40	150		Air
41–82	150		Pure O_2	41–82	150		Pure O_2
84–86		4000	Air	84–86		1000	Air
87–113		2000	Air	87–89		2000	Air
114–115		1000	Air	89–93		2000	Pure O_2
116–160		500	Air	94–95		16,000	Pure O_2
				96–136	150		Pure O_2
				136–160		16,000	Pure O_2

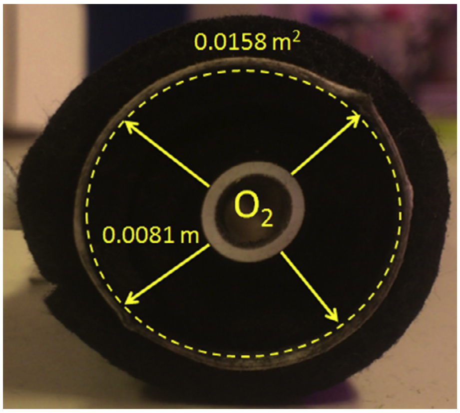

Fig. 2. Overview of chosen values for the calculations of the oxygen diffusion in the cathode. Arrows indicate total distance and direction of oxygen diffusion. Dashed circle is used to calculate the area in the equation.

3. Results and discussion

3.1. Biocathode was successfully started in peat soil PMFC with silicone gas diffusion layer

The three tubular PMFCs in the *Phragmites australis* peat soil started to generate electricity 26 days after installation in the wetland (Fig. 3). This shows that oxygen diffused through the silicone tube and silicone can therefore be used as a gas diffusion layer in the PMFC and other microbial fuel cells replacing the environmentally unfriendly PTFE [24]. The cathodes were controlled at 150 mV, because that resulted in a successful start-up of the biocathode in previous experiments [2,28]. This method also resulted in a successful start-up of the biocathode in this research as after day 26 a positive current was generated. This indicates that the onset potential (i.e. the open cathode potential) increased from a potential lower than 150 mV to a potential of more than 150 mV. Microorganisms catalysing the oxygen reduction reaction are known to decrease the overpotential of the cathode and as such increase the onset potential of the cathode [29]. Likely the increase in onset potential in this experiment can also be ascribed to these microorganisms.

All cathodes were connected electrically in parallel and thus operating as one working electrode. To analyse the start-up of the biocathode of the individual cells, polarization measurements were performed. Also the polarization graphs clearly show an increased onset cathode potential of each PMFC (Fig. 4). The onset potential increased from 264 mV on day 20–521 mV on day 160 for peat soil PMFC1 and from approximately −163/−198 mV (day 20) to 393/449 mV (day 160) for peat soil PMFC2 and PMFC3. The higher onset potential of PMFC1 compared to PMFC2 and PMFC3 on day 20 is likely caused by the differences in start-up of the biocathodes. Already on day 20 the biocathode of PMFC1 is catalysing the reduction of oxygen. The start-up of the biocathodes clearly varies. The start-up of PMFC2 is slower than the other two biocathode as can be seen in the polarization on day 88. A possible explanation of the quicker start-up of PMFC1 is the location of the used reference electrode. The reference electrode of PMFC1 was used to control the cathodes of the three PMFCs. The distance between the cathodes of PMFC2 and PMFC3 to the reference electrode resulted in potential losses which led to a lower and less stable cathode potential for PMFC2 and PMFC3. For example, from day 1 to day 30 the cathodes were controlled at 150 mV. The cathode potential of PMFC1 was on average 150 (±10) mV. At the same time the cathode potential of PMFC2 and PMFC3 were on average respectively 55 (±85) mV and 41 (±73) mV. Earlier oxygen reducing biocathodes were preferably started at a fixed cathode potential of 150 mV [28], which only occurs at PMFC1, possibly explaining the quicker start-up of PMFC1.

Even though the start-up of the biocathodes is different, the last polarization on day 160 is similar for all three PMFCs, for both the onset potential as the potential of the maximum current density. The maximum current density is respectively 167 mA m^{-2} PGA at 261 mV, 122 mA m^{-2} PGA at 225 mV and 132 mA m^{-2} PGA at 276 mV for PMFC1, PMFC2 and PMFC3. Further analysis of the maximum current generation is not possible, because the polarization of day 160 is performed by controlling the cell potential and

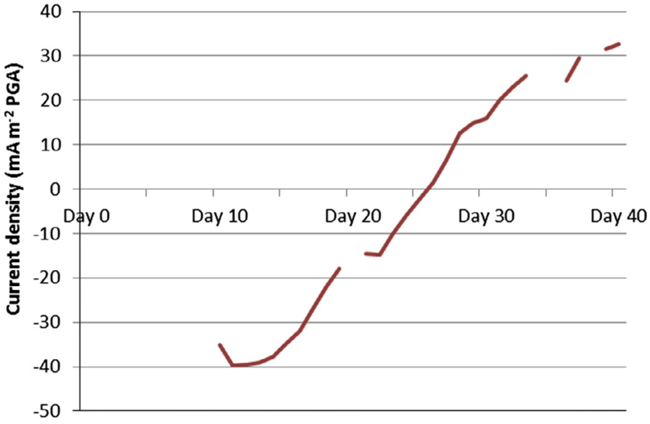

Fig. 3. Total current generation of the three PMFCs in parallel connected in the peat soil at a controlled cathode potential of 150 mV. In the first 10 days of the experiment the current generation of the PMFCs were not logged, however the cells were cathode controlled at 150 mV. The other periods without current generation were due to OCV operation.

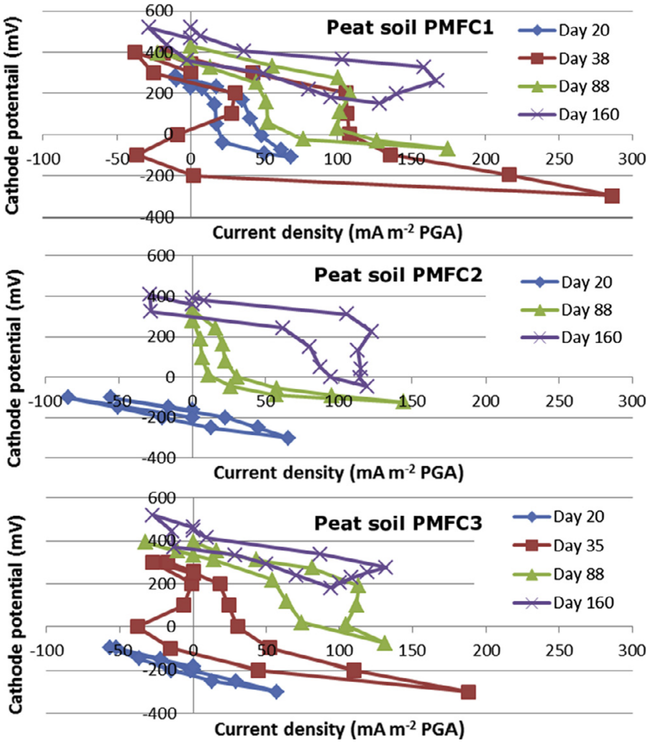

Fig. 4. Cathode potential and current density of the three individual PMFC in the peat soil during four polarizations. The polarizations on day 20 and day 35/38 were cathode potential controlled. The polarizations on day 88 and day 160 were cell potential controlled.

not by controlling the cathode potential. The maximum current density is therefore also determined by the oxidation reactions in the anode. Oxygen reduction is clearly catalysed likely by microorganisms in the cathodes of all three PMFCs as the overpotential decreased at all current densities. The selected start-up strategy, controlling the cathodes at 150 mV, was thus also successful for starting a biocathode in a *Phragmites australis* peat soil. Therefore, peat soil naturally contains microorganisms which can biologically catalyse the anode in the PMFC and microorganisms which can biologically catalyse oxygen reducing cathodes. As such a bioanode and biocathode were in situ started in the peat soil PMFCs.

3.2. Long term power generation with a bioanode and biocathode in the peat soil PMFC

From day 84, the PMFCs were controlled by an external resistance and power was continuously generated. For all three peat soil PMFCs most power was generated at 2000 Ω (Fig. 5). The maximum long term (two week average) power generation was the highest for peat soil PMFC2, 21 mW m^{-2} PGA from day 90 to day 103. Peat soil PMFC1 and PMFC3 generated on average respectively 12 and 8 mW m^{-2} PGA. This is clearly higher than the 1.3 mW m^{-2} which was earlier generated in the same wetland [27]. The higher power output is caused by an improved design and a better cathode performance. The previous experiment used a ferricyanide cathode which had a lower cathode potential than the oxygen reducing biocathode in this research. Lowering the resistance to 1000 Ω and further to 500 Ω did not result in a further increase in power. After decreasing the resistance the current generation directly increased and afterwards gradually dropped to a current density comparable to the current density at 2000 Ω. The lower resistance resulted in approximately the same current density and thus less power. Current generation in the peat soil PMFC was limited by the anode (figure in supporting information). Lowering the external resistance increased the anode potential without increasing the current of the PMFC and thus the limiting current is reached. Over time, the PMFCs in the peat soil became more limited in electron donors, possibly due to diffusion limitation [30], less exudation of the plants [31], slower hydrolysis of dead roots [32] and/or due to the presence of more alternative electron acceptor oxygen via radial oxygen loss [32] and/or via oxygen crossover from the cathode to the anode [33].

PMFC2 produces most power (Fig. 5), while the cathode potential of PMFC2 is lower than of the other two PMFCs (Fig. 4). The difference in power output between the PMFC is explained by the lower anode potential and resistance of PMFC2 (Table 2). The lower cathode potential of PMFC2 compared to PMFC1 and PMFC3 is not caused by a worse cathode performance, but by the higher current of PMFC2 (Fig. 5). This is confirmed by the cathode resistance of PMFC2, which is only slightly higher than the cathode resistance of PMFC1, while the cathode resistance of PMFC3 is clearly higher. The anode resistance of PMFC2 is clearly lower than the anode resistance of PMFC1 and PMFC3. This shows that the difference in power output is explained by the differences in anode performance.

Table 2
Power, potentials and resistances of the peat soil PMFCs during the two week maximum power generation.

	PMFC1	PMFC2	PMFC3
Power (mW m^{-2} PGA)	12	21	8
Anode potential (mV)	−41	−255	23
Cathode potential (mV)	375	265	336
Membrane potential (mV)	21	3	−10
Anode resistance (Ω m^2 PGA)	12.8	4.4	18.2
Cathode resistance (Ω m^2 PGA)	9.7	10.2	13.5
Membrane resistance (Ω m^2 PGA)	0.7	0.1	−0.4

The differences in anode performance can be explained by local conditions. A better anode performance (i.e. lower anode resistance) can be explained by higher local availability of electron donors, less electron acceptors, the microbial population and/or other beneficial local conditions. The electron donors depend on exudation, hydrolysis of dead roots and other organic matter and vary due to local variations in root growth. The main electron acceptor in the anode is oxygen, which can be present in the anode due to radial oxygen loss from the plants [32] or via diffusion from the cathode through the ultrafiltration membrane. Roots were clearly growing through the anode felt in the peat soil PMFCs (Fig. 6) which likely results in local variations in exudation and radial oxygen loss and thus in the availability of electron donors and acceptor. Differences in the cathode performance are caused by the same factors as for the anode: local variation in electron donors, acceptors, microbial community and local conditions. Also root growth likely affected the cathode performance as small roots penetrated through the ultrafiltration membrane to the cathode. Such roots may be beneficial while they can provide oxygen [20]; though it is expected that on the long term the roots provide more rhizodeposits which allow electron donor supply and oxidation in the cathode. As such, internal currents in the cathode can occur which may diminish the intended cathode function of the PMFCs.

3.3. Improving the design of the peat soil PMFC to avoid oxygen diffusion in anode

The current and power generation decreased when more oxygen was supplied to the cathode by pure oxygen diffusion instead

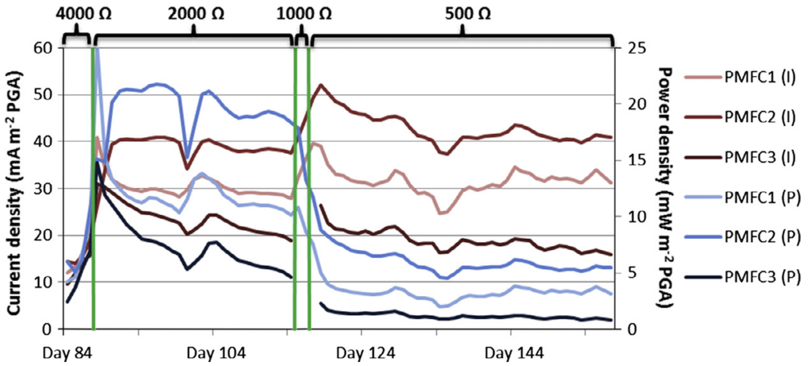

Fig. 5. Long term current (I) and power (P) generation of the three peat soil PMFCs at different external resistances to study the individual performance of the cells. The green lines indicate the moment that the external resistance was lowered. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Roots are growing through the anode felt of peat soil PMFC1. Picture from the inside of the anode felt of the dismantled peat soil PMFC1 at end of experiment.

of by air diffusion due to oxygen crossover from the cathode to the anode. This shows that oxygen supply is an important design criteria since it can be too high and too low. The polarization with pure oxygen diffusion on day 84 and air diffusion on day 88 illustrates this. The maximum power density of the PMFCs during the polarization on day 84 was on average 6.1 (±1.8) mW m^{-2} PGA and on day 88 on average 32 (±19) mW m^{-2} PGA. This difference can be mainly attributed to the anode as the anode resistance decreased on average from 11 (±6) Ω m^2 PGA to 2.6 (±0.7) Ω m^2 PGA. Clearly, the performance of the anode in the peat soil decreases when supplying more oxygen to the cathode. Therefore it is expected that oxygen in the cathode diffused through the ultrafiltration membrane, resulting in internal currents, lowering the voltage and coulombic efficiency and thus decreasing the power output [33].

Further optimization of the oxygen supply is necessary, because also oxygen crossover from the cathode to the anode occurred during air diffusion as the anode is also during that period the main resistance. This expectation based on the resistances is confirmed by the modelled coulombic efficiency of oxygen reduction. 55% of the oxygen available in the cathode is related to current generation. The rest is transported to the anode and/or reduced in side reactions. The coulombic efficiency was predicted using Fick's law, assuming an ideal wetland PMFC in which all the oxygen is consumed in the cathode and no electron donors diffuse from the anode to the cathode. The oxygen diffuses from the silicone tube into the cathode compartment. The dissolved oxygen concentration is 0.258 mol m^{-3} (20.9%) directly next to the silicone tube and diffuses through the complete cathode compartment (0.0081 m) were all oxygen is consumed. The diffusion coefficient for oxygen through water is $1.97{\cdot}10^{-9}$ m^2 s^{-1}. This results in an oxygen diffusion flux of $9.92{\cdot}10^{-10}$ mol O_2 s^{-1} (Table 3) which is equivalent to a current of 0.38 mA. The peat soil PMFCs produced on average a current of 0.21 mA/PMFC during the two weeks in which the maximum long term power was generated. The coulombic efficiency is calculated by dividing the measured current by the theoretical value. Only 55% of the available oxygen is thus used for oxygen reduction.

Table 3
Passive oxygen diffusion in the cathode compartment and the oxygen current equivalent in the peat soil PMFCs during air supply.

	Air diffusion	
Distance oxygen transport	0.0081	m
Diffusion coefficient	$1.95{\cdot}10^{-9}$	m^2 s^{-1}
Oxygen concentration difference	0.258	mol m^{-3}
Area ultrafiltration membrane	0.0158	m^2
Oxygen diffusion flux	$9.92{\cdot}10^{-10}$	mol O_2 s^{-1}
Oxygen current equivalent	0.38	mA

To increase the power output of the PMFCs in the peat soil, the design should be improved to make sure that all the oxygen is used in the cathode and no oxygen diffuses to the anode. This can be done by increasing the current density of the peat soil PMFCs to reduce more oxygen or by decreasing the oxygen diffusion in the cathode. The current density can be increased by using a larger anode. Based on Fick's law, possible improvements to the design for less oxygen diffusion to the cathode are the use of an air diffusion tube with a lower diffusion coefficient, a smaller size or a larger thickness. Also increasing the thickness of the cathode compartment or a lower oxygen concentration in the silicone tube will result in less oxygen diffusion. The search for the optimal design in which no oxygen diffuses to the anode is an important factor in development of the PMFC as oxygen diffusion to the anode results in internal currents and power losses. In this design, the tubular ultrafiltration membrane should be replaced by a cheaper alternative. The main function of the membrane is to physically separate the anode and cathode avoiding short circuit with a minimal distance between the electrodes. The membrane could thus also be replaced by a cheap spacer. This spacer should preferably be small (to minimize the ionic and transport losses), cheap, not electric conductive, ion conductive and should block roots avoiding roots and rhizodeposition in the cathode and the associated internal losses. For application, a possible replacement of the membrane is water permeable (woven) landscape fabric as it meets the set requirements. Any other non-woven plastic could also be used, for example plastic sheets with holes. Also the scale-up of the PMFC is important for the application. The PMFC is scaled-up by Plant-e B.V. The Netherlands. The developed tubular design can be elongated to tens of metres to increase the power output of a single tube. Pilot research is ongoing (see http://www.plant-e.com).

3.4. Biocathode in salt marsh PMFC only started with pure oxygen diffusion

The biocathode of the salt marsh PMFCs was started using the same method as the peat soil PMFCs, i.e. by controlling the cathode potential at 150 mV and by pumping pressurized air through the inner-side of the silicone tube. The oxygen diffuses passively from the inner-side of the silicone tube to the cathode. This method was not successful for the salt marsh PMFC, as there was no increase in current density in the first 40 days (Fig. 7). The start-up problems were caused by the limited availability of oxygen in the cathode. The cathode open circuit potential of the salt marsh PMFCs was −377 (±4) mV before the polarization on day 38, which is lower than the minimum cathode open circuit potential recorded for the peat soil PMFCs (−200 mV). The lower cathode open circuit potential of the salt marsh PMFC is likely caused by a lower oxygen concentration as can be calculated from the Nernst equation of the oxygen reduction reaction [15]. Possibly, the oxygen which diffused through the silicone tube was directly reduced in the cathode while oxidizing the sulphide (162 mg L^{-1} in the wetland [27]) present in marine sediment [12]. Due to these internal currents, not enough oxygen was present for oxygen reduction in the PMFCs. Therefore, the oxygen concentration in the cathode compartment was increased by pumping pure oxygen instead of pressurized air through the silicone tube resulting in more diffusion of oxygen from inside the silicone tube to the cathode. More oxygen diffusion to the cathode, resulted in a higher concentration of oxygen in the cathode and did result in the start-up of the biocathode as the current density increased at the same cathode potential (Fig. 7). The overpotential thus decreased and the oxygen reduction reaction was catalysed, likely by the microorganisms in the cathode [29].

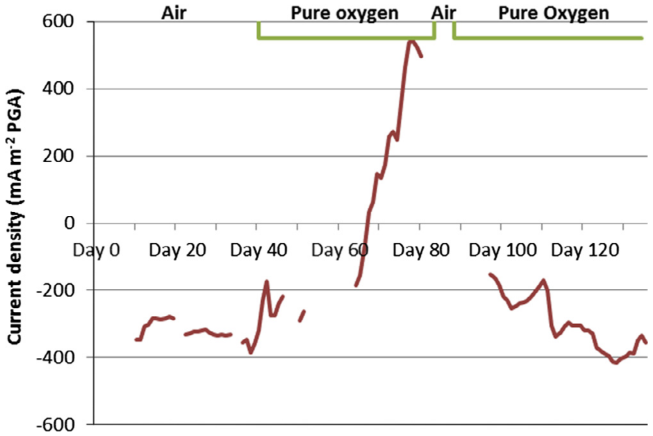

Fig. 7. Total current density of the three salt marsh PMFCs during 150 mV cathode control. Green line indicates period of pure oxygen diffusion instead of air diffusion. In the first 10 days of the experiment the current generation of the PMFCs were not logged, however the cells were cathode controlled at 150 mV. From day 84 to day 96, the cells were controlled by an external resistance. The other periods without current generation were due to OCV operation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

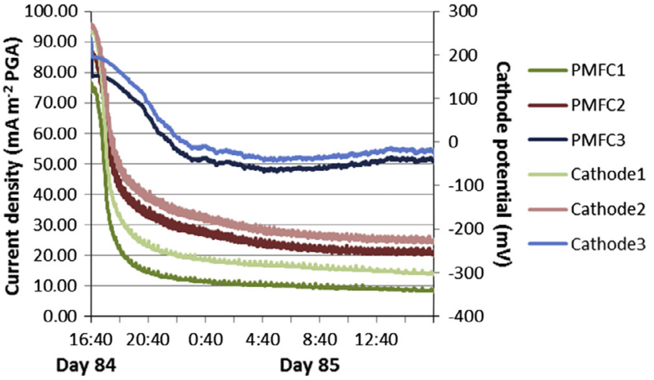

Fig. 8. Cathode potential and current density of the three salt marsh PMFCs during 24 h after the switch from pure oxygen diffusion to air diffusion at an external resistance of 1000 Ω.

The maximum daily average current density was achieved on day 78 and 541 mA m^{-2} PGA (i.e. 3.52 mA/PMFC) was generated. The coulombic efficiency for oxygen reduction was 192% that day calculated by dividing the generated current by the potentially available current (i.e. 1.83 mA/PMFC based on Fick's law). More oxygen was reduced in the cathode, than what was supplied through the ultrafiltration membrane. Pure oxygen was already supplied for 32 days likely resulting in more oxygen in the cathode than reduced by the PMFC. The extra oxygen was reduced once the biocathode started to catalyse oxygen reduction. The higher concentration of oxygen resulted in a higher current by the PMFC than what was supplied through the silicone tube and thus a coulombic efficiency of more than 100%. The current generation decreased on day 79 and 80, due to the decrease in oxygen concentration in the cathode compartment. Probably, a maximum current density of 1.83 mA could be maintained in a long term.

The salt marsh PMFCs did not generate power for a long term. Therefore, the maximum two week average power generation cannot be compared with the data from the peat soil PMFCs. However, for a shorter period both wetlands can be compared. The maximum daily average power density of the salt marsh PMFCs was 82 mW m^{-2} PGA on day 72. The current density increased after day 72 (Fig. 7), but no more power was generated due to a lower cell voltage. The maximum daily average power generation of the best peat soil PMFC was 22 mW m^{-2} PGA. Almost 4 times more power was generated by the salt marsh PMFCs than by the peat soil PMFCs. The higher power density of the salt marsh PMFCs is likely caused by the alternative electron donor sulphide, which is oxidized at the anode of the PMFC to elemental sulphur. The sulphide-sulphur couple is a mediator in the PMFC with organic carbon as the electron donor [27].

On day 84, again pressurized air was pumped through the silicone tube to analyse the current generation without pure oxygen. The individual PMFCs were connected with an external resistance of 1000 Ω. Directly after the change to pressurized air the current density and cathode potential dropped (Fig. 8). Clearly, again not enough oxygen diffused through the silicone tube to the cathode. The drop in current density and cathode potential of PMFC3 was smaller than of the other two PMFCs (Fig. 8), due to a broken connection of the silicone tube, resulting in air bubbles in the cathode compartment and thus more oxygen. The drop is expected to be comparable to the drop of the other two PMFCs if the connection was not broken. Also the polarization on day 84 with pure oxygen diffusion and day 87 with air diffusion shows a clear drop in cathode potential, current and power density. The maximum power density during the polarization decreased from 86 mW m^{-2} PGA to 0.5 mW m^{-2} PGA for salt marsh PMFC1, from 109 mW m^{-2} PGA to 5.2 mW m^{-2} PGA for salt marsh PMFC2 and from 156 mW m^{-2} PGA to 39 mW m^{-2} PGA for PMFC3. Pressurized air diffusion through a silicone tube with these dimensions results in an insufficient amount of oxygen for the oxygen reduction reaction at the cathode. Therefore, on day 87, pure oxygen was again pumped through the silicone tube. Unfortunately, the biocathode did not directly restart at the same current densities as before the air diffusion. Possibly sulphide was able to diffuse from the anode to the cathode as a result of a lower oxygen concentration and current density when switching from oxygen to air diffusion. This likely resulted in higher concentrations of sulphide in the cathode. The toxic sulphide may have killed the microorganisms [34]. Also the formation of elemental sulphur on the cathode may substantially decrease the oxygen reduction reaction [35]. The biocathode were controlled at 150 mV with pure oxygen diffusion until day 136 which did not result in the restart of the biocathode.

Deposition on the cathode felt directly at the silicone tube was clearly visible when dismantling the PMFC at the end of the experiment (figure in supporting information). Crushing the black formation resulted in a white powder. ICP analysis showed a clear increase in calcium concentration on the deposition compared to a part of the felt without deposition. Addition of HCl formed gas bubbles, likely carbon dioxide. Therefore, the deposition is probably calcium carbonate which may have been formed due to the pH increase caused by the reduction of oxygen. The black colour could be metal sulphide deposition. The addition of aqua regia may have caused the evaporation of hydrogen sulphide and as a result the sulphide was not measured by the IPC. The deposition may have limited or blocked the diffusion of oxygen to the cathode. The dismantling of the PMFC also showed that no roots were present in both the anode and cathode felts. The plants were vital at the start of the experiment and as such providing rhizodeposits. During the experiments, the plant vitality dropped until the plants died resulting in no roots growing through the felt. The plants likely died due to the not ideal growth conditions. Even at this time, the cells can still be considered PMFC as also dead plants generate electricity [32].

The current design is not suitable for PMFCs in this salt marsh with air diffusion. To also start-up the biocathode with air diffusion more oxygen should diffuse into the cathode and/or less sulphide should diffuse into the cathode. More oxygen will be present in the cathode when an air diffusion tube with a larger diameter, smaller thickness and/or a gas diffusion material with a larger diffusion coefficient for oxygen is used. Also a smaller cathode likely results in a start-up of the biocathode PMFC in the salt marsh. The diffusion of sulphide to the cathode can be blocked with the use of an ion selective membrane instead of the used ultrafiltration membrane. However, this will increase the costs of the PMFCs [36].

4. Conclusions

PMFCs with a silicone gas-diffusion oxygen reducing biocathode were successfully started in *Phragmites australis* peat soil. Oxygen reduction is clearly catalysed, likely by microorganisms in the cathodes as the overpotential decreased resulting in an increased current density and cathode potential. The long term two week average power generation of the best peat soil PMFC was 21 mW m^{-2} PGA with a maximum daily average of 22 mW m^{-2} PGA. The anode of the peat soil PMFC limits the current generation, due to oxygen crossover from the cathode to the anode. PMFCs with a biocathode in *Spartina anglica* salt marsh only started with pure oxygen diffusion reaching a maximum daily average power generation of 82 mW m^{-2} PGA. Start-up of the biocathode with pressurized air was not successful, likely due to crossover of sulphide from the anode to the cathode, resulting in insufficient amounts of oxygen and possible toxic conditions for the microorganisms in the cathode. To further increase the power, the design of the PMFCs in both wetlands has to be improved to limit the crossover of oxygen from the cathode to the anode for the peat soil PMFCs and to limit the crossover of sulphide from the anode to the cathode for the salt marsh PMFCs.

Acknowledgements

This project was carried out within the research programme of BioSolar Cells, co-financed by the Dutch Ministry of Economic Affairs. Furthermore, this research is financially supported by Alliander and Plant-e. We would like to thank It Fryske Gea and the province of Zeeland for their support with the collection of the wetlands.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2016.10.122.

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