Electricity generation from wetlands with activated carbon bioanode

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Abstract. Paddy fields are potential non-tidal wetlands to apply Plant Microbial Fuel Cell (PMFC) technology. World widely they cover about 160 million ha of which 13.3 million ha is located in Indonesia. With the PMFC, in-situ electricity is generated by a bioanode with electrochemically active bacteria which use primarily the organic matter supplied by the plant (e.g. as rhizodeposits and plant residues). One of limitations when installing a PMFC in a non-tidal wetland is the usage of "expensive" large amounts of electrodes to overcome the poor conductivity of wet soils. However, in a cultivated wetland such as rice paddy field, it is possible to alter soil composition. Adding a conductive carbon material such as activated carbon is believed to improve soil conductivity with minimum impact on plant vitality. The objective of this research was to study the effect of activated carbon as an alternative bioanode material on the electricity output and plants vitality. Lab result shows that activated carbon can be a potential alternative for bioanode material. It can continuously deliver current on average 1.54 A/m3 anode (0.26 A/m2 PGA or 66 mW/m2 PGA) for 98 days. Based on this result the next step is to do a test of this technology in the real paddy fields.

1. Introduction

Plant Microbial Fuel Cell (PMFC) is considered as a new source for sustainable bioelectricity production which does not compete with food production. It produces sustainable in-situ energy, without harvesting the biomass, by conversion of solar energy into electricity via plants and electrochemically active bacteria [1]. Hereby plant residues like rhizodeposits are used as fuel to produce electricity. For large scale electricity generation, PMFC should be applied in wetlands because they need waterlogged condition to maintain anaerobic condition and to facilitate ion transport [1]. Paddy fields are potential wetlands to apply PMFC technology (Figure 1). World wide they cover about 160 million ha of which 13.3 million ha of it is located in Indonesia [2].

It is known that in a non-tidal wetland such as rice paddy field, soil conductivity is relatively low compared to tidal wetlands [3]. Some researchers have tried to install PMFC system in a rice paddy field without any modification on the soil composition. The maximum power output of PMFC in the paddy field is about 140 mW/m² projected anode surface area [4]. This power output is half of the best performance of PMFC in the lab, which is 240 mW/m² [5].
In a cultivated wetland, most of the time before the growing season, soil composition of the paddy field is altered. The top layer soil and the lower layer is mixed while adding fertilizer. Considering this activity some inert conductive material such as carbon based material may be applied in the rice paddy fields. Researches have shown that adding biochar is not only increasing rice paddy soil fertility and the rice yield but it also reduces total methane emission [6, 7]. As biochar electrical conductivity (2-4.4 uS/cm) are typically about 1000 times lower than activated carbon [8], using activated carbon (AC) in a PMFC can allow electricity generation and potentially profiting on the additional advantages of biochar.

Based on this concept, this research aims to investigate the effect activated carbon as an alternative bioanode material on the electricity generation and plants vitality within PMFCs at laboratory condition.

2. Materials and Methods
This research was conducted with 2 identical flat plate PMFC reactors in a climate chamber (10 hours dark, 14 hours light, 25°C, 70% humidity). The flat plate reactor was made from plexiglas material. The reactors consist of 2 chambers (anode and cathode chamber) separated by a Cation Exchange membrane (CEM). Two graphite rods connected with titanium wire (18x1x0.2 cm) were place in both side of the anode chamber with a distance of 18 cm. The anode chamber had total volume 722 ml (19x19x2 cm) but only 650 ml were used. The anode chambers were filled with activated carbon Norit PK 1-3. Nitrate-less, ammonium-rich plant growth medium [9] was continuously pumped into anode chamber using minipuls-3 Gilson pump at a constant speed of 15 rpm. Anode plant growth area (PGA) was 19 cm x 2 cm. Cathode electrode was made from graphite felt (thickness: 3mm), FMI composites Ltd., Galashiels, Scotland. This electrode was woven with titanium wire (1 mm diameter) as a current collector. The same plant growth medium was used as catholyte and aerated with ambient air using aquarium pump.

There were two phase of operation of the experiment. The first phase was blank characterization without plants for 159 days (day 1 - 159) and the second one was with plant for 129 days (day 160 – 288). In the first 96 days, both reactors were operated only with plant growth media without bacteria.
inoculum. On day 97, 20 mL inoculum from previous PMFC’s research [5] was added in both anode reactor. One day later another 10 mL fresh inoculum from running MFC’s anode was also added into both anodes. Anode, cathode, cell and membrane potential were recorded every 60 minutes from day 23 until the end of experiment (day 288). All data were logged in a computer using field point data logger and LabVIEW software from National Instrument, The Netherlands. Anode and cathode potential were measured against Ag/AgCl reference electrode. Both PMFC reactors were controlled either with 1 kohm external load or at -100 mv anode potential using a potentiostat (16 channel Ivium BV, The Netherlands).

3. Results and Discussion
After 288 days of operation, AC bioanode PMFSs were successfully operated. Number of stems and total plant’s height were growing in both reactors.

3.1. Activated carbon (AC) bioanode can function as an alternative bioanode
When the experiment was started, AC anode was operated only with plant growth media without inoculation for 96 days. During this period both control modes did not show any current production. This result was predicted before due to absence of electrochemically active bacteria (EAB). The similar trend was also observed (data not shown) after adding bacteria inoculum on day 97 and 98 until day 160.

On day 160, plants (Spartina anglica) were planted into the anode PMFCs. Reactors were kept at open cell until day 163. From day 163 until 260, both anodes were controlled at -100 mV. During this period the PMFC reactors was starting to deliver current as can be seen on Figure 2. In the first 12 days after starting generating current, both PMFC delivered current of about 1 mA (equal to 0.25 mW). However, from day 175 current generation in PMFC 2 was gradually decreasing and reaching 0 on day 187. On day 260 PMFC 2 current was about –0.5 mA, meaning it functions as a cathode instead of an anode. At the same time, PMFC 1 continuously generated current on more stable condition around 1 mA (1.54 A/m3 anode or 0.26 A/m PGA) until day 260.

![Figure 2](attachment:pmfc_curves.png)

The drop on current generation of PMFC 2 was more likely caused by oxygen present in the anode. This oxygen can be (bio)electrochemically reduced to water [10]. As plant can deliver oxygen via its
root [11], it was confirmed that in the first 100 days after planting more plant’s stems and leaves were growing in PMFC 2 than PMFC 1 (Figure 3 and Figure 4). This effect was also indicated by clear day and night pattern on PMFC 2 during this period. The current production was decreasing during the day (light regime) and increasing during the night (dark regime). When reactors were controlled with external load, this effect was not observed. However due to cathode limitation, the current production both PMFCs were gradually decrease from about 0.1 mA (0.01 mW) to 0.02 mA(0.002 mW).

**Figure 3.** Number of living stems

**Figure 4.** Total stems' height

In either case, AC bioanodes were successfully operated in PMFC and delivering total electric charge as much as 4791 C for PMFC 1 and 4338 C for PMFC 2 for 129 days operation with plants (Table 1). Moreover, the activated carbon anode can also support plant growth. Plants on both reactors were growing (Figure 3 and Figure 4).

**Table 1.** Charge production (Coulomb).

|                  | PMFC 1 | PMFC 2 |
|------------------|--------|--------|
| Day 163-260 (98 days potentiostat control) | 4655   | 4103   |
| Day 260-288 (29 days 1000ohm ex load)       | 136    | 235    |
| Total            | 4791   | 4338   |

3.2. *AC PMFC generating cost is cheaper than other PMFCs*

Comparing costs among PMFC system is not always feasible because most of current production was reported based on PGA instead of anode material volume. As a normalise parameter, the PGA cannot give us a real amount of used electrode. The most fair comparison to calculate the effect of an anode material and its ability to deliver such amount of current in a PMFC system should be based on the number of used material itself. Therefore, a unit of electricity generating cost based on utilised anode material per unit power is calculated (Table 2). For this calculation the prices for graphite felt, graphite granule (high purity) and activated carbon are based on these data: 1. Graphite felt PGF grade, CGT carbon GmBh (0.12 g/cm³), thickness 3mm, €62/m² or equal to €172/kg [12]; 2. Huaming graphite granule (0.798 g/cm³); €0.76/kg[13]; 3. Taoshi activated carbon (0.55 g/cm³); €1.68/kg [14]. For comparison with other studies, average current production of 0.5 mA (0.125 mW) and 1 mA (0.25 mW) were used.

Based on our calculation we found that activated carbon is a promising material for anode on a PMFC system. Investment cost on bioanode electrode material per installed mW is about €2.4 – €4.8 (Table 2).
Table 2. Power density and electricity generating cost based on anode material price from various PMFC studies

| No | System                                | Plant species | Lab /field | average power density (mW/m² PGA) | Power (mW) | Anode material | Anode material weight (kg) | Anode cost (€) | Investment cost based on anode (€/mW) | Ref |
|----|---------------------------------------|---------------|------------|-----------------------------------|------------|----------------|---------------------------|----------------|----------------------------------------|-----|
| 1  | 2 chambers flat-plate PMFC with CEM  | Spartina anglica | lab         | 66                                 | 0.25       | activated carbon | 0.3575                  | 0.60           | 2.40                                   | This study |
| 2  | 2 chamber pot PMFC with CEM           | Reed manngrass (Glyceria maxima) | lab         | 67*                                | 0.258      | graphite felt+graphite granule | 0.0138 felt & 0.8288 graphite granules | 3.01           | 11.68                                  | [1] |
| 3  | without membrane                      | Paddy         | paddy field | 6*                                 | 0.810      | graphite felt   | 0.0486                  | 8.37           | 10.33                                  | [15] |
|    | container with CEM                    | Paddy         | lab         | 26                                 | 0.708      | graphite mat+graphite rod; in soil graphite mat+graphite rod; in graphite granules | 0.0165                  | 0.88           | 1.25*                                  | [16] |
| 4  |                                       | Paddy         | lab         | 15.8                               | 0.246      | graphite mat+graphite rod; in soil graphite mat+graphite rod; in graphite granules | 5.6479                  | 4.27           | 17.33b                                 |       |
| 5  | without membrane                      | Paddy         | paddy field | 14.44*                             | 0.907      | graphite felt   | 0.0226                  | 3.89           | 4.29                                   | [17] |
| 6  | 2 chamber pot PMFC with CEM           | Spartina anglica | lab         | 50                                 | 0.1        | graphite granules | 0.1650                  | 0.12           | 1.25                                   | [18] |
|    | PVC tubular PMFC, 2 chamber with ultra filtration membrane | Reed manngrass (Glyceria maxima) | lab | 10                                  | 0.020      | graphite felt   | 0.0426                  | 7.34           | 366.83                                 | [19] |
| 7  |                                       | Paddy         | lab         | 12                                 | 0.024      | graphite granules | 0.7500                  | 0.57           | 23.63                                  |       |
| 8  | 2 chamber Cylindrical PMFC with CEM  | Spartina anglica | lab         | 21                                 | 0.646      | graphite grain  | 4.6661                  | 3.53           | 5.46                                   | [20] |
| 9  | 2 chambers flat-plate PMFC with CEM  | Spartina anglica | lab         | 440*                               | 0.376      | graphite felt   | 0.0194                  | 3.35           | 8.91                                   | [9]  |
| 10 | 3 chambers: cathode-anode-cathode with BPM | Spartina anglica | lab | 240                                 | 0.6528     | graphite felt   | 0.1299                  | 22.38          | 34.29                                  | [5]  |
| 11 | Floating cathote without membrane; anode below | Paddy         | field      | 80*                                 | 0.64       | graphite felt   | 0.00288                 | 0.5            | 0.78                                   | [21] |
| 12 | Floating larger cathote than anode without membrane; anode below | Paddy         | field      | 140*                                | 0.7        | graphite felt   | 0.0018                  | 0.31           | 0.44                                   | [4]  |

Notes: *maximum; “graphite rod as a current collector is not considered; calculated only based on graphite granule
4. Conclusion
Based on the above result it can be concluded that activated carbon can be used as an alternative anode material for PMFC system. Plant vitality was shown with growing plants under laboratory studies. Investment costs on bioanode electrode materials per installed mW power are between €2.4 and €4.8. This is relatively cheaper compare than other PMFC anode materials.

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