Photosynthetic Microbial Fuel Cells With Positive Light Response

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ABSTRACT: The current study introduces an aerobic single-chamber photosynthetic microbial fuel cell (PMFC). Evaluation of PMFC performance using naturally growing fresh-water photosynthetic biofilm revealed a weak positive light response, that is, an increase in cell voltage upon illumination. When the PMFC anodes were coated with electrically conductive polymers, the rate of voltage increase and the amplitude of the light response improved significantly. The rapid immediate positive response to light was consistent with a mechanism postulating that the photosynthetic electron-transfer chain is the source of the electrons harvested on the anode surface. This mechanism is fundamentally different from the one exploited in previously designed anaerobic microbial fuel cells (MFCs), sediment MFCs, or anaerobic PMFCs, where the electrons are derived from the respiratory electron-transfer chain. The power densities produced in PMFCs were substantially lower than those that are currently reported for conventional MFC (0.95 mW/m² for polyaniline-coated and 1.3 mW/m² for polypyrrole-coated anodes). However, the PMFC did not depend on an organic substrate as an energy source and was powered only by light energy. Its operation was CO₂-neutral and did not require buffers or exogenous electron transfer shuttles.


KEYWORDS: microbial fuel cells; photosynthetic; self-sustainable; bioelectricity; cyanobacteria; electrochemistry

Introduction

In recent years, biological approaches for generating electricity in a self-sustainable manner have predominantly focused on microbial fuel cells (MFCs) (Logan and Regan, 2006). MFCs harvest energy from oxidation of organic compounds including those present in wastewaters. The majority of MFCs operate under anaerobic conditions, though a few aerobic MFCs have been developed recently (Biffinger et al., 2008; Mohan et al., 2008). Considering that sunlight offers an unlimited source of energy, development of self-sustainable microbial fuel cells that rely on light instead of organics as an energy source has become an increasingly popular area of research in recent years (Cao et al., 2008; He et al., 2009; Malik et al., 2009).

Previous light-powered fuel cells involved hydrogen production by a photosynthetic microorganisms/algae (Berk and Canfield, 1964; Kayano et al., 1981) or coupling of photosynthetic bioreactors with anaerobic oxidation of organic substrates produced through photosynthesis (Strik et al., 2008). Rosenbaum and coauthors introduced biohydrogen fuel cells that involved anode-catalyzed oxidation of hydrogen synthesized by the alga Chlamydomonas or the purple bacterium Rhodobacter (Rosenbaum et al., 2005a,b). In a recent study, Cho and coauthors described a fuel cell containing Rhodobacter that produced hydrogen under illumination. Hydrogen was then oxidized by the platinum-coated anode generating electrical current (Cho et al., 2007). This fuel cell functioned only under anaerobic conditions and required the presence of carbon and nitrogen sources. Strik et al. (2008) showed that sustainable electricity production could be achieved by coupling algal photosynthetic bioreactors with conventional MFC.

In 1980–1990s, Tanaka’s team published a series of studies that described aerobic photosynthetic microbial fuel cells (PMFCs) that operated entirely using cyanobacterial cultures (Tanaka et al., 1985, 1988; Yagishita et al., 1993). This work provided the first illustration that a positive light response (i.e., immediate increase in current upon illumination) could be achieved in a PMFC. An immediate positive light response is consistent with the idea that electrons could be supplied directly by the photosynthetic electron-transfer chain, and not derived only from the...
respiratory transfer chain or through oxidation of hydrogen (Yagishita et al., 1993). These studies, however, were performed using a two-chamber PMFC with potassium ferricyanide in cathode chamber, and phosphate buffer and exogenous electron shuttle in the anode chamber. Requirements for ferricyanide, electron shuttles or buffers impose serious limitations for exploiting PMFCs for sustainable generation of energy.

In the current study, we introduced a single chamber PMFC and tested its performance using two photosynthetic cultures, strictly planktonic cyanobacteria *Synechocystis PCC-6803* and natural fresh-water biofilm. PMFC showed a positive light response and did not require organic substrates, buffers, electron shuttles or potassium ferricyanide. The PMFC operation was CO2-neutral and did not depend on consumption of exogenous organic substrates as an energy source.

**Materials and Methods**

**PMFC Design**

The PMFC consisted of a single 125 mL chamber (anode chamber) made from a NALGENE Disposable Filter Unit (Nalgene, Rochester, NY) and an air-exposed cathode that was submerged ~0.5 cm beneath the surface of the medium 2 cm away from the anode (Fig. 1). The layer of air above medium surface connected with atmospheric air.

The anode electrode was the bottom of anode chamber (A\textsubscript{an} = 50 cm\textsuperscript{2}) coated with four layers of electrically conductive carbon paint (Item 05006-AB, SPI Supplies Division, Structure Probe, Inc., West Chester, PA) or a carbon cloth (5 x 5 cm\textsuperscript{2}, B1A no wet proof, E-Tek, Somerset, NJ). For each layer of carbon paint, 0.5 mL of paint was distributed with a brush, allowed to air-dry for 10 min, then dried at 70 °C in a furnace for 5 min, and cooled down at room temperature. To prepare polyaniline (polyA) or polypyrrole (polyP) treated anodes, the fourth layer was coated using carbon paint mixed with 10 mg polyaniline emeraldine salt (20 wt.% on carbon black, Cat.N. 530565 Sigma-Aldrich, St. Louis, MO) or 10 mg polypyrrole, undoped (20 wt.% on carbon black, Cat.N. 577565 Sigma-Aldrich), respectively, and dried as described. The carbon cloth was coated using polyaniline emeraldine salt (0.5 wt.% dispersion in mixed solvents, Cat.N. 649996 Sigma-Aldrich) diluted fourfold with isopropyl alcohol, by incubating in the polyaniline solution for 30 s followed by drying at 230 °C in a furnace for 2 min.

The cathode (A\textsubscript{ca} = 9.6 cm\textsuperscript{2}) consisted of (1) a platinum catalyst layer (0.5 mg of platinum/cm\textsuperscript{2}, E-Tek), (2) carbon cloth (B1B 30% wet proofed, E-Tek), (3) a carbon base layer, and (4) four PTFE diffusion layers; and was prepared according to a previously published procedure (Cheng et al., 2006). The cathode was permanently sealed using marine epoxy between two plastic caps with a hole in the bottom surface (Fig. 1). Titanium wire was attached to the anode and cathode.

**Photosynthetic Cultures**

Sediment was collected from a local pond in Columbia, MD and cultivated at room temperature in modified BG-11
medium (referred to as mBG-11) that lacked citrate (1.5 g NaNO₃, 0.04 g KH₂PO₄, 0.075 g MgSO₄·7H₂O, 0.036 g CaCl₂·2H₂O, 0.001 g EDTA, trace metal mix A5: 2.86 g H₃BO₃, 1.81 g MnCl₂·4H₂O, 0.222 g ZnSO₄·7H₂O, 0.39 g NaMoO₄·2H₂O, 0.079 g CuSO₄·5H₂O 0.0494 g Co(NO₃)₂·6H₂O per 1 L, pH 7.1) under aerobic conditions (but no air bubbling). After adaptation for 2 months, noticeable biofilm appeared on the bottom surface. The surface was scratched, gently vortexed to a homogenous cell suspension and transferred to the anode chambers; fresh mBG-11 was added. Prior to PMFC operation, the anode chambers were kept for 3–4 weeks to allow biofilm formation.

_Synechocystis PCC-6803_ was grown at room temperature in mBG-11 medium under constant bubbling with air. After two weeks of cultivation, the cultures were diluted with fresh mBG-11 to A = 0.6 o.e. as measured at 760 nm and transferred to the anode chamber. PMFCs were assembled and their performances were evaluated under stationary conditions (no air bubbling). During culture growth and PMFC operation, both _PCC-6803_ and pond cultures were placed in front of a day–light source (light intensity ~100 lux, color temperature 6,500 K) that operated under 12 h:12 h light/dark cycles.

**Characterization of PMFC Performance**

PMFCs were operated at 1 KΩ fixed external resistance and constant 22 ± 0.2°C temperature. The voltage was measured at 2-min intervals using a digital data acquisition system (PCI-6280, National Instruments, Austin, TX) and LabVIEW software (National Instruments). For recording the polarization curve, PMFCs were stabilized at an open circuit potential, then the voltage was measured at variable external resistances (from 100 KΩ to 10 Ω) after stabilization for 15 min at each resistance, and the current was calculated using Ohm's Law. An apparent internal resistance (R_{int}) was calculated from the linear region of the polarization curves using the equation R_{int} = -ΔE/ΔI as described by Logan (2008). The power curves were calculated from the polarization curves as previously described (Logan et al., 2006). Because the power output for planktonic PMFCs is dependent largely on the rector volume, whereas the biofilm PMFCs mostly on the anode surface area, the current density was normalized based on the cathode surface area (9.6 cm²) for the purpose of comparing the performance of planktonic and biofilm-based PMFCs.

**Electrochemical Analysis**

Cyclic voltammetry (CV) was conducted at scan rates of 5 or 50 mV/s in the potential range from −0.7 to 0.7 V using a potentiostat (Reference 600, Gamry Instrument, Inc., Warminster, PA). Electrochemical impedance spectroscopy (EIS) measurements were carried in a frequency range from 100 kHz to 1 mHz with an AC signal of 10 mV amplitude at open circuit potential. The equivalent circuit (EC) was used to analyze the anodic impedance spectroscopy. The EC model consisted of an ohmic resistance (R_s), followed by a Randle's type circuit of an electrochemical charge transfer resistance (R_{ct}) and a Warburg’s diffusion element (W) in parallel with a double layer constant phase element. The sum, R_{ct} + R_{int} is considered the total internal resistance. Instead of a capacitor element, a constant phase element was employed during simulation because of a dispersion effect that relates to a rough electrode surface. In all electrochemical measurements, the working electrode was the anode and the counter electrode was the cathode. An Ag/AgCl reference electrode was used as a standard constant potential.

For measuring the electrode potentials as a function of current density, two Ag/AgCl reference electrodes were inserted into the anode chamber at distance of 0.5 cm to the anode or cathode surface. The data was collected by varying the external resistance.

**pH and Dissolved Oxygen Measurements**

Dissolved oxygen (DO) and pH were measured in anode chambers every 10 min with an Orion meter (Thermo Orion, Beverley, MA), Ross Ultra glass pH electrode, DO probe (model 081010MD, Thermo Orion) and Star Navigator Plus software (Thermo Orion).

**Results**

**Positive Light Response**

A fresh-water photosynthetic culture that grows naturally as a biofilm was collected from a local pond and adopted to mBG-11 medium (no buffer or organic substrate) as described in Materials and Methods Section. Examination of photosynthetic culture seeded in PMFC anode chamber by intrinsic fluorescence microscopy imaging (Novitskaya et al., 2006) revealed that a biofilm with a complex multi-layered architecture was formed on anode surface (Fig. S1). During operation at 12 h:12 h light/dark cycles, PMFCs containing photosynthetic biofilm on non-treated carbon paint anodes showed weak positive light responses: the cell voltage increased slowly during the light-phases and dropped gradually during the dark-phases (Fig. 2A). PMFCs with the anodes coated with electrically conductive polymers polyA or polyP displayed a substantially higher amplitude of the light response (Fig. 2A). During each light–dark cycle, the cell voltage increased rapidly after the beginning of illumination reaching a maximum or plateau within 20–30 min (Fig. 2A) and then dropped during the dark stage. Turning on second light source of equal intensity resulted in additional rapid increase in voltage illustrating dose-dependence of the response (Fig. 2B). The positive light response phenomenon was not limited to the anodes made of carbon paint. PMFCs with carbon cloth anodes coated with polyA or polyP displayed positive light responses with amplitudes similar to that observed for carbon paint anodes (Fig. S2).
PMFCs loaded with strictly planktonic fresh-water cyanobacterium *Synechocystis* PCC-6803 (in mBG-11 media) instead of biofilm-forming culture showed very weak light response regardless of whether anodes were coated with conductive polymers (Fig. S3). PMFCs loaded with mBG-11 in the absence of any photosynthetic cultures showed no light response (Fig. 2A).

The difference in PMFC performances for non-modified and coated anodes can be attributed to (i) improved efficiency in electron transfer from biofilm to modified anodes and (ii) the positive effects of conductive polymers on biofilm formation. Indeed, visual examination of the anode surface prior to PMFC operation revealed that biofilm formation was much more extensive on the anodes coated with polyA or polyP than on non-treated anodes (Fig. S4).

**PMFC Performance**

Polarization curves were collected during the light-phase at 20th day of operation using a series of circuit external resistances (Fig. 3A). As judged from the slope that reflects the rate of voltage decline as a function of current production, biofilm PMFC with non-treated carbon paint anode showed fast voltage drop and an apparent internal resistance of $R_{\text{int}} = 12.1 \pm 0.4 \, \text{k\Omega}$, whereas PMFCs with polymer-coated anodes displayed relatively slow voltage decline with $R_{\text{int}} = 3.9 \pm 0.01 \, \text{k\Omega}$. Power density curves revealed the following power outputs: PMFC with non-treated anode, 0.35 mW/m²; with polyA anode, 0.95 mW/m²; and with polyP anode 1.3 mW/m² (Fig. 3B). As expected, the polymer-coated anodes performed much better than the non-treated anodes.
To test the extent to which exogenous electron mediators improve performance of PMFCs, polarization curves and the power density were analyzed for PMFCs operated in the presence of 1 mM HNQ for both planktonic and biofilm cultures. As expected, HNQ increase substantially the power output of *PCC-6803*-based PMFCs: from 0.2 to 0.59 mW/m² (195% increase) for PMFCs with non-treated anode, and from 0.63 to 1.47 mW/m² (133% increase) for PMFCs with polyA-coated anode (Fig. S5). The increase in the power output was much smaller for the biofilm-based PMFCs: from 0.35 to 0.45 mW/m² (28% increase) for PMFCs with non-treated anode, and from 0.95 mW/m² to 1.56 mW/m² (64% increase) for PMFCs with polyA-coated anode (Fig. S5). The experiments with HNQ showed that (i) planktonic PMFCs rely on electron shuttles to a much higher extent than biofilm PMFCs; and (ii) planktonic PMFCs could generate as high a power output as biofilm PMFCs if electron mediators are provided.

**Dissolved Oxygen (DO), pH, and Long-Term Performance**

Low power outputs produced in aerobic PMFCs were, in part, due to very low open circuit voltage (0.1–0.15 V). Measurement of electrode potentials revealed that such low open circuit voltage was attributed to high (positive) anode potential (Fig. 3C) that was presumably due to very high supersaturated level of DO in anode chamber (Fig. 4). The cathode potential was within the range similar to the previously reported for air-exposed cathodes in anaerobic MFCs.

Both DO and pH showed oscillations with periodicity of 24 h in both planktonic and biofilm PMFCs as a result of light-dependent oxygen evolution (Fig. 4). In contrast to the rapid jump of cell voltage, however, that occurred within 20–30 min in direct response to illumination (Fig. 2A), both DO and pH displayed much more gradual increase during 12 h illumination-phase. These marked differences between kinetics of the cell voltage increase and DO growth argue that the sharp positive light response was not caused by change in DO concentration or pH.

Although biofilm PMFCs showed positive light responses for as long as they were kept under operation (up to 8 weeks), the amplitude of response declined by 60–80% with the most substantial drop of up to 50% being observed in the first week (Fig. 2A). Decrease in the amplitude of light response could be due to several reasons including gradual accumulation of DO in the anode chamber, an increase in pH that causes insufficient supply of protons to the cathode reaction, depletion of the mBG-11 medium, a decline in performance of conductive polymers or some other reasons. Replacement of mBG-11 did not restore the amplitude of the cell voltage to the initial level suggesting that the voltage decline was not due to depletion of the medium (Fig. S6). The DO and pH values were found to gradually increase over the long-term (Fig. 4). In fact, in biofilm PMFCs, pH typically reached 8.5–9.0 during a few days of operation. In an attempt to control pH, mBG-11 medium was supplemented with phosphate buffer. Surprisingly, no light response could be detected for PMFCs containing phosphate buffer (Fig. S7). The effect of pH and DO on PMFC performance will be investigated in detail in future studies.

**CV and EIS**

To further examine the electrochemical activity we employed CV and EIS. Regardless of scanning speed rate (50 or 5 mV/s), CV did not show any oxidation/reduction peaks suggesting a lack of endogenously produced electron mediators in both biofilm- and planktonic-based PMFCs (Fig. S8). CV analysis showed that (i) biofilm PMFC had higher electrochemical activity than *PCC-6803* PMFCs, and that (ii) anodes coated with conductive polymers exhibited better electron-transfer properties than the non-coated anodes. The positive effects of polymer-coating can be attributed to an improvement of intrinsic conductivity of anode and/or the active involvement of polymers in transfer of electrons from cells. Because of their long chains, polyA and polyP could physically interact with or intercalate into cell membranes enabling direct discharge of electrons to the anode surface.
Table I. EIS analysis of biofilm-based PMFCs.

<table>
<thead>
<tr>
<th>Culture</th>
<th>Anode type</th>
<th>$R_{\text{total}}$ ($\Omega$)</th>
<th>$R_s$ ($\Omega$)</th>
<th>$R_{ct}$ ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biofilm, mBG-11*</td>
<td>Non-treated</td>
<td>383</td>
<td>63</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>PolyA-coated</td>
<td>298</td>
<td>58</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>PolyP-coated</td>
<td>212</td>
<td>62</td>
<td>150</td>
</tr>
<tr>
<td>mBG-11b</td>
<td>Non-treated</td>
<td>464</td>
<td>72</td>
<td>392</td>
</tr>
<tr>
<td></td>
<td>PolyA-coated</td>
<td>327</td>
<td>66</td>
<td>261</td>
</tr>
<tr>
<td></td>
<td>PolyP-coated</td>
<td>343</td>
<td>73</td>
<td>270</td>
</tr>
</tbody>
</table>

*EIS was performed 44 days after the pond culture was inoculated into anode chambers and at the 18th day of PMFC operation.

EIS analysis of biofilm PMFCs revealed remarkable differences in the total resistance ($R_{\text{total}}$) between three PMFCs (Table I, Fig. 5). These differences were attributed entirely to the differences in the anodic charge transfer resistance ($R_{ct}$) that reflects the transfer of electrons from biofilm to anode. As judged from $R_{ct}$, coating the anode with polyP and, to a lesser extent, with polyA improved the electron-transfer processes. Comparison of $R_{ct}$ for biofilm PMFCs and control PMFCs that lacked biofilm demonstrated that biofilm markedly improved the electron-transfer properties of the anodes in all three cells (Table I).

The ohmic or electrolyte resistance ($R_s$) was the same for all three biofilm PMFCs ($R_s = 60 \pm 3 \Omega$). The relatively high $R_s$ reflected intrinsically low ionic strength of mBG-11 medium. When mBG-11 was supplemented with 50 mM phosphate buffer, $R_s$ dropped from $60 \pm 3 \Omega$ to $20 \pm 1 \Omega$ in all three PMFCs (data not shown). EIS results were consistent with the CV tests and confirmed that polymer coating provided beneficial effects for anode performance.

Discussion

The current studies provided a direct illustration that electrical power can be generated in aerobic single-chamber PMFCs. The power density produced in the PMFC, although substantially lower than that reported for anaerobic MFC in recent years (Fan et al., 2007; Logan and Regan, 2006; Zuo et al., 2008), was compatible to the first generation of MFCs (Logan and Regan, 2006) or the recently reported sediment MFC installed in a fresh water rice paddy (Kaku et al., 2008). PMFCs in the current study are different from conventional MFCs in several key aspects. First, PMFC is 100% light-powered and does not require an organic substrate as an energy source. Second, the net production of CO$_2$ in PMFC is zero. Third, the PMFC does not require a buffer or exogenous electron shuttles for its operation. While these conditions are essential for establishing self-sustainable, CO$_2$-neutral PMFC-based technologies, substantial improvements are needed to determine the feasibility of this approach for converting light energy into electricity.

In the current studies, biofilm-based PMFCs displayed immediate response to light by showing rapid increase in the cell voltage that typically reaches a maximum within 20–30 min after beginning of illumination (Fig. 2). The light-phase voltage increase occurred despite the rise in DO concentration, which is expected to have a negative impact on power production. Turning off the light caused immediate and abrupt drop in cell voltage. The following features: (i) perfect coincidence between the light cycles and the oscillations of cell voltage, (ii) immediate response of cell voltage to light (regardless of whether it is on or off), and (iii) sharpness in cell voltage rise or drop suggest possible mechanisms for bioelectricity generation in biofilm-based PMFCs. All these features are consistent with the previously proposed mechanism postulating that the photosynthetic electron transfer chain is the source of the electrons harvested on the anode surface (Yagishita et al., 1993). This mechanism is fundamentally different from the one exploited in previously designed MFCs, including sediment MFCs and anaerobic PMFCs, in which the electrons are derived from the bacterial respiratory transfer chain (Chaudhuri and Lovley, 2003). The idea that electrons can originate from splitting of water molecules and be donated by photosynthetic electron transfer chain is not new. In the previous studies, photosystems I and II (PSI and PSII) from cyanobacteria were utilized for producing light-powered or light-sensitive electronic devices (Maly et al., 2005; Teresaki et al., 2007). When isolated and immobilized on gold nanoelectrodes, PSI or PSII were found to produce light-dependent electrical current. However, because of the high rate of photodamage, the devices consisting of immobilized enzymes are unlikely to be usable for energy production in a self-sustainable manner.

The alternative hypothesis for PMFCs described in the current work would be that the electrons are derived from the cyanobacteria/algae respiratory electron transfer chain during oxidation of organic compounds that are formed as a
result of carbon fixation during photosynthesis. If this mechanism is correct, one would expect (i) a delay between the beginning of illumination and the cell voltage rise (and, respectively, a delay between the start of the dark-phase and the cell voltage drop), and (ii) a gradual rather than abrupt increase/drop of cell voltage. The third mechanism postulating that electricity is produced by heterotrophs that consume organic compounds released by phototrophs is even less likely as this mechanism does not explain the perfect coincidence or lack of delay between the light cycles and voltage oscillation. In fact, this mechanism would predict a negative light response (a voltage increase during dark-phase), as has been reported recently (He et al., 2009). Nevertheless, our on-going studies using specific inhibitors of the electron transfer chains should provide further insight into the mechanism of light-powered electrogenic activity.

In recent studies, several sun-powered MFCs have been reported (Cao et al., 2008; Chiao et al., 2006; He et al., 2009; Malik et al., 2009). A sediment-type PMFCs inoculated with photosynthetic cultures were shown to display a negative light response (i.e., voltage drop during light-phase) (He et al., 2009). The negative light response is consistent with the mechanism where phototropic bacteria produce organics that feed heterotrophs and the respiratory electron-transfer chain of the heterotrophic bacteria is the source of electrons deposited on an anode. A voltage decrease during the light-phase was presumably due to the negative impact of photosynthetically evolved oxygen. Another study reported light-dependent voltage oscillation in marine-sediment PMFCs, where the open circuit voltage gradually increased upon illumination and maintained high steady-state level even during substantial portion of the dark-phase (Malik et al., 2009). Such kinetics of voltage oscillation is consistent with the mechanism proposing that phototrophs release organic compounds that feed heterotrophs. In the current study, we found that the intensity of dark-phase voltage gradually increases over several days of operation. This result may indicate accumulation of organics within photosynthetic biofilm and was consistent with the potential involvement of heterotrophs in generating power during the dark-phase. Interestingly, replacing of media in PMFC was found to reduce the dark-phase voltage which presumably occurred due to removing of organics (Suppl Fig. 6). The dark-phase voltage was restored in a few days. The current configuration of PMFCs appears to be suitable for harvesting electrons from both the photosynthetic and respiratory electron-transfer chains during light- and dark-phases, respectively.

The present work provided a useful framework for the future design and operation of PMFCs. Exploiting biofilm-forming photosynthetic cultures instead of planktonic cultures was shown to improve substantially the light response and remove the need for exogenous electron shuttles. We do not know whether nanowires were involved in electron transfer (Gorby et al., 2006; Reguera et al., 2005). Coating the anode with polyA or polyP was found to improve the yield of electron harvesting. Both polymers accelerated biofilm growth and altered favorably the electrochemical properties of the anodes. Positive effect on biofilm formation was consistent with previous findings that positively charged natural surfaces enhance adhesion of bacteria. In studies of mixed culture MFCs, the power production was increased upon treating the anode with ammonia that increased the positive charge on the surface (Cheng and Logan, 2007). Furthermore, consistent with previous studies with anaerobic MFC (Ramasamy et al., 2008), EIS revealed that the anodic charge transfer resistance was reduced upon initial biofilm formation indicating direct involvement of the biofilm in electron transfer.

The presence of oxygen in PMFCs appears to present the most significant challenge for achieving high power outputs, as it causes protons to be reduced to water before the electrons can reach anode. Supersaturated DO concentrations were found in both planktonic and biofilm cultures, as no precautions were employed to deprive DO. Despite an increase in DO and pH during the light-phase, PMFCs persistently showed higher cell voltage during the light-phase. Several strategies could be envisioned in future studies for reducing oxygen concentration including purging with CO2 or co-culturing with aerobic chemoheterotrophs that consumes oxygen for cellular respiration. Kayano et al. (1981) employed aerobic Bacillus subtilis for removing oxygen from the fuel cell reactor and increasing hydrogen production. In natural photosynthetic mats, DO concentration drops rapidly through the depth of mat reaching undetectable level at the depth of 2 mm (Stal, 2000). It should be possible to exploit the natural oxygen gradient for improving the design of the electron harvesting system in future PMFCs. Employing three-dimensional porous material instead of carbon paint should promote formation of a highly dense biofilm with higher yield of light energy harvesting per anode footprint area. Low conductivity of mBG-11 and high pH values were among other factors that contributed to the low PMFC power output. Exploiting marine photosynthetic cultures that grow in highly conductive saline media instead of freshwater cultures may help to overcome high PMFC internal resistance.

Photosynthetic biofilms or mats are completely self-sustainable communities that can grow on sediments in a variety of environments (Stal, 2000). The dense biomass of photosynthetic organisms in the mats results in high rates of photosynthesis. On a surface area basis, the photosynthetic productivity compares to that of rain forests, which are considered the most productive ecosystems on earth. Of the 1.5 x 1022 kJ of solar energy reaching the earth each day, 1% is absorbed by photosynthetic organisms and converted into biomass. These important characteristics provide unique opportunities for designing fully self-sustainable, solar-powered PMFC bio-devices or bioreactors. Further studies on PMFCs should advance our knowledge about alternative mechanisms for harnessing solar energy.
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