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Novel bufferless photosynthetic microbial fuel cell (PMFCs) for enhanced electrochemical performance

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ABSTRACT

Photosynthetic microbial fuel cells (PMFCs) are novel bioelectrochemical transducers that employ microalgae to generate oxygen, organic metabolites and electrons. Conventional PMFCs employ non-eco-friendly membranes, catalysts and phosphate buffer solution. Eliminating the membrane, buffer and catalyst can make the MFC a practical possibility. Therefore, single chambered (SPMFC) were constructed and operated at different recirculation flow rates (0, 40 and 240 ml/min) under bufferless conditions. Furthermore, maximum power density of 4.06 mW/m^2, current density of 46.34 mA/m^2 and open circuit potential of 0.43 V and low internal resistance of 611.8 Ω were obtained at 40 ml/min. Based on the results it was decided that SPMFC was better for operation at 40 ml/min. Therefore, these findings provided progressive insights for future pilot and industrial scale studies of PMFCs.

1. Introduction

The hovering demand for energy requires the development of new technologies that can provide alternatives to traditional energy sources in a sustainable fashion (Long et al., 2017; Dai et al., 2017). Microbial fuel cells (MFCs) are bioelectrochemical reactors, which could significantly accelerate ability of wastewater treatment by generating clean energy and renewable alternative energy (Wang et al., 2017). However, numerous studies have reported research works on toxic aqueous solutions such as potassium ferricyanide, which are not eco-friendly and unsustainable (Wetser et al., 2015). Therefore, the environmentally sustainable and affordable biocathode MFCs should be used for extensive research. In a Photosynthetic microbial fuel cell (PMFC), microalgae are inoculated in the cathode and it is a biocathode MFC (Walter et al., 2013). Inoculating microalgae in the cathode has myriad advantages that could generate oxygen (electron acceptor) in the catholyte via anodic carbon dioxide and also eliminate the requirement for mechanical air supply. This eventually reduces the cost of operation (Kakarla et al., 2015). PMFC can be mainly divided into two main categories according to its design as SPMFC and DPMFC. The difference is that the DPMFC has a membrane to separate the chambers, whereas the anolyte and catholyte are mixed in a SPMFC. Therefore, SPMFC not only eliminates the drawbacks of membrane in respect to low proton transfer and clogging (Rismani-Yazdi et al. 2008), but also reduces the cost (Jang et al. 2004; Jafary et al., 2017). Furthermore, the SPMFC have a syntrophic interaction between EAB (Electrochemically Active Bacteria) and microalgae. The mechanism is that the algae carries out the autotrophic reaction by employing CO_2 from anodic oxidation of organics and algae could as also be a substitute for substrate like acetate in MFCs. High power performance in MFCs has been reported by the usage of microalgae and minerals for the growth of EAB as the integration of bio cathode with MFCs could probably eliminate the problem of oxygen intrusion into the anolyte (Ieropoulos et al. 2010; Kouzuma and Watanabe, 2015; Wang et al. 2018). Moreover, photosynthetic biocathode could enhance the power density in the SPMFC (Commault et al., 2014). Nevertheless, PMFC still has drawbacks for scale-up since most of them employ expensive buffer solution to inhibit anolyte acidification, and this could result in a declined performance of the MFC (Zhang et al., 2015). The conventional buffer solution in MFC includes phosphate buffers or bicarbonate buffers and the negative effects are that they are non-biodegradable and result in eutrophication when released into the environment (Gil et al., 2003;

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Fan et al., 2007). The usage of bicarbonate buffers can also accelerate the growth of methanogens (Yang et al., 2016). Therefore, bufferless conditions can definitely enhance the feasibility of MFCs. Ahn and Logan (2013), employed saline catholyte to replace phosphate buffers in MFC and this increased the coulombic efficiency from 43% to 60%, and declined the maximum power density by only 17%. However, the adverse conditions for PMFC scale up include not only buffers but also noble and expensive metal catalysts such as platinum. This can cause clogging of organics and are highly toxic for a long time operation (Cristiani et al., 2013). Therefore, avoiding buffers and metal catalysts could be a more practical approach. In addition, the MFC used in this study was operated in a recirculation flow mode and therefore, the flow rate is a significantly important parameter for MFC scale-up as it could affect the performance (Ieropoulos et al., 2010). In addition, the recirculation flow mode which is similar to the flow mode adopted in wastewater treatment plants could enhance better flow mixing. This measure will obviously reduce the cost of stirring in DPMFC (Wang et al. 2014).

Honey comb pattern or flow-straightener is a common aspect in the field of fluid dynamics. This pattern is considered very advantageous as it maintains the flow geometry of a fluid inside a reactor in a homogeneous, symmetrical and uniform manner. This affects the mass transfer of substrates and ions and eventually enhances the reactor performance (Song et al., 2016). It could also reduce the swirl of incoming fluid from turbulent to laminar (Seo, 2013). As far as our knowledge is concerned this pattern has not been integrated into an MFC so far and we therefore consider it a novel attempt. The aim of this study was to investigate PMFC with cost-effective and environmentally sustainable methods for their scale-up. That includes construction and operation of MFCs without buffer, noble metal catalysts and mediators. These findings would clearly provide promising and feasible information about PMFC under bufferless conditions for the application of practical wastewater treatment in the future.

2. Materials and methods

2.1. Reactor configuration

Two different types of MFCs were used in this research study: dual chamber acclimation system (DA) and SPMFC (Fig. 1). The DA was used to enrich biofilm on the anode electrode and further place that acclimated electrode into SPMFC. The anode chamber (1000 ml) and cathode chamber (1000 ml) of the DA were separated by a proton exchange membrane (PEM, projected area of 80 mm × 80 mm; Nafion 117, Dupont Co., USA). Anode and cathode were made of pretreated carbon cloth (80 mm × 80 mm; W0S1002, CeTech Co., Taiwan) (Chen et al., 2013). PMFCs were constructed and operated to investigate the electrochemical performance and feasibility at different recirculation flow rates under bufferless conditions. Cuboid-shaped SPMFCs (4000 ml) were fabricated out of a plexiglass block, which consisted of reservoirs (each with 100 mm × 170 mm × 175 mm). Honeycomb pattern made of plastic straws (each with 100 mm × 100 mm × 100 mm) was inserted into the flow chambers and a test section (which harbours anode and cathode electrode) 100 mm × 100 mm × 120 mm) (Fig. 1). SPMFCs were operated in a recirculation loop mode. After successful start-up of the MFCs, bio anode (7450 mm^2) and bio cathode (microalgae electrode) (7450 mm^2) were arranged at the bottom and side wall of SPMFCs respectively.

2.2. Inoculation and operational conditions

To start-up a MFC in a short time and effectively treat large volumes of wastewater with high flow rates, developing a robust biofilm was a significantly important process (Ieropoulos et al., 2010). Therefore, before the SPMFCs were operated, the enrichment of the biofilm was carried out on the anode and cathode. The biofilm on the anode was acclimated by placing the electrodes in DA and this process was carried out in two stages. In the first stage, the reactor was filled with 50% wastewater from Lo-Tung wastewater treatment (pH 7.0–9.0) plant and 50% sodium acetate medium containing 50 mM PBS (Na_2HPO_4, 4.58 g/L; $NaH_2PO_4{\cdot}H_2O$, 2.45 g/L; NH_4Cl, 0.31 g/L; KCl, 0.13 g/L). 50 mM $K_3Fe(CN)_6$ and 50 mM PBS was filled in the cathode chamber. This method was repeated for three batch cycles. In the second stage, anolyte was replaced with 100% sodium acetate medium, when the voltage dropped less than 10% of the maximum value. This was repeated until the maximum voltage had been steady with 3 peaks. To further shorten the acclimation time, high external resistance (1000 Ω) was set. After that, lower resistance such as 500 Ω, 200 Ω, 100 Ω, 50 Ω were applied, as this may result in a denser biofilm and increase the current density (Ren et al., 2011). Marine algae (*Chlorella*) were taken in a glass beaker and illuminated for 12 h with a 6 W fluorescent lamp. The lamp was placed near the side wall of glass beaker and the distance between them was 50 mm. In addition an air pump (EAP-3 RAMBO Co., Taiwan) with an air stone and a stirring bar was placed in the glass beaker for solution mixing. The cathode electrode was placed into the beaker to allow the growth of algal biofilm on the cathode surface. The bio electrodes were later placed inside the SPMFCs and they were operated at different flow rates (0, 40, 240 ml/min with a peristaltic pump (Masterflex, Cole-Parmer, Vernon Hills, IL, USA) for the investigation on recirculation flow rate effects according to the previous study (Wang et al. 2018). Solution of SPMFC-B (buffer) contained 50 mM PBS and 1 g/L sodium acetate and that of SPMFC-BL (bufferless) contained 3.25 g/L and 1 g/L sodium acetate to maintain the same conductivity as that of the buffer condition. The artificial light was supplied with a 6 W fluorescent lamp (Kotobuki, JP).

2.3. Calculations and measurements

Cell voltage was recorded every min using a data acquisition system, which was connected to a personal computer. Current density and power density were calculated based on the cathode surface area (mW/m^2) as previously described (Ren et al., 2011). Polarization process and Electrochemistry Impedance Spectroscopy (EIS) were performed after open-circuit conditions for 4 h. Sine wave of (10 mV) was applied with a AC impedance spectroscopy (HIOKY 35522-50 LCR Hi-TESTER, Japan) within a frequency of 100 kHz to 2.5 mHz. The pH was measured using a pH meter (SP-701, WTW Co., GER).

3. Results and discussion

The main aim of this study was to construct and operate SPMFC reactors by eliminating metal catalysts, mediators, buffer solution and membrane. This can be more cost-effective for applications and scale-up. Therefore, the performance of SPMFCs was investigated in this study under bufferless and buffered conditions during light/dark cycles.

3.1. Variation of pH in SPMFCs

The pH variations in the SPMFCs are illustrated in (Fig. 2). The bufferless conditions are depicted in Fig. 2.a; whereas the buffered conditions in Fig. 2.b. In Fig. 2a, the starting pH of the anolytes with different recirculation flow rate were different (pH = 7.5–9.5) because this research aimed to imitate the conditions of the real WWTPs (the pH of the wastewater in the WWTPs cannot be the same always). In SPMFC, the concentration of OH^- were increased by photosynthesis of algae, therefore, it was possible that the photosynthesis carried out by microalgae generated OH^- to contribute to reduced acidification of anode and it could have maintained a suitable condition for bacterial growth (Cui et al., 2014; Kouzuma and Watanabe, 2015). Thus, the pH of BL = 40, 240 rose up when discharge stared at 20 h but as the increase in recirculation flow could have enhanced the OH^- transfer and mixing well in the anolyte. This may be the reason behind the alkaline