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Characterization of membrane biofouling and its effect on the performance of microbial fuel cell

Madiah Miskan^a, Manal Ismail^{a,b,*}, Mostafa Ghasemi^a,
Jamaliah Md Jahim^{a,b}, Darman Nordin^b, Mimi Hani Abu Bakar^a

^a Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Malaysia

^b Department of Chemical & Process Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

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ABSTRACT

During long-term operation of microbial fuel cells (MFCs), biofouling will gradually form on membrane surfaces. Biofouling is one of the major obstacles to the efficiency and economic operation of MFCs. The present study investigated and characterized the formation of biofouling on membranes at three different time frames within six months of MFC operations and the effect of biofouling on the performance of MFCs. The membranes were characterized by analyzing changes in the surface morphology, membrane structure, proton conductivity and resistance. The biofouling layer on the membrane increased over time during the MFCs' operation from $14.7 \pm 0.4 \mu\text{m}$ (at two months), $165.1 \pm 22.4 \mu\text{m}$ (at four months) to $250.1 \pm 10.7 \mu\text{m}$ (at six months). The morphology observed using scanning electron microscopy showed the enhancement of the growth and compactness of the bacteria formed on the membranes' surfaces. Organic and inorganic elements were identified as binding factors that could strengthen the biofouling layer. The increase in the thickness of the biofouling layer resulted in the reduction of the proton conductivity of the Nafion 117 membrane, which led to an increment in membrane resistance due to restrictions in proton transfer through the biofouling membrane. Based on the performance results, the power density of the MFC showed a 55% reduction from 1 W/m^2 at two months of operation to 0.45 W/m^2 at six months of operation. Therefore, the cumulative effect of biofouling on the membranes' surfaces during long-term operation obstructed the mobility of protons across the membrane, causing MFC performance to deteriorate.

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Introduction

Interest in renewable energy has grown rapidly due to the depletion of unsustainable fossil fuel resources and

awareness of environmental pollution [1]. Microbial fuel cells (MFCs) are an innovative technology being considered as a new to bioconversion process for energy production. MFCs differ from other types of fuel cells because they use microorganisms as a biocatalyst to convert organic matter

* Corresponding author. Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Malaysia. Tel.: +60 389216404; fax: +60 389216148.

E-mail address: manal@ukm.edu.my (M. Ismail).

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into electricity. To support microbial growth, substrates containing various solutes are added into aqueous electrolytes [2–4]. The energy production starts when microorganisms oxidize these substrates to produce electrons and protons. The electrons are transferred to the cathode compartment through an external circuit, whereas the protons are transferred to the cathode through a proton exchange membrane (PEM). Both the electrons and the protons then combine with oxygen at the cathode to form water [5–7]. The membrane is one of the most important components of the MFC system because it acts as a physical separator and allows only protons to pass through the membrane to the cathode. Moreover, the membrane must be able to hinder the passage of other materials and the crossover of oxygen from the cathode to the anode [5].

However, when MFCs are operated long-term, microbes grow and cause biofouling on the surface of the membrane [2,8]. Biofouling is an unwanted phenomenon in MFCs and occurs due to organic foulants such as extracellular polymeric substances (EPSs) that participate in bacterial aggregation and cluster during the formation of biofilms on the membrane surface [9,10]. Moreover, the negatively charged sulfonate groups in the membrane can easily bind with multivalent cations, especially at low pH [11]. This bond eventually contributes to the formation of a strong biofouling layer on the membrane [12–14].

To date, few studies have reported on the common causes of biofouling and the deterioration of MFC performance; however, no detailed discussions on membrane biofouling have taken place [2,8,15–17]. Choi et al. (2011) found a thin layer of biofouling after a year of MFC operation with a thickness of $15.5 \pm 4.6 \mu\text{m}$ in their study on dual-chambered MFCs. They reported that increases in electrical resistance of the membrane are due to cation replacement on the negatively-charged sulfonate group of the PEM instead of the biofouling layer [16]. In a different MFC study, Xu et al. [17] reported that their single-chamber MFC, which operated for almost three months, had deteriorated in performance due to a physical blockage of charge transfer caused by membrane fouling [17].

Therefore, this study was performed to gain an in depth understanding of the effect of biofouling behavior on membrane surface in long-term operations. Observations were conducted in three different time frames on changes in membrane characteristics; specifically changes in surface morphology, membrane structure, proton conductivity and membrane resistance, using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, energy dispersive x-ray (EDX) spectrometry and electrochemical impedance spectroscopy (EIS). Moreover, the effect of biofouling on the deterioration of MFC performance was also explored.

Experimental methods

MFC setup and operation

Three dual-chambered MFCs, as illustrated in Fig. 1, were constructed with a 220 ml volume for both their anode and

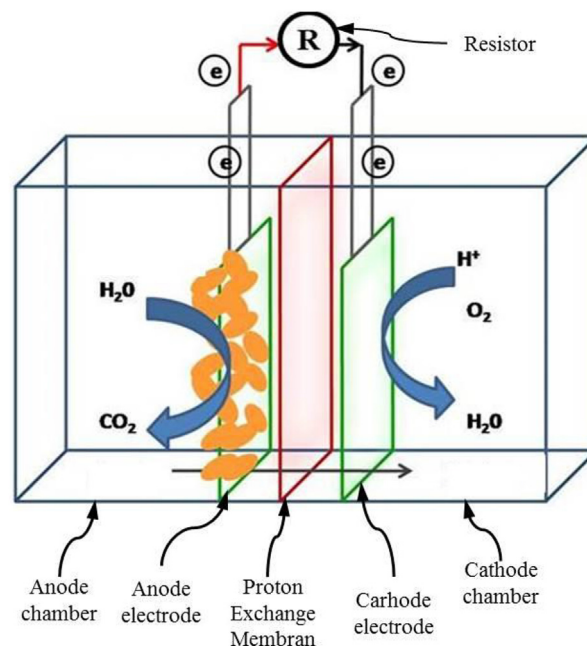


Fig. 1 – Schematic diagram of dual-chambered MFC with PEM (Nafion 117) as membrane separator.

cathode chambers and were equipped with inlets and outlets for feed and gas. Carbon paper (AvCarb™ P75T) with a surface area of 17.5 cm^2 was used for the anode and cathode electrodes. The cathode was coated with 0.5 mg/cm^2 of platinum catalyst. The anode and cathode chambers were separated using a Nafion 117 membrane with both electrodes placed adjacent to the membrane at 0.5 cm spacing to improve the efficiency of the electron flow. The MFC systems were then connected to a 1000Ω external resistor. The Nafion membranes were pretreated before being used by boiling in $80 \text{ }^\circ\text{C}$ distilled water and then $3\% \text{ H}_2\text{O}_2$ and $0.5 \text{ M H}_2\text{SO}_4$. Each stage was finished within an hour.

Anaerobic effluent from the Indah Water Konsortium Wastewater Treatment Plant containing a mixed bacterial culture was used as the anode inoculum. An artificial medium containing 0.62 g of glucose, 0.03 g of yeast extract, 0.1 g of KCl, 0.7 g of $\text{NaH}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$, 1.5 g of NH_4Cl , 2.5 g of NaHCO_3 , 10 ml of Wolfe's mineral solution and 10 ml of Wolfe's vitamin solution was then added into 1 L of deionized water [18]. The medium was sterilized by autoclaving, and the medium in the MFCs were replenished approximately every 3–4 days to maintain voltage at a maximum value. The anode chamber was kept under anaerobic conditions by purging with nitrogen gas for 10 min every time the medium were replenished. The cathode chamber was filled with phosphate buffer (pH 6.8–7.0) containing 2.76 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 4.26 g of Na_2HPO_4 , 0.31 g of NH_4Cl and 0.13 g of KCl in 1 L deionized water. The MFC system was agitated with a magnetic stirrer at 50 rpm . To evaluate the effect of biofouling on the changes in the membranes' characteristics and MFC performance, three sets of MFCs with the same configuration were operated for three different working durations as follows: MFC1 for 60 days (two months), MFC2 for 120 days (four months) and MFC3 for 180 days (six months).

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