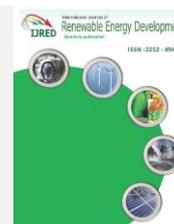




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Preliminary Study of the Use of Sulfonated Polyether Ether Ketone (SPEEK) as Proton Exchange Membrane for Microbial Fuel Cell (MFC)

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ABSTRACT. Sulfonated polyether ether ketone (SPEEK) was utilized as a proton exchange membrane (PEM) in Microbial Fuel Cell (MFC). The SPEEK performance in producing electricity had been observed in MFC using wastewater and glucose as substrates. The MFC with catering and tofu wastewater produced maximum power density about 0.31 mW/m² and 0.03 mW/m², respectively, lower than that of MFC with tapioca average power density of 39.4 W/m² over 48 h. The power density boosted because of the presence of *Saccharomyces cerevisiae* as inoculum. The study using of *S. cerevisiae* and *Acetobacter acetii*, separately, were also conducted in with glucose as substrate. The MFC produced an average power densities were 7.3 and 6.4 mW/m² for *S. cerevisiae* and *A. acetii*, respectively. The results of this study indicated that SPEEK membrane has the potential usage in MFCs and can substitute the commercial membrane, Nafion.

Keywords: Microbial Fuel Cell, sulfonated polyether ether ketone, electricity

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1. Introduction

Hydrogen or electricity could be one of the main components in CO₂ reduction efforts. Nowadays, as we know, the issues linked to the reduction of global CO₂ emissions have been proven able to divert the attention from conventional energy into renewable ones, such as biomass (Metcalf and Eddy, 2003, Notodarmojo, 2005). Hydrogen can be produced not only through Fuel Cell but also biologically through fermentation of saccharide groups at high concentration (Logan *et al.* 2002, Prestigiacomo *et al.* 2016) although no more than 50% of the potential maximum energy that can be generated. Mostly, the resulting energy is derived from advanced fermentation of organic acid such as acetic, butyric, and propionic acid, even solvents also like ethanol and butanol (Logan *et al.* 2002, Oh *et al.* 2008)

Beside hydrogen, it is recently known that electricity also can be directly generated from degradation of organic matters in Microbial Fuel Cell (MFC) system (Allen and Benneto, 1993, Katz *et al.* 2003, Bond and Lovely, 2003, Guerrini *et al.* 2014).

Some substrates commonly used in MFC are organic wastes (Aborached *et al.* 2013), pure substrates such as glucose and acetate (Christiani *et al.* 2013; Gal *et al.* 2016), domestic wastewater (Permana *et al.* 2015a; Rahyuningwulan *et al.* 2015), even from marine sediments (Bond *et al.* 2002). Meanwhile treating wastewater, MFC capable of generating electricity simultaneously (Santoro *et al.* 2013).

MFC system generally consists of two chambers, the anode, and cathode. The cathode takes place in aerobic, where the protons generated at the anode with oxygen to form water. At the anode usually lasts for anaerobes, wherein the substrate is oxidized by microbes to generate electricity as the electrons and protons are transferred to the cathode through the proton exchange membrane (PEM), such as membrane and salt bridge (Sukhla *et al.* 2008, Permana *et al.* 2013, Singh and Verma, 2015).

PEM is designed to facilitate the transfer of protons from the anode to the cathode while preventing the transfer other substrate and an electron acceptor (oxygen) (Park and Zeikus, 2000, Rabaey *et al.* 2003).

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Therefore, PEM has an important role in MFC. The using of appropriate PEM can increase the power output of MFC. One of the most popularly used in MFC is Nafion® 117 because of its high selective permeability to proton. However, Nafion® 117 being expensive, at the end, it will affect the production cost of MFC. PEEK is one of promising polymer to replace Nafion. PEEK is a low-cost polymer which having good thermal stability, mechanical properties (Handayani *et al.* 2007), and better ionic conductor (Neburchilov *et al.* 2007). Its proton conductivity can be achieved by sulphonation process.

Since have not been many reports of the using of SPEEK on MFC, in the present study, authors report electricity generation from various substrates comprise wastewater (tapioca, tofu, catering) and pure substrate (glucose) using MFC system. Sulphonated polyether ether ketone (SPEEK) is used as a membrane.

2. Materials and Methods

2.1 Substrates and inoculum sources

Two kinds of substrates are separately used in this study comprise glucose and wastewater. The first MFC setup, both of *Acetobacter aceti* and *Saccharomyces cerevisiae* were carried out in a sterilized nutrient medium (21,6 mg/mL glucose, 0.5% yeast, 0.5% peptone, 0.3% KH_2PO_4 , and 0.3% $(\text{NH}_4)_2\text{SO}_4$ at pH 7. These compositions were used as a single of inoculum and as a medium of growth (Permana *et al.* 2015b). Microbes were inoculated into 25 ml sterile medium and grown at 30°C for 18 h, 150 rpm.

Meanwhile, wastewater was collected and put into a sterile plastic bottle measuring 1 L. It was obtained directly from effluent at tapioca, tofu and catering industry. There was no amended with medium ingredients. It was intended like to be the condition of the waste field and used as the inoculum and growth medium. The initial pH of all solutions was adjusted to 7 and all MFCs were operated in a temperature-controlled room at 30°C.

2.2 Experimental setup

The fabricated MFC consist of two glass chamber (net volume of 900 ml) separated by SPEEK membrane (Figure 1). MFC system is supported by copper electrodes connected into the outer circuit. The first chamber (anode) is containing wastewater and potassium permanganate (KMnO_4) solution as an electron acceptor in the other room. The potassium permanganate solution had an average concentration of 50 ppm were conditioned under acidic conditions; the pH is about 3 to 4.

2.3 SPEEK membrane

Synthesis and characterization of SPEEK have been described in earlier reports (Handayani *et al.* 2007). In a typical experiment, 5 g of PEEK powder (450-P, Victrex) was dissolved in 100 ml of sulfuric acid (Merck,

95-97%). The sulphonated reaction was done during 3 h at 60°C. The resulting mixture was poured onto crushed ice and the innumerable fibers that were formed were recovered by filtration. Washing process with deionized water was done several times until the pH reached neutral. The acquired polymer was dried at 70°C for 48 hours.

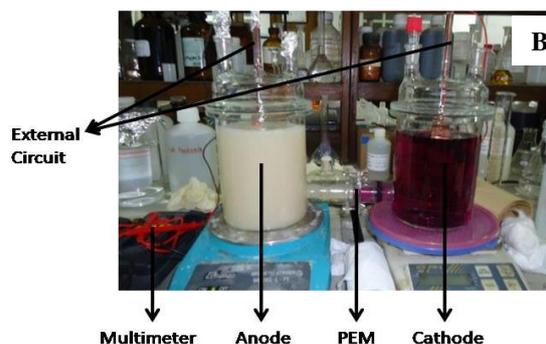
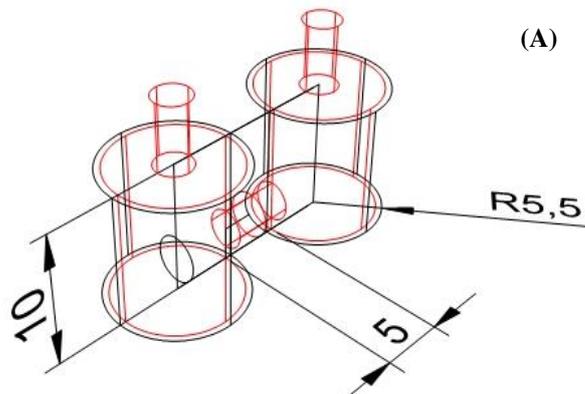


Fig. 1 Schematic of Double Chamber MFC (A). Dual Chamber MFC reactor used in this research that suggested by You *et al.* (2006) and Permana *et al.* (2013, 2015a). PEM (proton exchange membrane) that used was SPEEK. The volume of each chamber is 1000 mL.

Dried SPEEK was dissolved in *n*-methyl-2-pyrrolidone (composition 12.5% up to 15% by weight solution), then allowed to stand overnight. Membrane sonication for 15 minutes was done before its printing using *doctor blade* (size 850 μm) on the glass plate, then oven-dried. For this study, SPEAK give the value of ion exchange capacity, proton conductivity, and percentage water absorption were 2.1 meq/g, 0.045 S/cm, and 16% respectively.

2.4 Methods for Analysis

The MFC was a closed system. The circuit was completed with fixed load of 1 K Ω . Both of voltage and current was recorded by using a digital multimeter (Model Sanwa CD800a). Power was also calculated according to this formula, $P=IV$, where, P (W) is the power, V (mV) is the voltage, I (mA) is the current, and R (Ω) is the external resistance.

The power generated is calculated based on the data of potential and a strong current that is read by a multimeter with equation (1), power density is calculated using equation (2) (Rabaey *et al.* 2013).

$$P = V \times I \quad (1)$$

$$Pd = P \div A \quad (2)$$

where

P = Power (mW)

V = Potential (mV)

I = Current (mA)

Pd = Power density (mW/cm²)

A = Anode surface area (cm²)

The concentration of Chemical Oxygen Demand (COD) from wastewater was also determined (before and after the process) according to Indonesian National Standard SNI 6989.73:2009. The process took 48 hours. The SNI 6989.73:2009 is a standard method for COD analysis that based on the closed reflux titrimetry. Samples oxidized by the strong oxidizer, potassium dichromate (K₂Cr₂O₇) in the closed tube for 2 hours at 150°C. The amount of unreacted potassium dichromate then titrated with ferrous ammonium sulfate with feroin as an indicator. The analysis of samples was done with three replicates. The COD analysis methods maintained with the analysis of COD of standard samples, the use of pro analytical chemical reagents, special glassware, calibrated pippets, thermometer, burettes, and balance.

The Atomic Absorption Spectrometry (AAS) (Flame AAS, Hitachi) was used to determine the residue of permanganate ions (MnO₄⁻) in the catholyte. The reduced permanganate ions are written in percentage (%).

3. Results and Discussion

3.1. Profile of power density generated from wastewater

The MFCs with SPEEK membrane and using tofu and catering wastewater have produced a maximum power density of 0.03 mW/m² and 0.31 mW/m², respectively (Fig. 2). These values were very low because of mixture culture without any additional treatment.

Among of wastewater, electricity production showed that the greatest was tapioca wastewater. The MFC with tapioca wastewater achieved an average power density of 114 mW/m² over 16 h (6–20h) (Fig. 3). This level of average power generation was almost three times to that obtained using *Geobacter metallireducens* in the MFC reactor with Nafion and cereal wastewater as membrane and substrate around 38mW/m² over 71h. The maximum voltage reached about 666 mV higher than 400 mV which produced by MFC with SPEEK utilizing both dairy wastewater and domestic wastewater.

Power generation has increased since adding 0.025 ppm of *S. cerevisiae* as inoculum. This yeast concentration had greatly affected the value of the

generated voltage, more number of yeast cells the more the metabolic processes can take place.

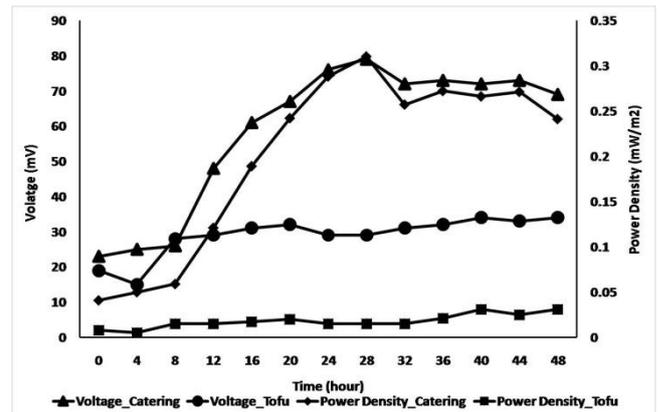


Fig. 2 Voltage and Power Density in MFC Using Tofu and Catering Wastewater

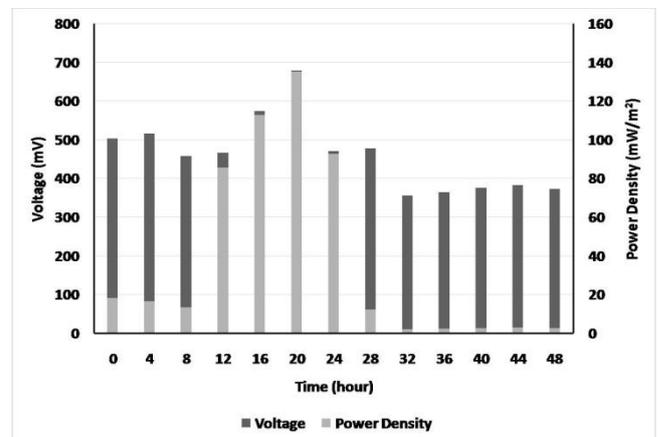
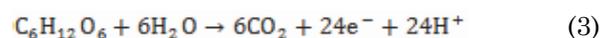


Fig. 3. Voltage and Power Density in MFC Using Tapioca Wastewater

3.2. Profile of power density generated from glucose

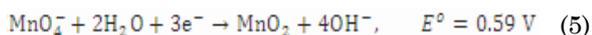
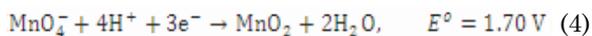
The MFCs with SPEEK membrane was also applied with glucose as a medium of growth for selected microbes; *A. aceti* and *S. cerevisiae*. Though these microbes are commonly used in the fermentation process, the process set at the semi-aerobic condition.

In the present study, glucose was also used as a substrate for the MFC. *S. cerevisiae* and *A. acetii* were used as biocatalysts in the MFCs used glucose as substrate and carbon source in the anode chamber and generate electrons and protons (H⁺). A total of 24 mol electrons and hydrogen ions were produced by oxidation of one mole of glucose in the anaerobic condition. The anodic reaction is taken place at the anode as summarized in equation (3).



The electron produced by microorganism and captured by anode surfaces and protons (H⁺) travel through SPEEK and react with oxygen in the cathode to produce water (H₂O). Electrons from anode then

captured by permanganate ions (MnO_4^-) that play a role as an electron acceptor that captured electrons that traveled from the anode. Permanganate ion was used as electron acceptor because it has high oxidation capacity and also more environmentally friendly (nondangerous reduced products). Either in acidic and alkaline conditions, permanganate ion accepts three electrons and reduced to manganese dioxide, as shown in equations (4) and (5).



Equations (4) and (5) explained that permanganate ion has higher potential in acidic condition. Therefore in the present study, the acidic condition was used for the cathodic electron acceptor expecting to maximize the electricity generation (Permana *et al.* 2015b).

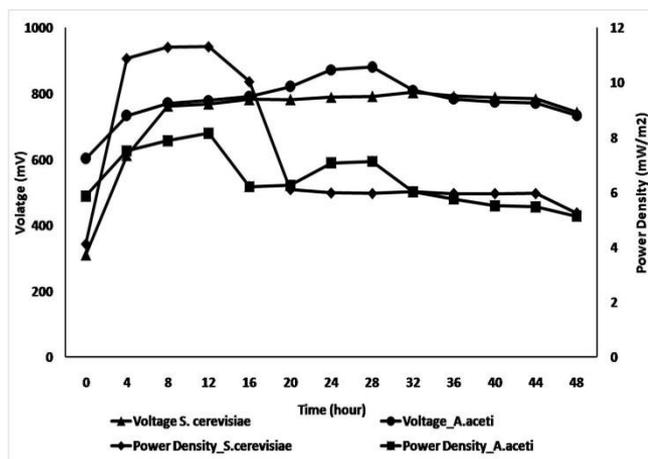


Fig. 4 Voltage and power density in MFC using glucose and selected microbes

During the process, the voltages kept elevated until 28 hours and tend to decrease afterward since glucose concentration has also diminished. Separately, the MFC using *A. aceti* shown that the maximum voltage was about 880 mV (after the 28h process) larger than 803 mV (after the 32h process) using *S. cerevisiae* (Figure 4). The average power density was higher around 6.4-7.3 mW/m² compared to 0.7 mW/cm² of maximum power density generated from one chamber air cathode MFC (Permana *et al.* 2015b).

The value of voltage and electricity current greatly dependent on substrate supply that used as oxidation medium for biocatalyst (Liu and Li, 2013, Li *et al.* 2014, Kim *et al.* 2015). Although the resulting voltage larger, a higher internal resistance on the system have resulted in small electricity current (data not shown) compared to Walker and Walker Jr's (Walker and Walker 2006). Double chamber MFC usually have large internal resistance (Permana *et al.* 2013; 2015a). Moreover, oxygen existed in system inhibited electron transport from the anode into the cathode. The electrons were more prone to the process of reduction

in aerobic condition (Abourached *et al.* 2013).

3.3. Profile of COD level after process

In this study, the tofu, catering, and tapioca wastewater were used to demonstrate electricity generation in a two-chambered MFC. Following startup and 48h process, the total COD of each wastewater was measured. COD level was significantly decreased for tapioca wastewater almost 97% in 2 days after MFC operated (Table 1).

Table 1. COD Removal.

Wastewater (COD in ppm)	MFC Process (hours)			Percentage of COD Removal
	0	24	48	
Tapioca	2000	96	64	96.80
Tofu	6750	6300	4320	36.00
Catering	18,840	13,800	11,100	41.08

MFC is a bioelectrochemical system that drives a current by mimicking bacterial interactions. Not only used for generating electricity, it also can be used for wastewater treatment. These results showed that organic substances concentration was decreased during 48 hours of the experiment. It was used by *S. cerevisiae* and *Acetobacter acetii* as a carbon source for growth and production of ethanol by the yeast, *S. cerevisiae*. The electrons produced as another output for electricity generation (Permana *et al.* 2015b).

3.4. Concentration of electrons acceptor

Permanganate ions (MnO_4^-) used as catholyte because it has manganese (Mn) atom with +7 of the oxidation number. It able to accept many electrons, although it caused its oxidation number reduced to +4 or +2 to form manganese oxide, MnO_2 or MnO . The initial concentration of permanganate ions was 50 ± 0.4 ppm. After MFC process finished for 48 hours the concentration dropped to 3.02 ± 0.1 ppm or 93.90 % of manganese reduced. This results confirmed that Mn atoms successfully reduced by the electrons that produced in MFC. Manganese reduced and formed a black-brown sediment of MnO_2 or MnO in the cathode chamber (Fig. 5).

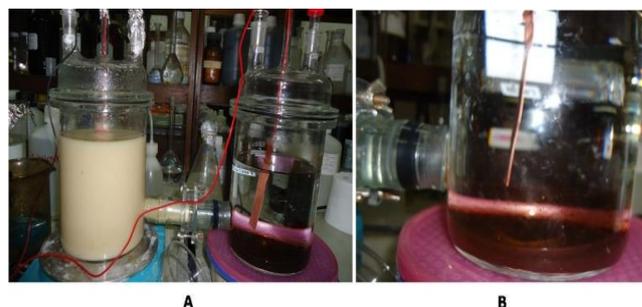


Fig. 5 The color of catholyte changed after 48 hours and concentration of manganese decreased (A). The formation of black-brown sediment of MnO_2 or MnO in the cathode.

The manganese also released two or three oxygen atoms when it reduced and formed manganese oxide (MnO_2 or MnO). The oxygen atoms then reacted with proton that permeates through SPEEK from the anode to form water molecules. We suggested that the concentration of free proton that entered into cathode was very low. Because protons directly reacted with oxygens. It was indicated by there is no significant pH change in catholyte.

4. Conclusion

The SPEEK membrane has the potential usage in MFC as proton exchange membrane. It is efficient and a cheap alternate the commercial membrane, Nafion®. It is also suitable to be applied for MFC with various substrates, for example, glucose and other wastewater. The MFC with catering and tofu wastewater generated maximum power density of 0.31 mW/m^2 and 0.03 mW/m^2 , respectively, lower than MFC with tapioca at the average power density of 39.4 W/m^2 over 48 hours. The power density boosted because of the presence of *S. cerevisiae* as inoculum. The study using of *S. cerevisiae* and *Acetobacter acetii*, separately, were also conducted in with glucose as substrate. The MFC produced an average power densities were 7.3 and 6.4 mW/m^2 for *S. cerevisiae* and *A. acetii*, respectively

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