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MICROBIAL FUEL CELL BASED POLYSTYRENE SULFONATED MEMBRANE AS PROTON EXCHANGE MEMBRANE

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ABSTRACT

Microbial fuel cell (MFC) represents a major bioelectrochemical system that converts biomass spontaneously into electricity through the activity of microorganisms. The MFC consists of anode and cathode compartments. Microorganisms in MFC liberate electrons while the electron donor are consumed. The produced electron is transmitted to the anode surface but the generated protons must pass through the proton exchange membrane (PEM) in order to reach the cathode compartment. PEM, as a key factor, affects electricity generation in MFCs.The study attempted to investigate if the sulfonated polystyrene (SPS) membrane can be used as a PEM in application on MFC. SPS membrane has been characterized using fourier transform infrared spectrophotometer (FTIR), scanning electron microscope (SEM) and conductivity. The result of the conductivity (σ) revealed that the membrane has a promising application for MFC.

Keywords: bioelectrochemical, conductivity, Microbial fuel cell, proton exchange membrane, sulfonated polystyrene.

INTRODUCTION

With their capability to produce renewable energy from the treatment of organic wastewater the Microbial fuel cells (MFCs) have attracted wide attention. As for chemical fuel cell, the MFCs are regarded as promising distributing power sources for mobile and stationary application. The MFC is a novel knowledge that can be used to obtain bioenergy in the form of hydrogen and/or electricity, directly from different organic and inorganic compounds, while simultaneously treating biodegradable contaminants in wastewaters (Oh and Logan, 2006). In MFCs, the electrons are provided from chemical bonds with the aid of active microorganisms such as enzymes or bacteria. Thereafter, the generated electrons are transported to the anode. The produced protons, however, are moved through a proton exchange membrane (PEM) toward the cathode compartment. Bacteria at the anode oxidize organic matter and transfer electrons to a cathode through an external circuit-producing current. Protons produced at the anode migrate through the solution across a

PEM to the cathode where they combine with oxygen and electrons to form water. As an approach, the MFCs exhibit promising results towards treating wastewater and also to produce electricity at the same time (Liu et al., 2003; Jang et al., 2004). Further, they can be used as biosensors to detect lactate, fructose, and the total organic strength of wastewater in terms of biological oxygen demand (BOD) (Chang et al., 2004). The MFCs have also been developed to be used in remote areas, such as the bottom of the ocean, where it is difficult to replace batteries (Chaudhuri and Lovley, 2003). Figure 1. shows a schematic diagram of a typical MFC for producing electricity. It consists of anodic and cathodic chambers partitioned by a PEM (Rahimnejad et al., 2014).

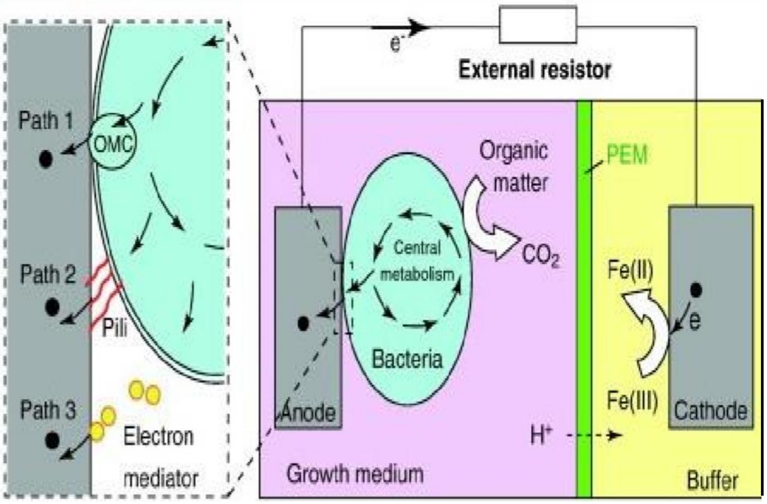

Figure 1. Principles of a two-chamber MFC.

Microbes in the anodic chamber of an MFC oxidize added substrates and generate electrons and protons in the process. Carbon dioxide is produced as an oxidation product. However, there is no net carbon emission because the carbon dioxide in the renewable biomass originally comes from the atmosphere in the photosynthesis process. Microbes in the anodic chamber extract electrons and protons in the dissimilative process of oxidizing organic substrates (Rabaey and Verstraete, 2005). Electric current generation is made possible by keeping microbes separated from oxygen or any other end terminal acceptor other than the anode and this requires an anaerobic anodic chamber.

The performance of MFC can be enhanced following several important process parameters, which are critical to its operation, such as: (i) cell metabolism, (ii) microbial electron transfer, (iii) proton exchange membrane transfer, (iv) external and internal resistances, and (v) cathode oxidation. These process parameters greatly influence the transfer of the electron and power generation (Jafary et al., 2012). In most studies of MFCs, Nafion 117 has been used as PEM, a few also used anion exchange membrane

(Rahimnejad et al., 2011; Xu et al., 2012; Ghasemi et al., 2013). However, one of the main reasons that still MFCs have not been commercialized is that these membrane are expensive and approximately account for 38% capital cost of the MFCs .Therefore, this issue call for more research on synthesis and application of novel types, economically viable, membranes. For instance, Rahimnejad et al. (2012) developed Fe_3O_4/PES nanocomposites membrane with various concentration of ferric oxide nanoparticles from 0 to 20 percent in PES polymeric matrix. While comparing the power output of the nanocomposites membranes with Nafion 117 as the common PEM in MFC, they concluded that Fe_3O_4/PES nanocomposites membrane produces more power than other types of fabricated membranes and even Nafion 117. The reason was higher conductivity of the nanocomposites membrane, lower pore size that prevents from movement of media from anode to cathode and oxygen from cathode to anode and also lower roughness. Recently, interests for development and application of conducting polymer as material for membranes due to unique properties like, high thermal and chemical stability ,have been interestingly increased. Among the family of conducting polymers, polyaniline (PANI) has mostly been used due to simple and cost effective synthesis, and high environmental stability. Moreover it has unique electroactive properties that can be controlled reversibly in the presence of acids such as hydrochloric acid (Dewan et al., 2008; Ghasemi et al., 2012). Considering these properties and also realizing high capital cost of Nafion 117, in thepresent investigation attempt was made to fabricate sulfonated polystyrene (SPS) membranes and apply it to the MFC system as PEM. Polystyrene (PS) has an aromatic group and a high performance polymer also possessgood thermal and mechanical properties. Synthetic methods have been developed to incorporate styrene as a graft on to a polymer backbone. Study succeeded in synthesizing the membrane and continued investigating membrane function as PEM MFC (Mulijani et al., 2014).

METHOD

Sulfonation of Polymers.

Typically 20 g of PS from Styrofoam waste was dried in a vacuum oven at 100 ºC and dissolved in 500 mL of chloroform and added H_2SO_4 sulfuric acid fume at room temperature under vigorous stirring held for the desired time ranging from 1 h to 3 h. In some cases the temperature was increased up to 50–80 ºC and the reaction time decreased correspondingly down to several hours. To stop sulfonation reaction the polymer solution was decanted into a large excess of ice-cold water under continuous mechanical agitation.

The polymer precipitate was filtered and washed several times with distilled water until the pH was neutral. The polymer was then dried under vacuum for 8–10 h at 25–100 ºC. The degree of sulfonation was determined by titration; 1–2 g of the SPS was placed in 0.5 M aqueous NaOH and kept for 1 day. The solution was back titrated with 0.5 M HCl using phenolphthalein as an indicator.

Membranes Preparation

Membranes were prepared by dissolving a known amount of sulfonated PS (SPS) in dichloridemethane with 10 % (w/v) composition under constant stirring. Resulting solution was casted in the form of thin film on a cleaned glass plate and dried at 60 ºC. These membranes were conditioned in 0.10 M HCl solution and 0.10 M NaOH solution alternately for several times and then equilibrated with experimental solution before being subjected to physicochemical and electrochemical studies. Before applying to the system, SPS membrane went under three stages of pretreatment as follow : 3 % H_2O_2, washed with deionized water, 0.5 M H_2SO_4 and finally washed with deionized water. In order to maintain the membrane for good conductivity, the cell anode and cathode compartments were filled with deionized water when the MFC was not in use (Ghasemi et al., 2012).

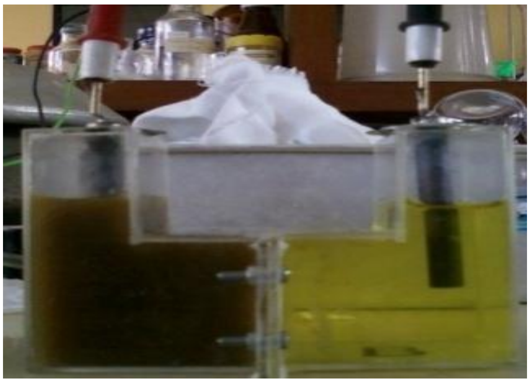

Figure 2. Design of MFC consisting of an anaerobic chamber and aerobic chamber and connected by a glass bridge containing a SPS membrane.

MFC Configuration

Two cylindrical and H-shaped chambers (Figure 2) were constructed from Plexiglas, with an inner diameter of 6.2 cm and a length of 14 cm, separated with SPS, which acted as the Proton Exchange Membrane (PEM). Oxygen was continuously fed to the cathode by an air pump (80 mL/min). Both the cathode and the anode surface areas were 12 cm^2 and the MFC operated in an ambient temperature and a neutral pH (6.5-7) in the anode and cathode compartments. The pH was adjusted using a phosphate buffer solution. The cathode consisted of carbon and acted as electrode.

Enrichment of the Electrochemically Active Bacteria (EAB) on Anode

Waste of rumen anaerobic sludge (Bogor, Indonesia) was used as an active biocatalyst to inoculate the anaerobic anode chamber. The media contained 3 g of glucose, 0.05 g of yeast extract, 0.1 g of KCl, 0.7 g of $NaH_2PO_44H_2O$, 1.5 g of NH_4Cl, and 2.5 g of $NaHCO_3$ (all obtained from the Merck). A 10 mL solution of mineral and 10 mL of vitamin solution was added per litre. All electrochemical tests were conducted in batch mode in a 30 ºC incubator. The cathode chamber contained a phosphate buffer solution that consisted of 2.76 g/L of NaH_2PO_4, 4.26 g/L of Na_2HPO_4, 0.31 g/L of NH_4Cl, and 0.13 g/L of KCl (Ghasemi et al., 2012).

Analysis of Membrane

FTIR was performed to identify the functional group of the membranes before pretreatment, after pre-treatment. Scanning electron microscopy (SEM) was employed to observe the attachment of microorganisms on the surface of the anode electrode. Special care was taken to remove the moisture from the biological samples by critical drying. They were then coated with a conductive material, such as gold, with a thickness of approximately 20-50 nm, in order to make them conductive for the SEM analysis.

Measurement of conductivity of membrane

Conductivity was measured using the conductivity cell and impedance analyzer LCR-meter. Length size of membrane was 5.6 cm dan wide 0.8 cm. The membrane was placed in between anode and cathode. Conductivity data were calculated using equation 1.

$$\sigma = G\,\frac{d}{A}\text{..}1$$

Note :

σ is conductivity

G is conductance

d is wide of membrane

A is area of membrane

DISCUSSION

PEM for MFC

In a two-chamber design of the MFCs, the anode and the cathode compartments are separated by an ionselective membrane, allowing proton transfer from the anode to the cathode and preventing oxygen diffusion in the anode chamber from the cathode compartment. The membrane in the MFCs plays an important role in determining MFC performance. The membrane needs to have good capability for exchanging protons. Generally, there are two types for PEM; porous proton exchange membranes and nonporous membranes called dense membranes (Mayahi et al., 2013). In fuel cells, the major role of dense membranes is to separate the anode and the cathode and to prevent the migration of the anode electrolyte to the cathode compartment as well as preventing the air from moving, which was purged in the cathode compartment, to the anode compartment (Leong et al., 2013). Figure 3. shows the micrograph for the cross section of a porous membrane. It should be noted that porous or nonporous membranes are distinguished by their cross sections.

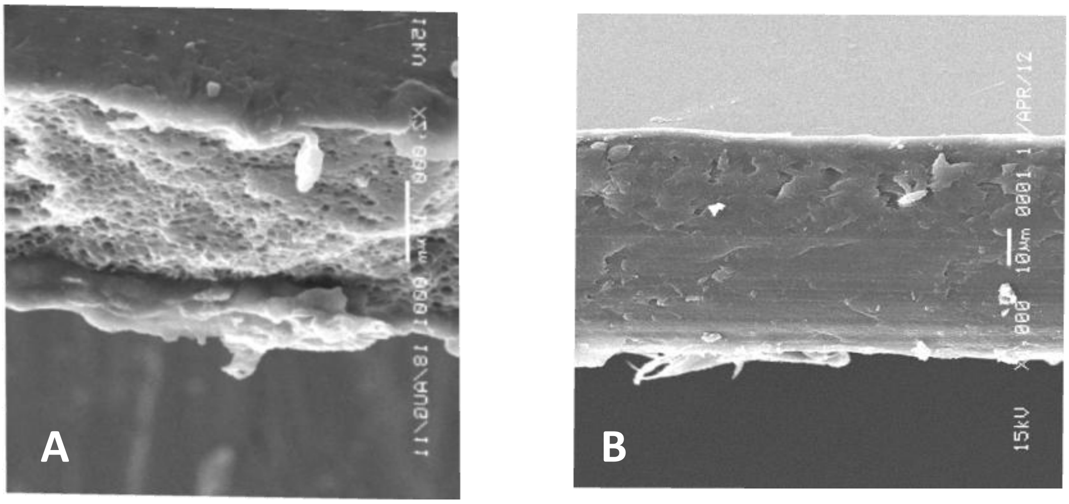

Figure 3. Cross section SEM image of membrane SPS, A). SPS porous membrane and B). SPS dense membrane.

From the SEM images Figure 3, it is apparent that the porous membrane has a lot of pores along its cross section whereas the same is not the case for the dense membrane. In the dense membrane, fouling process was possessed by death microorganism. The AFM images of a porous membrane and dense membrane are depicted (Figure 4, a-b). It clearly reveals a dense layer on top of the membrane without any pores (Figure 4b) due to fouling process and it contributes to decrease power of conductivity membrane. The anodic electron transfer mechanism in MFC is a key issue in understanding the theory of how MFCs work. Microbes transfer electrons to the electrode through an electron transport system that either consists of a series of components in thebacterial extracellular matrix or together with electron shuttles dissolved in the bulk solution.

The ideal performance of an MFC depends on the electrochemical reactions that occur between the organic substrate at a low potential such as glucose and the final electron acceptor with a high potential, such as oxygen. However, its ideal cell voltage remains uncertain as the electrons are transferred to the anode from the organic substrate through a complex respiratory chain that varies from microbe to microbe and even for the same microbe across varying growth conditions. Though the respiratory chain is still poorly understood, the key anodic reaction that determines the voltage is between the reduced redox potential of the mediator (if one is employed) or the final cytochrome in the system for the electrophile/anodophile if this has conducting pili, and the anode. For those bacterial species that are not capable of releasing electrons to the anode directly, a redox mediator is needed to transfer the electrons directly to the anode (Du et al., 2007).

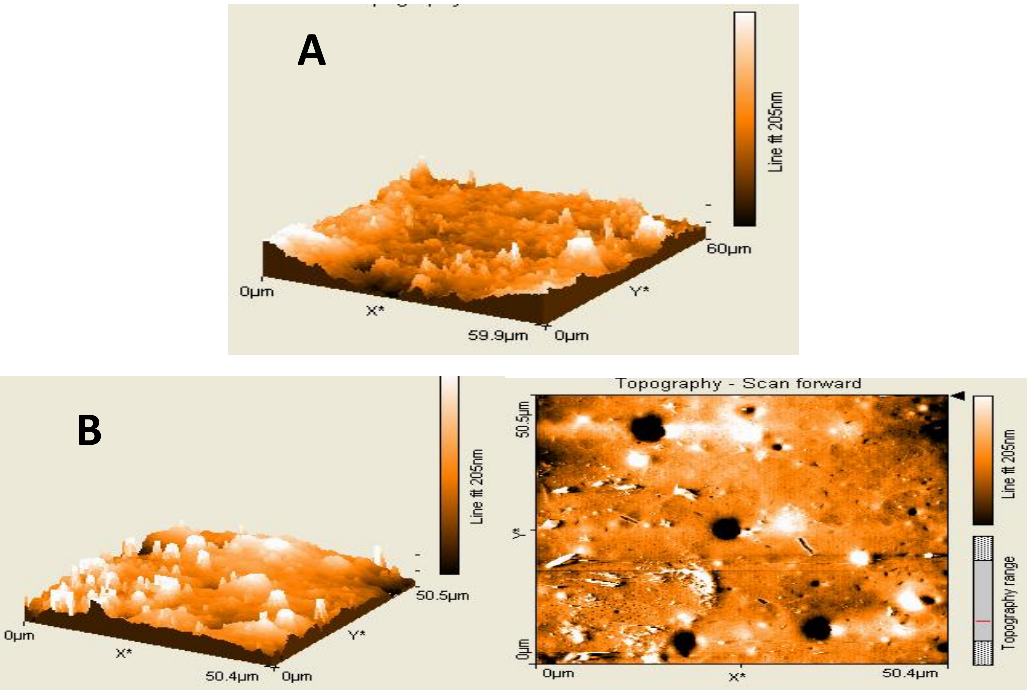

Figure 4. (A) AFM 3D image of membrane SPS before MFC application and (B) AFM 3D and 2D image of membrane SPS after MFC application.

In the study, the final anodic reaction is that the anode gains the electrons from metabolism reaction in the microbes (Liu et al., 2010). The proton H^+ then is transferred to the cathode through by PEM.

$$C_6H_{12}O_{6(s)} + 2H_2O_{\ (l)} \rightarrow 2CH_3COOH_{\ (aq)} + 4H_{2\ (g)} + 2CO_{2\ (g)}$$

$$\text{Anode} \quad : 2CH_3COO^-_{(aq)} + 8H_2O_{(l)} \rightarrow 4HCO_3^-{}_{(aq)} + 18H^+_{(aq)} + 16e^- \qquad (E°\text{red}=-0.279\ \text{V})$$

$$\text{Cathode} \quad : Fe^{3+}_{(aq)} + 8e^- + 8H^+_{(aq)} \rightarrow Fe^{2+}_{\ (aq)} \qquad (E°\text{red}= 0.791\ \text{V})$$

Rahimnejad et al. (2014) reported that in the MFC researchers utilized Nafion as a membrane, the Nafion membrane equilibrates with the cation species present in the anolyte and catholyte. This equilibration quickly changes the membrane from its proton form to a form in which mainly other cation species occupy the negatively charged sulfonate groups.

More than 99.99 % of the sulfonate groups are occupied with nonproton cations, as the sulfonate groups of Nafion have a higher affinity for most other cation species. Subsequently, these cations combined with the sulfonate groups of Nafion stop the movement of protons that are produced at the time of substrate degradation. In addition, other cation species have a higher concentration in the anolyte than protons which make proton transport slightly minor compared to the transport of other cations, causing a decrease in MFC performance. The diffusion coefficient of protons in the Nafion is relatively higher than other cations. Currently, the most available PEM for MFCs is Nafion from Dupont but this cannot operate efficiently at temperatures higher than 90 ºC due to thermal instability.

Conductivity of membrane SPS

We evaluated the membrane SPS for MFC. The sulfonation process on polystyrene has been successfully developed. SPS was found to even operate at high temperature, possess good proton conductivity, good current density and better thermal stability at 80 ºC as a membrane. Figure 5. exhibits the conductivity of SPS membrane. The concentration of sulfonate in sulfonation polystyrene process increased and the result of conductivity membrane also increased. The function of sulfonate group in the SPS has a higher affinity to attack proton from anodic.

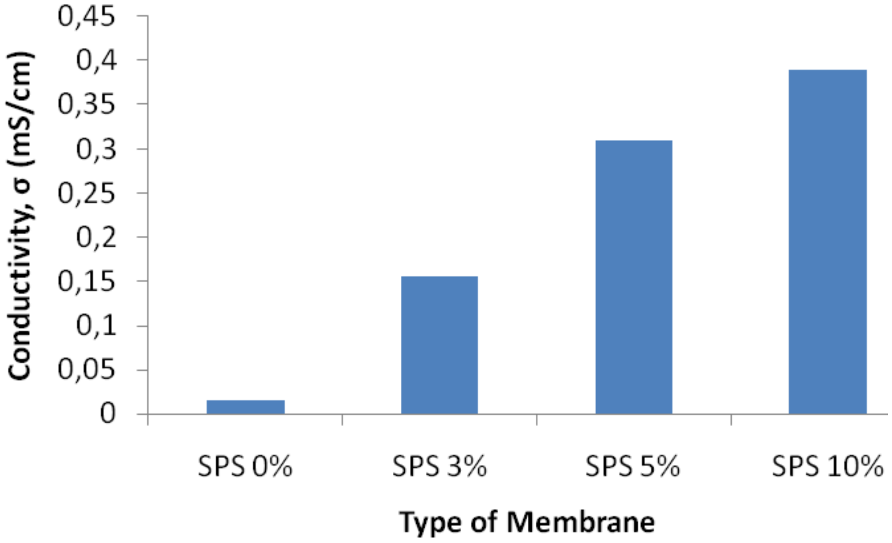

Figure 5. Conductivity of membrane SPS.

Increasing the sulfonate group function in the SPS can increase ionic strength of the medium which contributes to increase power by increasing the conductivity of the solution. However, bacteria cannot grow well under very high ionic strengths. SPS 10 % revealed highest conductivity in the membrane variant (Figure 5). The result, however, is still lower than conductivity of Nafion. Nevertheless, this study suggests SPS might be considered potential for PEM. Oh and Logan (2006) conducted research in determination of effect solution conductivity on power, and added KCl separately to the anode and cathode chambers to obtain different salt concentrations. The power was measured after voltage stabilization, with a minimum operation time of 18–30 h at each concentration. Unfortunately, adding KCl up to 0.4 M in each chamber resulted in decreased internal resistance from 1,087 to 625 Ω, thereby demonstrating that solution conductivity can limit power generation.

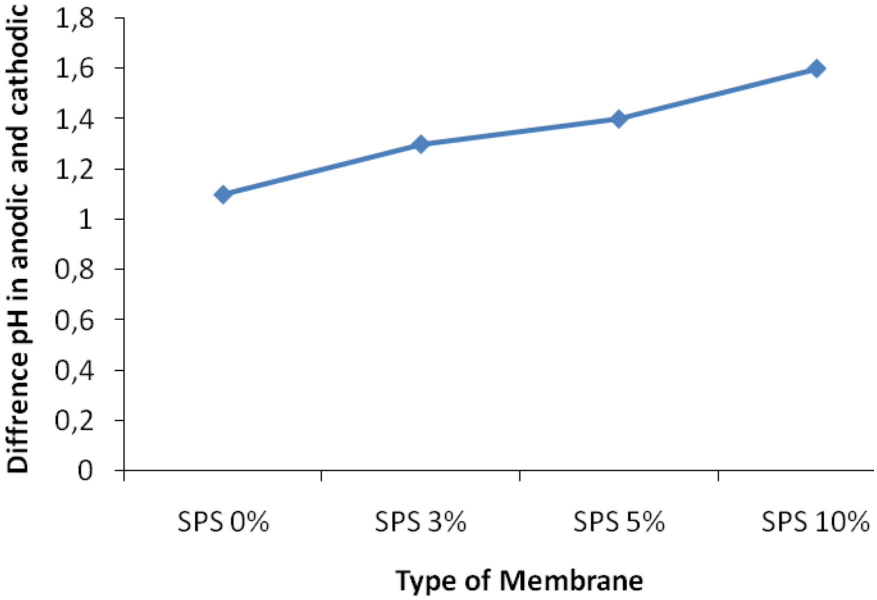

Figure 6. Condition of differences pH in the MFC compartment

Effect of pH differences

In cathodic compartment, $K_3[Fe(CN)_6]$ is an oxidation agent. Fe(III) in the solution of $K_3[Fe(CN)_6]$ is reduced to be Fe(II). Figure 6. reveals the condition of pH in the MFC process. pH is very important in MFC process. Due et al. (2007) reported if no buffer solution is used in a working MFC, there will be an obvious pH difference between the anodic and cathodic chambers, though theoretically there will be no pH shift when the reaction rate of protons, electrons and oxygen at the cathode equals the production rate of protons at the anode. The PEM causes transport barrier to the cross membrane diffusion of the protons, and proton transport through the membrane is slower than its production rate in the anode and its consumption rate in the cathode chambers at initial stage of MFC operation thus brings a pH difference. However, the pH difference increases the driving force of the proton diffusion from the anode to the cathode chamber and finally a dynamic equilibrium is formed. Some protons, generated with the biodegradation of the organic substrate and transferred to the cathodic chamber, are able to react with the dissolved oxygen while other protons are accumulated in the anodic chamber when they do not transfer across the PEM or salt bridge quickly enough to the cathodic chamber.

The study detected a pH difference of 1.6 (9.5 at cathode and 7.9 in anode) after 5-hour operations with an initial pH of 7 without buffering. It was possible that the buffer compensated the slow proton transport rate and improved the proton availability for the cathodic reaction. This suggests that the proton availability to the cathode is a limiting factor in electricity generation. Increasing ionic strength by adding NaCl to MFCs also improved the power output, possibly due to the fact that NaCl enhanced the conductivity of both the anolyte and the catholyte. Figure 7. shows the highest voltage achieved in MFC was 14 mV with graphite electrodes and a working surface area of membrane about 4.48 cm^2. The voltage showed was low due to microorganism growth decreased 8.3 %, it will contribute for power of voltage in the MFC. In the study, consortium microorganism was utilized for MFC which is capable to transfer electron spontaneously to the cathodic.

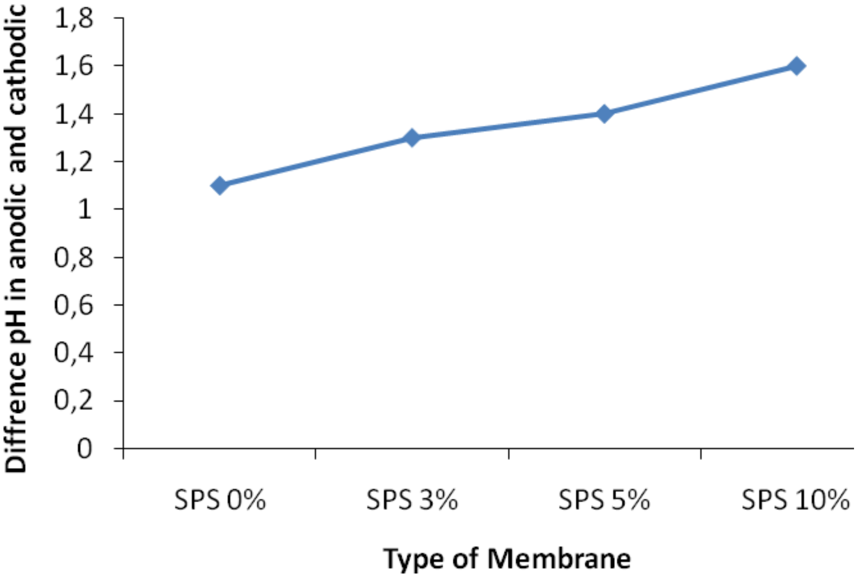

Figure 7. The voltage achieved on MFC.

Activity microorganism in respiration and metabolism process will affect the electron produced and transferred to cathodic. However, performances of laboratory MFCs still remain much lower compared the ideal performance. There could be several possible reasons. Power generation of an MFC is affected by many factors including microbe type, fuel biomass type and concentration, ionic strength, pH, temperature, and reactor configuration.

CONCLUSION

The Sulfonated process toward polystyrene has succeeded. Morphological cross section of membrane revealed a porous membrane. The AFM image, however, showed that the fouling process occurred in the membrane. Considering conductivity of SPS, it shows great potential to be utilized for MFC. Differences of pH in anodic and cathodic were very low. However, further performance investigation of MFC in laboratory is suggested to understand the effect of various microbe type, fuel biomass type and concentration, ionic strength, pH, temperature, and reactor configuration.

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