



Membrane Electrode Assembly based on Sulfonated Polystyrene as Proton Exchange Membrane for Application in Microbial Fuel Cell

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ABSTRACT

A novel membrane electrode assembly (MEA) based on sulfonated polystyrene was synthesized and applied to a microbial fuel cell (MFCs). In this study, membrane electrode assembly made of sulfonated polystyrene (SPS) and nafion membrane were fabricated by combining 20% AgNO₃/C catalyst ink. The performance of membrane electrode assembly based sulfonated polystyrene (SPS) and nafion were evaluated by measuring proton conductivity and power density. This sulfonated polystyrene of membrane electrode assembly (SPS-MEA) revealed power density was higher than that nafion non activated membrane, this is considered for membrane application of proton exchange membrane (PEM). The presence of sulfonation groups of polystyrene was characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. The membrane topography before and after the fuel cell process treatment was investigated by atomic force microscopy (AFM).

Keywords-- Membrane Electrode Assembly, Sulfonated polystyrene, Nafion, Microbial Fuel Cell

I. INTRODUCTION

The configurations of membrane electrode assembly (MEA) have been designed and widely investigated in chemical fuel cells. Membrane electrode assembly is a key component in fuel cell system as a proton distributor from the anode to the cathode, that generate electrical energy. Catalyst in the MEA fabrication allows to accelerate the reaction of proton to pass through the membrane. The MEA related studies that have been reported by Devrim and Albostan (2016) are producing higher power density than membranes without the MEA fabrication, using a nafion membrane combined with a Pt/graphene catalyst producing 1.267 W/cm² of a power density [1].

Microbial fuel cell (MFC) is a promising technology to resist the existing energy demand and pollution problem. While the environmental profits of MFC have been recognized to set a sustainable pattern of waste treatment, its potential as an energy producer has not been well addressed yet. In MFCs, the proton exchange membrane (PEM) is among the most promising electrochemical devices for convenient and efficient power generation, which functions as an electrolyte for transferring protons from the anode to the cathode as well as providing a barrier to the passage of electrons and gas cross-leaks between the electrodes [2,3]. Enhanced practical performance of MFCs requires further knowledge of structural and material modifications. Most relevant studies for MFCs, improvements are anticipated from the incorporation of a novel membrane electrode assembly in MFC construction [4, 5].

Nafion membrane is the most widely used in MFCs due to its good mechanical stability and superior proton conductivity resulting from the sulfonic acid groups present at the chain ends. However, the shortcomings of using nafion is its high permeability to oxygen and quite expensive, that is too costly for use in large-scale practical applications [6-8]. Many researchers have demonstrated various efforts for developing less expensive membrane and more durable substitutes to nafion membrane. Alternative polymers have been successfully used in MFCs, such as sulfonated poly(benzimidazole), poly(vinyl alcohol), poly(phenylene) sulphide, poly(-propylene), polystyrene [7,9-11]. The presence of aromatic polymers that possess good mechanical stability, high thermo-oxidative stability, and low cost. Furthermore, in order to obtain membrane materials with high proton conductivities, a high degree of sulfonation is required in polymers [12]. Sulfonation process of the polymer chain is required in order to improve the hydrophilicity and proton conductivity of polymer by

attaching sulfonic groups to the polymers' chain [13]. The polymer groups can be sulfonated through the using of some sulfonating agents such as sulfuric acid, chloro sulfonic acid and trimethyl silyl ester. The reaction of sulfonation is produced by via a direct electrophilic sulfonation mechanism and the sulfonate groups attach to the aromatic rings of the polymer backbone [14]. The increasing sulfonation level of the membranes leads to overall swelling in water that indicates high hydrophilicity and proton conductivity of the membranes.

In this study, we developed a low cost MFC membrane, which utilized the abundant waste of polystyrene to become environmentally friendly and high economic value, employing a MEA fabrication for MFCs construction. Investigation of performance MEA in a microbial fuel cell is the main focus of the research. Sulfonation process of the PS was confirmed by FTIR and ^1H NMR. Characteristic of topography MEA is also evaluated through by atomic force microscope (AFM).

II. EXPERIMENTAL

Material and Methods

The membrane electrode assembly consisted of the ion exchange membrane and carbon cloth electrode containing catalyst ink. Sulfonated polystyrene (SPS) membrane for MEA was synthesized in the laboratory by the sulfonation reaction of polystyrene. Typically 20 g of PS from Styrofoam waste was dried in a vacuum oven at 100 °C and then dissolved in 100 mL of chloroform and added oleum content 65% SO_3 from Merck at room temperature under vigorous stirring and held for the desired time ranging from 1 h to 3 h. In some cases the temperature was increased up to 60 °C and the reaction time decreased correspondingly down to several hours [13]. The polymer was then dried for 8–10 hour at 25°C. Before applying to the MEA, SPS membrane is activated by soaking in 3% H_2O_2 for 1 hour and the membrane was immersed in H_2SO_4 for 1 hour, after which the membrane was rinsed with deionized water. The membrane electrode assembly (MEA) was fabricated in combined with catalyst ink. The catalyst ink is prepared by mixing 20% AgNO_3/C catalyst with 5% SPS solution with dichloridemethane solvent and stirring to form a paste. The electrode layer is made by applying a catalyst ink mixture on the surface of the carbon paper. MEA is coated with two layers of catalyzed electrodes and printed using hot pressing at 120 °C [3].

Evaluation of Performance MEA

The performance of the MEA was evaluated by measuring proton conductivity and topography characterization of the membranes before and after the fuel cell process treatment was evaluated by AFM. Transverse proton conductivities of the SPS membranes were measured by impedance analyzer LCR meter over a frequency range from 42 Hz to 500 kHz with voltage limitation 10 mV. The sized membrane electrode assembly 1.5 cm^2 is enclosed with

two copper electrodes connected with positive and negative poles on the device. The membrane used was measured in thickness using a digital micrometer where the membrane thickness was directly proportional to the distance between the two carbons (L) electrodes. The conductivity (σ) of samples in the transverse direction was calculated from the impedance data using equation 1:

$$\sigma = G \times L/A \quad (1)$$

Where, G and A represent conductance and that area of the membrane sample.

MEA application in MFC measurement

A dual chambered MFC reactor is designed and fabricated in the laboratory with an inner diameter of 15 cm and a length of 15 cm respectively, separated with MEA, which acted as the Proton Exchange Membrane (PEM). Oxygen was continuously fed to the cathode by an air pump. The cell anode and cathode compartments consisted of carbon as electrodes. Electrochemically, waste of rumen anaerobic sludge (Bogor, Indonesia) was used as an active biocatalyst to inoculate the anaerobic anode chamber and contained 5 g of glucose. The pH of the rumen wastewater was adjusted using a phosphate buffer solution (pH 7). The cathode compartment was fed $\text{K}_3\text{Fe}(\text{CN})_6$ and phosphate buffer solution to control the process of the reduction reaction. The current and voltage from the MFC was measured using a digital multimeter. MFC performance in terms of power generation was comparatively evaluated using nafion 212 membrane spectra.

III. RESULTS AND DISCUSSION

Sulfonation Reaction of Polystyrene (PS)

The success sulfonation reaction was confirmed by FTIR and ^1H -NMR spectroscopy. Infrared analysis was performed on Agilent Cary 360 FTIR equipped with an attenuated total reflectance (ATR) is shown in Figure 1. In principle, FTIR serves to identify the structure of compounds by identifying the spectra of each compound [15]. The highlight of polystyrene transmission area appears in the band at 3058 and 3024 cm^{-1} which indicate the aromatic C-H stretching. The band of 2914 and 2850 cm^{-1} can be assigned to the aliphatic C-H. There is also a local band at 1598, 1489 and 1446 cm^{-1} , which are all representative of the C=C aromatic stretching [16]. Comparing both spectra, sulfonated polystyrene spectrum shows all these bands which do not change significantly.

Sulfonation reaction of polystyrene occurred by two new intense spectrum at 1365 and 1275 cm^{-1} , that indicate the presence of asymmetric and symmetric group of S=O stretching. The absence of this band in the PS spectrum confirmed the success in sulfonation reaction of polystyrene has been occurred. Strong band also found in 1065 cm^{-1} which indicates a C-S stretching group, then the emergence

of symmetrical band stretching from SO_3^- and in-plane bending of ring-substitution in phenyl at 1018 cm^{-1} . The broad and weak band at the region 3428 cm^{-1} of the SPS membrane has been ascribed to stretching of hydroxyl groups of $-\text{SO}_2\text{-OH}$ [15]. In summary, based on the depiction of FTIR spectra indicates the presence of $-\text{SO}_3\text{H}$ groups.

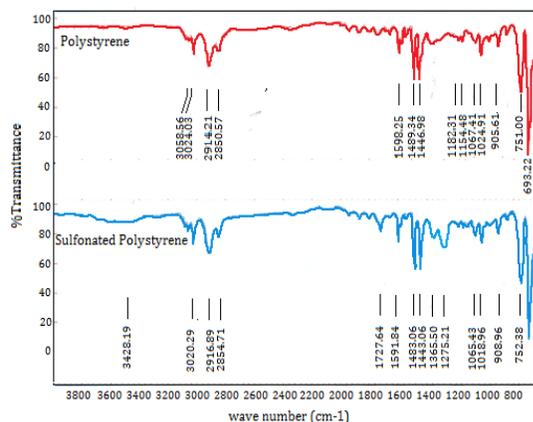


Figure 1: FTIR spectra of polystyrene and sulfonated polystyrene.

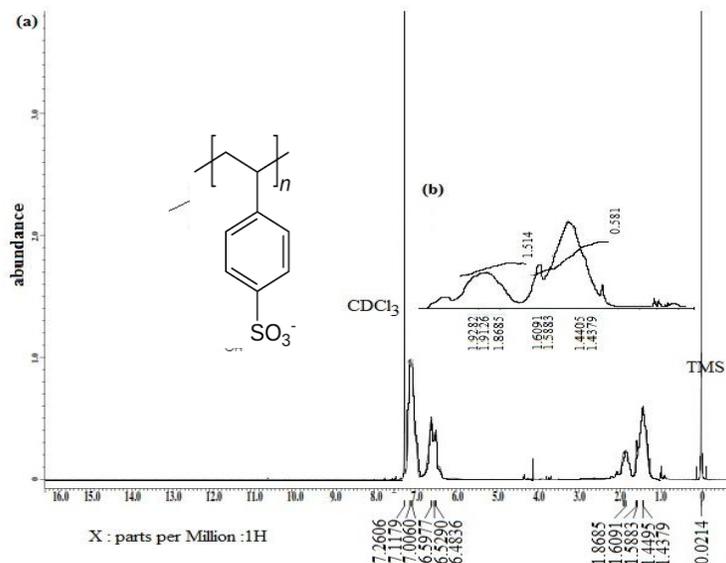


Figure 2: ^1H NMR spectrum of (a) SPS membrane, (b) peak magnification at 1-2 ppm.

Several spectra are shown, their single peak at 2 ppm region indicates $-\text{SO}_3\text{H}$ group, which reinforces the data indicating FTIR compounds were sulfonated. In addition, the results of ^1H -NMR analysis also contained a singlet peak at 4 ppm region that indicated H_2O existence. As well as the peaks in the region of 1.4 to 1.8 ppm, which indicates the peak of polystyrene.

Conductivity of Membrane

Proton conductivity of the membrane is the most important parameter for estimating the usefulness of a membrane as a PEM in MFCs. The sulfonate groups in the

^1H NMR was utilized for confirming the substitution reactions of proton toward benzene in polystyrene (Figure 2). Characterization of ^1H -NMR spectra proposed to view the structure and types of polystyrene sulfonated with CDCl_3 solvent. Some factors that may affect the results of the characterization. The using of different solvents allows for a slight shift in spectrum generated, the purity of the compound, concentration and molecular interactions will affect the outcome of the characterization [13,15]. The spectrum in Figure 2 shows that the aromatic protons of sulfonated polystyrene give a chemical shift between 6.0 and 7.3 ppm. Line broadening of the spectrum is observed because of both the somewhat large molecular weights and the viscosity of their solutions, which produce in slow molecular rolling over.

SPS have a higher affinity to attack the proton from anodic. Figure 3, exhibits the proton conductivity of membrane MEA is higher than that of non MEA.

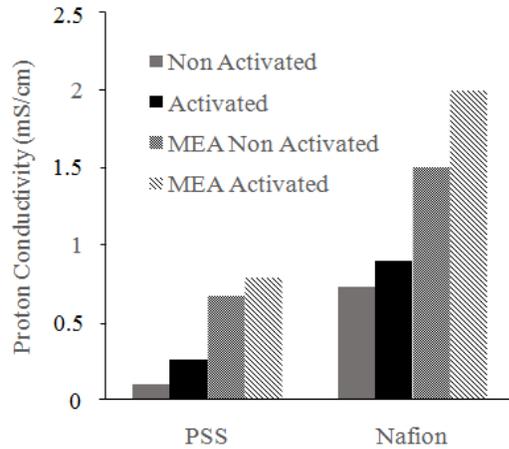


Figure 3: The proton conductivity of the membranes.

The addition of activated membrane increased the value of proton conductivity than non activated membrane. The highest value of proton conductivity resulted by MEA nafion activated membrane (2 mS/cm). Relatively, the nafion membrane has a higher proton conductivity value than SPS membrane, however MEA SPS activated membrane has a higher value (0.79 mS/cm) than the nafion non activated membrane (0.73 mS/cm). In any case, the

conductivity of SPS is still lower than the conductivity of Nafion. Nevertheless, this study suggests SPS might be considered potential for PEM in MFCs.

Power Density and Voltage Generation in MFC Application

The power density profiles of sulfonated polystyrene and Nafion are shown in Figure 4. The power density and voltage generation behavior of MFC during the operation were obtained with various maximum power density with a different type of membrane in the chamber MFC. The maximum power density MFC of 31.92 mW/cm^2 with the corresponding generated cell voltage of 0.38 V was higher at MEA nafion activated membrane as compared to MEA sulfonated polystyrene. Its can be confirmed from high conductivity of MEA nafion activated membrane. However, SPS membrane with the support of MEA fabrication can increase the power density value (7.54 mW/cm^2), which possess higher power density than nafion non activated membrane. Mulijani et al. Reported that the distance of electrode will affect the value of power density, it causes the proton is not transferred properly by a proton exchange membrane from the anode to cathode with the result that the potential of cathode decrease slightly [3].

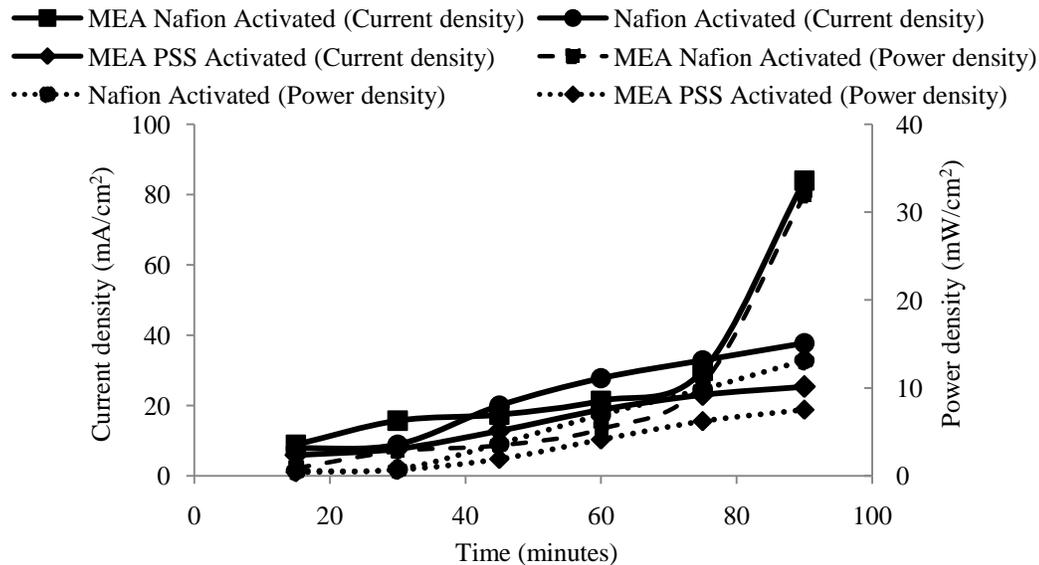


Figure 4: The current and power curves of the MFC.

Morphology Study by AFM

The changes in morphology of MEA sulfonated polystyrene and nafion before and after the fuel cell process treatment were analyzed by AFM. Based on the surface morphology analyzed by AFM, it was observed that the SPS belongs to asymmetric membrane. Before the fuel cell proces

treatment, the surface morphology of MEA SPS and nafion membrane show higher roughness surface area as compared to the membrane after treatment (Figure 5). This allows a potential decrease of the proton transport membrane to the system during the process treatment.

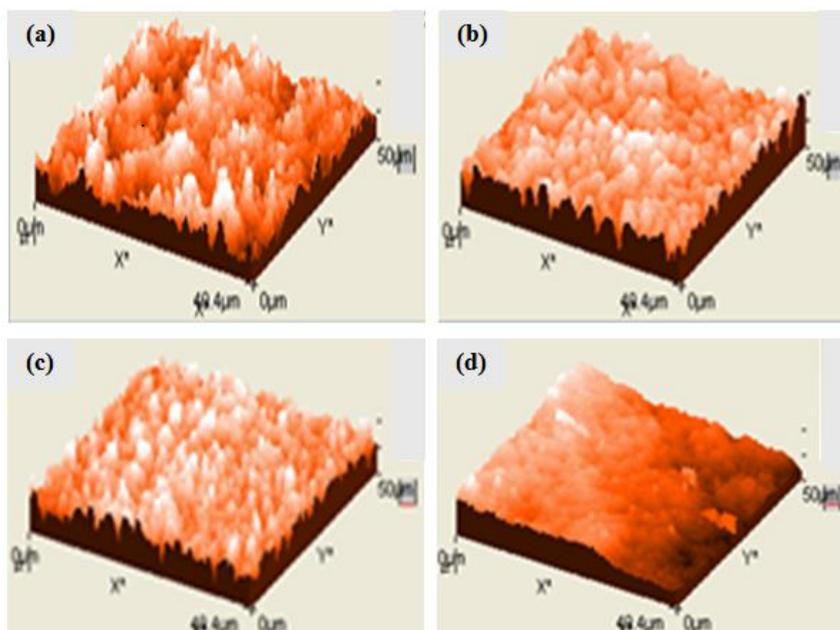


Figure 5: AFM Photograph (a) SPS Membrane before fuel cell treatment; (b) SPS Membrane after treatment (c) Nafion membrane before fuel cell treatment; (d) Nafion Membrane after treatment.

IV. CONCLUSION

Sulfonation process of polystyrene membrane has been successfully done. The success of sulfonation reaction is evidenced by FTIR spectra at 1365 and 1275 cm^{-1} and ^1H NMR studies. Evaluation of performance MEA fabrication for MFCs concludes that MEA nafion activated resulted highest generated voltage and power density, the proton conductivity is also increased. As for MEA SPS activated has a higher generated voltage and power density than nafion non activated membrane, which suggests SPS membrane might be considered potential for PEM in MFCs. AFM analysis revealed that the roughness of membrane before treatment showed rougher than the membrane after treatment.

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