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## Performance Improvement of Polysulfone Membrane Filled by Nanosilica Boiler Ash Sugarcane Industry on Direct Methanol Fuel Cell

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### Abstract

Nanosilica from boiler ash sugarcane industry can be utilized as filler for electrolyte membrane as it could increase hydrophilicity and performances. Electrolyte membrane is the key component of direct methanol fuel cell (DMFC). Polysulfone-nanosilica membrane has been developed to replace expensive nafion membrane. The objectives of this research were to analyze the effects of H<sub>2</sub>SO<sub>4</sub> concentration of 1.5 M, 2 M, and 2.5 M as sulfonating agent for polysulfone and the effects of Ag/ C or Cu/ C catalyst on membrane electrode assembly (MEA) performances. The sulfonation degree of polysulfone were increased with increased of H<sub>2</sub>SO<sub>4</sub> concentration. Sulfonated polysulfone membrane with H<sub>2</sub>SO<sub>4</sub> 2.5 M concentration gave the highest performances for this research with water uptake of 45.72%, methanol uptake of 28.33%, methanol permeability of 6.97x10<sup>-5</sup> cm<sup>2</sup>/s, proton conductivity of 6.55x10<sup>-3</sup> S/cm, and potential difference of 66.70 mV. Fabrication of MEA with Cu/C and Ag/C catalyst also increased proton conductivity and potential difference significantly. MEA 20% Ag/C catalyst gave proton conductivity of 23.79x10<sup>-3</sup> S/cm and potential difference of 281 mV MEA which were better than 20% Cu/C catalyst and electrolyte membrane without catalyst.

**Keywords:** boiler ash; direct methanol fuel cell; membrane electrode assembly; nanosilica; polysulfone.

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## **1. Introduction**

Boiler ash is by product of sugar industry from the combustion of bagasse on the boiler with burning temperature of 550-600 °C . Boiler ash contains of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> more than 70% [1]. The content of silica in the boiler ash of the sugarcane industry was 49.69% [2]. Utilization of bagasse is currently limited on organic fertilizers and burial material manufacturing, the rest is disposed as solid waste [3]. Silica synthesis from boiler ashes of sugarcane industry is an effort to utilize solid waste into value-added products. Its presence in industrial area caused environmental pollution, especially air pollution caused by dust [3]. Transformation of silica into nanosilica was done to enlarge the surface area causes its performances increased. Nanosilica has good stability, chemically inert, biocompatible character which is able to harmonize with the body's systems work [4]. One of utilization of Nanosilica wide applications is as filler of electrolyte membrane for direct methanol fuel cell (DMFC). Characteristic of Nanosilica is hydrophilic, and as filler it may increased the membrane hydrophilicity [5].

DMFC is a type of fuel cell that uses methanol and directly converts chemical energy into electrical energy and heat. Electrolyte Membrane which is an important component of direct methanol fuel cell (DMFC), serves as a medium for the transfer of proton (H<sup>+</sup>) from anode to catode and as a barrier between the electrodes. Membrane that commonly used is Nafion made from polytetrafluoroethylene (PTFE). Nafion membrane is hydrophobic and has high proton conductivity and good stability. However it has high cost, high methanol crossover, low stability at high temperatures, and low conductivity at low humidity or high temperature [6]. Polysulfone has been developed as it has good thermal, chemical, and mechanical stability with lower cost and widely available commercially [6]. Polysulfone as aromatic polymer is hydrophobic so it was sulfonated with H<sub>2</sub>SO<sub>4</sub> to increase the hydrophilicity. The addition of nanosilica into polysulfone membrane formula also increase the hydrophylicity of membrane.

In the present study, polysulfone-nanosilica membrane was developed as alternatif of Nafion membrane. Performance improvements of polysulfone-nanosilica membrane in this study were conducted by increasing the concentration of H<sub>2</sub>SO<sub>4</sub> as sulfonating agent and fabricating membrane electrode assembly (MEA) using Cu/C or Ag/C catalyst. Sulfonation of polysulfone was done to increase hydrophilicity of membrane. MEA is a key component of fuel cells consisting of an electrolyte membrane flanked by two catalyzed electrodes. The advantage of MEA is that it can increase electrical conductivity and accelerate electrochemical reaction. The catalyst used in commercial MEA is commonly Platinum (Pt/C). However, Pt/C catalysts have a relatively high costs. Therefore in this study, alternative catalyst Cu/C and Ag/C were developed which is cheaper and have good electrical conductivity [7]. Increasing the concentration of membrane sulfonation and fabricating membrane into MEAs with catalysts are expected can improve the performance of polysulfone-nanosilica membrane, specially in proton conductivity and potential differences.

## **2. Materials and method**

### **2.1. Materials**

Polysulfone was obtained from Aldrich (USA). Sulfuric acid, dichloromethane, sodium hydroxide, hydrochloric

acid was obtained from Merck. Hydrogen peroxide, distilled water, deionized water, methanol, AgNO<sub>3</sub>, CuSO<sub>4</sub>, carbon graphite (C), K<sub>3</sub>[Fe(CN)<sub>6</sub>], and Na<sub>2</sub>HPO<sub>4</sub> were used as received.

## 2.2. Method

**Sulfonation of polysulfone:** Polysulfone (Psf) was sulfonated with various sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) concentration of 1.5 M, 2 M, and 2.5 M as sulfonating agent. Dry polysulfone was sulfonated in various concentration of H<sub>2</sub>SO<sub>4</sub> (1:10) (wt%) at 80 °C and vigorously stirred for 3 hours. The sulfonated polysulfone (sPsf) was filtered and washed with distilled water to remove any residue. sPsf was dried in oven at 105 °C for 2 hours.

**Synthesis of electrolyte membrane:** sPsf-nanosilica membrane was synthesized by phase inversion method. sPsf was dissolved in dichloromethane with ratio of 3:13 (wt%). Nanosilica as much as 3% of the weight of sPsf was added to sPsf solution. The mixture was stirred with magnetic stirrer until homogen dissolved and there are no bubbles. The mixture was ultrasonicated for 30 minutes then casted on a glass plate and dried at room temperature to evaporate the solvent.

**Fabrication of Membrane Electrode Assembly (MEA):** Membrane electrode assembly (MEA) was fabricated by treatment of sPsf-nSi membrane firstly. Membrane was soaked in 3% H<sub>2</sub>O<sub>2</sub> solution then H<sub>2</sub>SO<sub>4</sub> 1 M each at 80 °C for 1 hour. Membrane was rinsed with deionized water and dried in a sheltered place of dust and sunlight. The catalyst ink was prepared by mixing Ag/C 20% or Cu/C 20% catalyst and 5% sPsf-nSi solution. The mixture was ultrasonicated for 10 minutes or until the catalyst was well dispersed. The electrodes were prepared by brushing catalyst ink onto the surface of carbon paper. MEA was formed by arranging electrode, membrane, and electrode, then merged.

## 2.3. Characterization

**Degree of sulfonation:** 0.1 g of polysulfone was soaked in 10 ml of NaOH for 3 days. The degree of sulfonation (DS) was determined by titration method using 0.1 N HCl until the color of sample was changed into clear. The degree of sulfonation can be calculated from the equation:

$$DS (\%) = \frac{(\text{Volume of HCl blank} - \text{Volume of HCl sample})}{\text{sample weight}} \times 100\% \quad (1)$$

**Water uptake:** Membrane sample of 1cm x 1cm was dried in oven at 120 °C for 24 hours and weighed as W<sub>dry</sub>. Dried membrane was immersed in distilled water for 24 hours at room temperature. Membrane was wiped with paper towels until no water is left on the surface and weighed as W<sub>wet</sub>. The value of water uptake can be calculated with the following equation:

$$\text{Water Uptake (\%)} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100\% \quad (2)$$

**Methanol permeability:** Membrane was placed between two vessels containing distilled water and methanol 1 M with respective volume of 300 cm<sup>3</sup>. The second vessel was stirred with a magnetic stirrer so that the mixture

remains homogeneous. Every 10, 20, 30, 40 min, a vessel containing distilled water was taken 10 mL of solution to determine the concentration of methanol. Determination of methanol concentration was done using pycnometer based on calibration curve between density with methanol concentration. The differences in methanol concentration every 10 minutes will resulted in slope (m) or mathematically written as follows:

$$m = \frac{\Delta [\text{MeS}]}{\Delta t} \quad (3)$$

Methanol permeability can be calculated by the equation:

$$\tau = m \frac{V \times L}{A \times [\text{MeF}]} \quad (4)$$

m: slope of the line (L mol<sup>-1</sup>s<sup>-1</sup>); Δ[MeS]: changes in methanol concentration of sample (M); Δt: change in time (s), V: Initial volume (L); L: thickness of membrane (cm); A: mass of wet membrane (g); [MeF] = methanol concentration of feed (M).

**Proton conductivity:** Proton conductivity of membrane and MEA were tested by means of an impedance analyzer LCR-meter HIOKI 3532. Membrane size of 1 cm x 1 cm was clamped between two electrodes that connected to the positive and negative poles of LCR-meter. The value of proton conductivity was obtained through the equation:

$$\sigma = G \frac{d}{A} \quad (5)$$

σ: proton conductivity (S.cm<sup>-1</sup>); D: membrane thickness (cm); G: conductance (S); A: area of electrode (cm<sup>2</sup>).

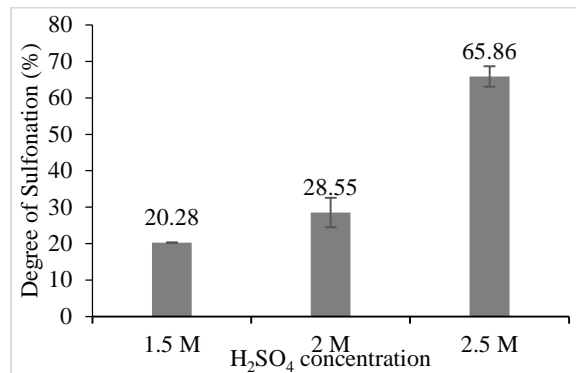
**Potential difference:** The potential difference of membrane was tested using a two vessel system, the system of anode containing 160 mL of methanol 0.3 N and the cathode containing 160 ml of solution mixture (1:1) of K<sub>3</sub>[Fe(CN)<sub>6</sub>] and 1 mM Na<sub>2</sub>HPO<sub>4</sub> 1 mM. The membrane was placed at the center of the two hollowed out vessels. Into the two vessels were inserted carbon electrodes. The membrane potential differences were measured by connecting the electrodes with a multimeter. The potential difference of MEA was tested by applying MEA to DMFC kit. The value of potential difference was measured by a digital multimeter.

### 3. Results and discussion

#### 3.1. Sulfonated polysulfone-nanosilica membrane

Electrolyte membrane is a key component of DMFC which had function as proton (H<sup>+</sup>) transfer media. The criteria for electrolyte membrane was had high proton conductivity, low methanol permeability, and good stability of thermal, chemical, and mechanical. Polysulfone membrane was developed as an electrolyte membrane on DMFC modified with sulfonation of polysulfone and addition of nanosilica as a filler. Sulfonation of polysulfone was done to increase the hydrophilicity of polysulfone membrane. Sulfonation is the entry process sulfonate group (-SO<sub>3</sub>H) into the polymer chain structure of benzene in polysulfone [8]. The sulfonate group were substituted with H group on the aromatic ring due to the addition of the sulfonating agent. The

presence of a sulfonate group caused the polysulfone becomes charged or becomes an ionomer. The success of the sulfonation process can be seen from the degree of sulfonation. The degree of sulfonation indicated the number of sulfonate groups included in the polysulfone framework. Figure 1 showed that sulfonation degree of polysulfone increased respectively by 20.28%, 28.55%, and 65.86% with increasing the H<sub>2</sub>SO<sub>4</sub> concentration of 1.5 M, 2M, and 2.5 M. Degree of sulfonation was influenced by the concentration of the sulfonation agent and the sulfonation time [8]. The formation of crosslinking in sulfonation process increased with the increasing number of sulfonate groups of the sulfonating agent [9]. The result showed that the higher degree of sulfonation, the higher hydrophilicity of membrane.



**Figure 1:** The sulfonation degree of sulfonated polysulfone (sPsf)

Figure 2 showed the sPsf nanosilica membrane which is tends to be transparent. White color signs the presence of nanosilica as filler that spread evenly on the membrane. Nanosilica could increase the hydrophilicity of membrane because the presence of silanol (Si-OH) groups that were amorphous will interact with water as proton transfer media [10]. The more hydrophilic of membrane, the membrane's ability as a proton transfer medium would increase so that it impacts the increased performance of the membrane, especially the proton conductivity. Besides that, silica also has high mechanical stability, resistance to chemicals, and can withstand the methanol crossover [11].

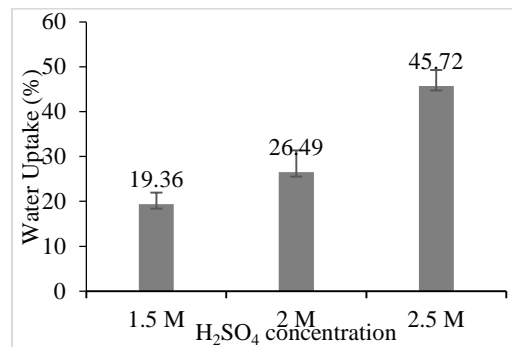


**Figure 2:** sPsf-nanosilica membrane

### 3.2. Water uptake

Water uptake showed the ability of membrane to absorb water. Water serves as a proton transfer media and it

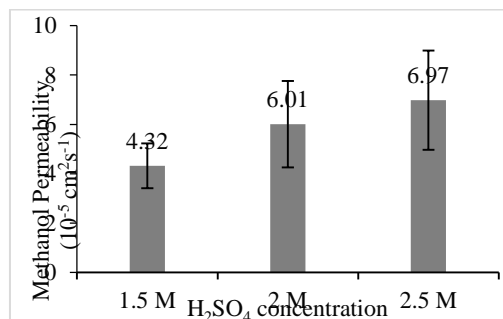
associated with proton conductivity of the electrolyte membrane. The more water absorbed by the membrane, the protons which transferred from anode to cathode were increasing so the value of proton conductivity increased [8]. The amount of water uptake was influenced by the presence of sulfonate groups on polysulfone and the presence of nanosilica as filler. Silica group contains four oxygen atoms which readily react with water because of the acidic silanol ( $\equiv\text{Si-OH}$ ) group, so that the silica has an easy to absorb water [10]. Nanosilica addition of 3% is the optimum amount for polysulfone membrane because the addition of more nanosilica will cover sulfonate groups on the membrane so that water uptake of the membrane decreased [5]. Increasing the concentration of  $\text{H}_2\text{SO}_4$  as the sulfonation agent increased the water uptake as more and more groups are included in the framework sulfonate polysulfone membrane so the hydrophilicity increased [8]. This is in accordance with the results presented in Figure 3.



**Figure 3:** Water uptake of sPsf-nanosilica membrane

### 3.3. Methanol permeability

Methanol permeability is the membrane's ability to pass methanol from anode to cathode. Increasing the concentration of  $\text{H}_2\text{SO}_4$  increased the permeability of methanol but not significantly (Figure 4). This is due to the similarity of the addition of 3% nanosilica in each membrane. Nanosilica has an important role in restraining the methanol permeability due to the presence of nanosilica as a filler could absorb the methanol, which affecting that most of the methanol does not pass through the membrane [11].



**Figure 4:** Methanol permeability of sPsf-nanosilica membrane

### 3.4. Membrane electrode assembly (MEA)

Membrane electrode assembly (MEA) is an important component of the DMFC that affected the overall performance of DMFC. MEA structure consists of an electrolyte membrane coated on both sides of the electrode catalyst and flanked by gas diffusion layer [12]. The catalyst layer serves to accelerate the oxidation reaction of methanol in the anode and the reduction of oxygen at the cathode thereby increasing the performance of DMFC. This study used alternative catalyst Ag/C and Cu/C on MEA sPsf-nanosilica. This is because Cu and Ag are transition metals that relatively inexpensive and have good electrical conductivity [7].

MEA sPsf-nanosilica has been displayed in Figure 5. MEA with Cu/C catalyst has an average thickness of 359  $\mu\text{m}$  whereas MEA with Ag/C catalyst has an average thickness of 356  $\mu\text{m}$ . The thickness of the membrane was increased due to the catalyzed electrode flanking the membrane. A good MEA is one that has a low thickness so that the resistance is low [13]. But MEA which too thin also not able to provide good electrical contact between the current collector plate with a catalyst layer and allow for a larger methanol crossover [13]. To determine the performances of MEA, proton conductivity test and potential difference test were done. The test also aims to determine the performance improvement experienced by the electrolyte membrane after being fabricated into MEA.



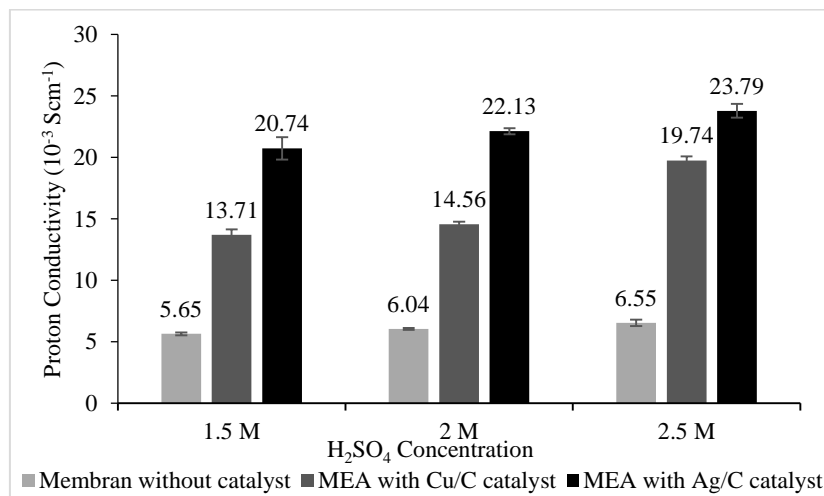
**Figure 5:** MEA sPsf-nanosilica

### **3.5. Proton conductivity**

The proton conductivity describe the membrane's ability to transfer protons from anode to cathode. One of the advantages of nafion membrane is have high proton conductivity 0.1 S/cm [11]. Polysulfone membrane in this study improved proton conductivity through sulfonation using  $\text{H}_2\text{SO}_4$  and the addition of nanosilica filler. Sulfonation improves proton conductivity, the more sulfonate groups contained in the polysulfone chain, the more hydrophilic of membrane, and the bigger number of protons that can be transferred [8]. Hydrophilic nanosilica also increases the membrane's ability to transfer protons. In addition, fabrication of the electrolyte membrane into MEA also increases the conductivity of the proton due to the influence of the catalyst on the electrode. The catalyst layer serves to accelerate the oxidation reaction of methanol in the anode and the reduction of oxygen at the cathode thereby increasing the performance of DMFC.

Proton conductivity increased with increasing the concentration of  $\text{H}_2\text{SO}_4$  as shown in Figure 6. SPsf-nanosilica

membrane with 2.5 M of  $\text{H}_2\text{SO}_4$  generated the highest proton conductivity of each type of membrane, MEA Cu/C, and MEA Ag/C. The proton conductivity also increased due to the addition of Cu/C and Ag/C catalysts onto the MEA. The proton conductivity of membrane to MEA increased significantly to one order. MEA sPsf-nanosilica 2.5 M of  $\text{H}_2\text{SO}_4$  with a catalyst Ag/C has the highest proton conductivity value is  $23.79 \times 10^{-3} \text{ S/cm}$ . This is because Ag has higher electrical conductivity  $6.8 \times 10^7 (\Omega \cdot \text{m})^{-1}$  compared to Cu  $6.0 \times 10^7 (\Omega \cdot \text{m})^{-1}$  [14]. Ag also has smaller resistivity (15.87 n  $\Omega \cdot \text{m}$ ) than Cu (16.78 n  $\Omega \cdot \text{m}$ ) so the electrical resistance is smaller [15]. The greater resistivity, the smaller conductivity because the resistance is greater. The proton conductivity of the membrane and MEA sPsf-nanosilica have qualified for the proton conductivity of DMFC electrolyte membrane which is greater than  $10^{-5} \text{ S/cm}$  [16].



**Figure 6:** Proton conductivity of membrane and MEA sPsf-nanosilica

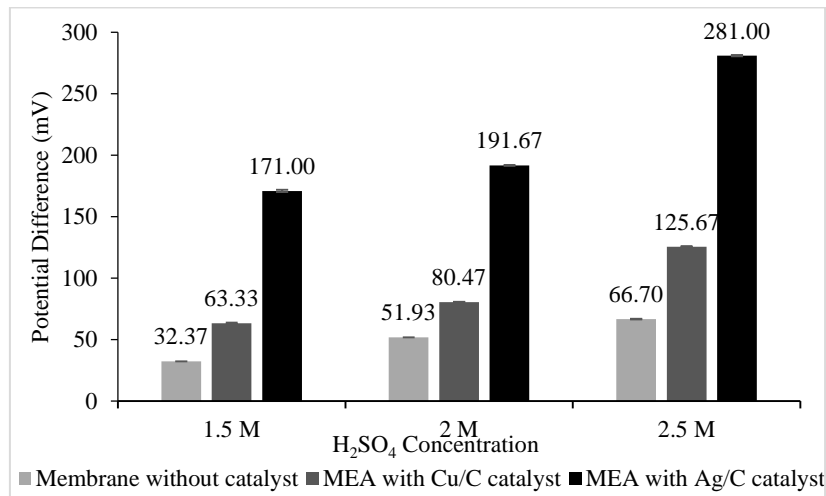
### 3.6. Potential difference

The potential difference in DMFC results from the reduction oxidation reaction. Methanol as a fuel in DMFC systems oxidized at the anode to  $\text{CO}_2$ , protons, and electrons. Gas of  $\text{CO}_2$  is removed from the system while the proton is transferred from the anode to the cathode pass through the electrolyte membrane and react with oxygen produces byproducts in the form of water vapor [12]. Electrons that accumulate in the anode are passed through a series of electrical devices that produce a potential difference between two electrodes.

The potential difference increased with increasing concentration of  $\text{H}_2\text{SO}_4$ . Figure 7 indicates that increasing the concentration of  $\text{H}_2\text{SO}_4$  as a whole affect the performance of the membrane and MEA. In addition, the potential difference is also increased due to the addition of catalysts to the MEA. The type of catalyst also affects the potential difference of MEA. The Ag/C catalyst generated higher potential difference than the Cu/C catalyst. This is because Ag has greater electrical conductivity and smaller electrical resistivity than Cu [14,15]. The magnitude of the potential difference is directly proportional to the proton conductivity. The higher proton conductivity, the greater the potential difference. The highest potential difference was in MEA sPsf-nanosilica 2.5 M  $\text{H}_2\text{SO}_4$  catalyzed by Ag/C 20% with value of 281 mV. The value of potential difference is influenced by the type of catalyst, the amount of catalyst loading, the concentration of catalyst, the thickness of the membrane,



and the concentration of methanol as a fuel [12,17].



**Figure 7:** Potential difference of membrane and MEA sPsf-nanosilica

MEA 2.5 M H<sub>2</sub>SO<sub>4</sub> with Ag/C catalyst has the highest performance in this study. The suitability of membrane and MEA performances compared with commercial membrane of Nafion can be seen at Table 1. Based on oxidation reduction reaction occurring in DMFC, it is known that the ideal DMFC cell potential is 1.18 V [17]. Therefore, to obtain a high potential difference DMFC, MEA application on DMFC need to be arrangement of series of cell unit as needed.

**Table 1:** Performances suitability of MEA Ag/C catalyst with Nafion Pt/C catalyst

Performances	MEA 2.5 M – Ag/C 20%	Nafion 117 – Pt/C 20%	References
Water uptake (%)	45.72	19 <sup>[18]</sup>	-
Methanol permeability (cm <sup>2</sup> /s)	6.97 x 10 <sup>-5</sup>	4,9 x 10 <sup>-6</sup> [18]	< 5.6 x 10 <sup>-6</sup> [19]
Proton conductivity (S/cm)	23.79 x 10 <sup>-3</sup>	100 x 10 <sup>-3</sup> [18]	>10 <sup>-5</sup> [16]
Potential difference (mV)	281	404 <sup>[20]</sup>	-

#### 4. Conclusion

Increasing the concentration of H<sub>2</sub>SO<sub>4</sub> as the sulfonation agent could increase the sulfonation degree of polysulfone, water uptake, methanol permeability, proton conductivity and potential difference of membrane. Fabrication of membrane electrode assembly (MEA) with an alternative catalyst Ag/C or Cu/C increased the proton conductivity and the potential difference significantly as a catalyst accelerating the electrochemical reaction. MEA 2.5 M H<sub>2</sub>SO<sub>4</sub> with 20% Ag/C catalyst had higher performance than the MEA with 20% Cu/C catalyst and membrane without catalyst. MEA sPsf-nanosilica 2.5 M with Ag/C catalyst had proton conductivity of 23.79 x 10<sup>-3</sup> S/cm and a potential difference of 281 mV.

## **5. Recommendations**

Polysulfone sulfonation should be optimized by combining the concentration of H<sub>2</sub>SO<sub>4</sub> and sulfonation time as independent variables. The testing of mechanical strength and thermal resistance should be done to see the optimum performance of polysulfone membrane. Exploration is needed especially in the methods of fabricating MEA, including catalyst concentration, loading catalyst, and the use of other catalysts such as Pb, Co, Fe, and Ni. The applications of MEA sPsf-nanosilica should be observed whether the DMFC could be used as an energy source for portable devices.

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