Influence of Silica/Sulfonated Polyether-Ether Ketone as Polymer Electrolyte Membrane for Hydrogen Fueled Proton Exchange Membrane Fuel Cells

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***Abstract* - The operation of non-humidified condition of proton exchange membrane fuel cell (PEMFC) using composite sPEEK-silica membrane is reported. Sulfonated membrane of PEEK is known as hydrocarbon polyelectrolyte membrane for PEMFC and direct methanol fuel cell (DMFC). The state of the art of fuel cells is based on the perluorosulfonic acid membrane (Nafion). Nafion has been the most used in both PEMFC and DMFC due to good performance although in low humidified condition showed poor current density. Here we reported the effect of silica in hydrocarbon sPEEK membrane that contributes for a better water management system inside the cell, and showed 0.16 W/cm^2 of power density which is 78% higher than that of non-silica modified.**

Keywords: composite membrane, polyether-ether ketone, silica, proton exchange membrane fuel cell.

I. INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) using polymer electrolyte membranes are promising to be applied in portable device and transportation [1], [2]. Recently, fuel cell at temperature operation more than 140^{o}C is very interesting because at this range temperatures, anode catalyst not poisoned by CO so the kinetics of fuel oxidation will be improved and the efficiency of the cell will significantly enhanced. At high temperature, cell operation will contribute in reducing the complexity of the hydrocarbon fuel cell systems [2].

Nowadays, perfluorinated membranes such as Nafion, Aciplex, Flemion, and Dow are widely accepted for commercial application. However, there is a major problem related to the application at both ambient and high temperature of PEMFC, i.e. lower conductivity due to hydration and it is very costly [2]. Therefore, the performance of membrane will decrease fuel cell efficiency. To solve this problem, many researches have been done developing alternative ways in finding more economical and efficient non-perfluorinated polymer proton exchange membranes. Many promising polymer are based on aromatic thermoplastic such as polysulfone, polyethersulfone, polybenzimidazole, polyether-imide, and polyether-ether ketone [3]-[7].

The polyether-ether ketone (PEEK) is an aromatic polymer in which 1,4-disubstituted phenyl groups are separated by ether (-O-) and carbonyl (-CO-) linkage. It was selected as polymer based membrane due to chemical resistance, good thermal stability, mechanical strength and adequate conductivity [7], [8]. In order to hydrophilicity polymer, polyether-ether ketone must be sulfonated using concentrated sulfuric acid to form sulfonated polyether-ether ketone (sPEEK). The process of sulfonation is being controlled by reaction time and temperature [7]-[11].

At high temperature, operation of PEMFC, membrane will decrease many performances like lower conductivity and lower water uptake. Indeed, sPEEK membrane has significant drawback compared to Nafion-117 i.e. low proton conductivity [12]. Thus it is hoped that the proton conductivity could be improved by incorporating proton conducting inorganic substance and sulfonated polyether-ether ketone. The hydrophilic inorganic materials was found to improve water uptake, which in turn leads to higher proton conductivity because water facilities proton conduction [5]. Apart from improving the properties of membrane, impregnating this inorganic substance in the polymer membrane is expected to further enhance its performance at high temperature, due to the structure stability and higher thermal resistance provided by inorganic substance.

In order to increase characteristic of electrolyte membrane like ionic conductivity, mechanical strength and thermal stability, some researchers conducted experiment by adding filler inorganic such as SiO_2, Al_2O_3, ZrO in Nafion membrane [13]. From this approach have been employed various filler to sPEEK [8], [14]. Nunes *et al.* [14] investigated composite membrane of tetraethoxy silane (SiO_2), titanium oxide (TiO_2), and zirconium oxide (ZrO_2) into sPEEK polymer by in situ hydrolysis, and showed that the membranes could reduce the methanol permeability of composite membranes. Although the silica powder in nano-sized particle have not been determined in recent studies. Thus, this experiment was done to study the effect of adding SiO_2 particles to sulfonated polyether-ether ketone. The aims of this experiment are to retain the absorbed water inside the cell, to prevent quick drying performance. The application in single PEM fuel cell has been described in this paper.

II. EXPERIMENTAL

2.1. Membrane preparation

Polyteher-ether ketone grade 450-P in powder form is obtained from by Victrex Inc., SiO_2 powder from Indonesia, sulfuric acid from Merck, 95-98 wt%, n-methyl pirrolidone from Aldrich Chemical Corp. Polyether-ether ketone (PEEK) was sulfonated as described [11]. PEEK powder (5 g) was added into concentrated sulfuric acid 100 ml under vigorous stirring for 3 hours at 60ºC temperature. To terminate sulfonation reaction, the polymer solution precipitated into a large excess of ice water. The polymer was washed repeatedly with deionized water until the rinse water was at pH 6-7. The recovered sPEEK were dried at in an oven overnight [11]. The pure sPEEK membrane (**1**) and composite sPEEK+Si membrane (**2**) was prepared by solution casting. The sPEEK polymer was first dissolved in n-methyl pyrrolidone (12.5 wt. %) to prepare a solution and then 3 wt. % of silica was added to the solutions. The resulting mixture was stirred for 7 h. Solution were cast onto glass plates then dried at 60^{o}C for 72 h to remove the solvents. The thickness of resulting membranes was in the range of 80-100 μm.

2.2. Characterization

Ion exchange capacity (IEC) and degree of sulfonation (DS) were measured by titration. A sPEEK was immersed in aqueous sodium hydroxide solution (NaOH) for three days. Dilute sulfuric acid was employed to back-titration of the NaOH aqueous solution. Phenolphtalein was used as indicator [8]. Proton conductivity was measured using standard bridge LCR (Impedance Capacitance Resistance), impedance spectroscopy (HIOKI 3522-50 LCR HiTESTER) with various frequencies from 3 kHz to 100 kHz and 20 mV oscillating voltage.

The conductance of each membrane was measured at 25^{o}C under fully hydrated condition. A conductivity cell was made up of two gold foils carrying the current and two gold wires sensing the potential drop, which was apart 1 cm [Sri Handayani et al., World Applied Journal Science]. The fully hydrated sPEEK membrane with deionized water during 24 h was cut in 1 cm wide, 4 cm long prior to mounting on the cell. After mounting sample onto two gold foils on the lower compartment, upper compartment was covered, and then the upper and lower compartments were clamped as described by authors (Zawodzinski *et al.*, 1991; Sancho *et al.*, 2007). The proton conductivity (σ) of the membrane can be calculated by $\sigma = G(L/W.d)$, where G, L, W and d are conductance (S), the length between the electrode (cm), wide (cm) and thickness of the membrane samples (cm), respectively.

Before measurement water uptake of membranes, the membranes were dried in an oven. Weighed films were immersed in deionized water at room temperature for 24 h. The membranes were saturated with water until no further weight gain was observed. The liquid water on the surface of wetted membranes was removed using tissue paper before weighing [8]. The membranes morphologies were investigated using a scanning electron microscope (Philips SEM XL 30), operated at 20 kV. Specimens for the SEM were prepared by freezing the dry membrane samples in liquid nitrogen and breaking them to produce a cross-section [8,9].

2.3. Cell performance

MEAs for each membrane were prepared for single cell using active area 5cm^2. The 40 wt% Pt supported on carbon black catalyst (Pt/C) from Gas Hub was used in all experiments for both cathode and anode. The ink preparation was applied in carbon paper teflon coated (NUS Japan) using brush technique with loading catalyst 5mg/cm^2. The nafion solution 5wt% content in the dry electrodes was 60wt%, respectively. The ink was stirred in an ultrasonic mixer or the ink composition was altered by using isopropanol 80% vol in aquadest as solvent. The membrane was set up to sandwhiched with the electrode. Both anode and cathode electrodes were applied in membrane and hot pressed in 120ºC and 28 kgf/cm^2 for 3 minutes to get MEA **1** for sPEEK membrane, and **2** were done in the same manner with sPEEK-silica membranes. Then each MEA were stacked into pairs of bipolar plate with parallel flow channel. Fuel cell test were carried out in a homemade 5 cm2 single cell with standard of Electrochem stack. The PEM fuel cell performance of the MEAs was tested by using in-house single fuel cell test set-up. Humidified hydrogen and oxygen gas were fed to the anode and cathode channel at 100 mL/min and 1 psi. The PEM fuel cell was operated at 50ºC and connected to ProDigit 3310F DC Electronic Load.

Figure 1. Pictures of MEAs and condition of fuel cell test.

III. RESULTS AND DISCUSSION

The size of silica particle estimated via TEM with magnification x 25,000 is shown in Figure 2. According to TEM image, it is clearly that the size of silica about 50-100 nm. Absorption analyzer is determined by BET surface area and pore diameter of particles, for silica are 183m^2/g and 8.3 nm.

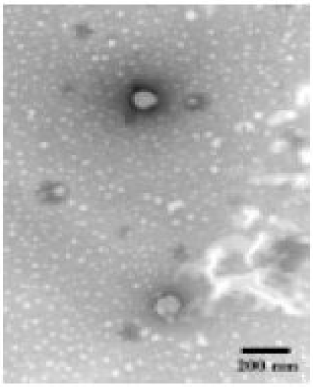
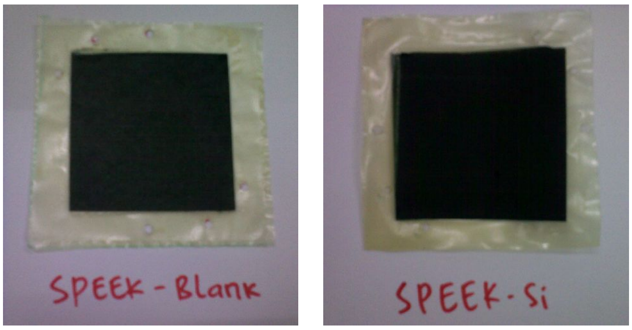


Figure 2. Transmission electron micrograph of silica powder.

The morphological observation of the blank membranes and modified membrane were determined by TEM (magnification x 25,000) as shown in Figure 3.



(a).sPEEK (b). sPEEK+Si

Figure 3. Transmission electron micrographs of: (a). sulfonated PEEK and (b). composite sPEEK.X-ray diffraction analysis of SiO_2 (Fig. 4(a)) shows an amorphous structure.

In this Figure, light region is hydrophobic domain (backbone polymer matrix) and dark region is hydrophilic domain (sulfonic acid group and particles). In Figure 3(a), it is indicates that unmodified membrane sPEEK has no pores. The addition of silica at membrane (Figure 3(b)) showed homogeneous distribution and little separated phase between hydrophobic domain and hydrophilic.

And in Fig 4 (b), the blank sPEEK membrane shows an amorphous structure. That's it in Fig. 4(c) shows the XRD pattern of composite sPEEK membrane containing 3 wt. % SiO_2, is amorphous structure. The SiO_2 present in the polymer matrix is more of an amorphous structure leading to a well associated network. Amorphous structure in membrane will provide an environment conducive to ionic transport.

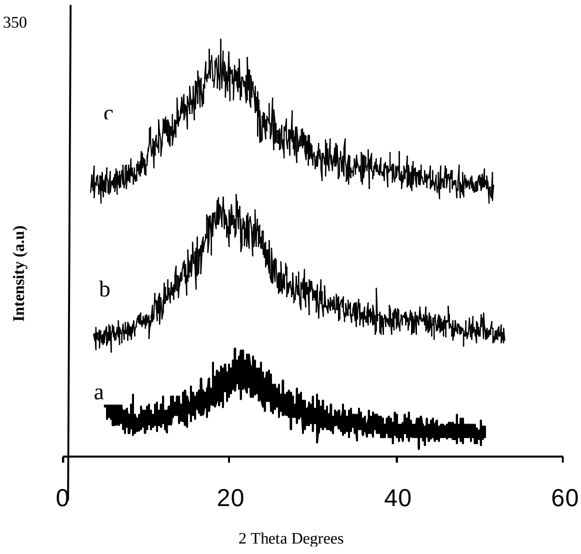


Figure 4. X-ray diffraction of (a) SiO_2 powder, (b) sPEEK membrane and (c) sPEEK membrane containing SiO_2.

The modification of composite membranes with additional of hydrophilic silica are aimed to improve the overall hydrophilicity of composite membrane. The addition of silica to membrane will retain water at high temperature due to the composite membrane 2 which has higher thermal stability compare to blank membrane **1**; transition temperature (T_g) composite sPEEK-silica membrane **2** is 230°C and sPEEK **1** is 197°C. DSC results show the T_gs of sPEEK and composite sPEEK membranes in Fig. 5.

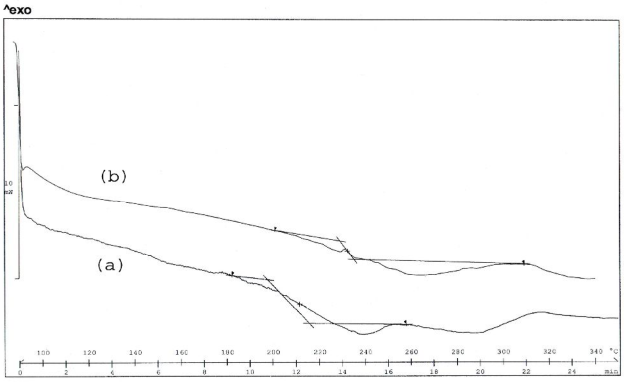
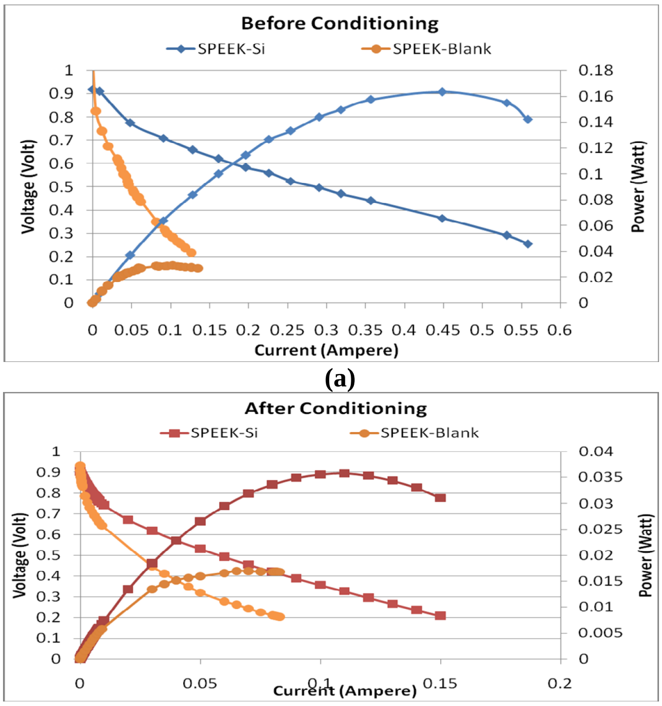


Figure 5. Typical DSC curves of (a) sPEEK and (b) composite sPEEK membranes.

Effect of membrane type on the ionic conductivity can be seen in Table 1. The addition particles on sPEEK membrane **2** caused the increasing of water uptake. It is also indicates that silica particles is a hygroscopic (easy absorb water). The increasing of water uptake of composite membrane sPEEK **2** that incorporating silica is followed by increasing of ionic conductivity.

TABLE 1. THICKNESS DATA, IONIC CONDUCTIVITY AND WATER SWELLING OF MEMBRANES

	Ionic Conductivity (S/cm)	Water uptake (% b/b)
sPEEK	0.02	15
Composite sPEEK (sPEEK+Si)	0.045	30



(a)

(b)

Figure 6. The I-V curve polarization of fuel cell performance with MEA **1** and **2** in (a) before conditioning and (b) after conditioning.

The observed fuel cell performances with composite membranes were compared and evaluated by 5 cm^2 PEM fuel cell and used H_2/O_2 at humidified conditions. As seen from Fig. 6 (a) there is a significant cell voltage and power density values with sPEEK-silica membrane **2** than sPEEK membrane **1**. In high humidified condition which means after conditioning with water vapor for 30 min, the silica contain membrane 2 showed lower power density compared to non-humidified condition that might be due to water flooding as shown in Fig. 6(b). This is correlated by water drops inside the parallel flow field at bipolar plate after test. Indeed, it is clearly showed that the silica particle was keeping the electrolyte wet enough to act as polyelectrolyte without the additional humidified hydrogen as fuel.

IV. CONCLUSIONS

A composite membrane using silica powder particle was newly developed for PEMFC applications. The characterization of those membranes have been determined and showed a high power density with silica particle contained membrane (sPEEK-silica) **2**. The PEMFC performance result clearly showed that silica particle act as a hydrophilic domain in non-humidified condition.

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