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THE EFFECT OF MEMBRANE THICKNESS OF HYDROCARBON COMPOSITE POLYMER TO FUEL CELLS PERFORMANCES

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ABSTRACT

THE EFFECT OF MEMBRANE THICKNESS OF HYDROCARBON COMPOSITE POLYMER TO FUEL CELLS PERFORMANCES. Polymer type's fuel cell generator are depends on oxidant as fuels. For hydrogen and methanol fuel's oxidant, there are proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC)'s type. Each type of fuel cells needs suitable membrane as electrolyte in order to get high density of proton transfer reaction. In this research the conductivity and water uptake of sulphonated polyether-ether keton (sPEEK) with silica modified composite hydrocarbon membrane in various thickness up to 100 µm were investigated. The selectivity of proton transfer reaction had been calculated. In summary, the ionic conductivity showed about 10^{-2} $S.cm^{-1}$ to 2 $S.cm^{-1}$ and water uptake about 30-45 (% w/w). In the thickness between 70 µm to 100 µm, the influence of the thickness membrane on ionic conductivity was increased by two times the ion conductivity. The sulphonated PEEK with silica modified composite membrane have clearly shown as a good candidate for DMFC applications with 90-100 µm thickness and for PEMFC's is 70 µm.

Key words : Polymer electrolyte membrane, Sulphonated hydrocarbon polymer, Ionic conductivity

ABSTRAK

PENGARUH TEBAL MEMBRAN POLIMER KOMPOSIT HIDROKARBON PADA KINERJA *FUEL CELL*. Pembangkit *fuel cell* tipe polimer bergantung pada oksidan sebagai bahan bakar. Pada oksidan bahan bakar hidrogen dan metanol, terdapat tipe *Proton Exchange Membrane Fuel Cell* (*PEMFC*) dan *Direct Methanol Fuel Cell* (*DMFC*). Masing-masing tipe *fuel cell* memerlukan membran yang sesuai sebagai elektrolit untuk mendapatkan densitas yang tinggi dari rekasi transfer proton. Pada penelitian ini dilakukan pengukuran konduktifitas dan *water uptake* oleh polieter eter keton tersulfonasi (sPEEK) dengan membran komposit hidrokarbon termodifikasi silika dalam berbagai tebal hingga 100 µm. Selektifitas dari reaksi transfer proton telah dihitung. Dapat disimpulkan bahwa konduktifitas ionik menunjukkan nilai sekitar 10 $S.cm^{-1}$ hingga 2 $S.cm^{-1}$ dan *water uptake* sekitar 30 %w/w hingga 45 %w/w. Pada ketebalan antara 70 µm hingga 100 µm, pengaruh ketebalan membran pada konduktifitas ionik meningkat 2 kali lipat. Membran PEEK dan komposit termodifikasi silika secara jelas menunjukkan potensinya sebagai kandidat yang baik untuk aplikasi *DMFC* dengan ketebalan 90 µm hingga 100 µm dan *PEMFC* 70 µm.

Kata kunci : Membran elektrolit polimer, Polimer hidrokarbon tersulfonasi, Konduktifitas ionik

INTRODUCTION

Fuel cells are efficient devices that generate electricity via chemical reaction of fuels and oxygen from air. Fuel cells technology using hydrogen or alcohol as fuel is a promising candidate system for portable electronic device and automotive applications. This is because of their attributes of high power density, low weight, simplicity of operation, high energy conversion efficiency and zero harmful emissions. Energy carrier of fuel cells is more than 50 %, it is higher comparing to internal combustion engine (15 %) [1, 2].

Some of the most promising Proton Exchange Membrane (PEMs) are developed at low temperatures below 80°C using hydrated perfluorosulfonic acid (PFSA) polymers, such as Nafion® (Dupont), Flemion® (Asahi Glass), Aciplex® (Asahi Chemical Industry), Neosepta-F® (Tokuyama) and Gore- Select® (W.L. Gore and Associates). Although some of these membranes were originally developed for chlor alkali electrolysis, they demonstrate good proton conductivities when used as electrolytes in a PEM fuel cell. Some of the requirements of PEMs, apart from high proton conductivity, include good chemical, morphological and thermal stability, excellent chemical durability and low cost.

In order to increase characteristic of electrolyte membrane like ionic conductivity, mechanical strength and thermal stability and to decrease methanol permeability, some researchers conducted experiment by adding inorganic filler such as SiO_2, Al_2O_3, ZrO in Nafion membrane [3-6]. From this approach various filler to sPEEK have been employed [7-9]. Synthesized composite membrane of boron orthophosphate into polymeric matrix of sulfonated PEEK producing ionic conductivity higher than the blank sPEEK membrane [8]. But the composites membrane has pores, which is not suitable for application of DMFC due to high methanol cross over value. Compositing membrane of tetraethoxy silane (SiO_2), titanium oxide (TiO_2), and zirconium oxide (ZrO_2) into sPEEK polymer have been done by in situ hydrolysis [9]. The results show that the membranes lowering methanol permeability but also could reduce the ionic conductivity of composite membranes.

Influence of membrane thickness on the characteristics of the membrane has been studied by previous researchers. The thicker membrane will effect on lower methanol permeability and lower ionic conductivity. For DMFC application, the thicker membrane produces a higher OCV values due to the reducing of methanol crossover [10]. This paper discussed about the characteristics of the composite membrane sPEEK (sPEEK + silica) and their effects on membrane thickness variations. Addition of silica (which is hygroscopic) into the polymer electrolyte are expected to increase the water adsorption on the membrane surface. The presence of water in the membrane will increase the transport of protons.

EXPERIMENTAL METHOD

Polyether ether ketone (PEEK) 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.

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 60 °C 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 in an oven overnight [11].

The composite sPEEK+Si membrane 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 24 hours. Solution were cast onto glass plates then dried at 60 °C for 72 hours to remove the solvents. The thickness of resulting membranes was in the range of 70 µm, 90 µm and 100 µm.

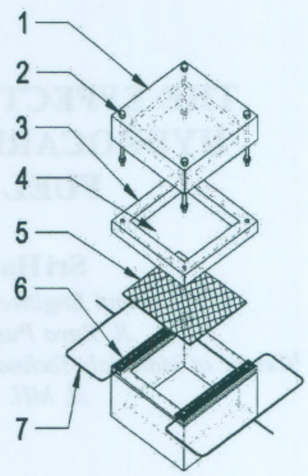

Figure 1. Conductivity cell

The morphology of membranes is analyzed by transmission electron microscopy TEM-1010. The crystal structure of particles and membranes were investigated using X-Ray Diffractometer (XRD) Shimadzu XD-610.

Water uptake was measured by immersing membranes into water at ambient temperature for 24 hours. Then the film was take out, wiped with tissue paper and weight at microbalance. Water uptake (swelling) of the membrane was calculated from Equation (1) :

$$(W_{wet} - W_{dry}) / W_{dry} \times 100(\%) \quad\quad (1)$$

Where :
W_{dry} = Weight of dry membrane
W_{wet} = Corresponding water swollen of membrane film

Water uptake of membrane was estimated from the average value of water uptake of each film.

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 room temperature 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 1 cm apart as shown in Figure 1. The fully hydrated sPEEK membrane with deionized water for 24 hour 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

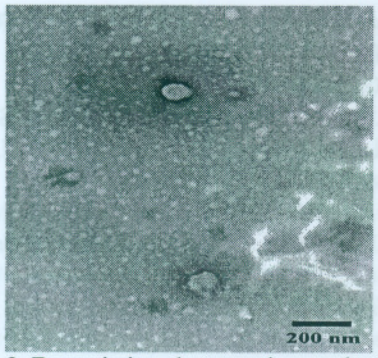

Figure 2. Transmission electron micrograph of silica powder

compartment was covered, and then the upper and lower compartments were clamped as described by authors [12]. The proton conductivity (σ) of the membrane can be calculated using Equation (2),

$$\sigma = G \times \frac{L}{W.d} \qquad (2)$$

Where :

G = Conductance (S)

L = The length between the electrode (cm)

W = Wide (cm)

d = Thickness of the membrane (cm)

RESULTS AND DISCUSSION

The size of silica particle estimated via TEM with magnification 25,000 is shown in Figure 2. From this figure the size of silica is about 50 nm to 100 nm.

The crystal structure of particles was also analyzed by XRD, as shown in Figure 3. Figure 3 showed amophous structure of silica powder and sPEEK +silica membrane.

Surface properties of particles are analyzed by pH slurry. The slurry was composed by 0.5 g of particles powder per 0.1 of bi-distilled water which stirred for about 24 h and then analyzed by pH meter. The pH of silica slurry is 3.5. Absorbsion analysis is carried out by BET method, which gave surface area and pore diameter of particles, for silica are 183m²/g and 8.3 nm respectively.

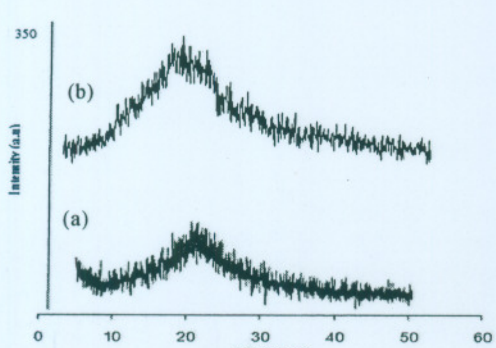

Figure 3. X-Ray diffraction of (a). SiO_2 powder and (b). sPEEK membrane containing SiO_2

Figure 4. Transmission electron micrographs of silica modified membrane of sPEEK

Table 2. Thickness data, ionic conductivity and water swelling of membranes

Membrane Thickness (μm)	Ionic Conductivity (S/cm)	Water uptake (% b/b)
70	0,045	30
90	0,038	38
100	0,025	40

The morphologycal observation of the composite membranes was done by TEM (magnification of 25,000) as shown in Figure 4. In this Figure, light region is hydrophobic domain (backbone polymer matrix) and dark region is hydrophilic domain (sulfonic acid group and particles). Figure 4 showed homogeneous distribution and little separated phase between hydrophobic domain and hydrophilic.

Effect of membrane thickness on the ionic conductivity can be seen in Table 2. The ionic conductivity increased as the thickness membrane decrease. It is because ion move in relatively short distances. Based on Table 2, it also showed that water uptake increase as the thickness membrane increase. The amount of water uptake did not effect on higher ionic conductivity. These results suggest that membrane thickness has more effect than the membrane water uptake to increase the ionic conductivity. In other words, the thin membrane will influence on greater ionic conductivity.

The higher ionic conductivity will result in better fuel cell performance [12]. Therefore, the effective thickness of sPEEK composite membrane for PEMFC applications is 70 μm, while for DMFC application is about 90 μm to 100 μm.

CONCLUSION

Ionic conductivity and water uptake were investigated at room temperature. The morphology of cross section membranes and silica powder were observed by TEM. In the composite membrane (sPEEK+silica), ionic conductivity increases with the decrease of membrane thickness. In the other hand, water uptake increases with the increases of membrane

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thickness. The appropriate selection of the membrane thickness for the application of solid polymer electrolyte fuel cells will improve the performance of fuel cells.

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REFERENCES

[1]. LAMINIE, JAMES and DICKS A., *Fuel Cell System Explained*, John Wiley & Sons, Ltd., Baffins Lane, Chichester, England, (2000)

[2]. L. LI, JUN ZHANG, YUXIN WANG, *Journal Membrane Science*, **226** (2003) 159-167

[3]. T. ARIMURA, D. OSTROVSKII, T. OKADA, G. XIE, *Solid State Ionics*, **118** (1999) 1-10

[4]. ENIYA L. DEWI and ROHMADI, *Indonesian Journal of Materials Science*, **8** (3) (2007) 198-204

[5]. P. DOMITROVA, K.A. FRIEDRIECH, U. STIMMING, B. VOGT, *Solid State Ionics*, **150** (2002) 115-122

[6]. A.S. ARICO, V. BAGLIO, A. DI BLASI, P. CRETI, P.L. ANTONUCCI, V. ANTONUCCI, *Solid State Ionics*, **161** (2003) 251-265

[7]. M.H.D. OTHMAN, S.L. HO, A. MUSTAFA, A.F. ISMAIL, Organic/Inorganic Hybrid Membrane for Direct Methanol Fuel Cell Aplication. *The 3rd Regional Symposium on membrane Technology for Industry and Enviromental Protection, ITB-Bandung, Indonesia*, (2005)

[8]. S.D. MIKHAILENKO, S.M.J. ZAIDI, S. KALIAGUINE, *Catalysis Today*, **67** (2001) 225-236

[9]. S.P. NUNES, B. RUFFMANN, E. RIWOKOWSKI, S. VETTER, K. RICHAU, *J. Membr. Sci.*, **203** (2002) 215-225

[10]. A. HEINZEL and BARRAGAN V.M., *Journal Power Source*, **84** (1999) 70-74

[11]. S. HANDAYANI, WIDODO W.P., ENIYA L.D., ROEKMIJATI W.S. *Indonesian Journal of Materials Science*, **8** (2) (2007) 129-133

[12]. T. SANCHO, J. SOLER, PINA M.P., *J. Power Sources*, **169** (2007) 92-97