Vol. 19, No. 2, Desember 2016, hal: 87-96
Majalah Polimer Indonesia ISSN 1410-7864

A Comparison of Physical Properties of Nafion and Lapindo-Nafion-SiO_2 Composite Membrane as Electrolyte for High Temperature Fuel Cell

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Diterima: 30-Okt-2016 Diperbaiki: 30-Nov-2016 Disetujui: 29-Des-2016

ABSTRACT

A Comparison of Physical Properties of Nafion and Lapindo-Nafion-SiO_2 Composite Membrane as Electrolyte for High Temperature Fuel Cell. The physical properties of Nafion-d2020 and composite Lapindo-Nafion-SiO_2 membranes are compared. The composite membrane was prepared by mixing 5% of Nafion-d2020 solution and nanosilica (3 w.t% of Nafion-d2020) using dispersion and casting methods. Silica was synthesized from Lapindo mud through co-precipitation method using NaOH 6 M and HCl 3 M continued with NaOH 2.5 M including H_2SO_4 3 M. Membrane composites structure was characterized by FTIR and TEM to study the hydrogen bonds between nanosilica against Nafion-d2020. TEM analysis showed that the silica has particle size of 30-100 nm applying NaOH 6 M and HCl 3 M and 5-16 nm using NaOH 2.5 M and H_2SO_4 3 M. The proton conductivity, swelling water, and high temperature durability of the Lapindo-Nafion-SiO_2 composite membranes were higher than those of Nafion-d2020 membranes. Proton conductivity of Lapindo-Nafion-SiO_2 composite membrane was 6.09 x 10^{-2} S/cm, swelling water was 55.27 % and high temperature durability on fuel cell operating system was 120˚C. Proton conductivity of nafion-d2020 membrane was 5.34 x 10^{-2} S/cm, swelling water was 45.15 % and high temperature durability on fuel cell operating system was 80˚C.

Keywords: Lapindo mud, nanosilica, coprecipitation, Nafion-d2020, composite

ABSTRAK

***Perbandingan Sifat Fisis Membran Komposit Nafion dan Membran Lapindo-Nafion-SiO_2 sebagai Elektrolit untuk Sel Bahan Bakar Suhu Tinggi*.**

Sifat fisis dari membran Nafion-d2020 dan membran komposit Lapindo-Nafion-SiO2 dibandingkan. Membran komposit dibuat dengan mencampur 5% larutan Nafion-d2020 dan nanosilika (3% berat Nafion-d2020) menggunakan metode dispersi dan casting. Silika disintesis dari lumpur Lapindo melalui metode co-presipitasi menggunakan NaOH 6 M dan HCl 3 M dilanjutkan dengan NaOH 2,5 M termasuk H_2SO_4 3 M. Struktur komposit membran dikarakterisasi dengan FTIR dan TEM untuk mengetahui ikatan hidrogen antara nanosilika dengan Nafion-d2020. Analisis TEM menunjukkan bahwa silika memiliki ukuran partikel 30-100 nm menggunakan NaOH 6 M, HCl 3 M dan 5-16 nm menggunakan NaOH 2,5 M dan H_2SO_4 3 M. Konduktivitas proton, pembengkakan air, dan ketahanan pada suhu tinggi dari Lapindo-Nafion-SiO_2 membran komposit lebih tinggi dari membran Nafion-d2020. Konduktivitas protonik membran komposit Lapindo-Nafion-SiO_2 adalah 6,09 x 10^{-2} S/cm, pembengkakan air adalah 55,27% dan daya tahan pada suhu tinggi pada sistem operasi sel bahan bakar adalah 120˚C. Konduktivitas proton membran Nafion-d2020 adalah 5,34 x 10^{-2} S/cm, pembengkakan air adalah 45,15% dan ketahanan suhu pada sistem operasi sel bahan bakar adalah 80˚C.

Kata Kunci: *lumpur Lapindo, nanosilika, ko-presipitasi, Nafion-d2020, komposit*

INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) is an electrochemical system that converts chemical energy directly into electrical energy. In general, this fuel cell system that operated at low temperature (< 80ºC) often leads to major problems on a Pt catalyst poisoning caused the amount of carbon monoxide (CO). For this, an approach is made to acquire the durability of CO in the presence of free energy absorption of CO on the catalyst and depends on temperature [1]. High-temperature fuel cell has a weakness against the adjustment of moisture and water content. The weakness in fuel cell system relates to an electrolyte membrane, in which the quality of the Fuel Cell's performance is determined by the electrolyte membrane.

The commercial membrane used in fuel cell is a type of polymer perfluorosulfonated Nafion, which is made from polytetrafluoroethylene (PTFE) sulfonated produced by Dupont TM. Teflon is the material that is resistant to chemical attack and strong hydrophobic. In general, Nafion has advantages in selectivity of ion transfer (IEC 0.91 mmol/g), high ionic conductivity (0.05 to 0.14 S/cm), and resistance to chemicals [2]. Nafion has advantages in ion selectivity transfer and chemical durability. In high temperature fuel cell (> 100ºC), dehydration and lack of water will occur in Nafion membrane. Dehydration membranes cause the membranes to shrink, reduce the contact between the electrodes and the membrane, cause a hole in the membrane, and gas crossovers [1]. In addressing this problem, it is necessary to modify the structure of Nafion, thus increasing humidity at high temperatures.

Modification of Nafion structure has been done with the addition of inorganic additives such as metal oxides as an absorber of water including ZrO_2 [3]. However, the addition of SiO_2 (silica) as a water absorbent was depend on reaction rate of bonding formation with Nafion. The addition of silica is needed to obtain nanometer-size dimensions (nano pores structure) of Nafion [4]. Some studies prepared a modification of nafion with silica derived from synthetic materials through the sol-gel method and dispersion [5-7]. In this study, silica was derived from bursts of Lapindo, East Java, Indonesia. Silica separation process from Lapindo mud through coprecipitation method was using a solution NaOH 6 M and it produced amorphous silica with 95.7% purity, but unknown particle size. Nanosilica synthesis of natural materials can also be performed by coprecipitation method such as waste rice husk ash. Nafion membrane was modified by nanosilica from Lapindo mud to provide the effect of moisture membrane fuel cell at high temperatures. Modification of nafion membranes with nanosilica through dispersion method and sonication was done in this research.

EXPERIMENTAL METHOD

Materials

Lapindo mud was obtained from the mud volcano in Porong, Sidoarjo Regency East Java province. Nafion solution d2020 5 % was purchased from Dupont, NaOH pellet was purchased from Sigma Aldrich. H_2O_2 38%, H_2SO_4 97%, and HCl 37% were purchased from Merck.

Sample Preparation of Lumpur Lapindo

Lapindo mud was dried, crushed, and sieved to smaller size, and followed by washing it with H_2O for 24 h.

Silica Extraction and Synthesis of Nanosilica

Clean Lapindo mud was soaked in 2 M HCl for 24 h and then washed with H_2O until pH 7. The material was refluxed with 6M NaOH for 16 h at 80°C and filtrated. The solution was titrated with 3 M HCl until it reached pH 7-9 and formed a white precipitate. The precipitate was then filtered, washed, and dried at temperature of 100°C for 24 h and 50°C for 48 h. Silica powder was refluxed with HCl for 4 h at 50°C and washed until pH 7. After that, the reflux was performed with 2.5 N NaOH for 16 h and the samples were treated with H_2SO_4 to pH 7. The precipitate was washed and dried at 50°C for 48 h.

Preparation of Nafion-d2020 Membrane

Nafion solution d2020 5% was sonicated for 30 min at 30°C, cast in the petri dish, and dried in an oven at 80 °C for 20 h. In fabricating Lapindo-Nafion-SiO_2 composite and membranes, nanosilica powder was dissolved in DMF and hot water under sonication for 15 min, then Nafion solution d2020 5% was added into it. The mixture was then sonicated for 30 min at 30°C, cast in the petri dish, followed by drying in an oven at 80°C for 20 h. The next step was the membrane activation. The activation was performed by soaking the membrane in a solution of 5% H_2O_2 50 ml at 80°C for 1 h and then washed with aquabidest 2 times. Afterwards, the membrane was boiled in a solution of 1 M H_2SO_4 50 ml for 30 min and washed 2 times by soaking in aquabidest for 30 min.

Characterization

Bonding in the membrane was analyzed by using Nicolet iS50 FT-IR Thermo Scientific. Hitachi-9500 Transmission Electron Microscopes (TEM) was used to analyze the particles of membrane. Ionic conductivity measurement of membrane was conducted using ac impedance spectroscopy complex Solatron 1260 with spectroscopic methods in distilled water at room temperature. Swelling property of the membranes was performed with the following method. The samples were dried in an oven to obtain the dry weight of the membrane (W_{dried}). Then, dry membrane was immersed in water for 24 h at room temperature. After the water was removed from the sample by wiping with a tissue, the samples were then weighed and recorded as W_{wet}. Swelling degree of the membrane was calculated using the following equation.

$$\text{Swelling} = \frac{W\ wet - W\ dry}{W\ dry} \times 100\ \% \qquad (1)$$

RESULT AND DISCUSSION

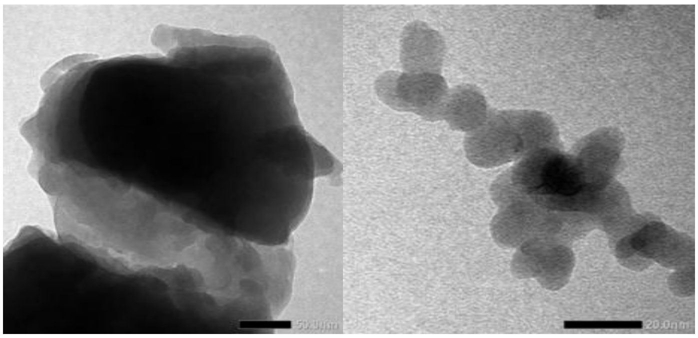
Silica content after every step of procedures are shown in Table 1.

Tabel 1. Silica content (%) from various treatments

Treatment	Lapindo Mud	Washed H_2O	Soak with HCL 2 M	Silica	Nano Silica
Silica Content	34.3	34.5	44.8	81.7	94.1

Vol. 19, No. 2, Desember 2016, hal: 87-96
Majalah Polimer Indonesia ISSN 1410-7864

The result shown in Table 1 indicates that the synthesis procedure influence the purity of the obtained nanosilica. This is in agreement with the previous result [8]. Silica and nanosilica synthesis were through two stages. Firstly, synthesis with NaOH to produce sodium silicate, which silicate ions bind with salt alkalin. NaOH also affects the purity of silica and silica-bound lot number. Then it was reacted with a strong acid such as HCl and H_2SO_4 which produces silicic acid ($SiOH_4$). At the time of reaction with acid salt protonation reaction of sodium silicate (Na_2SiO_3) and the hydrolysis reaction which produces silanol and condense to form silica polymerization [9]. By using TEM, it was showed that silica produced by reaction with 6 M NaOH and HCl 3M has particle size of about 30-100 nm in which the particles undergo agglomeration to form larger particles. The role of HCl was slowing down condensation reaction, so that the siloxane groups (Si-O-Si) can be increased and the resulting higher particle size. TEM images show that nanosilica synthesized has a smaller size than the silica in the synthesis of Lapindo mud. Nanosilica produced has a size of about 6-15 nm and spherical / spherical accordance with previous research [8].



(a) Silica (b) Nanosilica

Figure 1. The TEM of Synthesis of Lapindo Mud

FT-IR data showed that the silica and nano silica has almost the same absorption wave numbers. This is because the synthesis of nano silica has no effect on the functional groups, but it only affects the structure, size and purity. The differences are seen in the intensity of 3448.72 cm^{-1}. The higher the concentration of acid is added, the greater the intensity of the absorption that indicates more hydroxide functional group (-OH) there. It is quite groundless because during the formation of the gel, the use of relatively high concentrations of acid resulting -Si-O- groups are protonated also more and more and will be carried over until the gel is formed.

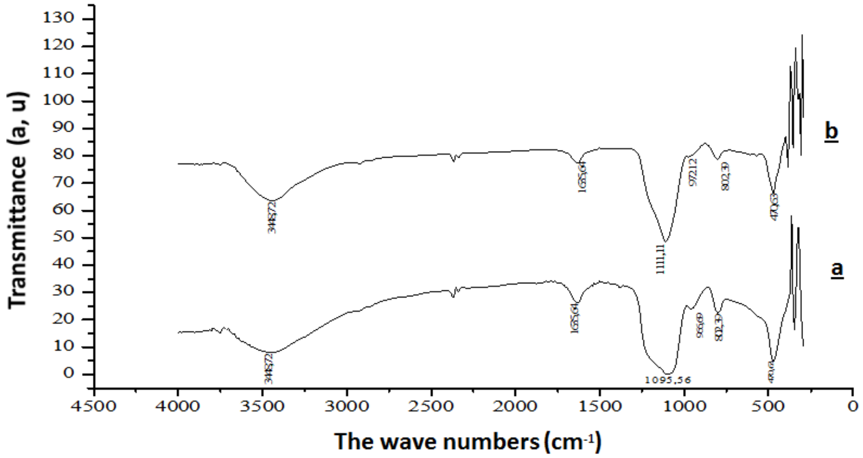


Figure 2. FT-IR (a) Silica lapindo Mud (b) Nanosilica

The addition of additives aims to increase the absorption and retention of water in low humidity conditions (high temperatures). This will affect the ion conductivity and water swelling. Nano silica additions to the cluster ions in Nafion d2020 must have a size that matches the size of the cluster. The increasing of swelling and proton conductivity due to the hydrogen bonds of the sulfonate group to the surface of the silica, so that the silica bound and absorbed more and more dependent on the silica silanol groups. The more silanol groups on the surface, the more water will be absorbed. The addition of nano silica, which is not homogeneous size, causes an increase in conductivity and swelling were not significant. This is described in Figure 3.

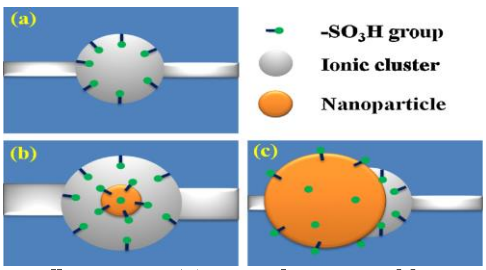


Figure 3. Systematic illustration (a) Ion Cluster , Addition Silica (b) Small size below 4-5 nm (the size of the Cluster Ion) and (c) Large size in Nafion d2020 [10]

Figure 3(b) indicates that nano silica is bound by size according to the cluster ion, thus increasing conductivity and water swelling, which occurs in nano silica Lapindo size of 5-10 nm. However, in Figure 3(c), nano silica is larger than the size of the cluster ions, thus blocking the transfer of protons and water absorption occurs only in the silica surface and do not occur in the sulfonate group. This will result in a decreasing in proton conductivity and water swelling.

Table 2. The Proton Conductivity and Water Swelling of Membrane Nafion d2020 and Lapindo-Nafion-SiO2 Composite Membrane

Membrane	Proton Conductivity (S/cm)	Water Swelling
Nafion d2020 Membrane	$5.34x10^{-2}$ – 5.47 x10^{-2}	45.15 %
Lapindo-Nafion-SiO2 Composite Membrane	$6.07x10^{-2}$-$6.09x10^{-2}$	55.274%

The bond between Lapindo nano silica-Nafion d2020 is shown with the analysis results of FT-IR. Spektra Nafion-d2020 membrane and the membrane composite are shown in Figure 4.

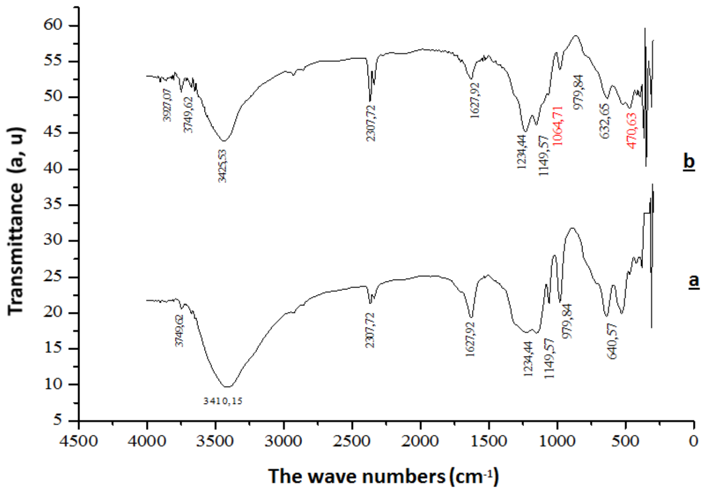


Figure 4. FT-IR (a) Nafion d2020 membrane and (b) Lapindo-Nafion-SiO2 composite membranes

Spectra of Nafion d2020 membrane showed a typical cluster group of Nafion d2020 with absorption band 979.84 cm^{-1} correspond to the strain symmetry –CO. IR spectra of Lapindo-Nafion-SiO_2 composite membrane shown specific absorption band similar to Nafion d2020 membrane but with different intensities.

TG analysis shows the degradation temperature of the membrane which reveals the resilience of the fuel cell operation and interaction interface. The resilience of fuel cells could be predicted from the membrane as the TG analysis temperature was considered as an external stimulus to evaluate the decomposition patterns. TG experiments also carried out at higher temperature than the actual operating temperature of fuel cells [11]. TG results on the Figure 5 shows the decomposition mechanism Nafion membrane where the membrane Nafion experienced a weight reduction begins at a temperature of 80°C and a maximum temperature of 130°C, this suggests that a reduction H_2O in the matrix nafion. TG of Lapindo-Nafion-silica membrane shows the difference that the initial weight loss occurs at a temperature of approximately 120°C which is the weight of water that is bound in silica.

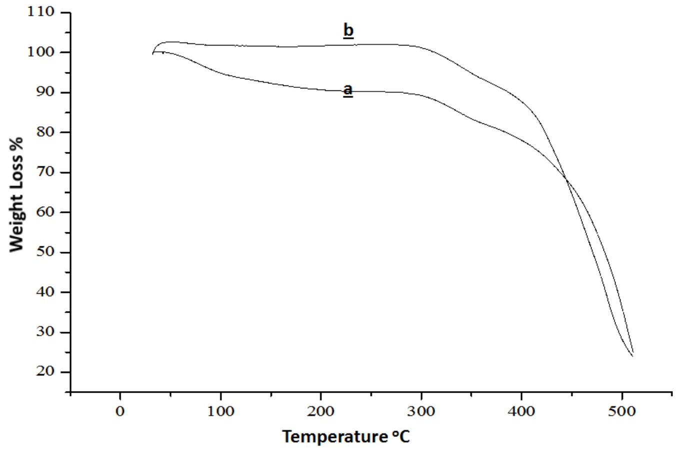


Figure 5. Thermal Gravimetry (a) Membran Nafion d2020 and (b) Lapindo-Nafion-SiO2 Composite Membrane

Compared to the Nafion, Lapindo-Nafion-Silica membrane showed quite good properties. It was also an economic reason to use the waste from Lapindo and preparing a modified composite. It also has higher temperature resistance compared with the commercial ones. Thus, it is necessary to do scale up production to validate the quality of Lapindo-Nafion-Silica membrane.

CONCLUSION

The particle size of synthetic silica Lapindo Mud produced through co-precipitation method of measuring 30-100 nm (6 M NaOH and HCl 3 M) with a purity of 81.7% and the size of 5-16 nm (2.5M NaOH and H2SO4 3 M) as well as the purity of about 94.1%. The process of making a composite membrane of Lapindo-Nafion-silica through dispersion method and casting shows the interaction between nano silica with Nafion d2020 that form hydrogen bonds. Proton conductivity of the composite membrane of Lapindo-Nafion-silica $6.09 x 10^{-2}$ S / cm at 55 274% water swelling and resistance at a temperature of 120^0C. This composite membrane increased membrane properties compared to the use of fuel cell Nafion membrane

D2020 that produce proton conductivity of 5.34x10^{-2} S / cm by 45.15% water swelling and durability at a temperature of 80°C.

ACKNOWLEDGMENT

This work was carried out under the auspice and financial support of INSINAS RISTEK 2013&2014 that is research award under The Ministry of Research & Technology.

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