Synthesis and Characterization of Chitosan – Rice Husk Ash Silica Composite As Polymer Electrolyte Membrane (PEM)

Eva Mardiningsih, Ella Kusumastuti

Abstract

Direct methanol fuel cell (DMFC) is an alternative technology which environmentally friendly and very prospective to be developed. Polymer electrolyte membrane (PEM) is a solid polyelectrolyte membrane which plays a big role as ionic carrier in a DMFC. In this research, it has been synthesized a solid polyelectrolyte membrane by using chitosan as matrices and silica from rice husk ash as a filler. Membrane was synthesized by phase inversion method with addition of rice husk silica in chitosan matrices. The mass ratio of chitosan-rice husk silica were 1: 0; 1: 0.0049; 1: 0.0097; 1: 0.0194; 1: 0.0292; 1: 0.0486 and 1: 0.0972 (w/w). Polymer electrolyte membrane was characterized by analysing the water swelling, proton conductivity and methanol permeability. Interaction between silica and chitosan was studied by analysing functional groups of membrane by Fourier transform infra-red (FTIR). The result showed that the addition of silica had significant effect on the water swelling, proton conductivity and methanol permeability. The greater of silica addition, the greater of water swelling, proton conductivity and methanol permeability. Modified silica had hygroscopic properties so the water molecules could use as a proton and methanol transport media. The optimum membrane properties performed by the membrane with mass ratio of chitosan-rice husk ash silica is 1:0.0049 (w/w) with water swelling, proton conductivity and methanol permeability respectively 29.00%, 5.35×10⁻⁴ s/cm and 2.09×10⁻⁷ cm²/s. It were selected by reason of water swelling must less than 50%, proton conductivity must more than 5×10⁻⁵ s/cm and methanol permeability must be under 5.6×10⁻⁶ cm²/s. FTIR spectra show that there were not new functional groups in membrane, indicated there have not been cross linking interaction between silica as a filler and chitosan as matrices but the interaction were physical one.

Keywords: chitosan; polymer electrolyte membrane (PEM); rice husk ash silica

Introduction

Nowadays, the source of widely used energy is the unrenewable energy from fossil material. Fossil fuel produces byproducts that would pollute the environment. Fuel cell technology is one of the environmentally friendly alternative to overcome this problem. Based on the type of its electrolyte, currently known fuel cell is referred to as Direct Methanol Fuel Cell (DMFC). The primary key of this type of fuel cell is a solid polyelectrolyte membrane or polymer electrolyte membrane (PEM) that acts as a carrier of ions in the cell. of the many types of membranes were studied, Nafion membranes were found to give maximum performance (Neburchilov et al., 2007). Nafion 112 as a separator of the reactants and as a proton conductor have a conductivity about 1.2 × 10⁻² S/cm. The main problem of Nafion for the application in DMFC is its high methanol permeability that is equal to 6.21 × 10⁻⁶ cm²/s. The high methanol permeability will drive the methanol crossover (Smitha et al., 2004) and decrease its voltage (Dhuhita, 2010).

One of the potential polymers replacement for Nafion is chitosan (Chakrabarty et al., n.d.). Chitosan has free amine groups that can be protonated, and chitosan also has hydroxy groups. Both of these groups allow for proton exchange so chitosan potentially to be developed as a polyelectrolyte membrane with high proton conductivity. One of the disadvantages of chitosan is its hydrophilic property (because of their amine and hydroxy groups) lead to the high methanol permeability. This property can be reduced by addition some hydrophobic species to produce high proton conductivity but low methanol permeability (Vaghari et al., 2013). One of the hydrophobic species is silica. Rice husk ash as a solid waste contains silica which is quite high at 72.28% (Bakri, 2009). Therefore, rice husk
ash is considerable potential as the raw material for biosilica source from renewable sources (Chandra et al., 2012). Rice husk ash silica particles were expected to be able to cover the pores in the chitosan membrane so that the movement of methanol through the membrane is obstructed (Suka et al., 2010). It will also form some blocks which act as proton conduction (Li et al., 2011).

Methodology

The equipment used in this research were analytical balance (AND GR-200), glassware, 100 mesh sieve, oven (Memmert), furnace (Barnstead Thermolyne), magnetic stirrer (Ika-mag), glassware, incubator (Memmert), LCR meters (Agilent U1733C Series 20.000-Count Dual-Display Handheld LCR Meter), desiccator, a set of reflex device, a set of membrane permeability test equipment, digital calipers, FT-IR (Shimadzu-B201PC), X-ray fluorescence (XRF) (Bruker). The materials used in this study are chitosan, rice husk ash, distilled water, filter paper, pH indicator paper, \( \text{H}_2\text{SO}_4 \), \( \text{NaOH} \), \( \text{CH}_3\text{OH} \) (methanol) 99%, \( \text{CH}_3\text{COOH} \) 100%, and aquademin (p.a., E. Merck).

Preparation of rice husk ash from rice husk is performed by washing and then drying. Dry and clean rice husk roasted in furnace at 600 °C for 7 hours to obtain rice husk ash (Yunica, 2008). A sample of 20 g rice husk ash was stirred in a 160 mL of 2.5 M \( \text{NaOH} \) at 100 °C with a speed of 400 rpm for 3 hours and then filtered. The residue was then washed with 40 mL of boiling water. The obtained solution was allowed to cool down at room temperature. As 5 N \( \text{H}_2\text{SO}_4 \) was then added under constant stirring at controlled conditions until it reached pH 2. Then \( \text{NH}_4\text{OH} \) was added up to pH 8 and was allowed to stand at room temperature for 24 hours formed gel of silica. Silica gel was filtered and rinsed with distilled water until neutral pH. Silica gel was dried for 24 hours at a temperature of 80 °C. silica powder was analysed by XRF to determine the content of silica (Rafiee et al., 2012).

Synthesis of chitosan-silica membrane was carried out by phase inversion method. As much as 1 g of chitosan was dissolved in 50 mL of acetic acid 2% (v/v) (Bhuvaneshwari et al., n.d.) in another container, silica was stirred with 50 mL of 2% acetic acid (v/v) for 4 hours. Both of chitosan and silica in acetic acid solution were mixed in an erlenmeyer and stirred for 2 hours. The solution was poured onto a glass plate with size of 20×20 cm². The solution was dried in an incubator at temperature of 50 °C for 24 hours. The formed membrane then soaked in a solution of NaOH 5% (v/v). The solution of NaOH was used to neutralize the acetic acid in the membrane. It will be easier to peel the membrane from the glass plate. The resulted solid membrane was washed with distilled water until neutral pH and then dried at room temperature.

Chitosan–rice husk ash silica membranes were analysed their characteristics respectively water swelling, proton conductivity, methanol permeability, and its functional groups by FTIR.

Results and Discussion

Preparation of silica from rice husk ash

The results of the composition analysis by XRF of the silica content in rice husk ash are shown in Table 1.

Table 1. Composition of Rice Husk Ash Silica by using X-Ray fluorescence (XRF)

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>Amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \text{SiO}_2 )</td>
<td>97.24%</td>
</tr>
<tr>
<td>2.</td>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>0.89%</td>
</tr>
<tr>
<td>3.</td>
<td>( \text{CaO} )</td>
<td>0.58%</td>
</tr>
<tr>
<td>4.</td>
<td>( \text{P}_2\text{O}_5 )</td>
<td>0.41%</td>
</tr>
<tr>
<td>5.</td>
<td>( \text{K}_2\text{O} )</td>
<td>0.12%</td>
</tr>
<tr>
<td>6.</td>
<td>( \text{ZnO} )</td>
<td>0.02%</td>
</tr>
<tr>
<td>7.</td>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>0.01%</td>
</tr>
</tbody>
</table>

Table 1 showed that rice husk ash contained 97.24% of silica (\( \text{SiO}_2 \)) particle and trace of other compounds. As a source of silica, rice husk ash were very good. Preparation of rice husk ash was done by burning rice husk at a temperature of 600 °C with the expectation that the obtained silica is amorphous. Amorphous silica in a variety of conditions considered to be more reactive than crystalline silica. silica reactivity was desired to easily bind with chitosan. Reactions which may occur in rice husk ashing process is as follows (Nuryono & Narisito, 2004):

\[
\text{Compound C, H, and Si + O}_2 \rightarrow \text{CO}_{2(g)} + \text{H}_2\text{O}(g) + \text{SiO}_2
\]

Combustion at high temperature will produce silica and organic compounds turned into \( \text{CO}_2 \) and \( \text{H}_2\text{O} \).

Purification of silica in rice husk ash was done by the extraction method. It was performed at a temperature of 100 °C with 2.5 N \( \text{NaOH} \). Slowly heating will transform silica into water-soluble silicate. The reaction is (Sugiyarto, 2004):

\[
\text{SiO}_2(\text{SiO}_2) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SiO}_3(\text{aq}) + \text{H}_2\text{O}(l)
\]

At high temperatures, NaOH melted and formed a perfect dissociated ions of sodium and hydroxide ions. in \( \text{SiO}_2 \) molecules, high electronegativity O atoms lead to more electropositive Si and formed intermediates [\( \text{SiO}_2\text{OH} \)] unstable. Then there will occur dehydrogenation reaction and the second hydroxyl ions will bind with hydrogen to form water molecules. Two \( \text{Na}^+ \) ions will balance the formed negative charge and interact with ions to form \( \text{Na}_2\text{SiO}_3 \) or \( \text{SiO}_2\text{H}_2 \) (Mujiyanti et al., 2010). by transforming silica into
Na$_2$SiO$_3$ molecules, it were expected to be more hydrophilic so interaction with chitosan will be more effective.

**Synthesis and characterization of chitosan-rice husk ash silica membrane**

Synthesis of chitosan-rice husk ash silica membrane was carried out by phase inversion method. It is the simplest method used in membrane synthesis because it transforms the liquid phase into solid phase. Chitosan and rice husk silica were dissolved respectively in acetic acid solution as a solvent to get the homogeneous reactants. In this study, investigation were performed on the effect of rice husk silica addition to the properties of membrane.

The analysis of water swelling of chitosan-rice husk ash silica membranes are presented in Table 2.

**Table 2. Water Swelling Membranes Chitosan-Rice Husk Ash Silica**

<table>
<thead>
<tr>
<th>Membranes Chitosan-Silica (w/w)</th>
<th>Water Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>15.38%</td>
</tr>
<tr>
<td>1:0.0049</td>
<td>29.00%</td>
</tr>
<tr>
<td>1:0.0097</td>
<td>32.83%</td>
</tr>
<tr>
<td>1:0.0194</td>
<td>36.89%</td>
</tr>
<tr>
<td>1:0.0292</td>
<td>43.28%</td>
</tr>
<tr>
<td>1:0.0486</td>
<td>48.84%</td>
</tr>
<tr>
<td>1:0.0972</td>
<td>56.96%</td>
</tr>
</tbody>
</table>

Water swelling test was conducted to determine the water absorption capacity of the membrane. It can be seen from Table 2 that the water swelling percentage increased with the addition of rice husk ash silica because this silica has hygroscopic properties and has a large surface area so easily absorb water on the their surface so finally increase the water uptake properties (Handayani et al., 2007). For fuel cell applications, the degree of water absorption membrane must fulfill requirement of less than 50% (Handayani, 2009). If the water absorption are more than 50% of the membrane will be soft because bind with H$_2$O so that the membrane life time is shorter. This result showed that a good membrane for polymer electrolyte membrane is chitosan-rice husk ash silica membrane with the mass ratio of chitosan-silica are 1:0; 1:0.0049; 1:0.0097; 1:0.0194; 1:0.0291; and 1:0.0972 with the percentage of water swelling respectively for 15.38%; 29.00%; 32.83%; 36.89%; 43.28% and 48.84%.

The measurement results of proton conductivity of chitosan-rice husk ash silica membrane can be seen in Table 3. Proton conductivity indicates the ability of a membrane in delivering protons (Putro, 2013). From the data it can be seen that the addition of silica enhanced the proton conductivity because silica as SiO$_2$ molecules can absorb water as a medium for proton transport H$^+$ across the membrane. Silica from rice husk ash will also form some blocks among chitosan matrices which act as proton conduction (Li et al., 2011). Ionic conductivity (protons or hydroxyl) will only occur when the membranes in the wet state (hydrated). In chitosan membranes, their mechanism is estimated involving OH$^-$ species as a carry charge species. When water is inserted into the membrane, the free amino group on chitosan will partially protonated to produce NH$_3^+$ and OH$^-$ ions. Because NH$_3^+$ group is bound strongly to chitosan chains, only the OH$^-$ ions are free to move and give ionic currents and contribute to conductivity (Zulfikar et al., 2009). The mechanisms is:

\[
\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_3^+ + \text{OH}^-
\]

Membrane can still be used for fuel cell if it has a proton conductivity greater than 1×10$^{-5}$ S/cm (Suka et al., 2010), so in this variation, all of membrane potentially to be used in DMFC according their high proton conductivity.

**Table 3. Proton Conductivity Membranes Chitosan-Rice Husk Ash Silica**

<table>
<thead>
<tr>
<th>Membranes Chitosan-Silica (w/w)</th>
<th>Proton Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>2.8988 x 10$^{-4}$</td>
</tr>
<tr>
<td>1:0.0049</td>
<td>5.3453 x 10$^{-4}$</td>
</tr>
<tr>
<td>1:0.0097</td>
<td>5.8275 x 10$^{-4}$</td>
</tr>
<tr>
<td>1:0.0194</td>
<td>5.8510 x 10$^{-4}$</td>
</tr>
<tr>
<td>1:0.0292</td>
<td>5.9269 x 10$^{-4}$</td>
</tr>
<tr>
<td>1:0.0486</td>
<td>6.4770 x 10$^{-4}$</td>
</tr>
<tr>
<td>1:0.0972</td>
<td>6.0821 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

Another important characteristic of a polymer electrolyte membrane for direct methanol fuel cell applications (DMFC) is the methanol permeability. Data of methanol permeability on chitosan-rice husk ash silica membrane can be seen in Table 4.

**Table 4. Methanol Permeability of Chitosan-Rice Husk Ash Silica Membrane**

<table>
<thead>
<tr>
<th>Membranes Chitosan-Silica (w/w)</th>
<th>Methanol Permeability (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>1.0469 x 10$^{-7}$</td>
</tr>
</tbody>
</table>
Table 4 showed that there was an increase in methanol permeability with increasing silica addition. Methanol permeability is the ability of the membrane to withstand methanol so as not to pass to the anode (Dhuhita, 2010; Dewi, 2009). Supposedly, the addition of silica can decrease the methanol permeability due to silica particles able to form crosslink with chitosan so that the structure will be more compact and dense (Handayani, 2009). Silica can also close the pores in the membrane so that the movement of methanol through the membrane can be obstructed (Suka et al., 2010). of the few studies that have been made, it known that the water does not just pass through the pores but also can seep through silica particles (Handayani, 2009). The increasing of methanol permeability because of the increasing of water swelling. Silica as SiO$_2$ molecules can absorb water as a medium for proton transport H$^+$ across the polymer membrane (Dhuhita & Arti, 2010). The requirement of methanol permeability of polymer electrolyte membrane for the DMFC application is <5.6 x 10$^{-6}$ cm$^2$/s at 25 °C (Neburchilov et al., 2007).

Although the addition of rice husk ash silica to chitosan membranes improved the methanol permeability, but it can still be used as a polymer electrolyte membrane because the methanol permeability is still under 5.6 x 10$^{-6}$.

The addition of rice husk ash silica to chitosan actually increased the proton conductivity, methanol and water swelling. This is consistent with the hygroscopic nature of silica as SiO$_2$ molecules (Handayani et al., 2007). of all variation performed, the membranes give an optimum result with the mass ratio of chitosan-rice husk ash silica 1:0,0486 which the proton conductivity is 6.4770 x 10$^{-6}$ S/cm, water swelling is 48.84% and the methanol permeability is 2.1985 x 10$^{-6}$ cm$^2$/s. It was selected with the consideration of requirements for PEM, proton conductivity >1 x 10$^{-5}$ S/cm (Suka et al., 2010), water swelling < 50% (Handayani, 2009), and methanol permeability <5.6 x 10$^{-6}$ cm$^2$/s at 25 °C (Neburchilov et al., 2007).

Functional groups analysis were performed by FTIR to compare if there was a new the functional group parallel to the addition of silica. FTIR spectra of chitosan-rice husk ash silica with the mass ratio of chitosan-silica is 1:0,0486 (membrane with optimum properties) and 1:0 (membrane without silica) can be seen in Figure 1. FTIR spectra showed that there was not a significant change in wavelength of both membranes.

FTIR spectra of rice husk ash silica membrane-chitosan 1:0 and 1:0,0486 (w/w) has a similar pattern. The absorption at 1070-1150 cm$^{-1}$ region is the C-O-C asymmetric stretching vibration absorption. Absorption in 1580-1650 cm$^{-1}$ region indicated the presence ofN-H$_2$ groups. Absorption peak at 2877.79 cm$^{-1}$ indicated the presence of a C-H (Lambert et al., 1989). Absorption peak at 3448.72 cm$^{-1}$ indicated the presence of O-H (Sudiarta et al., 2013). The addition of silica as SiO$_2$ molecules increases the peak intensity at 3448.72 cm$^{-1}$ region which shows the O-H absorption. All of these facts indicated that there was not new functional group in both of membranes. It also indicated there have been no cross linking interaction between silica as a filler and chitosan as matrices but the interaction were physical one. This fact in accordance with the high of water swelling and methanol permeability as a result of silica particle cannot cover the pores in the chitosan membrane so that the movement of methanol through the membrane is not obstructed. It mean there have been no chemical bond among the chitosan and rice husk ash silica.

**Figure 1.** FTIR Spectra of Chitosan-Rice Husk Ash Silica Membrane with Mass Ratio 1:0 and 1:0,0049 (w/w)

**Conclusions**

The membranes with optimum properties is the mass ratio of chitosan-rice husk ash silica 1:0,0486 with the proton conductivity is 6.4770 x 10$^{-6}$ S/cm, water swelling is 48.84% and the methanol permeability is 2.1985 x 10$^{-6}$ cm$^2$/s. It was selected with the best meet the requirements for PEM. Generally, the addition of rice husk ash silica into chitosan increases the water swelling and methanol permeability due to hygroscopic nature of silica as SiO$_2$ molecules and it cannot cover/ pass through the pores of chitosan so the movement of methanol through the membrane is not obstructed. The addition of silica also increases the proton conductivity as silica forms some blocks among chitosan matrices which act as proton conduction. Functional groups analysis with FTIR showed that there have been no cross linking interaction between silica as a filler and chitosan as matrices but the interaction were physical one.
References


