Synthesis of Composite Membrane Based Biopolymer Chitosan With Silica From Rice Husk Ash For Direct Methanol Fuel Cell Application

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Abstract. A membrane chitosan with silica from rice husk ash was fabricated as alternative membrane electrolyte for direct methanol fuel cell (DMFC) application. Chitosan is made from shrimp shell powder which is processed through deproteination, demineralization and deacetylation steps. Furthermore, the phase diversion technique was used to synthesis membranes by mixing chitosan and silica in acetic acid solution. The resultant membrane characterized with FTIR, water and methanol uptake, ion exchange capacity, and methanol permeability. FTIR analysis showed that chitosan and silica was successfully synthesized. Water uptake for the chitosan-silica membrane increased with increasing silica loading, but the methanol uptake value decreased. The chitosan-silica with 15 wt% silica loading exhibited the best ion exchange capacity and methanol permeability which were 1.290 meq/gram and 2.42 x 10⁻⁴ cm²/s, respectively. All the result obtained from this study shown that chitosan-silica membrane is a promising electrolyte membrane for direct methanol fuel cell application.

Keywords: membrane, chitosan, silica, fuel cell

1. Introduction

The membrane is a very selective thin layer between the two phases that regulates the transportation of certain substances [1]. Based on the type, the membrane is divided into two, namely composite membranes and non-composite membranes. The composite membrane is a membrane made from organic polymers as a matrix and inorganic materials as a filler. These materials are widely used because they have special properties that mutually reinforce each other when combined. Organic polymers are flexible, high dielectric and easy to use. Inorganic materials have high thermal stability and are rigid [2].

In membrane manufacturing, several techniques are used, namely sintering, stretching, track-etching, template leaching, coating, and phase inversion. The process of making membranes generally uses the phase inversion method, which is a change in the form of the polymer from the liquid phase to the solid phase. This solidification process begins with a transition from a one-liquid phase to a two-liquid phase (liquid-liquid demixing). A stage during demixing, one of the liquid phases (high concentration polymer phase) will become solid to form a solid
matrix. Chitosan is a biopolymer that is similar in structure to cellulose and can form a membrane. Chitosan has hydroxyl and amino reactive groups that allow it to be modified chemically, one of which is a membrane [3, 4].

Chitosan is a polysaccharide produced from deacetylation of chitin which can be easily obtained, namely from crab shells which contain 25-30% chitin. Chitosan has hydrophobic properties (insoluble in water), in alcohol, and dissolves in dilute acids and alkalis [5]. The manufacture of the membrane will collaborate with organic materials in the form of chitosan and inorganic fillers in the form of silica which are easy to obtain and come from agricultural waste that does not get more attention, namely rice husks [6]. Rice husk (rice hull) or unhulled rice is the outermost part of rice grains and has the highest silica content compared to other rice processing by-products. The by-products of rice processing include straw (4.0–7.0)%; bran (0.6–1.1)%; bran (0.2–0.3)% and husks (18.0–22.3)%. This study focused on the use of chitosan as an organic matrix for composite membrane synthesis. The composite membrane was made in collaboration between silica from rice husk ash and the addition of vanillin as an additive. The additive in the membrane base material is used as a constituent material in the membrane structure layer.

2. Method

2.1 Synthesis Chitosan

The extraction process of chitosan from crab shells was conducted according to the previous study [7]. The crab shells was dried and crushed into fine powder prior to the extraction process. The powder was added into 1 M NaOH solution with a ratio 1 : 10 (w/v) and stirred for 2 hours at 65 °C. Then, the mixture was filtered to retrieve the precipitate. The precipitate was washed with distilled water until pH 6-7 then dried at 105 °C. Then dried powder was demineralized using 2 M HCl solution with a ration 1 : 10 (w/v) and stirred for 30 minutes at 65 °C. After that, the filtered precipitate was washed and dried until it became dried powder called chitin. The chitin powder was deacetylation process using 50% NaOH solution with a ratio 1: 10 (w/v), stirred for 4 hours at 90-100 °C, washed and dried until it became dried powder called chitosan.

2.2 Synthesis of silica from Risk Husk

The risk husk was washed and dried, then the dry rice husks was burned with fire to produce white rice husk ash. Ashes were carried out by means of flushing at a temperature of 600 °C for 3 hours. After that, the ashes was pulverized using a grinder, then the mashed ash was sieved using a 200 mesh sieve. Then the sample was purified so that the silica was separated from the rice husk ash. As much as 20 grams of rice husk ash that has passed the 200 mesh sieve was washed with 150 mL of 6 M HCl and heated with a hot plate for 2 hours. The sediment was washed with distilled water to pH 6-7. The washing results were dried in an oven at 105 °C for 1 hour, then mashed using a mortar and called silica.

2.3 Synthesis Membrane

Chitosan powder was dissolved in 50 mL of 2% acetic acid, and stirred at 80°C and 400 rpm. Another 50 mL of 2% acetic acid was used silica powder and ultrasonic treatment for 30 minutes. Then, both the mixtures were mixed together and stirred for 30 minutes at 80°C. After that, the mixture was given an ultrasonic treatment for 30 minutes, stopped 30 minutes and then an ultrasonic treatment was carried out again for 30 minutes. After degaification, the mixture was poured onto a caston glass panel and dried at room temperature.

2.4 Membrane Characterizations

2.4.1 Water and methanol uptake. The water and methanol uptake of membrane were determined by measuring the weight difference of membrane before and after immersion in water or an aqueous solution of methanol. Membrane samples dried at room temperature for 24 h then weighted, and immersed in water or 5 mol L⁻¹ aqueous solution of methanol at room temperature for 24 h. After that wipe using tissue residual water or methanol solution on the surface membrane, then weighted. water and methanol uptake is calculated based on Equation. 1:
Uptake (%) = \( \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100 \) \hspace{1cm} (1)

Where, \( M_{\text{wet}} \) and \( M_{\text{dry}} \) are the weights of the membrane in the wet and dry states, respectively.

2.4.2 Ion Exchange Capacity (IEC). The test was carried out by cutting the membrane with a size of 1 x 1 cm for each membrane variable and then oven for 30 minutes and weighing the mass. Each membrane was immersed in HCl solution for 1 hour, then drained and followed by soaking 1 M NaCl for 3 hours. The soaked sample was then dripped with the phenolphthalein indicator and titrated using 0.01 M NaOH until it turned pink and the volume of the titration was recorded. Then the IEC value can be calculated using the following equation 2.

\[
\text{IEC} = \frac{\text{Titrating Volume} - C_{\text{NaOH}}}{\text{Sample mass}}
\] \hspace{1cm} (2)

2.4.3 Methanol Permeability. Methanol permeability was analyzed using two compartment diffusion cells. The membrane with a size of 2x2 cm which has been prepared with a dry and flat surface, is clamped and placed between the two compartments. Compartment A is filled with 1M methanol solution and compartment B is filled with 300 ml distilled water each. Next. Samples in compartment B were taken with a pipette every 30 minutes for 3 hours to determine the concentration of methanol. Determination of the concentration of methanol is carried out using a pycnometer based on a calibration curve between density and methanol concentration. The difference in methanol concentration every 30 minutes will produce a slope. The permeability value of methanol can be calculated using the equation 3.

\[
P = \left( \frac{\Delta C_B}{\Delta t} \right) \frac{L C_B}{A C_A}
\] \hspace{1cm} (3)

\( P \) is the methanol permeability from the membrane (cm² / s), \( \Delta C_B / \Delta t \) is the slope of the variation in methanol concentration in compartment B with a function of time (mol / Ls), \( L \) is the thickness of the membrane (cm), \( V_B \) is the volume of water in compartment B (cm³), \( A \) is the surface area of the membrane (cm²), and \( C_A \) is the methanol concentration in compartment A (mol / L).

3. Results and Discussions

3.1 Synthesis chitosan

Synthesis chitosan from crab shell powder, deacetylation is carried out three times, with the aim of obtaining a higher purity or deacetyl degree according to the target. At each stage of deacetylation of the material, the chitosan obtained was set aside a little to be tested using the FTIR tool to see the content of the functional groups in the chitosan and to determine the percentage of the addition of deacetylation degrees of each deacetylation. FTIR spectra for chitin and chitosan are presented in Figure 1.
Based on Figure 1, it can be seen that the absorption peak at wave numbers of 2965 cm\(^{-1}\), 2923 cm\(^{-1}\) and 2893 cm\(^{-1}\) shows the stretching vibrations of CH\(_3\) and C-H aliphatic alkanes which are typical peaks of chitin [8, 9]. And the absorption at the wave number 1652 cm\(^{-1}\) which indicates the presence of a stretching vibration of the C=O group (-NHCOCH\(_3\)) which has a weaker absorption intensity. This indicates the release of acetyl groups from chitin compounds, which proves that there has been deacetylation of chitin compounds into chitosan [10].

Another parameter to determine the success rate of the transformation of chitin into chitosan is to determine the degree of deacetylation. The degree of deacetylation is a quality parameter of chitosan which indicates the percentage of acetyl groups that can be removed from the yield of chitin. The more acetyl groups of chitin that turn into amino groups in chitosan, the chitosan formed will have many amino groups (NH\(_2\)) which are more nucleophilic [11]. In addition, with the number of amine groups formed, the ion interaction with hydrogen bonds increases. [12].

### 3.2 Silica From Rice Husk Ash

The dry rice husks are treated with a furnace at a temperature of 600°C for 3 hours. This ashing process aims to remove carbon compounds that make up the husk. The temperature of 600°C is the optimum temperature for ashing process for rice husk ash, while the ashing at 500°C is still incomplete oxidized carbon so the silica content in the ash is still relatively low. Rice husks have the main component of carbon compounds. Ashes conversion rate is expressed as the amount of ash weight to the initial husk. During the ashing process hydrocarbons will break down into H\(_2\)O vapor and CO\(_2\) gas. After the ash is produced, it is continued with a refining process using acid. Furthermore, the purification of rice husk ash was carried out by dissolving rice husk ash with HCl solution for 1 hour using a magnetic stirrer. Purification of rice husk ash in acidic conditions such as HCl aims to eliminate the metal and non-metal content contained in rice husk ash such as Al, Ca, Fe, Mg and Ti and to obtain a silica content of 99.39% [13, 14]. The silica results obtained were characterized using an infrared spectrophotometer with the results in Figure 2.

Figure 2 shows the spectra of the wave number 3440 cm\(^{-1}\) which indicates the presence of an O - H group, due to silanol vibrations or the interaction of water molecules absorbed on the silica surface. The wave number 1633 cm\(^{-1}\) shows the elastic vibration absorption band O-H, which indicates that water molecules cannot be completely lost. At the wave number 1095 cm\(^{-1}\) there is a strong decrease due to the asymmetric vibrations of the silaxon bond from Si - O - Si, this bond indicates the presence of a silica matrix. This is also reinforced by the presence of Si-O-Si strain vibrations at a wavelength of 806 cm\(^{-1}\). This is in accordance with previous research [15].
3.3 Membrane Characterizations

3.3.1 Water and methanol uptake. Water and methanol uptake shown at Figure 4. Membrane Ch/Sil shows an increase in water uptake along with the addition of silica loading. This is due to the presence of silanol groups from silica which can increase the hydrophility of the membrane. The addition of silica in the chitosan-silica membrane caused an increase in the bonding interaction between the silanol groups from the silica and the amine and acetyl groups from chitosan. High water uptake is favourable for high performance PEM to facilitate great numbers of protons hopping and diffusion through the membrane [16]. In Figure 4b, Membran Ch/Sil shows a decrease in Methanol Uptake along with the addition of silica filler. This is because the addition of silica in chitosan can strengthen the chitosan chain, resulting in decreased ability to absorb water molecules. Water Uptake for composite membrane Ch / Sil 5% had the lowest water uptake value at 64.83% and methanol uptake for composite membrane Ch / Sil 5% had the lowest methanol uptake value of 5.25%. From the width of the membrane the methanol uptake value has a lower value compared to the water uptake value. The lower methanol uptake value shown membrane performance will be very good, therefore there will be no methanol cross-over on the membrane. This phenomenon is possible because of the good interaction between silica and chitosan which can increase the density of the composite membrane, so that it can suppress methanol and reduce its diffusion into the composite membrane [17, 18, 19].
3.3.2 Ion Exchange Capacity and Methanol Permeability. Based on the analysis that has been carried out, the addition of silica filler in the chitosan membrane has a significant effect on the value of the ion exchange capacity. The addition of 5% silica obtained an ion exchange capacity value of 1.024 meq / gram. If the silica concentration is increased to 10% and 15% tended to decrease the ion-exchange capacity of the chitosan membrane to 0.860 and 0.759 meq / gram, respectively, as shown in Figure 4a. This is because the too much SiO$_2$ in chitosan will trigger the formation of silicic acid which will interfere with the process of proton exchange in the chitosan membrane.

From Figure 4b, it can be seen that the addition of silica can reduce the methanol permeability. This is because silica can absorb methanol into the membrane surface so that most of the methanol does not pass through the membrane. In addition, the addition of silica can cover the pores on the membrane so that the transfer of methanol through the membrane is very small, this shows that methanol is only absorbed on the membrane surface but does not penetrate or pass through the membrane. It can be seen that the 5% chitosan-silica membrane was 3.96 x 10$^{-4}$ cm$^2$/s and decreased in the 15% silica concentration of 2.42 x 10$^{-4}$ cm$^2$/s. However, the 10% chitosan-silica membrane experienced an increase from the 5% chitosan-silica membrane this was due to the formation of aggregate pores on the 10% chitosan-silica membrane. These pores affect the increase in methanol permeability, because methanol mass transfer can occur through porous aggregates. Aggregate pores are large cavities that surround polymer aggregates which allow a period of methanol transport so that the high methanol permeability. The composite membrane must have the ability to withstand the movement of methanol into the membrane. This is because the presence of methanol molecules in the membrane structure can interfere with the performance of the electrolyte membrane in the fuel cell operation process, besides this methanol movement can cause the
methanol to run out quickly [20, 21]. Therefore, low methanol crossover is an important factor that an electrolyte membrane must have in order to achieve high performance in DMFC applications.

4. Conclusion
Composite membrane based biopolymer chitosan with silica from rice husk ash was successfully prepared using solution casting method. FTIR analysis showed that chitosan and silica was successfully synthesized. Water uptake for the chitosan-silica membrane increased with increasing silica loading, but the methanol uptake value decreased. Water uptake for composite membrane Ch/Sil 5% had the lowest water uptake value at 64.83% and methanol uptake for composite membrane Ch/Sil 5% had the lowest methanol uptake value of 5.25%. The chitosan-silica with 15 wt% silica loading exhibited the best ion exchange capacity and methanol permeability which were 1.290 meq/gram and 2.42 x 10⁻⁴ cm³/s, respectively. Based on the obtained results, it can be concluded that chitosan membrane consisting silica filler from rice husk ash has a high potential to be a promising low cost and environmental friendly polymer electrolyte membrane for DMFC applications.

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