

Synthesis and Characterization of Chitosan-Ssodium Alginate Composite Membrane for Direct Methanol Fuel Cell (DMFC) Application

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Abstract: Direct methanol fuel cell is one type of direct alcohol fuel cell, where methanol in liquid form enters the anode cell without going through reforming process. Methanol has the advantage of being relatively cheap and has high electrochemical activity. However, direct methanol fuel cells have several disadvantages, namely low efficiency (about 60%), slow methanol oxidation reaction rate, the occurrence of methanol cross over and also the price of the membrane used as an electrolyte membrane in direct methanol fuel cells. The procedure in this research are composite membrane fabrication; characterization and performance composite membrane are membrane functional group analysis; morphology of membrane analysis; density of membrane measurement; methanol permeability measurement; swelling membrane. The result from this research are based on FTIR analysis, The entire membrane has amino and carboxylic acid groups that are bonded to each other and have hydrogen bonds; based on SEM analysis, chitosan: sodium alginate membrane has good pore performance; the density of the membrane increases as the composition of sodium alginate increases. The highest of membrane density is 1.3676 g/mL at 5:2 w/w; there is no methanol crossover so that the membrane can answer the problems of conventional Nafion® membranes; Swelling methanol at 5:1 and 5:2 w/w have the same swelling value, which is 10; Composite membrane from chitosan – sodium alginate can be used as a substitute for the nafion membrane in DMFC.

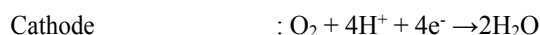
1 INTRODUCTION

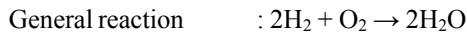
The increase in population and industrial growth contributes to the increasing demand and demand for energy. On the other hand, the availability of energy sourced from fossil fuels such as coal, oil and natural gas used in conventional power plants is decreasing from time to time. This is an important challenge and problem that will be faced by the world. New renewable energy sources will answer energy challenges and problems in order to meet future energy needs. New renewable energy sources that can be developed include wind, geothermal, biomass, solar, tidal, hydropower, waves, hydrogen and fuel cell energy.

Fuel cell is one of the promising power plants because it has high efficiency, clean energy and low environmental impact. The fuel cell system is designed to consume hydrogen and oxygen directly and produce products in the form of water, heat and

electricity. There is without fuel combustion from a furnace or boiler turned to electrical energy, so it cleanest and potential energy.

Fuel cell is an electrochemical cell that converts the chemical energy in hydrogen and oxygen fuels into electrical energy directly through a redox reaction. Fuel cell have two electrodes, anode as negative electrode and cathode as positive electrode. Fuel such as hydrogen is placed at the anode cell and oxygen at the cathode cell. The catalyst in the anode cell releases hydrogen molecules into protons and electrons. Electrons pass through an external circuit to generate electricity, while protons migrate through the electrolyte to the cathode, where protons react with oxygen and electrons, producing heat and water. The overall reaction have been done in the fuel cell in following:





Fuel cells can be applied portable in consumer electronics, battery chargers, miniature toys, kits, and gadgets; transportation application on auxiliary power units, marine propulsion, stationary application in distributed power generation, combined heat and power, combined cooling, heat and power, back up power supply, remote area power supply.

Fuel cells can be classified based on operating conditions, such as pressure, temperature, type of electrode, catalyst, interconnection, and type of electrolyte used. Based on the type of electrolyte, fuel cells can be classified as follows (1) solid oxide fuel cell with ceramic electrolyte; (2) carbonate fuel cell; (3) proton exchange membrane fuel cell with its electrolyte consisting of proton membrane; (4) phosphoric acid fuel cell; (5) alkaline fuel cell with alkaline electrolyte solution such as potassium hydroxide, sodium hydroxide. The following details the differences types of fuel cell:

Table 1: Types of Fuel Cell.

Different	PEMFC	AFC	PAFC	MFC	SOF C
Electrolyte	Hydrated Polymer Ion Exchange Membranes	Mobilized or Immobilized Potassium Hydroxide in asbestos matrix	Immobilized Liquid Phosphoric Acid in SiC	Immobilized Liquid Molten Carbonate in LiAlO ₂	Perovskites (Ceramics)
Electrodes	Carbon	Transition metals	Carbon	Nickel and Nickel Oxide	Perovskite and perovskite / metal cermet
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material

Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or	Nickel, ceramic
				Nickel	ic, or steel
Operating Temperature	40 – 80 °C	65°C – 220 °C	205 °C	650 °C	600-1000 °C
Charge Carrier	H ⁺	OH ⁻	H ⁺	CO ₃ ⁻	O ⁻
External Reformer for hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell designs
External shift conversion of CO to hydrogen	Yes, plus purification to remove trace CO	Yes, plus purification to remove CO and CO ₂	Yes	No	No
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Liquid Cooling Medium	Process Gas + Electrolyte Circulation	Process Gas + Liquid cooling medium or steam generation	Internal Reforming + Process Gas	Internal Reforming + Process Gas

Based on the type of electrolyte dan operation temperature, fuel cell can be classified as follow : at the high temperature fuell cell are molten carbonate fuel cell and solid oxide fuel cell, and at the low temperature are phosphoric acid fuel cell, polymer electrolyte membrane fuel cell, alkaline fuel cell and

direct methanol fuel cell.

Direct methanol fuel cell is one type of direct alcohol fuel cell, where methanol in liquid form enters the anode cell without going through reforming process. Direct methanol fuel cells are widely applied in cell phones, vehicles, laptops, cameras, home appliances. Methanol has the advantage of being relatively cheap and has high electrochemical activity. However, direct methanol fuel cells have several disadvantages, namely low efficiency (about 60%), slow methanol oxidation reaction rate, the occurrence of methanol cross over and also the price of the membrane used as an electrolyte membrane in direct methanol fuel cells.

Nafion is a membrane that has a high proton conductivity value, strong chemical stability and has high mechanical strength. However, the Nafion membrane can cause methanol cross over in direct methanol fuel cells and cause environmental pollution.

Nur Rokhati fabricated a chitosan – alginate composite membrane for use in DMFC. The fabricated membrane was then characterized. The film characterization carried out included tests of: permeability, degree of swelling, mechanics, morphology (by SEM), and surface chemical structure (by FTIR). The results showed that the alginate film had a higher permeability and swelling degree than the chitosan film. Both chitosan and alginate give the phenomenon that the greater the concentration of the solution, the smaller the permeability value and the degree of swelling, with the degree of swelling to water being the largest followed by technical methanol ($\pm 95\%$) and the smallest being methanol PA ($> 99, 9\%$). The mechanical strength of chitosan film is greater than that of alginate film. The alginate/chitosan composite film made by layer by layer method provides better characteristics than the composite film made by mixing alginate solution and chitosan solution.

Romadhoni Anto conducted research on chitosan and sodium alginate composites. Composite membranes were produced with various concentrations of chitosan-sodium alginate. The composites were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectrophotometer (FTIR). The FTIR spectrum shows the NH₃C group at 1637.29 cm⁻¹ and the COO group is symmetrical at 1253.68 cm⁻¹ which shows the interaction between chitosan and sodium alginate. SEM micrographs showed that the composite membrane was non- porous. The 3:5 chitosan-sodium alginate composite membrane has the highest proton conductivity is 9.594×10^{-7} S/cm.

Based on the results of this study, the chitosan-sodium alginate composite membrane can be applied properly in the Direct Methanol Fuel Cell system.

Riki Siswanto conducted a research by making a chitosan-alginate composite membrane. The results showed that there was an effect of adding more chitosan composition to the membrane characteristics. In physical properties, the more addition of chitosan composition causes the formation of smaller pore sizes. While the mechanical properties resulted in increased tensile strength and elongation values. The results of the filtration test resulted in a decrease in the flux value to urea and an increase in membrane rejection. Chitosan alginate 4:1 (v/v) membrane has optimal results and is better to be used as a membrane candidate in hemodialysis applications. The pore size formed is in the range of 29.14 – 105.1 nm. Tensile value of chitosan:alginate membrane 4:1 (v/v) is 31.23 N/mm² and % elongation is 13.27%. Then the value of the flux to urea is 0.03 ml.cm⁻².menit⁻¹ and a membrane rejection is 60.87%.

(Eldin, 2017) conducted research on chitosan by chemically cross linked it by activation with an alginate biopolymer which has a low molecular weight with various molar ratios. The results show that the covalently cross linked CS/Alg-GA membrane has low permeability with range methanol 2.179×10^{-9} until 2.5×10^{-10} cm²/s compared to nafion membrane (1.14×10 cm²/s).

So, in this paper, the focus is on the use of low cost, low methanol cross over and environmental friendly membranes to overcome the weaknesses of the Nafion membrane, but in terms of characteristics and performance it has the same advantages and even exceeds the Nafion membrane. The types of membrane used in this study were chitosan and alginate.

2 EXPERIMENTAL

2.1 Materials

Chitosan, sodium alginate, acetic acid glacial (CH₃COOH), tchloric acid, aquadest, methanol, black platinum powder, platinum-ruthenium powder, carbon paper, acrylic, syringe, oxygen cylinder, printer hose, acrylic 3 and 5 mm.

2.2 Method

2.2.1 Composite Membrane Fabrication

In this study, the variation of chitosan: sodium alginate of 5:1, 5:2 (w/w). The process of making chitosan – sodium alginate composite membrane includes the following steps:

1. Mixing chitosan: sodium alginate according to variation (5:1, 5:2 (w/w)) with 1% glacial acetic acid.
2. Stirring using a hot plate magnetic stirrer for 30 minutes so that the solution becomes homogeneous.
3. Each homogeneous solution was allowed to stand for 1 night to wait for the entire reaction to become even.
4. The solution that has been allowed to stand is then each added with 32% hydrochloric acid (HCl) with a volume of 1 mL HCl for every 100 mL of solution volume, then stirred until homogeneous. After that, the two solutions were mixed and stirred for 1 hour using a hot plate magnetic stirrer and then stirred until homogeneous. After that, the two solutions were mixed and stirred for 1 hour using a hot plate magnetic stirrer and then filtered using filter paper, so that the residue of the mixture could be eliminated.
5. The homogeneous solution mixture was left for 1 night to remove air bubbles contained during the mixing process. The solution mixture is placed in the refrigerator so as not to spoil.
6. The mixture that has been free of bubbles is then printed on the surface of the glass whose edges have been given foam double-sided tape as a 2 mm thick mold barrier. Ensure that the solution is evenly distributed, so that the resulting membrane has an even thickness. The membrane printing process is carried out in a room with good air circulation without conditioning the room temperature and left to dry evenly. If the environmental conditions support the drying process, then the drying can take place only in 1 night. After the mold is dry, the membrane is slowly removed from the mold.

2.2.2 Characterization and Performance Composite Membrane

- a. Membrane Functional Group Analysis.** Membrane functional groups analysis using Fourier transform infrared (FTIR)

spectroscopy.

- b. Morphology of Membrane Analysis.** Surface and cross-sectional morphology transverse films were observed using a scanning electron microscopy (SEM) with 10000X magnification.

c. Density of Membrane

1. The steps for testing the density of composite membranes can be broken down into the following points:
2. Cut the composite membrane with a uniform size, which is 2 x 7 cm.
3. Measure the empty weight of the pycnometer, which is then recorded as W_0 .
4. Measure the weight of the pycnometer with a piece of composite membrane sample, which is then recorded as W_1 .
5. Measure the weight of the pycnometer filled with water, and then record it as W_3 .
6. Insert the composite membrane sample piece into the pycnometer which has been filled with water. In this measurement, you must first make sure that there are no air bubbles in the pycnometer. Then weigh the pycnometer filled with water and the membrane which has been confirmed that there are no air bubbles in it and the results are recorded as W_2 .
7. For density data from air (ρ_a), take the reference density, i.e 1.2 kg/m³, atau 0.0012 g/mL.
8. Collecting water density data (ρ_1) by utilizing data on W_3 and W_0 , with the following equation:

$$\rho_1 = \frac{(W_3 - W_0)}{10 \text{ mL}}$$

d. Methanol Permeability

In this analysis, a vessel with a barrier is required, where a chitosan-sodium alginate composite membrane acts as a barrier. The methodology is described as follows:

1. Prepare test vessels and samples of fabricated chitosan – alginate composite membranes that have been cut according to the size of the bulkhead of the vessel.
2. Clamp the chitosan-alginate composite membrane between the two sides of the vessel and ensure that it is tight so that no methanol seeps out of the vessel through the gaps between the vessel and the membrane that may exist.
3. One side of the vessel is filled with 50 mL of methanol, while the other side is left

empty. After that, the vessel was positioned upright, with the composite membrane as the base from the side of the methanol vessel.

4. This test is carried out for one hour.
5. Checking whether there is methanol seeping

e. Swelling Membrane

The swelling test requires an oven to dry the fabricated composite membrane sample, a balance to weigh the sample weight, a vessel as a container to soak the sample in methanol, and methanol. The testing methodology can be described as follows:

1. Each membrane is cut to the size of 5 x 2 cm.
2. Put the sample into the oven and dried at a temperature of 125°C for 24 hours so that the water content evaporates.
3. After the membrane is dry, weigh the membrane using a balance to determine its dry weight (D).
4. Soak the sample in methanol for 48 hours.
5. After the immersion process is complete, then the surface of the sample is dried using a highly absorbent cloth or tissue so that there is no methanol remaining on the surface of the membrane. Setelah permukaannya kering, membran ditimbang untuk mengetahui bobot basahnya (*W*).
6. The wet and dry weight data are then used to find the percentage of methanol absorption through the equation:

$$Swelling = \frac{W - D}{D} \times 100\%$$

3 RESULT AND DISCUSSION

Membrane Functional Group Analysis

FTIR analysis was carried out to determine the functional groups contained in the fabricated chitosan – sodium alginate composite membrane. The FTIR results are in the form of a spectrum that states the functional groups contained in the sample which are expressed by wave numbers. The classification of specific functional groups based on the wave range can be seen in table 2 below:

Table 2: Specific groups and wavelength ranges of FTIR.

Compound	Functional Group	Absorption Area (cm ⁻¹)
Alkana	C-H	2850-2960, 1350-1470
Alkena	C-H	3020-3080, 675-870
	C=C	1640-1680
Alkuna	C-H	3300
Aromatik	C-H	3000-3100, 675-870
	C=C	1500-1600
Alcohol, eter, carboxylic acid, eter	C-O	1080-1300
Aldehida, keton, carboxylic acid, ester	C=O	1690-1760
Alcohol, phenol (monomer)	O-H	3610-3640
Alcohol, phenol (bond of H)	O-H	2000-3600 (length)
Carboxylic acid	O-H	3000-3600 (length)
Amine	N-H	3310-3500
	C-N	1180-1360
Nitro	NO ₂	1515-1560, 1345-1386

The FTIR spectrum on the chitosan – sodium alginate composite membrane with a variation of the ratio 5/1 (w/w), based on Fig.1 which refers to table 2 shows the C – N functional group (amino acids) at wave numbers 1739.39 cm⁻¹ (x₁) and group C – O – O (carboxylic acid) on wave number 1216.77 cm⁻¹ (x₂). The two spectra indicate that there is an electrostatic interaction of the carboxylate group of sodium alginate with the protonated amino group of chitosan which indicates that the composite membrane produced is homogeneously mixed. At wavenumber 3442.52 cm⁻¹, there is an OH group (x₃). The presence of the OH group is expected to increase the strength of the intermolecular interactions of the fabricated composite membrane, for example hydrogen bonds between chitosan and sodium alginate.

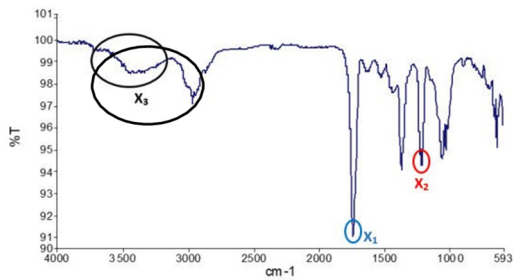


Figure 1: FTIR spectrum of chitosan - sodium alginate composite membrane 5/1 (b/b).

The FTIR spectrum on the chitosan – sodium alga composite membrane with a variation of the ratio 5/2 (w/w), based on Fig.2 which refers to table 2 shows the C – N functional group (amino acids) at wave numbers 1739.25 cm^{-1} (x_1) and group C – O – O (carboxylic acid) on wavenumber 1216.77 cm^{-1} (x_2). The two spectra indicate that there is an electrostatic interaction of the carboxylate group of sodium alginate with the protonated amino group of chitosan which indicates that the composite membrane produced is homogeneously mixed. At wavenumber 3396.74 cm^{-1} , there is an OH group (x_2). The presence of this OH group produces a more drastic peak than the 5/1 variation, so it is expected to increase the strength of intermolecular interactions of the fabricated composite membrane, for example hydrogen bonds between chitosan and sodium alginate.

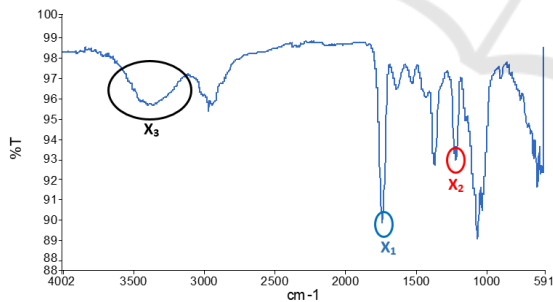


Figure 2: FTIR spectrum of chitosan - sodium alginate composite membrane 5/2 (b/b).

Morphology of Membrane

SEM characterization was carried out with a magnification of 2000 times, where the results for each variation showed a tendency for the chitosan – sodium alginate composite membrane to have no pores (non-porous).

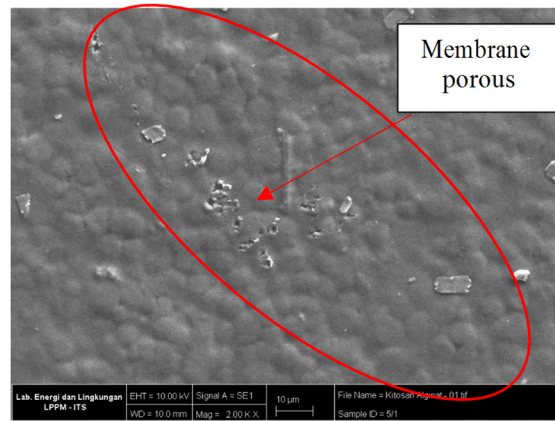


Figure 3: SEM morphology on composite membrane samples with a ratio of 5/1 (w/w) with a magnification of 2000x.

In the variation of chitosan – sodium alginate 5/1 (w/w), it was found that there were quite a number of pores formed on the surface of the chitosan – sodium alginate composite membrane. However, even though there are pores formed, the number is not too large, so the membranes produced from the variation in the ratio of 5/1 tend to have no pores. This indicates that the solution of chitosan and sodium alginate has been homogeneous. From the morphological results, the chitosan – sodium alginate composite membrane with a variation of 5/1 (w/w) has good potential to be applied in DMFC.

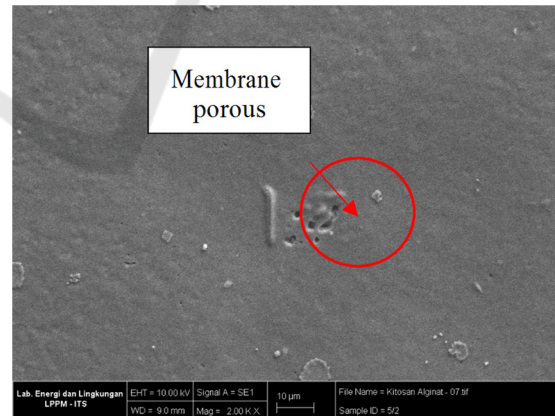


Figure 4: SEM morphology on composite membrane samples with a ratio of 5/2 (w/w) with a magnification of 2000x.

The results of SEM morphology on the chitosan – sodium alginate composite membrane variation 5/2 (w/w) showed that the number of pores formed was decreasing. The decrease in the pores formed on the composite membrane is due to the increased

composition of sodium alginate, thus closing the pores that may be formed from chitosan. The decrease in the pores formed also indicates that the chitosan and sodium alginate solutions are mixed until homogeneous.

From the results of the SEM analysis of the chitosan – sodium alginate 5/2 (w/w) composite membrane, it shows that the membrane has the potential to be used as a replacement composite membrane in DMFC applications, because the tendency of the presence of pores on the membrane is only slightly.

Figs 1 and 2 show that the entire composite membrane fabricated has the potential to be applied to the DMFC and become an alternative choice for the Nafion® membrane. The absence of pores formed allows the chitosan – sodium alginate composite membrane to be more resistant to methanol, so that methanol crossover can be minimized.

For comparison, the SEM morphology results from Nafion® (Dang, 2014) are listed below.

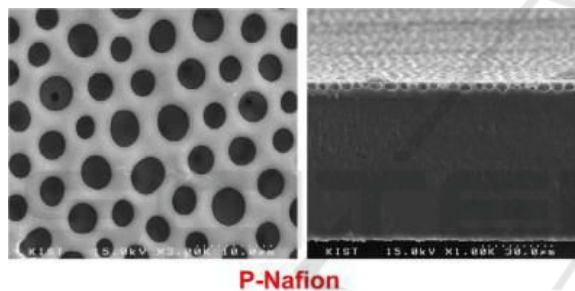


Figure 5: Nafion® membrane morphology with 1000x magnification.

From the morphology, it can be seen that Nafion® 211 has pores all over its surface. These pores cause Nafion® 211 to easily undergo methanol crossover, which has an impact on decreasing DMFC performance because Nafion® 211 has pores that can be occupied by methanol, and can even be passed as a transport medium for methanol across from the anode to the cathode.

Density of Membrane

From the results of density testing using a pycnometer, the results are shown in table 3 below:

Table 3: Data on the weight of the pycnometer (W₀), the empty pycnometer and the membrane sample (W₁), the weight of the sample in a pycnometer filled with water (W₂), the weight of the pycnometer with water (W₃) and the density of water (ρ₁).

Chitosan: Sodium Alginate (w/w)	W ₀ (g)	W ₁ (g)	W ₂ (g)	W ₃ (g)	ρ ₁ (g/m L)
5:1	10,99	11,07	21,22	21,21	1,02 2
5:2	10,95	11,07	21,24	21,21	1,02 6

Where:

W₀ = Weight of the pycnometer (grams)

W₁ = Weight of pycnometer and sample (grams)

W₂ = Weight of pycnometer and sample filled with water (grams)

W₃ = Weight of the pycnometer filled with water (grams)

ρ₁ = Density of water (gram/mL)

The membrane density in each variation was evaluated through the following equation:

$$\rho = \frac{W_1 - W_0}{(W_3 - W_0) - (W_2 - W_1)} \times [\rho_1 - \rho_a] + \rho_a$$

The value of water density (ρ₁) is obtained through the following equation:

$$\rho_1 = \frac{(W_3 - W_0)}{10 \text{ mL}}$$

And the results of the evaluation of these equations can be seen in table 4. below:

Table 4: The results of the calculation of the sample density for each variation.

Chitosan: Sodium Alginate (w/w)	ρ (g/mL)
5:1	1,167829
5:2	1,3676

The density value obtained can be seen through the graph in Fig.6 below:

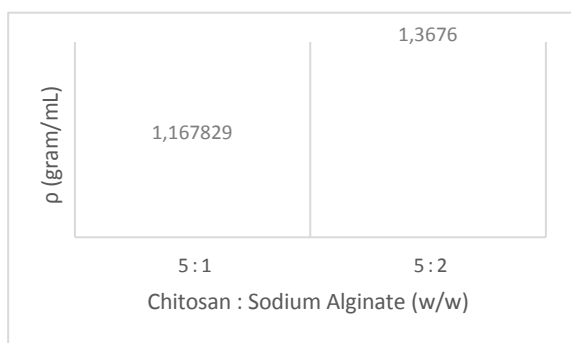


Figure 6: Comparison of the density of the chitosan – sodium alginate composite membrane fabricated for each variation.

The addition of sodium alginate will improve the cross-linked structure of the chitosan in the gel so that it becomes stiffer and the gel will be stronger. Because sodium alginate has the property of absorbing water, the addition of sodium alginate will decrease the breaking point of the gel, which means that the strength of the gel will increase. The increasing gel strength of this membrane has an impact on increasing the density of the chitosan-alginate composite membrane.

Because the strength of the membrane increases, then when viewed from the calculation results, the membrane density from the smallest to the largest is a variation of 5:1 with the result 1.167829 g/mL; 5:2 with the result 1.3676 g/mL.

Permeability of Membrane

From the membrane permeability test, the following results were obtained:

Table 5: Membrane permeability analysis.

Chitosan: Sodium Alginate (w/w)	Membrane permeability
5:1	No
5:2	No

From the test results, there is no methanol crossover, namely the crossing of methanol to the side of an empty vessel through or through the membrane. The sides of the membrane in empty vessels in all variations remained dry when wiped with a tissue, after each test was carried out for 1 hour. This is an indication that the chitosan – alginate composite membrane can be used as an alternative proton transfer membrane to replace Nafion® in DMFC, because it is able to hold methanol, so it can solve the problem of methanol cross over.

Methanol crossover is the event of displacement of methanol particles from the anode (high methanol concentration) to the cathode (low to zero methanol concentration) and is caused because the proton transfer membrane is unable to hold methanol. The methanol crossover event will reduce the performance of the DMFC because the resulting potential difference will decrease. The underlying reason for the methanol crossover is that there are differences in the concentration of methanol on the anode and cathode sides, where on the anode side the concentration of methanol is high, and there is no concentration of methanol at the anode. high concentration towards the other side of lower concentration.

Composite Membrane Swelling Analysis

The swelling test requires uniform sample pieces for each variation, container, digital balance, oven, and methanol. The dry weight of the membrane was obtained after the sample was oven-baked for 24 hours at a temperature of 125°C. Then, the wet weight was obtained after the membrane was soaked in methanol for 48 hours. Swelling of methanol is obtained through the following equation:

$$Swelling = \frac{W - D}{D} \times 100\%$$

The results obtained can be seen in table 6 below:

Table 6: dDy sample data (D) and wet sample (W).

Chitosan: Sodium Alginate (w/w)	D (g)	W (g)	swelling	% swelling
5:1	0,1	0,11	0,1	10
5:2	0,1	0,11	0,1	10

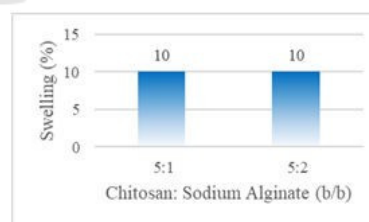


Figure 7: Swelling of fabricated chitosan-sodium alginate composite membrane.

From the test results, it was found that the addition of alginate concentration could increase the membrane's ability to adsorb methanol. This is due to the nature of sodium alginate which only has anionic groups (hydroxyl and carboxyl) which causes the molecular bonds between polymer chains to be less dense, so that there is a larger space for liquid to

occupy which makes the membrane absorption large. While the nature of chitosan, besides having a cationic group that can form a strong and tight film, it also has an acetyl group which is hydrophobic (does not absorb water). So that the absorption of chitosan is smaller than alginate.

Thus, in this paper, data were obtained that the more concentration of sodium alginate in the composition of a membrane, the higher the absorption of methanol, which is because sodium alginate has a higher absorption capacity than chitosan.

4 CONCLUSIONS

1. Based on FTIR analysis, The entire membrane has amino and carboxylic acid groups that are bonded to each other and have hydrogen bonds.
2. Based on SEM analysis, chitosan: sodium alginate membrane has good pore performance.
3. The density of the membrane increases as the composition of sodium alginate increases. The highest of membrane density is 1.3676 g/mL at 5:2 w/w.
4. There is no methanol crossover so that the membrane can answer the problems of conventional Nafion® membranes.
5. Swelling methanol at 5:1 and 5:2 w/w have the same swelling value, which is 10.
6. Composite biomembrane from chitosan – sodium alginate can be used as a substitute for the nafion membrane in DMFC.

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