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Synthesis and Characterization of Electrolyte Membrane Based Biopolymer Chitosan and Fly Ash Combinations for Fuel Cell Application

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***Abstract*— A composite membrane biopolymer chitosan filled fly ash was fabricated as alternative membrane electrolyte for fuel cell application. The membrane was synthesized from chitosan from deacetylation of shrimp shells and then cross-linked with sulfonic acid network by introducing fly ash. The aim was to investigate fly ash adding to the performance of membrane. The membranes were studied by scanning electron microscopy (SEM), water uptake, methanol uptake, permeability, and proton conductivity assessment. SEM images analysis showed that the fly ash was successfully incorporated in chitosan polymer matrix. Water and methanol uptake for the composite membranes decreased with increasing fly ash loadings. The resulting membranes exhibited proton conductivities up to 6,863 mS/cm. The obtained results indicated that the optimum composite membrane could be considered as a promising candidate to developed membrane electrolite for fuel cell applications.**

***Keywords*— Chitosan, Fly Ash, Membrane, Fuel cell.**

I. INTRODUCTION

Fuel cell is electrochemical cell that converts chemical energy into electrical energy based on redox reactions. In the application of fuel cell, a membrane acts as semipermeable layer between cathode and anode which only let hydrogen pass through and generate electricity. The specialized membrane in this application is called electrolyte membrane and well known as proton exchange membrane (PEM). The popular membrane which is widely used is perfluorosulfonic acid membrane (Nafion). Nafion works well since it has good chemical stability and excellent conductivity[1]. Nafion showed the highest conductivity 4.7 x10-2 S/cm under 100^0C but high in methanol permeability at 27.6 x10-8 cm2/s. Higher the permeability, the faster hydrogen pass through membrane and reduce the efficiency. Also, Nafion is consiredably expensive. Some research found the alternative way to overcome these lackings and suggest using biopolymer based membrane, one of those is chitosan[2]

Chitosan is biopolymer which composed of N-acetyl glucosamine residues with 1,4 β linkage[3]. It is derived from deacetylation of chitin, which is produced from shells of crustaceans. Shrimp shells contain much chitin and widely used in Indonesia as filter membrane and some medical artificial human parts. As biopolymer, chitosan is biocompatible, non-toxic, and soluble at aqueous media[4]. Chitosan is compatible for electrolyte membrane due to its structure and proton conductivity. To maintain its stability against acid solution and physically strong, a filler is used. Anorganic filler such as fly ash is needed since it has good conductivity and lower the methanol permeability[5]. In the present paper, we attempt to synthesize chitosan based electrolyte membranes which are modified with addition of fly ash composite. The properties such as proton conductivity, methanol permeability, and morphological surface are investigated systematically.

II. EXPERIMENTAL METHODS

A. Chitosan Preparation

First, shrimp shells is grinded into powder and then stir it at 60-70ºC in NaOH 3,5% wt solution by the composition 1:10 (gr powder/mL NaOH) for about 2 hours. The shells then filtered from the solution, washed it by demineralized water (aquadest), and dried it in oven at 100ºC for about 4 hours. The shells then demineralized in HCl solution at 60-70ºC by the composition 1:15 (gr powder/mL HCl) for about 2 hours. The shells turned into chitin this time and underwent the same procedure to get dried chitin. Chitin then deacetylized in NaOH 50% wt solution by the composition 1:10 (gr powder/mL NaOH) for about 1 hour at 90-100ºC. Chitin was degraded into chitosan and lastly, same procedure is applied to get dried chitosan.

B. Membrane Preparation

The electrolyte membrane were prepared using sol-gel process. Initially, the experiments were performed by preparing various concentrations (5%, 10%, and 15% wt fly ash) chitosan membrane. Chitosan and fly ash were dissolved in 75 grams of acetic acid 2% v/v at 80ºC until the solution formed gel. The solution was placed to cool in petri dish for about 2 days. After the thin film were formed, the

membrane then poured with NaOH solution to faster the peeling. The membrane then washed to remove remaining solvent and re-immersed with H_2SO_4 1 M for about 24 hours. The resultant membrane then washed and dried at room temperature.

C. Chitin and Chitosan Characterization

Membrane characterization was attempted by the use of instrumental analysis. *Fourier Transport Infra Red (FTIR) Spectroscopy* was used to characterize functional group of chitin and chitosan. The sample was directly hit by electromagnetic radiation to get the absorbance and then correlate between the absorbance and the functional group.

The main parameter of chitin deacetylation was the disapperance of acetyl group. The amount of liberated acetyl groups would determine *degree of deacetylation* (DD) which indicated the purity of chitosan. The higher the DD, the purer chitosan would be which lead the better membrane synhesize. A good DD of chitosan for synthesizing membranes were in range 70%-100%. DD was determined based on *base line* method. This method was based on the infrared absorbtion value of wavelength of 1655 cm^{-1} and 3450 cm^{-1}. The equation were shown below:

$$DD = [1-(A_{1655} / A_{3450}) * (1/1.33)] * 100\% \quad (1)$$

Where : A_{1655} = absorbance value of 1655 cm^{-1} (amide group absorbance)
A_{3450} = absorbance value of 3450 cm^{-1} (hydroxil group absorbance)
1.33 = constant of perfect deacetylation (100%)

D. Water and Methanol Uptake Measurements

Water uptake and methanol uptake were determined by measuring the wet membrane and dried membrane. First, the membranes were dried at 60ºC for 20 minutes and then weighed. The membranes were immersed in water or methanol for 24 hours to get maximum hydration. The surface of membrane then wiped with tissue and the weighed again. The formula for water and methanol uptake are shown below:

$$Uptake (\%) = ((Wwet – Wdry) / Wdry) \times 100\% \quad (2)$$

Where Wwet and Wdry are the mass of membrane before and after immersion (gram).

E. Methanol Permeability Measurements

Methanol permeability is one of parameter that evaluates membrane performance. To determine mthanol permeability, two diffusion cell compartments is needed. Membranes were cut into 2 x 2 cm in rectangular size and then placed it in between the compartments. Compartment A filled with 1M methanol solution and compartment B filled with water. Methanol solution was sampled every 30 minutes for about 2.5 hours. Methanol concentration can be determined by using piknometer and corrected it with calibration curve. The sampled concentrations were regressed to get its slope. Methanol permeability formula as follows :

$$P = [\Delta C_B/\Delta t] * [L*V_B/(A*C_A)] \quad (3)$$

Where : P = methanol permeability (cm^2/s)
$\Delta C_B/\Delta t$ = slope determined by function of time (mol/L.s)
L = membrane thickness (cm)
V_B = volume of water in compartment (cm^3)
A = membrane surface area (cm^2)
C_A = methanol concentration in compartment (mol/L)

F. Ion Exchange Capacity Measurements

The miliohmmeter was used for calculating the bulk resistance of the membrane. The bulk resistance values would simulated in *z-view* application to get the approximate R values. This R value was used to determine conductivity by the following equation:

$$Conductivity (\delta) = [d/(R*A)] \quad (4)$$

Where R is resitance (ohm), d and A are thickness and area of membrane tested, respectively.

G. Membrane Morphology Examinations

Scanning Electron Microscopy (SEM) was used to observe the membrane's morphology by multiple magnifications. The magnification is ranging from 1000x to 10000x.

III. RESULTS AND DISCUSSION

A. Membrane Structure and Functional Group Study

FTIR assessments were to determine the group functionality of chitin and chitosan. The results were shown in the diagram below:

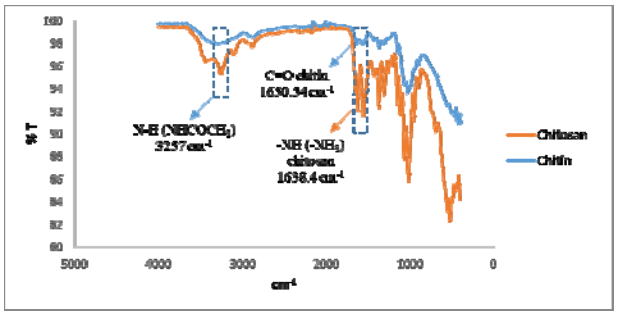


Fig 1. Chitin and Chitosan Infrared Spectroscopy Wavelengths

Numerous wavelengths were caught in FTIR spectrum. Chitin wavelengths were in about 3400-3500 cm^{-1} which indicated the OH group existed. Another absorption were in 3257.14 cm^{-1} which came from –NH groups of amide and supported with 1620.69 cm^{-1} wavelength. CH_3 groups were found in wavelength 2878.36 cm^{-1}. CN groups were on the peak at wavelength of 1308.35 cm^{-1}. C=O groups were in a range of 1700-1650 cm^{-1}. C-H groups were shown on the peak of 1376.56 cm^{-1} and 1416.48 cm^{-1} wavelength. C-O groups were seen on the wavelength of 1070.38 cm^{-1}. Another characteristic from chitin was C-O-C groups on the wavelength of 1203.72 cm^{-1}.

There were enough proof that chitosan were formed by chitin deacetilation. Chitosan wavelength were shown at 3282.5 cm^{-1}. This absorption shown there were bending of

OH and NH chains. This could be happened by intersection between OH and NH from amine group of chitosan. Moreover, the disapperance of C=O from amide group were shown no wavelength. A comparative study were shown in the table below:

Table 1. Comparative Analysis of Structure and Funcional Groups For Chitin and Chitosan

Num.	Vibration	Wavelength (cm^{-1})	
		Kitin	Kitosan
1	O-H	3480	3282.85
2	N-H (-$NHCOCH_3$)	3257.14; 1620.69	-
3	-CH3	2878.36	2850
4	-C-N	1308.35	1340
5	-C-H	1376.56; 1416.48	1375.39
6	C=O	1650	-
7	NH (-NH3)	-	1638.54
8	-C-O	1070,38	1149.17; 1050

From these results, chitosan was succesfully formed by deacetylation of chitin and the degree of deacetylation chitosan was confirmed of 75.34%. This result indicated that chitin was partially deacetylated into chitosan and it was fair enough to make a good membrane.

B. Water Uptake and Methanol Uptake Study

As can be seen in figure 2, the % uptake for both water and methanol increase by the addition of fly ash content. This phenomenon is primarily caused by the role of fly ash that may create selective voids in the interfacial area. There were large uptake for water than methanol. This could happen due to hydrophilic properties that fly ash have could take up much water solution instead of methanol[6]. Moreover, there were many possibilities for the membrane able to absorb solutions such as porosity, cristalinity, and surface area of membrane which were explained in another study. The presence of water is needed to help the proton crossing to cathode. The higher the water content would increase the chance of proton crossing and also increase proton conductivity. Methanol uptake was proportional to water uptake which can absorb as much as hydrogen[7]. The result were consecutively shown 63.52%, 78.46%, 80.39% for water uptake and 41.25%, 45.87%, 56.06% for methanol uptake.

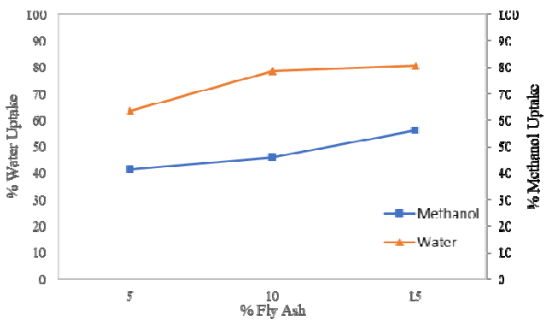


Fig.2 . Uptake for Various Fly Ash Addition at 25ºC

C. Methanol Permeability Study

Methanol permeability tests showed a comparative result which shown in the table below:

Table 2. Methanol Permeability Test Results of Various Membranes

Membrane	**Methanol Permeability ($x10^{-6}$ cm^2/s)**
Chitosan / Fly Ash 5%	8,93
Chitosan / Fly Ash 10%	6,30
Chitosan / Fly Ash 15%	2,85

From these results, the membranes still have high methanol permeability due to their morphological structure which were not good enough. The blending between membrane and filler was not uniformly so there was still methanol passed through. From table 2, the permeability decrease as more fly ash were added. It has been suggested that, this phenomenon is might due to the existence of filler which increases the tightness of composite membrane so it can suppress the methanol movement [8]. The addition of fly ash would make the membrane more difficult for solution to breakthrough as the grains made formation and covered the pore. Also, the lacks interaction between ionic clusters and methanol could affect the permeability due to larger interfacial free volume[9]. The best result shown in the table is membrane with 15% fly ash addition.

D. Ion Exchange Capacity Study

Ion exchange capacity test was to determine membrane conductivity. Conductivity is an important value for membrane to transfer proton in fuel cell application. Conductivity data were shown in table 3.

Table 3. Membrane Conducivity Test Results of Various Membranes

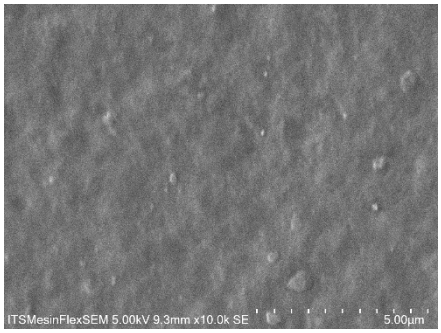
Membrane	**Membrane Conductivity ($x10^{-3}$ S/cm)**
Chitosan / Fly Ash 5%	6.693
Chitosan / Fly Ash 10%	6.863
Chitosan / Fly Ash 15%	0,485

Addition of fly ash would increase small amount of conductivity. Higher concetration of fly ash would increase the conductivity, and also it depends on the distribution of fly ash in membrane matrix. The distribution was initiated by crosslinking membrane matrix with H_2SO_4 so fly ash particles easily integrated in matrix. But take notice that adding too much fly ash would decrease the conductivity. The grains were aggregated in the matrix and blocked the solution[10]. The best conductivity shown was membrane

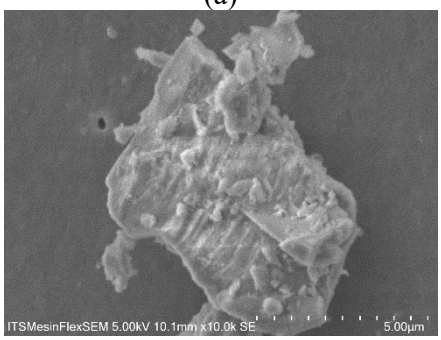
with 10% fly ash because of its distribution and methanol permeability.

E. Morphological Surface Study

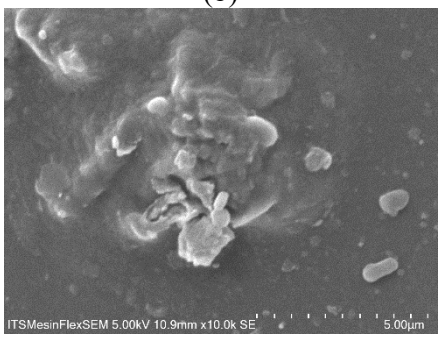
Scanning Electron Microscopy (SEM) was used to examine the morphological surface. The results were shown in figure 3.



(a)



(b)



(c)

Fig 3. Morphological Surface of Membrane with 10.000x Magnification. (a) 5% Fly Ash Membrane, (b) 10% Fly Ash Membrane, (c) 15% Fly Ash Membrane.

From figure 3a, 5% fly ash membrane showed that fly ash grains were distributed uniformly and the pore sizes were the same. In figure 2b and 2c, addition of fly ash 10% and 15% affected the morphological structure of membrane. It were shown the bulk formation of grains in particular places of matrix and there were bigger pores among them. Addition of fly ash would generated bigger *pore density* which the amount of pores in the membrane's surface and reduce the pore size but increasing the chance the grains would aggregate rather than mixing uniformly. Higher pore density means the membrane could take up fuel as much as possible which explained the methanol permeability[10]..

IV. CONCLUSIONS

Chitosan / Fly ash membrane for fuel cell application was prepared with addition of fly ash. Membrane characterization including water uptake, methanol uptake, methanol permeability, membrane conductivity, and morphological surface have also been performed. It has been shown that the resultant membranes were good in water uptake which are in range of 60%-80% and methanol uptake in range of 40%-60%. The methanol permeability result showed that the maximum value of 2.85 x 10^{-6} cm^2/s is reached with 15% fly ash membrane. The membrane conductivity reached maximum conductivity value of 6.863 x 10^{-3} S/cm with 10% fly ash membrane. Based on the results, it can be concluded that Chitosan/Fly ash composite membrane has a high potential to be electrolyte membrane for fuel cell application.

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