Effect of Calcium Carbonate as Filler at the Chitosan/Calcium Carbonate Composite Membrane

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***Abstract* – Membrane is the most important part of Direct Methanol Fuel Cell (DMFC) because of its function as a proton transfer. The purpose of this research was studying the effect of calcium carbonate filler to the performance of chitosan (CS)/Calcium Carbonate (CC) composite membrane using 0.02; 0.04; 0.06; 0.08; and 0.10 g of CC. In this study, CS/CC membranes showed high performance for DMFC application. The best concentration of CS/CC was obtained with 0.06 g of CC based on proton conductivity, methanol permeability, and TGA measurements.**

***Index Terms* – Chitosan, calcium carbonate, DMFC, thermal stability.**

INTRODUCTION

Main sources of energy are from coal and petroleum, which were a natural source that cannot be re-newable because it comes from fossils. Using it continuously without product efficiency, new research discovery, or change to other energy sources can lead to scarcity of energy, causing great influence on humanity, and also produce harmful pollutants, like CO_2 [1].

Many researches have focused on using fuel cells due to its product reactions, water, which is eco-friendly and capable to convert chemical energy to electrical energy with good efficiency. Five types of fuel cells are distinguished by the type of electrolyte, PEMFC, AFC, SOFC, PAFC, and MCFC. Among this five, PEMFC become one of the most widely recommended as an alternative energy source due to easy operation, low operating temperature, and high density [2]. The fuel that commonly used in PEMFC is methanol, and then called as DMFC (Direct Methanol Fuel Cell).

Component of DMFC is anode (oxidation reaction), cathode (reduction reaction), and membrane. Membrane was not only tribute to separate cathode and anode, but also to transfer protons [3]. Good membrane has to have high proton conductivity and thermal stability, and low methanol permeability [4]. Commercial membranes have been widely studied for DMFC is Nafion®. Nafion® is perfluorosulfonat acid-based membrane that has high chemical stability and proton conductivity. But it has high methanol permeability and expensive due to complicated production process. High methanol permeability not only reduces fuel efficiency and performance, but also reduces the performance of cathode [4-5].

Chitosan (CS) is a natural biopolymer with a unique character as a biocompatible, non-toxic, good chemical and thermal stability, and low methanol permeability. Chitosan can be obtained from chitin, a polysaccharide that contains N-acetyl-D-glucosamine [4]. Proton conductivity of CS membrane lowers than Nafion®. Because of that, CS needs to be modified to improve membrane performance [2]. The existence of inorganic materials plays important role in rejecting methanol. Use Calcium Carbonate (CC) as filler has made a significant contribution. The effect of CC on a CS membrane could improve thermal properties based on the TGA results [6].

In this study, CS will be used as the matrix polymer, CC as filler in various concentrations (0.02; 0.04; 0.06; 0.08; and 0.10 g), and sulfuric acid as a crosslink agent. Hopefully, the interaction between hydrophilic CS with hydrophobic CC can improve properties of the membrane for DMFC application. Properties and performance of CS and CS/CC membranes will be characterized by Thermogravimety Analysis (TGA), analysis of proton conductivity and methanol permeability.

EXPERIMENTAL

A. *Synthesis of CS/Calcium carbonate membranes*

2.0 g of CS powder and CC in various concentration (0.02; 0.04; 0.06; 0.08 and 0.10 g) dissolved in 80 ml and 20 ml of acetic acid solution 2% (at 65°C). CC solution dissolved by ultrasonic treatment for 30 min. Subsequently, two portions of solution were mixed, and stirred at 65°C for 30 min, then treated by sonication for 30 min. The resulting viscous solution was cast onto a flat dry glass plate and dried at room temperature for 72 h. The resulting membrane subsequently neutralized using 1N of NaOH solution, washed by demineralized water, and dried at room temperature. Furthermore, the membrane was soaked by 2M of sulfuric acid solution (cross-link process) for 24 h, soaked with demineralized water for 24 h, and finally dried at room temperature. The thickness of all membranes was 1.5×10^{-2} cm. The membranes were denoted as CS, CS/CC1, CS/CC2, CS/CC3, CS/CC4 and CS/CC5.

B. *Characterizations*

All membranes were characterized with Mettler Toledo Thermal Gravimetry Analysis (TGA) and analyzed for its proton conductivity and methanol permeability.

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RESULT AND DISCUSSION

A. Thermal property

Good membrane can be analyzed by its thermal stability. Higher thermal stability is required to guarantee a long lifetime of PEMs in DMFCs. According to TGA results in Fig. 1, increasing CC concentration significantly could increase the thermal stability of the CS/CC.

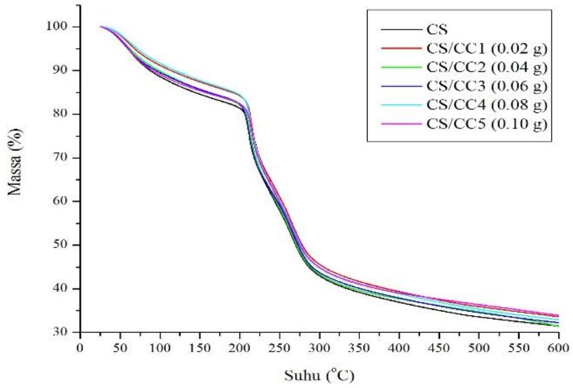

Figure 1. TGA curves of CS and CS/CC membranes.

B. Proton conductivity and methanol permeability

Proton conductivity of CS and CS/CC membranes was determined by impedance method. All impedances were carried out after hydration process of the membranes. The results clearly seen that adding CC into CS increased the proton conductivity at temperature 40-60°C.

Table 1. Proton conductivity (σ) and methanol permeability (p) of CS and CS/CC membranes.

Code	σ (25°C) (S/cm)	σ (40°C) (S/cm)	σ (60°C) (S/cm)	P (x 10^{-6} cm^2/s)
CS	$1.83x10^{-4}$	-	-	3.44
CS/CC1	$1.06x10^{-4}$	$5.32x10^{-5}$	$6.92x10^{-5}$	3.01
CS/CC2	$1.60x10^{-4}$	$6.38x10^{-5}$	$7.45x10^{-5}$	2.58
CS/CC3	$1.70x10^{-4}$	$7.02x10^{-5}$	$8.03x10^{-5}$	1.96
CS/CC4	$1.42x10^{-4}$	$5.85x10^{-5}$	$6.44x10^{-5}$	2.82
CS/CC5	$1.18x10^{-4}$	$5.36x10^{-5}$	$5.76x10^{-5}$	3.30

Modifying CC into CS membrane give other effect in methanol permeability, that decreased as much as concentration of CC. It is indicated that CC has hydrophobic parts that could improve the ability of membrane to reject methanol. The result of proton conductivity and methanol permeability shows in Tab. 1. The best composition of composite membrane was obtained in CS/CC3 (0.06 g) with $8.03x10^{-5}$ S/cm and $1.96x10^{-6}$ cm^2/s for proton conductivity and methanol permeability.

CONCLUSION

In conclusion, the increase of calcium carbonate concentration from 0.02 to 0.10 g causing the increase of thermal properties, proton conductivity and decrease methanol permeability. The best composition of membrane was obtained in CS/CC3 (0.06 g) with the highest proton conductivity and lowest methanol permeability. Proton conductivity of CS/CC membrane is bigger than unmodified CS membrane when treated at high temperature, either do methanol permeability. This result implies that this composite membrane is a good candidate for DMFC in fuel cell application.

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