Effect of Glutaraldehyde Concentration Variation toward Properties and Performance of Composite Membrane (Chi-Mmt) for DMFC Application

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Abstract – Membrane CS/MMT-GA were synthesized by inversion phase method. In this study, CS as matrix, MMT as filler and GA as cross linking agent. CS-GA-MMT showed high performance as good candidate for DMFC. The best composition was obtained to CS/MMT-GA2 with highest proton conductivity and lower methanol permeability.

Index Terms –Chitosan, DMFC, Glutaraldehyde, MMT.

Introduction

Polyelectrolyte membranes (PEMs), as the key part of DMFC systems, have crucial role as the transport medium for generated protons from oxidation of fuel in fuel cell [1-2]. Nafion is currently the most commonly utilized Proton Exchange Membrane (PEM) for DMFCs because of superior chemical stability and high proton conductivity. However, it still has some drawbacks such as reduction in conductivity at high temperature, high methanol permeability and high production cost [3]. Therefore, the development of new alternative hybrid membranes that will provided improved character, environmental benign, and low production cost for fuel cell application is highly required. The new DMFCs membranes require several important properties, including good film formation, high methanol rejection, good mechanical stability and hydrophilic character to allow sufficient ionic conductivity [4-5].

Chitosan (CS), a polysaccharide bio resource, has been attracting considerable interest to substitute Nafion as DMFCs in fuel cell application [6]. It was pointed out that cationic polyelectrolyte such as chitosan has unique character due to the presence of both amine and hydroxyl groups [7]. Although it has low ionic conductivity compared to Nafion, but it has low methanol permeability. Therefore, it makes chitosan membrane an excellent material to be further developed [8].

In this study, DMFCs membranes were prepared from mixture of chitosan (CS) as matrix and montmorillonite (MMT) as filler. Meanwhile, glutaraldehyde with various concentration as cross linking agent has been chosen for enhance proton conductivity of hybrid membrane. The formation of polyelectrolyte hybrid composite membrane from both CS/MMT and CS/GA are expected to improve their conductivity, rejecting methanol, mechanical properties and thermal stability. The aim of this research is to study the effect of glutaraldehyde in various concentration toward composite membrane, for DMFC by analysis the thermal stability, mechanical properties, proton conductivity and methanol permeability.

Experimental

A. Synthesis of CS/GA-MMT membranes

2.0 g CS powders were dissolved in 75 mL of acetic acid solution at 80 °C. Subsequently, 80 mL of glutaraldehyde with various concentration of 0.10; 0.15; 0.20 and 0.25 were added into chitosan solution [9]. A certain amount of montmorillonite was dispersed in the portion of @% of acetic acid solution by ultrasonic treatment for 30 min. Subsequently, two portions of solution were mixed, and stirred at 80 °C for 30 min. Then, ultrasonic treatment and stirring were carried out alternatively, each for 30 min. After thorough degasification, the mixture was cast onto clean glass plate and dried at room temperature for 72 h. Next, 1 N sodium hydroxide solution was added to the dry membranes in the Petri dishes several times. The neutralized membranes were washed several times with deionized water. Finally, the membranes were dried at 25 °C. The thickness of all membranes was in the range of 2.0 to 4.0 (10^{-2}) cm. the membranes were denoted as CS as pure chitosan, CS-MMT as chitosan/montmorillonite, CS/GA1-MMT, CS/GA2-MMT, CS/GA3-MMT and CS/GA4-MMT as chitosan/glutaraldehyde-montmorillonite.

B. Characterizations

Fourier transform infrared spectra (4,000-500 cm^{-1}, resolution 4 cm^{-1}) of modified-montmorillonite samples and membranes were recorded with a Shimadzu FTIR spectrometer. Thermal Gravimetry Analysis (TGA) and Scanning Electron Microscopy (SEM), as well asa proton conductivity and methanol permeability were used to characterised the membrane.

Result and Discussion

A. Synthesis of CS/GA-MMT membranes

Generally, the CS/GA-MMT membranes in various concentration of glutaraldehyde were successfully synthesized by inversion phase method. Fig. 1 shows the FTIR spectra of CS, CS-MMT and CS-GS-MMT.

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The characteristic bands at 3420 cm^{-1}, 1650 cm^{-1}, and 1550 cm^{-1} are attributed to hydroxyl group, amide I and amide II groups of chitosan, repectively. The peaks at 1650 cm^{-1} and 1550 cm^{-1} shifted to higher wavenumber at 1655 cm^{-1} (C=N) and 1560 cm^{-1} (C=C), providing support that cross-linking between amine groups of chitosan and the aldehyde groups of GA has occurred [10].

B. Mechanical and thermal property

Good mechanical and thermal properties are required for PEMs in DMFCs to guarantee a long lifetime of fuel cells. Tensile strength results of all membranes were listed in Table 1. According to TGA results the increasing glutaraldehyde concentration will significantly increased the thermal stability of the CS/GA-MMT membranes.

Table 1. Tensile strength of CS, CS-MMT and CS/GA-MMT

Membranes	Tensile Strength (MPa)
CS	22.0
CS-MMT	14.0
CS/GA1-MMT	20.5
CS/GA2-MMT	27.6
CS/GA3-MMT	38.0
CS/GA4-MMT	11.8

C. Proton conductivity and methanol permeability

Proton conductivity of CS, CS -MMT, and CS/GA-MMT membranes was determined by means of the complex impedance method. All impedances were carried out after hydration of the membranes. The results clearly seen that adding glutaraldehyde into chitosan increased the proton conductivity in wide range temperature. The best composition was obtained for CS/GA2-MMT with highest proton conductivity of 26.24x10^{-4} S.cm^{-1} at 60 °C.

The methanol permeability decreased as increasing concentration of glutaraldehyde which added to modified chitosan. It is indicated that glutaraldehyde was taken place in membrane to improve the methanol rejecting. The lower methanol permeability was obtained in CS/GA1-MMT of 6.28x10^{-7} cm^2.s^{-1}.

CONCLUSION

The increase of glutaraldehyde concentration from 0.10 to 0.25 caused the increase of mechanical and thermal properties, proton conductivity and enhance methanol rejecting. The best composition of membrane was obtained in CS/GA2-MMT which possesed the highest proton conductivity and lower methanol permeability. However, the proton conductivity was still an order magnitude lower than Nafion at 3.84 x 10^{-1} S.cm^{-1}. This result implies that this novel complex-composite membrane is a good candidate for DMFC in fuel cell application.

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