Effect of Phosphotungstic Acid toward Composite Membrane for DMFC Application

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Abstract* – *Fuel cell consists of an electrolyte, which connected to the anode and cathode through a polyelectrolyte membrane in which the membrane is capable of delivering protons from the anode toward the cathode. The aim of this study is to know the effect of acid on the membrane composite phosphotungstic chitosan/montmorillonite-silane 10% of the ion exchange capacity, proton conductivity and methanol permeability using a variation of the 0; 0.5; 1.0; 1.5%, respectively. The additions of phosphotungstic acid increased the proton conductivity and ion exchange capacity. However, in this study, the highest proton conductivity on chitosan/ montmorillonite-silane 10%/1.0% phosphotungstic acid caused by a strong hydrophilic nature phosphotungstic acid.

Index Terms* – *Membrane, Methanol Permeability, Proton Conductivity and Ion Exchange Capacity.

INTRODUCTION

Fuel cells are electrochemical devices that convert chemical energy of reactants directly into electricity and heat with high efficiency. DMFC is one of the fuel cells used that is the liaison between the reaction at the cathode and anode through a membrane [1]. At this time, the membrane is widely used Nafion© which has high proton conductivity and good chemical stability but it is expensive. Therefore, alternative membrane is required to other materials that have a high conductivity at a cheaper price [2].

Heteropoly acid is one of donor proton conductivity and good thermal stability include phosphomolibdate acid (PMA), silicotungstic acid (Shiva), and phosphotungstic acid (PWA). Phospotungstic acid has been known as an inorganic material which acts as a proton conductor super ionic in type-Keggin HPA, which has a proton conductivity, value of 0.02 to 0.1 S/cm at room temperature [3]. In this study, DMFC membrane made of chitosan and mixing chitosan (CS) as a matrix and montmorillonite (MMT) modified by silane 10% as filler that both added additives phosphotungstic acid at 0; 0.5; 1.0 and 1.5%. The aim of this research is to study the applicability of this polyelectrolyte complex - a composite membrane, for DMFC by analysis Proton Conductivity vs. Ion Exchange Capacity.

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EXPERIMENTAL

A. *Synthesis of CS/PWA and CS/MMT-Silan/PWA Membranes*

2 g 2.0 wt.% Aqueous solution of acetic acid equally divided by into two portions. (i) 1 g CS powders were dissloved in one portion of acetic acid solution at 60-70ºC, (ii) 0,9 g CS powders were dissolved in one portion of acetic acid solution at 60-70ºC, a certain amount of montmorillonite was dispersed in the portion of acetic acid solution by ultrasonic treatment for 30 min. Subsequently, two portions of solution were mixed, and stirred at 60-70ºC for 30 min. Then, ultrasonic treatment and stirring carried out alternatively, each for 30 min. After thorough degasification, the mixture cast onto clean glass plate and dried at room temperature for 10-15 days. The neutralized membranes were washed several times with deionized water and soaked in PWA solution 0; 0, 5; 1,0 and 1,5% for 24 h. Then, the membranes washed and immersed in deionized water for 24 h to remove the physically absorbed PWA. Finally, the membranes dried at 25ºC. The membranes were denoted as CS/PWA (0; 0,5; 1,0; 1,5%) and CS/MMT-Silan 10%/PWA (0; 0,5; 1,0; 1,5%).

B. *Characterizations*

Proton conductivity using Impedance Analyzer, methanol permeability using density method, and ion exchange capacity using classical titration.

RESULT AND DISCUSSION

A. *Proton conductivity, methanol permeability and ion exchange capacity*

Proton conductivity of membranes was determined by means of the complex impedance method. All impedances were carried out after hydration of the membranes. The result clearly seen that adding PWA into chitosan increased the proton conductivity. In table 1, the best composition was obtained for CS/PWA 1,5% of 0,0033 S/cm at 60ºC and CS/MMT-Silan 10%/PWA 1,0% of 7,90 x 10^{-5} S/cm at 80ºC.

The methanol permeability decreased as increasing concentration of phospotungstate acid which added to modified chitosan. It is indicated that PWA was taken place in membrane to improve the methanol rejecting. The lower methanol permeability was obtained in CS/MMT-Silan 10%/PWA 1,0% of 1,15 x 10^{-6} cm^2/s. Ion exchange capacity (IEC) indicates the density of ionizable hydrofilic functional groups in the membrane and was determined by the classical titration. In table 1,the biggest of ion exchange capacity of CS/PWA 1,0% is 5,10 meq/g while modification membrane (CS/MMT-Silan 10%/PWA 1,0%) is 4,78 meq/g. This proves adding PWA into chitosan indicates many density of ionizable hydrofilic functional groups in the membrane.

Table 1. Proton Conductivity, Methanol Permeability and Ion Exchange Capacity of CS/PWA and CS/MMT-Silan 10%/PWA.

Membrane	σ (x 10^{-3} S/cm) (60°C)	P (x 10^{-6} cm^2/s)	IEC (meq/g)
CS/PWA 0%	1,1	2,29	0,81
CS/PWA 0,5%	2,86	1,72	3,77
CS/PWA 1,0%	3,08	2,87	5,10
CS/PWA 1,5%	3,30	3,44	4,62
CS/MMT-Silan 10%/PWA 0%	0,0582	3,44	0,85
CS/MMT-Silan 10%/PWA 0,5%	0,064	4,59	1,21
CS/MMT-Silan 10%/PWA 1,0%	0,070	1,15	4,78
CS/MMT-Silan 10%/PWA 1,5%	0,063	1,72	3,39

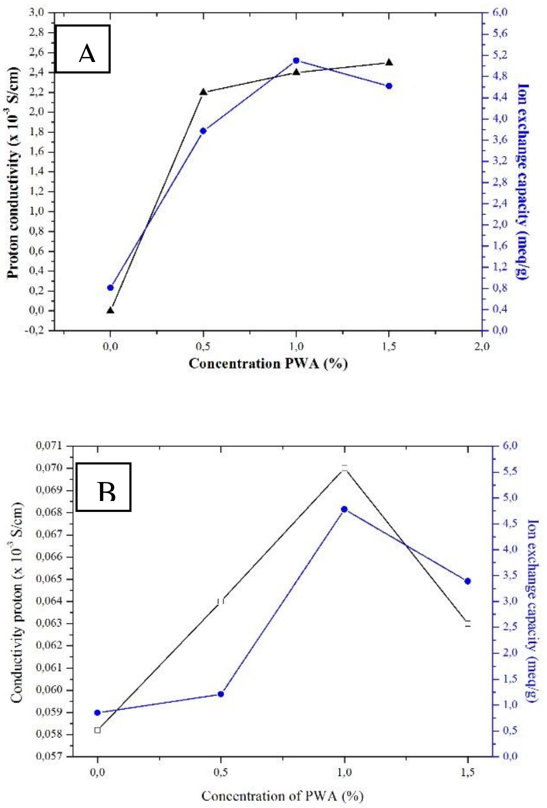

Figure 1. The proton conductivity vs ion exchange capacity of membrane (a) cs/pwa and (b) cs/mmt-silan 10%/pwa.

Figure 1 shows correlation between increasing concentration of PWA, conductivity and ion exchange capacity. It obtained that increasing concentration of PWA increased proton conductivity and ion exchange capacity.

CONCLUSION

In conclusion, increasing concentration of PWA lead to increase proton conductivity and ion exchange capacity. The best composition of membrane obtained in CS/PWA 1,5% and CS/MMT-Silan/PWA 1.0%.

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