## Ionic Conductivity of Carbon Black-Filled Chitosan-Grafted-Poly (Vinyl Alcohol)/Poly (Vinyl Alcohol) Membranes

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#### Abstract

Chitosan-grafted poly(vinyl alcohol)/poly(vinyl alcohol) (CS-g-PVA/PVA) membrane has been synthesized and studied for use as a polyelectrolyte membrane for direct methanol fuel cells because of its high water absorbability and low methanol permeability. Besides, it has high mechanical strength in the wet state. In this work, the increase of ionic conductivity is our focus. The enhancement was by filling the membrane with self-dispersible carbon black (SDCB) nanoparticles having hydrophilic carboxylic group (COO) on their surfaces. Moreover, crosslinking with sulfuric acid was also used to increase ion conductivity of the membrane. The conductivity of CS-g-PVA/PVA membrane obtained had a low ionic conductivity of 0.258 mS/cm, slightly greater than that of chitosan membrane, which was 0.223 mS/cm. Upon crosslinking with increasing concentration of sulfuric acid solution up to 6%, the ionic conductivity was found to increase. At its maximum, the conductivity was 7.713 mS/cm, 30 times the original. In addition, filling with SDCB without crosslinking increased the conductivity slightly. However, filling with SDCB together with crosslinking showed synergistic effects on the ionic conductivity. The best membrane in this study was the one filled with 6% SDCB and crosslinked with 6% sulfuric acid, which had an ionic conductivity of 9.640 mS/cm, 37 times the plain CS-g-PVA/PVA membrane.

Keywords: chitosan membrane, chitosan-grafted poly(vinyl alcohol), carbon black, direct methanol fuel cell, crosslink

### **1. Introduction**

Chitosan (CS) is a high-molecular weight polysaccharide, generally prepared by partial deacetylation of chitin in a hot alkali solution. Because of several unique and interesting biological properties such as biocompatibility, biodegradability and nontoxic properties, chitosan has been considered for the development of membranes, fibers and other forms. In this work, the aim was to use it in a polyelectrolyte exchange membrane for a Direct Methanol Fuel Cell (DMFC). Direct methanol fuel cell is known as clean alternative energy which is a candidate for portable devices or transportation application. Different from general proton exchange membrane, it requires methanol as the supply fuel instead of hydrogen which needs a complicated storage system, thereby being inconvenient in transportation. So it is of interest to use DMFC as a possible commercial alternative energy.

An efficient membrane for DMFC should have high proton conductivity, good water absorption and low methanol permeability. Chitosan is a good candidate for DMFC membrane because a chitosan membrane can prevent methanol permeability as was reported in a previous work [1]. However, the membrane consisting of only chitosan is still not an appropriate membrane for DMFC because of its low ionic conductivity and low water absorbability. Therefore, incorporating an appropriate hydrophilic polymer such as poly (vinyl alcohol) with chitosan could be a possible alternative. In this work, chitosan-grafted-poly (vinyl alcohol)/poly (vinyl alcohol) or CS-g-PVA/PVA mem brane was studied and it was found that this kind of membrane had better mechanical properties in the wet state than the membrane of CS/PVA blend [2].

To increase proton conductivity of the membrane, any method to increase anionic sites inside the membrane should be explored. Surface modified carbon black (CB) such as self-dispersible carbon black (SDCB) nanoparticles was selected for this purpose because the hydrophilic carboxylic group (COO<sup>-</sup>) on the surface can enhance proton (H<sup>+</sup>) movement in the membrane [2,3]. In addition, crosslinking with anionic groups has been proved to be beneficial before [4]. Therefore, in this study sulfuric acid and glutaraldehyde solution were also applied for crosslinking.

### 2. Experimental

### 2.1 Raw Material

High molecular weight chitosan (CS) with degree of deacetylation (DDA) of 98.6% was obtained from A.N. Lab, Co. Ltd. Acetic acid and sodium hydroxide were from Merck KGaA, Germany. Vinyl acetate monomer (VAc) was from Merck Schuchardt OHG, Germany. Cerium Ammonium nitrate (CAN) for initiator was from Fluka, Australia. 51% Sulfuric acid was obtained from J.T. Baker NEUTRASORB® or

TEAM®, USA. Acetone was from SK Chemicals, Korea. 25% glutaraldehyde was from Ajax Funechem, Australia. Carbon black was obtained from Loxley, Thailand. **2.2 Synthesis of chitosan-grafted-poly** 

### (vinyl alcohol)/poly (vinyl alcohol)

The synthesis followed the two-step reactions proposed by Don *et al.* [5].

### 2.2.1 Graft copolymerization

30 g of chitosan ( $W_{CS}$ ) was dissolved in 2,000 ml of 2% acetic acid solution. After it was completely dissolved, 23.672 g of CAN initiator were added while the solution was stirred at 300 rpm. Ten minutes later, 200 g of distilled VAc monomer  $(W_{VAc})$  were added to the solution and the polymerization was carried out at 60°C. After 2 hrs, a dispersion containing chitosan copolymer was obtained. To calculate monomer conversion (X%), the solution was dried to find a constant weight  $(W_1)$ . To obtain grafting efficiency (GE%) and grafting ratio (GR), PVAc homopolymer was removed by pure acetone extraction. After 72 hrs of extraction, the remaining chitosan-g-PVAc copolymer was weighed  $(W_2)$ . dried and Monomer conversion, grafting efficiency and grafting ratio were all calculated by gravimetric method according to the equations,

$$\% X = \frac{(W_1 - W_{CS})}{W_{VAc}} \times 100$$
 (1)

$$\% GE = \frac{W_2 - W_{CS}}{W_1 - W_{CS}} \times 100$$
 (2)

$$GR = \frac{W_2 - W_{CS}}{W_{CS}} \tag{3}$$

### 2.2.2 Alcoholysis of PVAc to PVA

80 g of NaOH were dissolved in 20 ml water, and subsequently 2,000 ml CH<sub>3</sub>OH added to the solution. The alkali methanol solution was heated to 40°C and stirred at 300 rpm. The previously prepared dispersion solution (CS-g-PVAc/PVAc)

was added dropwise into the solution in 45 min. The reaction was continued for another 15 min. The alcoholysis reaction proceeded immediately once the dispersion latex was added into the methanol solution and a sediment product was observed. After filtration, methanol was used to wash the reaction product.

### 2.3 Membrane preparation 2.3.1 CS-g-PVA/PVA Membrane

2.3 g of CS-g-PVA were dissolved in 40 ml of 10% acetic acid v/v. The solution was heated to 60°C and stirred until CS-g-PVA had been fully dissolved. Chitosan solution was filtered and poured onto a glass plate. It was left to dry in open air for 24 hrs and then heated at 60°C for 6 hrs. The dried membrane was neutralized in 1 M NaOH solution, and then washed thoroughly and kept in deionized water.

### 2.3.2 CS-g-PVA/PVA membrane filled with SDCB

2.3 g of CS-g-PVA were dissolved in 40 ml of 10% v/v acetic acid solution and filtered. After that, the solution was left to cool down to room temperature. SDCB with concentration 1, 2, 4, 6, 8% of CS-g-PVA/PVA by weight was then gently added into the solution. The suspension was stirred to assure the dispersion of SDCB throughout the liquid by a magnetic stirrer. The suspension was poured onto a glass plate and left to dry in open air for 24 hrs and then heated at 60°C for 6 hrs.

### **2.3.3** Crosslinking with glutaraldehyde and sulfuric acid

CS-g-PVA/PVA membranes and CS-g-PVA/PVA membranes filled with SDCB were immersed in mixed solution prepared from 1.5 ml of glutaraldehyde and 60 ml of sulfuric acid with different sulfuric acid concentration of 2, 4, 6 and 8% v/v. After 24 hrs, membranes were thoroughly washed and kept in deionized water.

### 2.4 Ionic conductivity measurement

Each membrane was cut to a piece of 3x3 cm<sup>2</sup>. It was fully hydrated by storing in water at least 24 hrs. The ionic

conductivity of the membranes was measured by Frequency Response Analysis program using four-probe-points cell at a frequency of 10 kHz and amplitude of 0.35 mA. The proton conductivity was calculated by using the following equation [6]:

$$\sigma = \frac{I}{Z \, x \, S} \tag{4}$$

where I, Z and S denote the distance between the two probe wires, the resistance of the membrane, and the cross-section area of the membrane, respectively.

### 3. Results and Discussions

### **3.1** Monomer conversion, grafting efficiency and grafting ratio

Monomer conversion (X%), grafting efficiency (*GE*%) and grafting ratio (*GR*) after 2 hrs of reaction at 60°C were 61.84%, 22.22% and 0.92, respectively.

### **3.2 Effect of modification of chitosan to** CS-g-PVA and crosslinking on ionic conductivity

The comparison of ionic conductivities of various membranes is displayed in Figure 1.



**Fig. 1** The ionic conductivities of various membranes are compared: CS and CS-g-PVA/PVA is in the small figure. The effect of crosslinking on ionic conductivity is shown.

As shown in Figure 1, the ionic conductivity of the membrane of CS-g-PVA/PVA is slightly greater than that of the CS membrane. When chitosan is dissolved in acetic acid solution, the amino groups on chitosan chains will be protonated, transforming it to a polycationic polymer. Therefore, it may be considered as an alkaline polyelectrolyte conducting hydroxyl ions in the membrane [7]. The modification of chitosan to CS-g-PVA/PVA increases the degree of hydrophilicity which increases the mobility of protons moving from one water molecule to another inside the membrane. Adding PVA introduces the interaction between hydroxyl groups and protonated amino groups of chitosan.

The effect of crosslinking is also seen in the figure, where the concentration of sulfuric acid was varied. The ionic conductivity of the CS-g-PVA/PVA increased with increasing sulfuric acid concentration. The electrostatic interaction between SO<sub>4</sub><sup>2-</sup> groups and protonated amino groups,  $NH_3^+$ , is favorable, leading to crosslinking among chitosan chains and making the membrane stronger. However, by jumping mechanism of protons in the membrane, increasing anionic sites of  $SO_4^{2}$ could increase the mobility of the protons [8], thereby increasing proton conductivity of the membrane. The increase was seen up to a concentration of sulfuric acid solution of 6%. Beyond that point, the conductivity dropped since the hardening of the membrane by excessive crosslinking hinders the diffusion of protons inside the membrane.

# **3.3** The effect of carbon black loading on the ionic conductivity of CS-g-PVA/PVA membranes

The membrane was filled with small amounts of self-dispersible carbon black particles up to 8%. It is observed in Figure 2 that when filling only 1% of carbon black particles, it could double the proton conductivity in the membrane. Carbon black particles with carboxylic groups act as anionic sites in the membrane, interacting with the moving protons. It was reported that, adding carbon black also obstructs water absorption [3]. Therefore, both effects of carbon black loading for increasing the anionic sites and preventing water absorption could compete with each other. Upon increasing the loading to 2% and beyond, it was likely that water absorption reduced, resulting in the drop of ionic conductivity.



**Fig 2** Ionic conductivities of CS-g-PVA/PVA membranes filled with different amounts of self-dispersible carbon black.

## 3.4 Synergistic effect of carbon black loading and crosslinking on ionic conductivity.

The results of ionic conductivities of membranes with varying percentage of SDCB and sulfuric acid concentration are shown in Fig 3.

Ionic conductivity of the membranes crosslinked with 2% sulfuric acid solution was raised when the amount of SDCB was increased from 1 to 8%. Separately considering the effect of carbon black loading and sulfuric crosslinking, it was seen that the ionic conductivity was twice and twenty times that of the original membrane, respectively.



**Fig 3** Ionic conductivities of membrane CSg-PVA filled with self-dispersible carbon black and undergoing cross linking with sulfuric acid

When applying both carbon black filling and crosslinking to the membrane, it was seen from Fig. 3 that the conductivity was twenty-two times that of the original. This shows that the total effect is a linear combination of both.

For membranes crosslinked with 4% sulfuric acid solution, the conductivity increased until the amount of SDCB was up to 6%. Membranes crosslinked with 6% sulfuric acid solution showed the best trend with a maximum of ionic conductivity of 9.640 mS/cm when using 6% SDCB. For the highest concentration of sulfuric acid solution used here, at 8%, the conductivity showed some inconsistency. It seemed to be that when a large amount of sulfate ions interacted with  $\widetilde{NH}_3^+$  groups of chitosan, the excessive ionic interaction between  $SO_4^{2-}$ and  $NH_3^+$  made the membrane too rigid. This caused less water permeability and less number of ions transferring through the membrane. Therefore, the ionic conductivity of the membrane was decreased.

The synergistic effect was observed for the case of using carbon black greater than 1%. For example, the membrane with carbon black loading of 2% had ionic conductivity of about 0.30 mS/cm, 1.2 times the original, while the membrane crosslinked with 4% sulfuric acid solution had ionic conductivity of about 7.5 mS/cm, 30 times the original. If the membrane was filled with carbon black loading of 2% together with crosslinking with 4% sulfuric acid solution, the ionic conductivity would be 9 mS/cm, 37 times the original. So both crosslinking and anionic loading play synergistic roles in promoting the ionic conductivity of the membrane.

### 4. Conclusion

Both carbon black filling and sulfuric acid crosslinking increased the ionic conductivity of the membrane. The optimum loading of carbon black alone is 1% of CS-g-PVA weight and the optimum of sulfuric acid concentration is 6% v/v. When the two methods were incorporated, the synergistic effect brought about high ionic conductivity. The best performance was observed for the membrane with 6% SDCB crosslinked with 6% sulfuric acid solution, which gave the ionic conductivity 37 times that of the plain CS-g-PVA/PVA membrane.

However, other experiments are required to support the appropriate use of the membrane. These concern water absorption and methanol permeability. Our aim is that the membrane should have high selectivity, which is defined as the ratio of proton conductivity to methanol permeability. Both filling with carbon black and crosslinking with sulfuric acid solution would increase the strength of the membrane and this could help prevent methanol from permeating through the membrane. Such studies are still ongoing.

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