Research Article

An Investigation of Chitosan-Grafted-Poly(vinyl alcohol) as an Electrolyte Membrane

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The membrane of chitosan-grafted-poly(vinyl alcohol)/poly(vinyl alcohol) (CS-g-PVA/PVA) was investigated along with chitosan (CS), PVA, CS/PVA, and Nafion 117 membranes for transport properties of water and methanol, mechanical properties, and ionic conductivity. The ionic conductivity, σ, of the crosslinked CS-g-PVA/PVA membrane was about 4.37 mS cm^{-1} and the methanol permeability, P_S, was 1.8×10^{-7} cm^{2}s^{-1}. These gave the selectivity, σ/P_S, of 23.95 mS·s·cm^{-3} compared with 16.35 mS·s·cm^{-3} of Nafion 117 membrane. The conductivity of the crosslinked CS-g-PVA/PVA membrane was greater than others including Nafion 117 when the membranes were saturated with methanol solution of which concentration was greater than 20%. This fact and that the mechanical properties of the wet crosslinked CS-g-PVA/PVA membrane were comparable to those of other membranes made it a promising material to be used as an electrolyte membrane in a direct methanol fuel cell.

1. Introduction

The direct methanol fuel cell (DMFC) is a device converting chemical energy to electrical energy. Nowadays, it is used as an energy source for transportation and other portable applications such as mobile phones and laptop computers [1]. The enhancement of DMFC via improving the electrolyte membrane and increasing effectiveness of the catalysts have been investigated by many researchers for several decades. To increase the fuel cell performance, the polymer electrolyte membrane should be modified to yield higher proton conductivity. The membrane currently used is a Nafion membrane, which is basically composed of perfluorinated sulfonic acid. However, it has some disadvantages. First of all, it is an expensive material costing about $600–1200 per square meter [2]. In addition, it has high methanol permeability, leading to methanol crossover as much as 40% during the process [3]. There are many research works investigating low-cost polymers, which have high proton conductivity and low methanol permeability, one of which is chitosan, which has been investigated widely for this purpose [3–6].

Chitosan is a linear polysaccharide composed of randomly distributed β-(1–4)-linked D-glucosamine (or deacetylated unit) and N-acetyl-D-glucosamine (or acetylated unit). It is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans such as crabs and shrimps. Chitosan consists of two attractive functional groups: amine (–NH$_2$) and hydroxyl (–OH) groups, thereby, being used in many applications including waste water treatment, biomedical engineering, and fuel cell. Chitosan is easily cast into a membrane from the solution of a weak acid. Being dissolved in a weak acid, the amine groups of chitosan could be protonated and these protons can move in the membrane, leading to the ionic conductivity of the membrane [7]. Moreover, it could also be protonated when it is submerged in water [8]; so water plays an important role in ionic conductivity of any chitosan membrane [9].

Even though chitosan has many good properties due to its functional groups, a chitosan membrane has poor mechanical properties. These could be improved by incorporating another polymer such as poly(vinyl alcohol) (PVA), which

is also easily formed as a membrane with good mechanical properties. Moreover, PVA is a good methanol barrier [10–12], which is beneficial in case where methanol permeability is concerned. There was, however, a report on poor miscibility between chitosan and PVA [13]. To solve this problem, a graft copolymer of PVA and chitosan was introduced as a compatibilizer in the composite. In addition, crosslinking with glutaraldehyde and sulfuric acid was found to enhance properties of chitosan membranes and importantly increase their ionic conductivities due to additional sulfate ions in the membranes [3, 7].

So far, there has not been any investigation into the electrical properties of chitosan-grafted-PVA membrane before to see whether it is appropriate to be used as an electrolyte membrane. Therefore, in this study, we report the ionic conductivity along with mechanical properties for both in dry and wet states of such membrane and compare with those of chitosan-based, PVA-based, and the commercial Nafion membranes. In addition, crosslinking with glutaraldehyde and sulfuric acid as a method to increase the proton conductivity of the membrane is also explored.

2. Materials and Methods

2.1. Materials. Chitosan (CS) from shrimp with a degree of acetylation of 98.6% was provided by Aquatic Nutrition Lab Co., Ltd., Thailand. Vinyl acetate monomer, methanol, and acetic acid were supplied by Merck, Germany. Ammonium cerium(IV) nitrate (CAN) was obtained from Sigma-Aldrich, Austria. Hot water soluble poly(vinyl alcohol) and glutaraldehyde (GLA) were received from Ajax Finechem, Australia. Sulfuric acid was purchased from J. T. Baker, USA. Nafion 117 membrane was obtained from Ion Power, Inc., USA.

2.2. Synthesis of Chitosan-Grafted-Poly(vinyl alcohol)/Poly (vinyl alcohol) (CS-g-PVA/PVA). The synthesis follows the method proposed by Don et al. [14], which is a two-step reaction. Briefly, in the first step, 15 g of chitosan flakes were dissolved in 2 wt% acetic acid solution. After that, 2.16×10^{-2} mol of ammonium cerium(IV) nitrate (CAN) was added the solution as an initiator for polymerization. Then, 100 g of vinyl acetate monomers were added. The reaction was carried out at 60°C for 2 hours. The solution contained the products of chitosan-grafted-poly(vinyl acetate) (CS-g-PVAc) together with vinyl acetate homopolymer (PVAc). The second step involved methanolysis of the product. It was accomplished by adding the obtained solution from graft copolymerization dropwise into the mixture of 20 mL of 100 wt% NaOH solution and 500 mL of methanol at 40°C and stirring at a speed of 100 rpm for 45 min. The reaction continued for another 15 min. The sediment was filtered and washed several times with methanol to remove unreacted vinyl acetate monomers. Subsequently, it was dried at room temperature for 24 h and then heated in a vacuum oven at 60°C for 6 h. The product from this step was chitosan-grafted-poly(vinyl alcohol) blended with poly(vinyl alcohol) homopolymer (CS-g-PVA/PVA).

2.3. Membrane Preparation. Several membranes were prepared. Those included membranes from chitosan (CS), poly(vinyl alcohol) (PVA), chitosan blended with poly(vinyl alcohol) (CS/PVA), and chitosan-grafted-poly(vinyl alcohol) blended with poly(vinyl alcohol) (CS-g-PVA/PVA). To complete dissolution, the solution might have to be heated. To prepare CS/PVA membrane, chitosan and PVA solutions were prepared separately and blended at the same CS : PVA ratio as it was in CS-g-PVA/PVA membrane. Each polymer solution was cast on a clean glass plate and left to dry at room temperature for 48 h and then it was dried in a vacuum oven at 70°C for 24 h.

In crosslinking a membrane, it was submerged into a mixture of 1.5 mL of 10 wt% glutaraldehyde (GLA) solution and 60 mL of 2 M sulfuric acid solution for 24 h. Glutaraldehyde acts as a crosslinking agent, while sulfuric acid acts as a catalyst [15]. In addition, it was also found that an acid could increase the degree of protonation in a membrane [16]. After that, the membrane was washed thoroughly and kept in deionized water, ready to be characterized. The assigned name for each crosslinked sample is ended with X. For example, CS-g-PVA/PVA_X means that the membrane is made of CS-g-PVA/PVA and is then crosslinked with GLA solution.

2.4. Membrane Characterization

2.4.1. Water and Methanol Uptake. The membrane sample was cut into 25.4 mm × 25.4 mm pieces. Each piece was placed into a bottle containing either 10 mL of deionized water or 10 mL of methanol. The submerged piece was drawn every minute and the liquid attached to its surface was removed by a piece of filter paper before weighing it. This was repeated until the mass of the swollen membrane was constant. The water and methanol uptakes can be calculated from

$$\%\text{Water Uptake (or Methanol Uptake)}$$
$$= \left(\frac{W_t - W_d}{W_d} \right) \times 100\%, \tag{1}$$

where W_t and W_d are the mass of a wet membrane at any time t and that of a dry membrane, respectively.

2.4.2. Methanol Permeability. The methanol permeability of each membrane was measured with the procedure explained by Mukoma et al. [7]. Basically, the measurement was done in a vessel with two compartments, one of which contained a 40% methanol mixture (denoted by A) and the other contained deionized water (denoted by B). The membrane placed between two compartments could allow methanol and water molecules to pass through. Liquids in both compartments were stirred at 200 rpm and they were sampled for methanol concentration measurement at several time intervals. The methanol permeability, P_S, was determined from

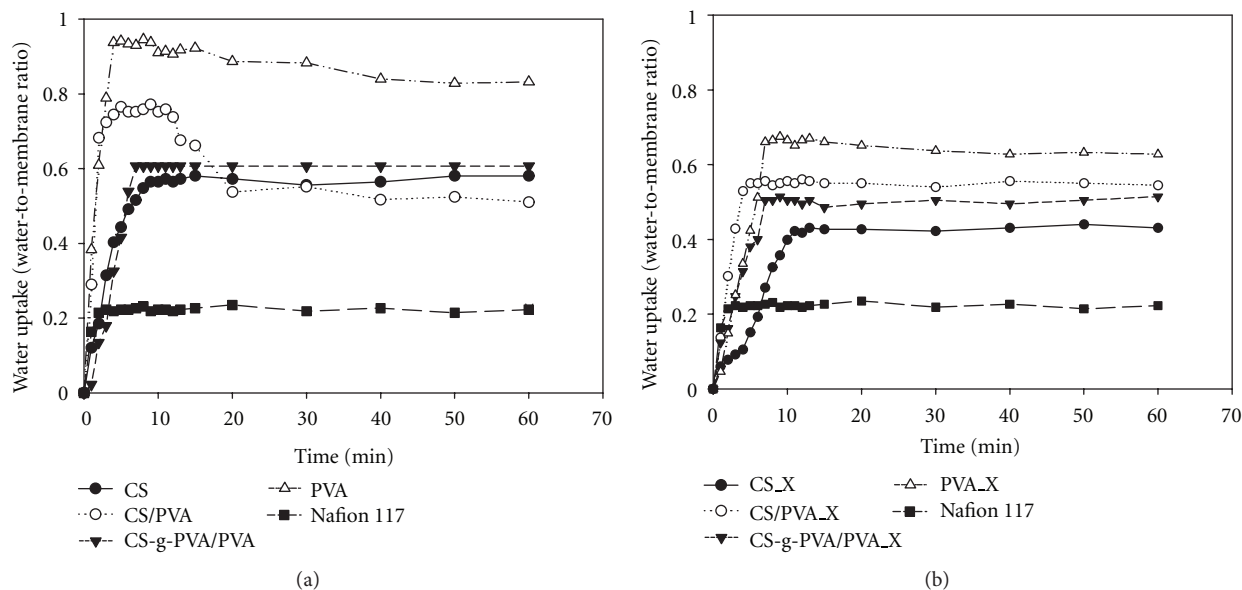$$P_S = \frac{k_B V_B L}{A_P (C_A - C_B)}, \tag{2}$$

FIGURE 1: Water uptakes of several membranes at various times: (a) uncrosslinked membranes and (b) crosslinked membranes.

where k_B is the slope of a plot of the methanol concentration in compartment B versus time, V_B is the liquid volume in compartment B, L is the membrane thickness, A_P is the projected area of the membrane, and C_A and C_B are the initial methanol concentrations in compartments A and B, respectively.

2.4.3. Mechanical Property.

Tensile strength of each membrane was measured with the Universal Testing Machine (Instron 4502). The method complies with ASTM D 882, which is a standard test method for tensile properties of thin plastic sheeting. A specimen was cut into small pieces (15 cm × 2.5 cm). The testing gauge length was 10 cm and the testing speed was 50 mm/min. All specimens were tested at room temperature. The maximum load, ultimate tensile strength, elongation at break, and modulus were recorded and calculated by a computer.

2.4.4. Ionic or Proton Conductivity Measurement.

Ionic or proton conductivity of a fully hydrated membrane was investigated by the impedance method using Potentiostat Testing Machine (PGSTAT 30) with four-point probe cell [17]. The membrane was saturated with a certain solution and then placed between two Teflon blocks and fixed together by four screws. Impedance measurement was carried out at a frequency of 10 kHz and at an open-circuit potential with an AC voltage of 3 mV. Ionic or proton conductivity, σ, can be represented by

$$\sigma = \frac{l}{Z \times A}. \tag{3}$$

Here, l is the length between two electrodes, Z is the measured impedance of the membrane, and A is the cross-sectional area of the membrane. Additionally, the proton conductivity of the membrane saturated in the solution of

various methanol concentrations was investigated in order to understand the effect of methanol crossover on the proton conductivity of the membrane.

3. Results and Discussions

3.1. Characterization of CS-g-PVA/PVA.

The conversion of graft copolymerization was 99.2% and the grafting efficiency, which is defined as the ratio of the mass of vinyl acetate grafted to chitosan to the total mass of vinyl acetate, was 13.5%. Furthermore, the composition of chitosan and PVA in the obtained CS-g-PVA/PVA product could be estimated to be 13.3% and 86.7%, respectively. The Fourier transform infrared spectroscopy (FTIR) was used to characterize the functional groups of CS-g-PVA/PVA product and the results were consistent with Don et al. [14].

3.2. Water Absorption.

The kinetics and equilibrium of water absorption carried out at 30°C are shown in Figure 1. The experiments were performed up to one hour. It can be seen that the absorption equilibrium was reached within 10 min. The kinetics studied in the short-time analysis of mass transport through the membrane can be expressed using the relation [18]:

$$\log \left(\frac{W_t}{W_\infty} \right) = \log k + n \log t, \tag{4}$$

where W_t and W_∞ are the uptake at anytime and the equilibrium uptake, respectively, k and n are parameters, and t is the absorption time. The parameter k describes the interaction between a material and liquid, whereas n represents the mechanism of molecules of substance diffusing in the membrane matrix. The values of n and k are shown in Table 1, along with R^2.

TABLE 1: The values of parameters, n and k, of water and methanol transports in membranes.

Membrane	Water			Methanol		
	n	$k\,[1/s^n]$	R^2	n	$k\,[1/s^n]$	R^2
CS	0.523	0.232	0.968	0.512	0.324	0.994
CS_X	0.465	0.138	0.919	0.497	0.279	0.944
CS/PVA	0.471	0.452	0.912	0.503	0.285	0.916
CS/PVA_X	0.486	0.270	0.970	0.516	0.228	0.978
CS-g-PVA/PVA	0.532	0.249	0.966	0.492	0.227	0.908
CS-g-PVA/PVA_X	0.484	0.222	0.976	0.514	0.213	0.974
PVA	0.479	0.547	0.999	0.481	0.187	0.942
PVA_X	0.505	0.383	0.985	0.502	0.161	0.902
Nafion 117	0.432	0.140	0.984	0.495	0.662	0.941

TABLE 2: The value of diffusion, sorption, and permeation coefficients of water and methanol transports through various membranes.

Membrane	Water			Methanol		
	$D_{ab} \times 10^6$ $(cm^2\,s^{-1})$	S $(-)$	$P \times 10^6$ $(cm^2\,s^{-1})$	$D_{ab} \times 10^6$ $(cm^2\,s^{-1})$	S $(-)$	$P \times 10^6$ $(cm^2\,s^{-1})$
CS	0.36	0.572	0.21	1.70	0.434	0.74
CS_X	0.31	0.432	0.13	2.35	0.267	0.63
CS/PVA	2.59	0.768	1.99	0.55	0.473	0.26
CS/PVA_X	2.57	0.545	1.40	0.49	0.397	0.19
CS-g-PVA/PVA	0.82	0.611	0.50	1.11	0.235	0.26
CS-g-PVA/PVA_X	0.72	0.503	0.36	1.28	0.177	0.23
PVA	3.35	0.934	3.13	1.94	0.147	0.28
PVA_X	2.60	0.671	1.76	1.42	0.132	0.19
Nafion 117	1.60	0.223	0.36	4.26	0.709	2.98

For any pair of membrane-water, the value of n is close to 0.50, implying that the transport through such membrane is Fickian diffusion [19]. Consequently, the diffusion coefficient, D_{ab}, of water into the membrane could be estimated by using the equation for uptake during a short-time period [18],

$$\frac{W_t}{W_\infty} = 4\left[\frac{D_{ab}t}{\pi h^2}\right]^{1/2}, \qquad (5)$$

or equivalently,

$$D_{ab} = \pi\left[\frac{h\Theta}{4W_\infty}\right]^2. \qquad (6)$$

Here, h is the initial thickness of the membrane and Θ is the slope of the linear portion of the curve of W_t versus $t^{1/2}$, where t is the absorption time.

Table 2 displays the values of diffusion coefficients for each pair of membrane-liquid together with the sorption coefficient, S, and the permeation coefficient, P. They are defined in the following:

$$S = \frac{W_\infty}{W_d}, \qquad (7)$$

where W_∞ is the mass of liquid at equilibrium sorption and W_d is the initial mass of a dry membrane, and

$$P = D \times S. \qquad (8)$$

Sorption involves the initial penetration and dispersion of liquid molecules into a membrane, so the sorption coefficient is dependent on the strength of membrane-liquid interaction. Permeability of liquid molecules into a membrane depends on both diffusion and sorption. Permeation coefficient is, therefore, defined as the product of diffusion coefficient and sorption coefficient.

The analysis shows that the diffusion coefficient of water in PVA was the highest and lower in CS/PVA, CS-g-PVA, and CS, respectively. This is not surprising since PVA is a highly hydrophilic material. It was also found that the stabilities of both PVA and CS/PVA membranes are very poor in water. As seen in the figure, while CS and CS-g-PVA/PVA membranes could withstand the dissolution, PVA and CS/PVA membranes began to dissolve at about 12 min after being immersed in water. Therefore, these membranes could not be used unless they were crosslinked.

Table 2 also shows the equilibrium uptake (S or sorption coefficient) of water for all membranes, including Nafion 117. For PVA and CS/PVA membranes, the equilibrium uptakes were identified at the maximum. It can be seen that PVA membrane absorbed the greatest amount of water, which is about its own weight. The hydroxyl groups on PVA chains could hold up large amount of water by hydrogen bonding. It is known that PVA hydrogel could be formed very easily because there are favorable intramolecular and
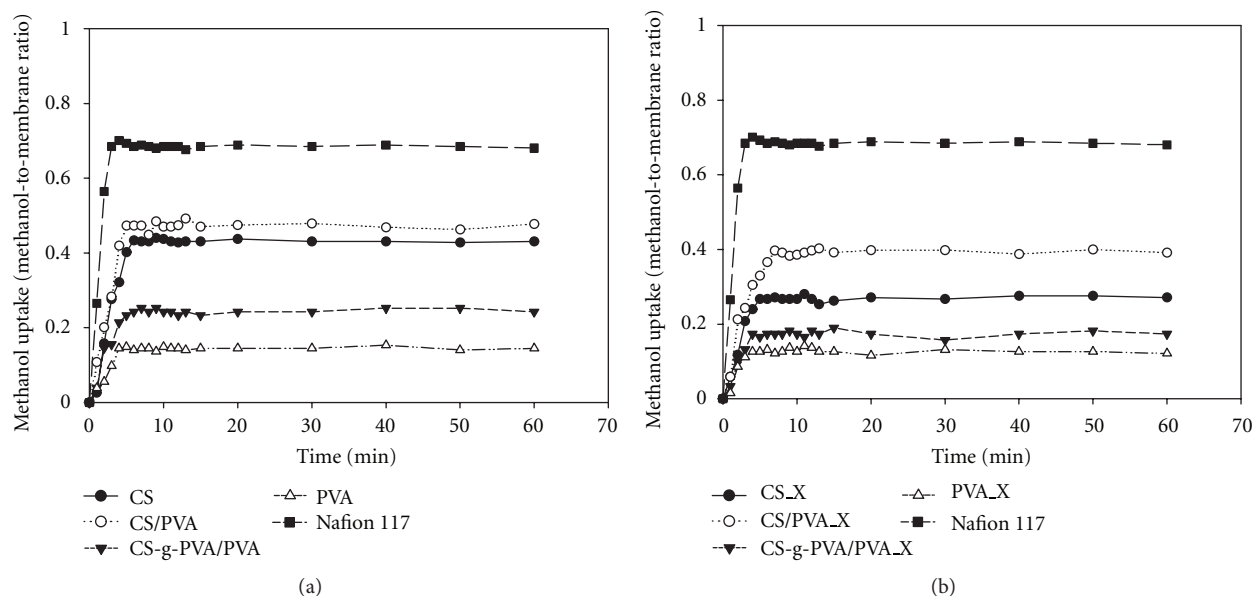
Figure 2: Methanol uptakes of several membranes at various times: (a) uncrosslinked membranes and (b) crosslinked membranes.

intermolecular interactions among PVA chains themselves and water molecules [20].

CS membrane was found to absorb less amount of water than other membranes excluding Nafion 117, which was good at water resistance. As commonly known, chitosan cannot be dissolved in water since the hydrogen bonding between amine groups ($-NH_2$) and hydroxyl groups ($-OH$) on chitosan chains is too strong. However, some amine groups are still left to participate in protonation, which is the main mechanism of proton conductivity of the material [21]. When chitosan was blended with PVA as in CS/PVA and CS-g-PVA/PVA membranes, hydrophilicity of PVA could increase water uptakes of membranes [22]. CS/PVA membrane, nonetheless, gave higher water uptake than CS-g-PVA/PVA membrane. It was possible that in CS-g-PVA/PVA membrane, the entanglement between macromolecules occurred more easily than in CS/PVA membrane due to the branched structures of CS-g-PVA. The entanglement could increase the interactions between amine groups and hydroxyl groups, thereby decreasing hydrophilicity of the membrane.

Comparison between the water uptakes of the uncrosslinked and crosslinked membranes can be made. For each pair of membrane-liquid, the uptake of the crosslinked membrane was evidently less due to less flexible structures of the crosslinking network. Upon crosslinking, the water uptake dropped as much as 30%, 20%, 15%, and 10% for PVA, CS/PVA, CS, and CS-g-PVA/PVA membranes, respectively. It should be noted that water uptakes of CS/PVA_X and CS-g-PVA/PVA_X were comparable.

3.3. Methanol Absorption.
The kinetics of methanol absorption at 30°C is displayed in Figure 2 and the equilibrium uptakes are reported in Table 2. Similarly, the diffusion coefficient, D_{ab}, of methanol through various membranes

can be obtained. In Table 1, the values of n for all pairs of methanol-membrane are close to 0.5; so the transport of methanol through a membrane is also Fickian diffusion. The diffusion coefficient of methanol in Nafion 117 was the greatest, followed by those of CS, CS/PVA, PVA, and CS-g-PVA/PVA, respectively.

Table 3 contains the results of methanol uptakes at saturation. Nafion 117 membrane could absorb the greatest amount of methanol, followed by CS/PVA, CS, CS-g-PVA/PVA, and PVA membranes, respectively. As can be seen, the presence of PVA in the membrane could prevent methanol permeation as was observed in [11]. Being compared among chitosan-based membranes, CS-g-PVA/PVA could obstruct methanol crossover most effectively since the uptake was the least. In addition, for each membrane-methanol pair, the crosslinked membrane had lower methanol uptake than the uncrosslinked membrane because of the higher degree of crystallinity in the structure [22].

3.4. Methanol Permeability.
It is of interest to compare the methanol permeability (by performing the experiment mentioned in Section 2.4.2 and using (2)) to the permeation coefficient (as expressed by (8)), as shown in Figure 3. It is seen that the results of methanol permeability obtained by both calculations are in the same order of magnitude and are close to each other. However, considering the convenience of the method, it is easier to obtain the permeation coefficient. It is restated here that the Nafion 117 was prone to methanol permeation and CS-g-PVA/PVA_X could also prevent the methanol permeation.

3.5. Mechanical Properties of Membranes.
The mechanical properties of dry and wet membranes are provided in Table 4. Dry PVA membrane was the strongest membrane yielding the greatest tensile strength and elongation at break. CS

TABLE 3: Mechanical properties of dry and wet membranes at room temperature.

| Membrane	Dry membrane			Wet membrane		
	Tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)
Chitosan (CS)	32.51	1.92	16.96	18.18	6.23	2.92
CS_X	31.45	4.23	7.43	20.65	10.27	2.01
CS/PVA	28.45	115.67	0.25	0.97	24.17	0.04
CS/PVA_X	53.59	154.67	0.35	2.17	82.67	0.03
CS-g-PVA/PVA	9.67	107.83	0.09	9.23	125.33	0.07
CS-g-PVA/PVA_X	17.17	134.50	0.13	15.13	162.67	0.09
PVA	46.86	262.50	0.18	2.05	95.22	0.02
PVA_X	52.99	285.43	0.19	6.63	148.22	0.04
Nafion 117	28.57	260.17	0.11	20.64	121.75	0.17
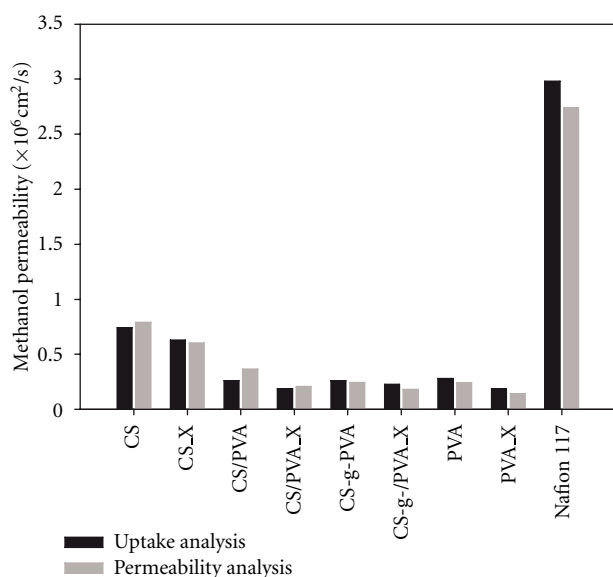
FIGURE 3: The comparison of the methanol permeation coefficient obtained from the methanol uptake analysis and the methanol permeability.

membrane had poor mechanical properties, especially for the elongation at break. Obviously, incorporating PVA to CS membrane resulted in enhancing the mechanical properties. It can be seen that CS/PVA gave higher mechanical properties than CS-g-PVA/PVA membrane. The commercial membrane, Nafion 117, gave the tensile stress as high as CS/PVA membrane and the elongation at break as high as PVA membrane. Upon crosslinking, the mechanical properties of all membranes were increased because a large number of generated chemical bonds linking between polymer chains could absorb more energy exerted to the membrane.

While mechanical properties of a dry membrane may be important when it is handled outside the fuel cell, those of a wet membrane should also be investigated since the membrane is in contact with water all the time during the cell operation. The results are shown in Table 3.

The results of mechanical properties of wet membranes show the same trend as those from water uptake experiments. Crosslinking membrane with glutaraldehyde suited its purpose well in increasing the mechanical properties of the membranes. When PVA and CS/PVA membranes were saturated with water, the mechanical properties, both tensile strength and elongation at break, decreased. This is closely related to the dissolution of PVA in water as already discussed in Section 3.2. For saturated CS and CS-g-PVA/PVA membranes, tensile strength decreased but elongation at break increased due to higher degree of molecular flexibility of polymer chains in the presence of water. The mechanical properties of Nafion 117 membrane also decreased when it was wet. Although the strength of Nafion 117 membrane, at fully hydrated state, is the most attractive, CS-g-PVA/PVA membrane gave reliable properties since its properties at wet state did not changed much from those at dry state. Therefore, CS-g-PVA/PVA membrane showed this advantage over PVA and CS/PVA membranes as it was more stable when it was in contact with water than PVA and CS/PVA membranes.

3.6. Ionic or Proton Conductivity. It is found from Table 4 that proton conductivity of fully hydrated Nafion 117 membrane is superior to those of other membranes due to sulfonate groups in the structure of Nafion [23–26]. Table 4 also indicates that the proton conductivity of the uncrosslinked membrane decreases in the following order: CS/PVA, PVA, CS-g-PVA/PVA, and CS membranes.

As discussed by Wan et al. [8] for the ionic conductivity of a chitosan membrane, the conductivity of CS membrane resulted from the mobility of hydroxide ions moving from protonated amine groups to others. This is known as Grotthuss or jump mechanism. Another possible mechanism is the vehicle mechanism, where the protons stick to water molecules diffusing inside the membrane. PVA is a hydrophilic substance holding a large amount of water, thereby increasing the number of protons in the membrane. However, PVA membrane may absorb water molecules so strongly that the motion of protons is not efficient. This implies that hydrophilicity is one of the important factors to increase proton conductivity even though the material

Table 4: Ionic conductivities from the impedance method, methanol permeabilities, together with the selectivities, σ/P_S, of the membranes.

Membrane	σ, ionic conductivity (mS cm^{-1})	$P_S \times 10^6$, methanol permeability (cm^2 s^{-1})	$\sigma/P_S \times 10^{-6}$ (mS $\cdot$ s $\cdot$ cm^{-3})
CS	0.69	0.79	0.87
CS_X	1.50	0.60	2.49
CS/PVA	4.05	0.36	11.10
CS/PVA_X	4.17	0.21	20.15
CS-g-PVA/PVA	0.96	0.24	3.92
CS-g-PVA/PVA_X	4.37	0.18	23.95
PVA	1.43	0.24	5.94
PVA_X	2.24	0.14	15.61
Nafion 117	44.82	2.74	16.35

is nonelectrolyte. PVA molecules in CS/PVA and CS-g-PVA/PVA membrane could increase water absorbability when compared with CS membrane, leading to higher ionic conductivity. The blended membrane, CS/PVA membrane, however, performed better than CS-g-PVA/PVA membrane because the latter had a fewer number of amino groups. During graft copolymerization process, some of amino groups were grafted with PVA chains, resulting in the reduction of proton conductivity channels.

Table 4 also indicates that proton conductivity increases when the membrane is crosslinked. In a crosslinked membrane, in addition to more number of ions in the membrane, the hopping of protons from sulfate groups to others in the crosslinking network should be responsible for the increase in proton conductivity. Upon crosslinking, the conductivity of the PVA, CS, and CS/PVA membranes increased. The comparison can be made in terms of selectivity defined as the ratio of ionic conductivity and the methanol permeability (σ/P_S). The values are given in Table 4. The selectivity of CS-g-PVA/PVA membrane is close to that of CS/PVA membrane, which is in turn greater than that of Nafion 117 membrane.

Besides, the effect of methanol on proton conductivity of the membrane is of importance. In DMFC, the concentration of the mixtures of water and methanol will change during the reaction in the cell. The proton conductivity of the crosslinked membrane saturated with methanol solution of varied concentration was observed and reported in Figure 4. The initial concentration of the methanol solution was varied to be 0%, 20%, 50%, 80%, and 100% by weight. Figure 4 reveals that the proton conductivity of the membrane decreases as the methanol concentration increases. When the methanol concentration was increased up to 20%, the proton conductivity of Nafion 117 membrane dropped drastically from 49.5 to 5 mS cm^{-1}, while others slightly decreased. The conductivity of Nafion 117 membrane was even lower than others when the methanol concentration reached 100%. This drawback of Nafion 117 membrane is consistent with its methanol uptake result. Methanol may block the proton conductivity channel in the membrane causing the reduction of proton conductivity. Therefore, in actual DMFC which contains methanol at concentration about 6% or about 2 M [27] Nafion 117 membrane is not a good membrane at all. The CS-g-PVA/PVA membrane seems to be a potential candidate
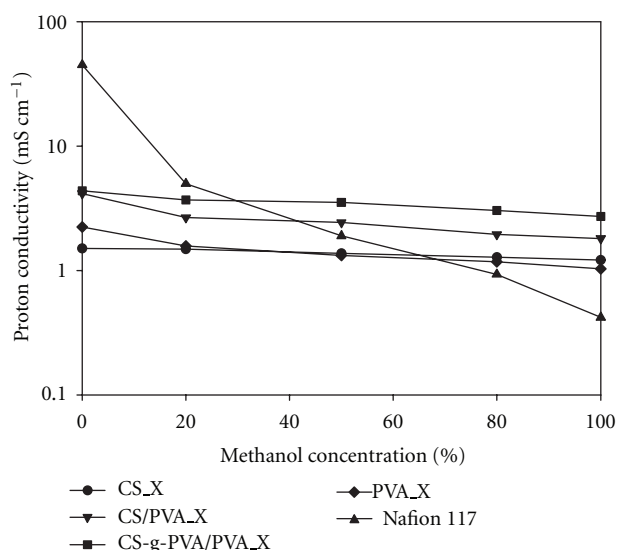

Figure 4: Proton conductivities of crosslinked membranes at various concentrations of methanol solutions.

in DMFC, provided that the methods to enhance the proton conductivity have to be thoroughly investigated. This is our focus and the investigation is still going on.

4. Conclusions

Even though Nafion 117 membrane had better properties, including mechanical properties and proton conductivity, than CS-g-PVA/PVA membrane, the obvious drawbacks of Nafion 117 membrane are its high cost and high methanol uptake which could lessen proton conductivity dramatically. The ionic conductivity, σ, of the crosslinked CS-g-PVA/PVA membrane was about 4.37 mS cm^{-1} and the methanol permeability, P_S, was 1.8×10^{-7} cm^2 s^{-1}. These yielded the selectivity, σ/P_S, of 23.95 mS$\cdot$s$\cdot$cm^{-3} compared with 16.35 mS$\cdot$s$\cdot$cm^{-3} of Nafion 117 membrane.

This study showed that CS-g-PVA/PVA was a potential alternative material to be utilized as an electrolyte membrane in a direct methanol fuel cell because of the following reasons. Firstly, CS-g-PVA/PVA membrane consisted of PVA

that could absorb greater amount of water, compared with CS membrane. Moreover, PVA could prevent methanol from crossing over the membrane. Secondly, CS-g-PVA/PVA membrane had an advantage over CS/PVA membrane in the aspect of mechanical properties particularly in wet state. PVA chains in CS-g-PVA/PVA made CS-g-PVA/PVA membrane stronger and more flexible in dry state and the membrane still had good stability in wet state. Finally, CS-g-PVA/PVA membrane had higher proton conductivity than pure chitosan and pure PVA membranes. Although the proton conductivity of CS-g-PVA/PVA membrane seemed to be lower than CS/PVA membrane, CS-g-PVA/PVA membrane was more durable than CS/PVA membrane, that is, not being dissolved in water and the mechanical properties did not change much when it was wet. In addition, the proton conductivity of CS-g-PVA/PVA membrane changed only slightly when the membrane was tested with methanol solutions with various concentrations. Besides, its performance was easily enhanced by using a crosslinking agent and by adding some electrolyte fillers, which should be investigated further.

Conflict of Interests

The authors do not have any conflict of interests in this research work.

Acknowledgments

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