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Development of polystyrene sulfonate/glycol chitosan hybrid membrane for direct methanol fuel cell

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ABSTRACT

The direct methanol fuel cell (DMFC) is the battery of the system, which directly supplies methanol to the cell containing a polyelectrolyte membrane. As for DMFC, a miniaturization and weight saving in the whole system are possible, because device does not have to constitute reformer. Therefore, DMFC is expected as a power source of a mobile device. Polyelectrolyte membranes for DMFC need a characteristic of the proton conductivity and the reduction of methanol crossover (MCO). In this research, hybrid membrane comprising a polystyrene sulfonate (PSS) and a glycol chitosan (G-Ch) was investigated. PSS/G-Ch hybrid membranes were prepared by cast method and were cross-linked with glutaraldehyde (GA) to reduce the water content. From the Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) measurement, the amino group of the G-Ch origin and the sulfonate group of the PSS origin in hybrid membranes generated ionic bond. On the other hand, the proton conductivity of the hybrid membranes increased with increasing amount of PSS and/or concentration of GA, and maximum value was 0.013 S/cm in case of composition of 4/2/2 (PSS/G-Ch/GA).

Keywords: Direct methanol fuel cell; Polyelectrolyte membrane; Glycol chitosan; Polystyrene sulfonate

1. Introduction

The direct methanol fuel cell (DMFC) has attracted considerable attention in fuel cell technology owing to their stable operation, high-energy efficiency, portable power source, and low environmental burden for mobile electronic devices [1–3]. Protons transfers from anode to cathode are important components in a polyelectrolyte membrane (PEM) with a DMFC system. In addition, methanol crossover (MCO) is another important component. MCO is phenomenon that methanol is transported to the cathode, which decreases the fuel cell efficiency [4,5]. Thus, both high proton conductivity and low methanol permeability are required for PEM of DMFC. However, these two

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factors are trade-off relationship. Because, though existence of water is indispensable for protons transfers so that water has methanol and high affinity.

Currently, Nafion®, a perfluorinated polymer that contains small proportions of sulfonic or carboxylic ionic functional groups, is used most commonly in DMFC. In a hydration state, they provide high proton conductivity as well as excellent thermal stability and chemical stability [6,7]. However, Nafion is expensive to use fluorinated hydrocarbon for membrane material.

Recently, novel membranes has been developed which have low methanol permeability, high proton conductivity, and low cost [8,9]. The most common alternatives are hybrid membranes based on non-perfluorinated hydrocarbon series. In this study, we focused on chitosan, and its derivative as material of membrane. Hydrophilic materials, such as chitosan, are widely used in a membrane separation of alcohol by characteristics such as high hydrophilicity, chemical reactivity, a formability, heat stability, and resistance of organic solvent. Chitosan has many hydroxyl and amino groups, and the cross-linked structure and the salt formation occur by chemical reaction and modification between these active groups. These hydrophilic groups in chitosan membrane hold important role in a selective water permeation and adsorption [10].

In our study, a glycol chitosan (G-Ch) and a sodium salt of polystyrene sulfonate (PSS) were selected as materials of membrane. G-Ch, which is water-soluble derivative of chitosan, can prepare uniform aqueous solution without an acetic acid. This characteristic is used in a protonation of amino groups after mixture of anionic polymer. In addition, we expected to PSS having many sulfonate groups gives PEM the high proton conductivity. However, both PSS and G-Ch having high hydrophilic characteristic, the excessive swelling is expected. Thus, control of swelling in materials of membrane by cross-linking or hydrophobization is necessary. We employed glutaraldehyde (GA) that is typical cross-linking agent for chitosan and is easily reacted at room temperature.

We investigated about preparation methods and characteristics in PSS/G-Ch hybrid membrane cross-linked with GA. We estimated superiority of the hybrid membrane by comparison with Nafion 117.

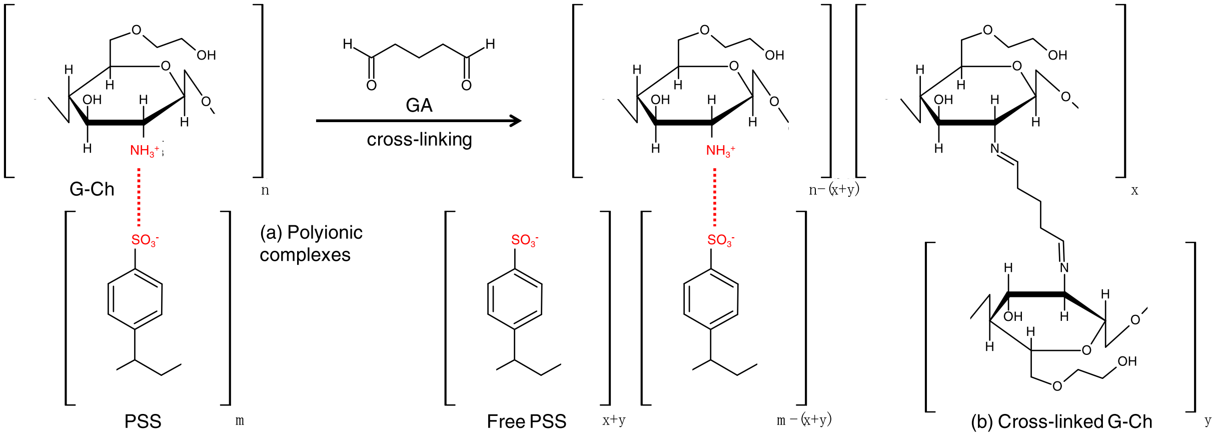
2. Experimental

2.1. Materials

Poly (sodium 4-styrene sulfonate) with an average molecular weight of 1,000,000 g/mol was purchased from Sigma–Aldrich Japan. Glycol chitosan with about molecular weight of 100,000 g/mol was purchased from Wako Pure Chemical Ind., Ltd. Methanol, acetic acid, and 50% glutaraldehyde solution was purchased from Kanto Chemical Co.

2.2. Preparation of membranes

The PSS powder and G-Ch powder of predetermined quantity were added to ion-exchanged water, and it was stirred and was dissolved at 298 K for 24 h. This PSS and G-Ch mixture solution was cast on the glass Petri dish and placed at 298 K for three days. Subsequently, dry membrane was immersed by acetic acid/methanol aqueous solution (volumetric ratio, 5:80:15) for 24 h to form polyionic complexes between the sulfonate group of PSS and the amino group of G-Ch, as shown in Scheme 1(a). Furthermore, it was immersed by GA/methanol solution of predetermined concentrations for 24 h to



Scheme 1. The reaction scheme of the formation of polyionic complexes between PSS and G-Ch and the cross-linked G-Ch.

cross-linked between amino groups of G-Ch, as shown in Scheme 1(b). Finally, the free-standing membrane was obtained by desorption from glass Petri dish with immersing in ion-exchanged water for 24 h. The obtained membrane was saved in ion-exchanged water. In this work, notation of a membrane sample is described as follows: PSS/G-Ch/GA. The number of notation stands for the gravimetric concentration of PSS in cast solution, the gravimetric concentration of G-Ch in cast solution, and the volumetric concentration of GA in methanol solution, respectively.

2.3. Structural characterization (ATR-FTIR)

The Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) spectrum of the sulfonate group in PSS and the amino group in G-Ch were measured by FT/IR-6100 (JASCO Co., Ltd.). The samples of ATR-FTIR measurement were prepared by drying the wet membrane at 333 K for 24 h.

2.4. Water content measurements

The membranes are stored in ion-exchanged water. As for membrane taken out from ion-exchanged water, the mass of wet membrane (M_w) was measured after excessive surface water was removed quickly.

Subsequently, the mass of dry membrane (M_d) was measured after having dried at 333 K for 24 h.

In this work, the water content of membrane was calculated based on a swelling condition as following Eq. (1).

$$\text{Water content } (\%) = \frac{M_w - M_d}{M_w} \times 100 \tag{1}$$

2.5. Methanol permeability measurements

The methanol permeability of the membrane was determined using a side-by-side cell (Fig. 1), which consisted of two identical compartments separated by a vertical test membrane. Before the experiment, the membranes were immersed in 30 vol.% methanol solution over night. The compartment A contained 30 vol.% methanol solution and the compartment B contained ion-exchanged water. Throughout the entire permeation experiment, the contents of both compartments were stirred with a magnetic stir bar at 303 K. The change in the concentration of methanol over time in both compartments was determined by gas chromatography. The methanol permeability (P) was calculated as following.

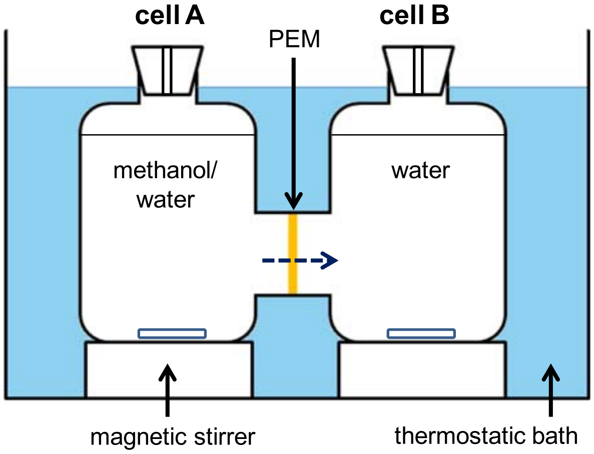


Fig. 1. Schematics of the side-by-side cell for measurements of methanol permeability.

The total molar flux can be represented as (from Fick's Law diffusion):

$$J = K(C_A - C_B) \tag{2}$$

$$K = \frac{P}{l} \tag{3}$$

where K [cm s^{-1}] is overall mass transfer coefficient, C_A and C_B [mol cm^{-3}] are the methanol concentration of compartment A and B, P [cm^2 s^{-1}] is the methanol permeability, and l [cm] is the thickness of the membrane. Here, the material balance is considered, the number of methanol molecule which increased in the compartment B is equal to the number of methanol molecule which permeated the membrane. Thus,

$$V_B dC_B = K(C_A - C_B)A\, dt \tag{4}$$

where A is the area of the membrane (about 12.6 cm^2) and t [s] is a time. Moreover, from initial condition:

$$C_A V_A + C_B V_B = \text{constant} = C_A(0)V_A \tag{5}$$

where V_A and V_B are the volume of the compartment A and B (300 cm^3). Therefore, from Eqs. (3)–(5):

$$\ln\left[\frac{C_A(0)V_A - C_B(t)(V_A + V_B)}{C_A(0)V_A}\right] = -\frac{V_A + V_B}{V_A V_B} \times \frac{P}{l} \times A \times t \tag{6}$$

P can be determined from the slope of the plot of Eq. (6).

2.6. Proton conductivity measurements

The proton conductivity of the hybrid membrane was measured by the four probe method using the Impedance/Gain-phase analyzer SI1260 (Solartron Metrology Ltd.). The custom-made Teflon cell consists of two outer platinum black foils and two inner platinum wires, as shown in Fig. 2.

The samples and Teflon cell were immersed in ion-exchanged water for at least 24 h at room temperature beforehand. A part of samples (about 1 cm square) was fixed in the Teflon cell for measuring an electric current and voltage. The resistance (R [Ω]) of the membrane was measured by applying 100 mV of constant AC voltages in frequency ranges from 1 to 0.1 Hz. The proton conductivity (σ [S/cm]) of membrane was calculated using the following Eq. (7), d (0.5 [cm]) means the distance between the two electrodes, w (1 [cm]) means the width of membrane, and t [cm] means the thickness of membrane, respectively.

$$\text{Proton conductivity} \quad \sigma\ [\mathrm{S/cm}] = \frac{d}{R \times t \times w} \qquad (7)$$

3. Results and discussion

3.1. Visual observation

Fig. 3 shows the optical photograph of the hybrid membrane without cross-linked reaction. The size of a membrane conspicuously increased when amount of PSS on a composition of membrane was doubled. Thus, we investigated about control of swelling of a membrane by cross-linked with GA.

Fig. 4 shows the optical photograph of the hybrid membrane of with cross-linked reaction. The diameter of hybrid membranes 4/2/0.1, 4/2/1, 4/2/1.5, and 4/2/2 were 16, 8, 7.5, and 7, respectively. Thus, the diameter of membranes decreased with increasing the concentration of GA.

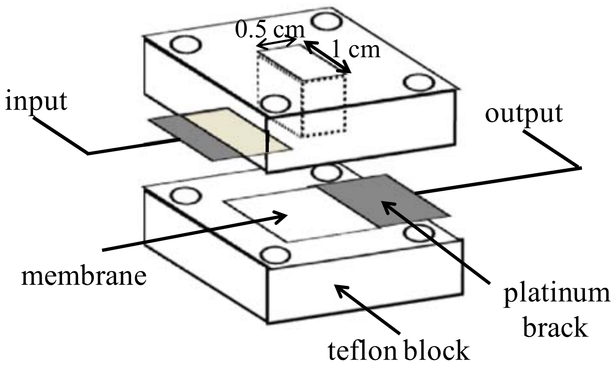


Fig. 2. Schematics of the custom-made Teflon cell for measurements of proton conductivity.

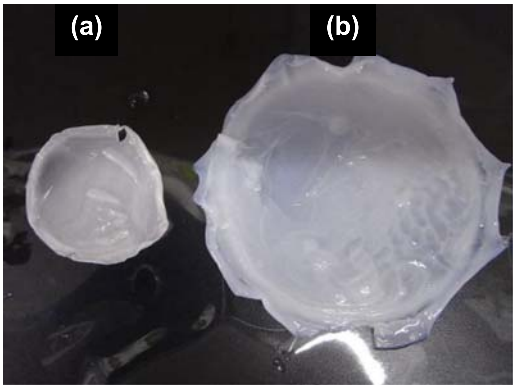


Fig. 3. The optical photograph of the hybrid membrane of 2/2/0 (a), and 4/2/0 (b) without cross-linked reaction.

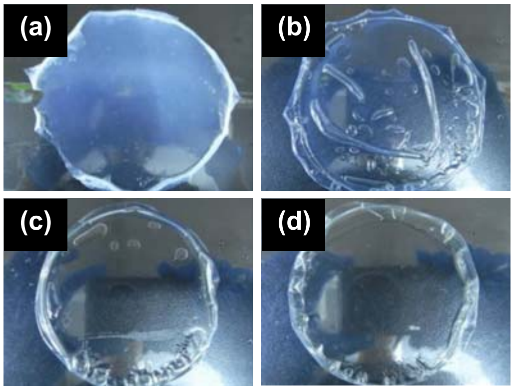


Fig. 4. The optical photograph of the hybrid membrane of 4/2/0.1 (a), (b) 4/2/1 (b), 4/2/1.5 (c), and 4/2/2 (d) with cross-linked reaction.

3.2. Structural characterization (ATR-FTIR)

Fig. 5 shows ATR-FTIR spectrum for the PSS, G-Ch and hybrid membrane 4/2/2. The peak near 1,000 cm^{-1} as shown in Fig. 5(a) was characteristic of the PSS, and correspond to the vibration peak of S=O group. The broad peak near 1,050 cm^{-1} as shown in Fig. 5(b) was characteristic of the PSS, and corresponds to the vibration peak of C–O group etc. The hybrid membrane 4/2/2 formed a polyion complexes because a characteristic peak of PSS and G-Ch appears in Fig. 5(c). However, the peak of the C=N group by cross-linked with GA was not appeared.

3.3. Water content

At first, we explained of the meaning of water content. It is indispensable there is a fluid in the membrane, because a proton moves in the situation fluid exist in the membrane. On the other hand, control of the MCO becomes difficult when membrane has

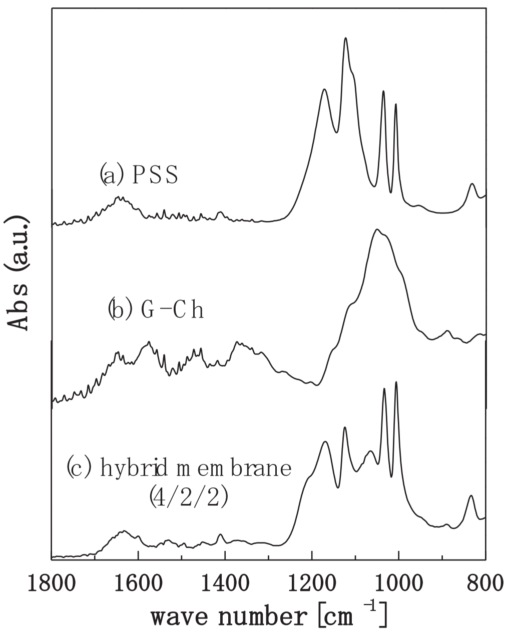


Fig. 5. ATR-FTIR spectrum of PSS (a), G-Ch (b), and hybrid membrane of 4/2/2 (c).

much water, because a methanol which is a fuel has a high affinity with water. We aims a value less than or equal to the Nafion membrane.

Fig. 6 shows the effect of GA concentration on the water content of hybrid membrane at room temperature. The more increase GA concentration, the lower water content of the hybrid membranes. But it was still higher than that of Nafion membrane. Because the more increase the quantity of PSS, the more increase sulfonate group, and it occurs water content is not lower than Nafion by hydrating of sulfonate group of more PSS. We think from now on that the further reduction in water content is required for the reduction of MCO.

3.4. Methanol permeability

Fig. 7 shows the effect of GA concentration on the methanol permeability of hybrid membrane at 303 K. As the concentration of GA increased, the methanol permeability of hybrid membrane decreased from 5.4×10^{-6} to 2.1×10^{-6} cm^2 s^{-1}, which is as much as that of Nafion membrane. It indicated that cross-linking by GA made membranes reduce water content. Though hybrid membrane consisted of hydrocarbon series, methanol permeability of that was lower than that of Nafion totally, because both PSS and G-Ch are highly hydrophilic polymers. PSS has many sulfonate groups. And for sure chitosan membrane can block alcohol series well, but water-soluble derivative of chitosan cannot

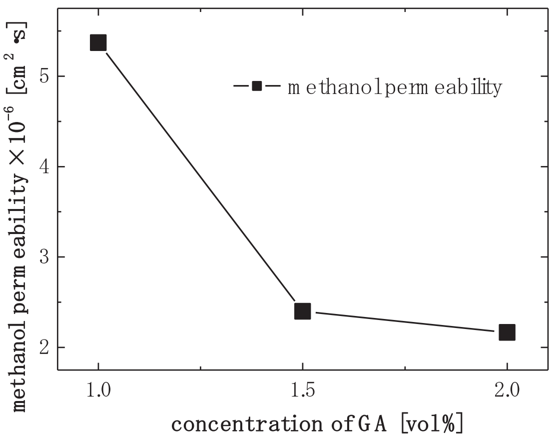


Fig. 7. Effect of GA concentration on the methanol permeability of hybrid membrane.

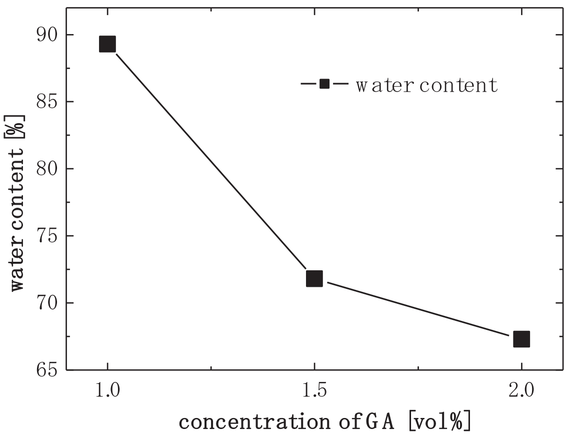


Fig. 6. Effect of GA concentration on the water content of hybrid membrane.

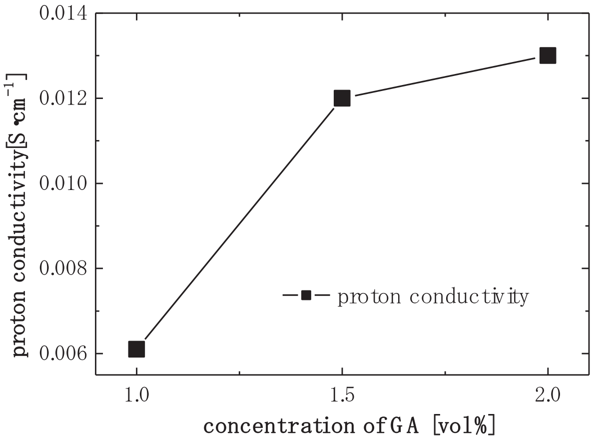


Fig. 8. Effect of GA concentration on the proton conductivity of hybrid membrane.

Table 1
The properties of PSS/G-Ch hybrid membranes and Nafion 117 membrane

Membrane (PSS/G-Ch/GA)	Thickness [μm]	Water content [%]	Methanol permeability $\times 10^{-6}$ [$cm^2 s^{-1}$]	Proton conductivity [S cm^{-1}]	Selectivity [$S s cm^{-3}$]
4/2/1	165	89.3	5.4	0.0061	1,136
4/2/1.5	102	71.8	2.4	0.0120	5,003
4/2/2	97	67.3	2.1	0.0130	6,003
Nafion 117	183	23	2.0	0.1000	–

block alcohol series. From Fig. 7, methanol permeability and water content were decreased in the same way with increasing GA concentration. Thus, it is necessary to reduce water content for the reduction of MCO.

3.5. Proton conductivity

Fig. 8 shows the effect of GA concentration on the proton conductivity of hybrid membrane and Nafion membrane at room temperature. The proton conductivity of 2/2/0 was 0.001 S/cm. In the case of hybrid membranes of 4/2 system which doubled PSS, the proton conductivity increased. This is because quantity of the sulfonate group in the membrane increased. Moreover, the proton conductivity of the hybrid membranes increased with increasing of GA concentration. Because matrix structure of a membrane became minuteness by progress of cross-linked reaction, the distance between sulfonate groups became short. As a result, the proton conductivity of 4/2/2 hybrid membrane was 0.013 S/cm. This value was about 10 times in comparison with Nafion membrane.

From the results of proton conductivity and methanol permeability, we calculated the selectivity parameter to directly compare the applicability for DMFC between the membranes. Table 1 shows the properties of PSS/G-Ch hybrid membranes and Nafion 117 membrane. Higher value of selectivity means that a performance of a hybrid membrane is superior. In addition, the hybrid membrane cannot directly compare value of selectivity with Nafion membrane because the measurement methods are different. The selectivity was increased with increasing of GA concentration. In our experiment, 4/2/2 hybrid membrane was optimal composition from selectivity.

4. Conclusions

In this study, we prepared PSS/G-Ch cross-linked by GA hybrid membrane for DMFC and measured structure of hybrid membrane, water content, methanol permeability, and proton conductivity. It was possible the PSS/G-Ch hybrid membrane of the swelling controlled, the methanol permeability reduced, and the proton conductivity increased by cross-linked with GA. It reveals that the chitosan-based hybrid membrane of polyionic complexes have higher proton conductivity value than that of the other polyionic complexes membranes, but lower than that of Nafion membrane and have just about equal methanol permeability as compared with Nafion. The experimental results revealed that the 4/2/2 hybrid membrane exhibited high performance compared with other. From now on, we think of using the other cross-linking agent to decrease the water content and methanol permeability, more and more PSS to increase the proton conductivity.

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