Sulfonic acid group을 갖는 PVA/Silica Hybrid막의 DMFC 응용

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PVA/Silica Hybrid Membrane Containing Sulfonic Acid Group for Direct Methanol Fuel Cells Application

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요 약: 본 연구에서는 설폰기를 함유한 sulfosuccinic acid를 가교제로 사용하였다. 또한, 메탄올 투과도를 줄이기 위해 실리카를 졸-겔 방법을 사용하여 성장시킨 PVA/Silica 하이브리드막을 제조하여 수소 이온 전도도 및 메탄올 투과도에 관하여 연구하였다. 수소 이온 전도도 및 메탄올 투과도는 가교제 농도 및 친수성 SO3H의 함량에 영향을 받았으며, 제조된 막의 수소 이온 전도도는 $10^{-3} \sim 10^{-2}$ S/cm 범위에 있었고, 메탄올 투과도는 $10^{-8} \sim 10^{-7}$ cm²/s 를 갖는다.

Abstract: In the present study, crosslinked poly(vinyl alcohol) (PVA) membranes were prepared at various crosslinking agent content using sulfosuccinic acid (SSA) containing sulfonic acid group (SO_3H). To reduce methanol permeability, silica was introduced to the membrane using sol-gel process. The hybrid membranes were studied in relation to proton conductivity and methanol permeability. It was found that both these properties were very dependent on the effect of SSA content as a crosslinking agent and as a donor of hydrophilic SO_3H group. The proton conductivities of these PVA/SSA/Silica membranes are in the range from 10^{-3} to 10^{-2} S/cm and the methanol permeabilities are in the range from 10^{-8} to 10^{-7} cm²/sec.

Keywords: PVA-SiO₂ hybrids; Sol-gel process; sulfosuccinic acid; proton conductivity

1. Introduction

A direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are one of the most attractive power sources for a wide range of application from vehicles to portable utilities due to the stable operation at a rarely low temperature, the high energy generation yield and energy density, the simplicity of system [1,2]. Most DMFC research has concentrated on polymer electrolyte membrane fuel cells (PEMFC) fed directly with methanol [3]. Methanol itself is a fuel that possesses significant electroactivity and can be oxidized directly to carbon dioxide and water in so called direct methanol fuel cells [4,5]. The proton diffusion across the membrane is associated with water transport in the membrane and methanol is also transported to the cathode by electro-osmotic drag, that is, methanol crossover, due to the similar properties of methanol (such as its dipole moment), and consequently, a decrease in cell performance [6,7]. In order to improve the performance of the DMFC, it is necessary to eliminate or, at least, to reduce the loss of fuel across the cell [8].

Considerable effort has been developed in order to

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reduce methanol crossover as well as to reach high proton conductivity ($\sim 10^{-2}$ S/cm). Membranes containing metallic blocking layers were proposed [9]. Organic-inorganic composite membranes containing Zr-phosphonates [10], tin doped mordenites [11], zeolites [12] or silica [13] was investigated.

The preparation of hybrid organic-inorganic composites has attracted much attention because such hybrids may show controllable properties such as optical, electrical and mechanical behaviors by combining the properties of both organic polymer and inorganic compound [14,15]. In the organic-inorganic hybrid, inorganic minerals precipitate in situ regularly in the organic polymer matrix, and the strong interaction between the organic polymer and inorganic mineral may result in a hybrid of markedly improved mechanical properties. Stating materials for the sol-gel process are metal alkoxides and a small amount of acid or base as catalyst. Hybrids are prepared usually through a sol-gel process by incorporating organic polymers with alkoxysilanes, mainly tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) [15].

Commercial poly (vinyl alcohol) (PVA) is derived from poly(vinyl acetate (PVAc), and major applications of PVA are paper and textile sizing, oxygen resistant films, adhesives, food wrappings, desalination membranes, and pervaporation membranes [16]. In particular, PVA membrane has been used in ethanol dehydration to break the ethanol-water azeotrope because it selectively passes water molecule over ethanol or methanol [17-19].

In this study, the PVA/SiO₂ nanocomposites hybrid membranes containing sulfonic groups have been synthesized through sol-gel processes. The introduction of sulfonic acid group into PVA matrix was achieved by the modifications of PVA chemical structure through esterification with sulfosuccinic acid (SSA) having carboxylic groups. Here, we might expect that the introduction of sulfonic acid group and silica together with crosslinking into hydrophilic PVA matrix might lead to both high proton conductivity due to addition of sulfonic acid and low methanol permeability due

to crosslinking between PVA chains and Silica domain as a methanol barrier.

2. Experimental

2.1. Materials

Polymer used in this study was PVA (99% hydrolyzed, average Mw = 85,000 146,000; Aldrich) and sulfosuccinic acid (SSA, 70 wt% solution in water) as a crosslinking agent was purchased form Aldrich Co. (Milwaukee, USA). The tetraethyl orthosilicate (TEOS) and methanol (MeOH) were analytical grade from Aldrich Co. and the distilled and deionized water was used in this study.

2.2. Membrane preparation

The PVA was dissolved in pure water at 90°C with a concentration of 10 wt% and was stirred constantly to ensure homogeneity.

Inorganic-organic hybrids based on PVA and sol-gel derived silica were prepared by dissolving PVA in water followed by the addition of TEOS mixture to the solution. A homogenous TEOS mixture was prepared by mixing H₂O/HCl/TEOS in a mole ratio of 4/0.1/1, which were stirred at room temperature for 2 hr. After homogenization, the PVA/TEOS solutions were mixed together with the SSA by varying each component composition and stirred at room temperature for 12 hr. The homogeneous solution was poured into a Petri dish. The membranes were allowed to dry in air at room temperature, and completely dried membranes were then peeled off. The dried membranes were then heated in an oven at 120°C for 1hr to induce crosslinking. The PVA/SiO₂/SSA hybrid membrane (named as PVTS-) was obtained. The experimental condition of polymer solution was shown in Table 1.

2.3. Membrane characterization

FT-IR spectra of membranes were measured by Nicolet IR 760 spectra E.S.P in the 4000-500 cm⁻¹ ranges.

To investigate the morphology of films, fracture

Table 1. Experimental Conditions of Polymer Solutions

Sample	PVA (wt%)	TEOS (wt%)	SSA (wt%)
PVTS 5	10	5	5
PVTS 10	10	5	10
PVTS 15	10	5	15
PVTS 20	10	5	20
PVTS 25	10	5	25

surfaces were investigated by field emission scanning electron microscope (FE-SEM, Jeol Model JSF 6340F, Tokyo, Japan).

The process of degradation and thermal stability of films were monitored by thermogravimetric analysis (TGA, Perkin-Elmer TGA7). The TGA measurements were carried out under the nitrogen atmosphere at a heating rate of 10°C/min from 50 to 700°C.

## 2.4. Measurement of water swelling ratio

After soaking the samples in distilled water for more than 24 hr, they were wiped filter paper and weighed immediately. The samples were then dried at 60°C under a vacuum condition until a constant weight was obtained. Water swelling ratio was determined by the following equation:

$$\text{Water swelling ratio} = \frac{W_{wet} - W_{dry}}{W_{dry}} \qquad (1)$$

Where, W_{wet} and W_{dry} are wet and dried membrane weight, respectively.

2.5. Ion-exchange Capacity (IEC)

The ion exchange capacity (known as IEC value) was measured by the classical titration (ASTM 2187). After immersing the samples in distilled water, they were soaked in a large volume of 0.1 mol/L HCl solution to change them into H$^+$-form. They were washed with distilled water to remove excess HCl and then equilibrated with exact 100 mL of 0.1 mol/L NaOH solutions for 24 h. IEC was determined from the reduction in alkalinity measured by back titration. IEC of the cation-exchange was calculated by the following equation:
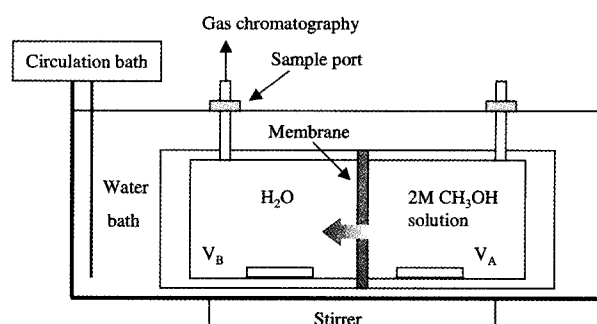
Fig. 1. Two chamber diffusion cells used to measure methanol permeability through membranes in this study.

$$\text{IEC} = \frac{M_{o,NaOH} - M_{E,NaOH}}{W_{dry}} \qquad (2)$$

Where, $M_{o,NaOH}$ is milli-equivalent (meq.) of NaOH in the flask at the beginning of titration, $M_{E,NaOH}$ is meq. of NaOH after equilibrium, and W is the weight of dry membrane (g).

2.6. Ion Conductivity Measurement

The ion conductivity of membrane was determined using LCR hitester (Reactance Capacitor Resistor, Hioki Model 3522). Prior to the measurement, the membrane samples were immersed in 1mol/L H$_2$SO$_4$ solution at 25°C over 1day and then inserted into the cell and current (1V) was supplied by LCR hitester with a frequency 1000 Hz. The ion conductivity (σ) was obtained by a following equation;

$$\sigma = \frac{l}{R \cdot S} \qquad (3)$$

where σ is proton conductivity (S/cm), l is membrane thickness (cm), R is resistance (Ω) and S is surface area for ion to penetrate through (cm^2).

2.7. Methanol Permeability

Methanol permeability of the membranes was determined using the diaphragm diffusion cell (Fig. 1) [20]. This cell consisted of two reservoirs each approximately 60 mL, separated by a vertical membrane. The membrane was clamped between the two reservoirs and they were stirred during the experiment. Prior to

the test, the membranes were equilibrated in deionized water for at least 12 h. Initially, one reservoir (V_A) contained 2 M methanol-water solutions and the other reservoir (V_B) contained only pure ionized water. Concentration of methanol in the initially pure water reservoir was measured versus time using gas chromatography. For gas chromatography, 1 μL samples were analyzed using a Shimadzu GC-14B gas chromatograph. During permeability tests the temperature was controlled by means of a thermostatic water bath.

A flux of methanol penetrates across the membrane as a result of the concentration difference between the two compartments. Under pseudosteady-state conditions, which prevailed during our experiments and for $c_B \gg c_A$, the methanol concentration in the receiving compartment as a function of time is given by:

$$c_B(t) = \frac{A}{B_B} \frac{DK}{L} c_A(t - t_0) \qquad (4)$$

where C is concentration, A and L the membrane area and thickness; D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The assumptions are made in this study that D inside the membrane is constant and K does not depend on concentration. The product DK is the membrane permeability ($P(cm^2/s)$).

$$P = \frac{1}{A} \cdot \frac{c_B(t)}{c_A(t - t_0)} \cdot V_B L \qquad (5)$$

C_B is measured several times during the experiment and the permeability is calculated from the slope of the straight line.

3. Results

3.1. FT- IR Spectroscopy

The FT-IR spectra of the prepared membranes are shown in Fig. 2 for PVA film, pure silica and hybrid membranes. The pure silicate shows a characteristic band at 800 cm^{-1} (symmetric Si-O-Si stretching), 1080 cm^{-1}
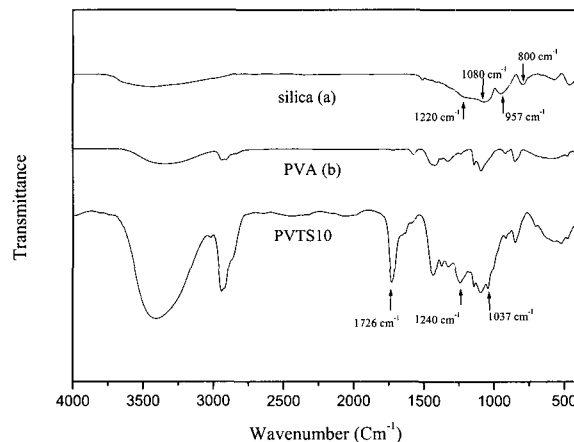

Fig. 2. FT-IR spectra of the membranes. (a) Pure silica (b) PVA film (c) Crosslinked PVA/Silica/SSA membrane.

and 1220 cm^{-1} (asymmetric Si-O-Si stretching), and 957 cm^{-1} (Si-OH stretching). The hybrid membranes (PVTS10) with sulfosuccinic acid show the characteristic ester absorption band at 1726 cm^{-1} (-CO-O-, sulfosuccinic acid). The 1240 cm^{-1} absorption band arose from the C-O stretch mode in the ester group. Furthermore, the absorption band of 1037 cm^{-1} means that of SO$_3$H. Therefore, it is clear that the spectral changes are evidences of crosslinking reaction between the hydroxyl groups of PVA and the carboxylic groups of SSA In addition, the broad band at around 1080~1220 cm^{-1} (Si-O-Si asymmetric stretching) are seen to the spectra of PVTS10 hybrid membrane. This indicates that the esterification reaction was completed between PVA chains and SSA and hybridization was done via sol-gel reaction. The broad absorption peak at around 3400 cm^{-1} in PVTS10 hybrid membrane indicated that there was a significant amount of -OH group. These non-condensed -OH groups provided the sites for hydrogen bonding between PVA and hydrated silicate and/or SSA, resulting the homogeneous membranes.

3.2. Scanning Electron Microscope

Fig. 3 shows SEM images of the hybrid membranes. Silica microparticles are observable. The average size of the silica microparticles is about <50 nm. The silica microparticles was confirmed by energy-dispersive X-
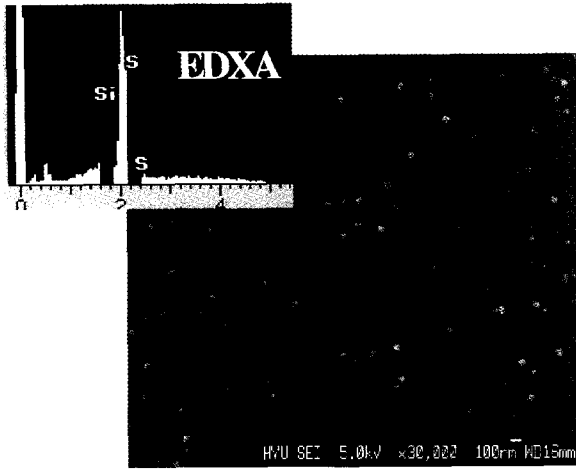
Fig. 3. FE-SEM image of hybrid membrane of top surface.
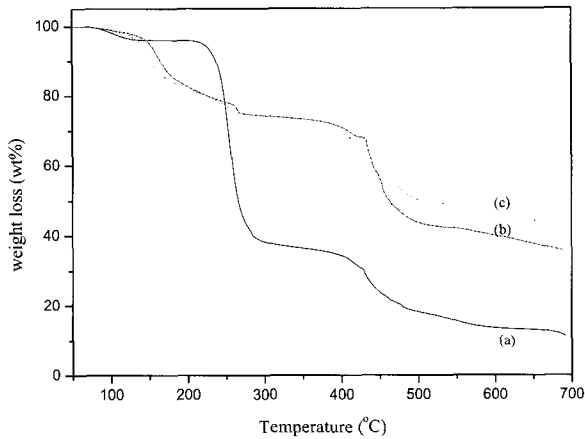

Fig. 4. TGA curves of membranes (a) Pure PVA (b) PVTS 10 (c) PVTS 20.

ray analysis (EDXA).

We expect that the silica microparticles distribution in PVA matrix might lead to reduce methanol permeability.

3.3. Thermal Analysis

The TGA curves of membranes under nitrogen are shown in Fig. 4. TGA curve of membranes can be fitted by three main degradation steps. They are due to the process of thermal salvation, thermal desulfonation and thermooxidation of a polymer matrix, respectively. The first weight loss process above 100°C was associated with the loss of absorbed water molecules or water molecules formed after esterification in

membranes. Most of the absorbed water molecules in the membranes are supposed to exist in a bound state rather than in a free molecular state [21]. The water molecule seem to be bound directly to the polymer chain and/or the SO3H due to hydrogen bond.

As observed in Fig. 4, there is a weight loss of 60% at a temperature of 260°C for the pure PVA membrane. The weight loss around 450°C was considered to reflect the decomposition of main chain (T-dm) of PVA.

However, for PVA/SSA/silica membranes, the second weight loss process (between 250 and 400°C) corresponded to a loss of sulfonic acid by the desulfonation of sulfosuccinic acid and a breakage of crosslinking bonds (-CO-O-). In the third weight loss process (after 400°C), the polymer residues were further degraded at approximately 450°C, corresponding to the decomposition of main chain of PVA.

In the case of hybrid composite membranes, the weight remained after decomposition is dependent on the content of inorganic component and crosslinking density. That is, the weight residue of PVTS10 and PVTS 20 hybrid membranes containing silica at 700°C is higher than that of pure PVA membrane. Also, the weight of residue of PVTS20 membranes at 700°C is higher than that of PVTS10 due to crosslinking density.

These results suggest that the crosslinking density and the introduction of silica into PVA chain clearly enhance of the thermal stability of the given hybrid materials.

3.4. Ion Exchange Capacity (IEC) and Water Content

Fig. 5 and Table. 2 show ion exchange capacity (IEC) and water content as a function of SSA content (wt%). As shown Fig. 5, the experimental values were comparable to theoretical ones. The prepared proton exchange membranes at each preparation condition possessed the IEC in the range of 0.2~1.1 meq./g-dry membrane. These results confirmed that experimental IEC values by a titration fit well. The IEC increase
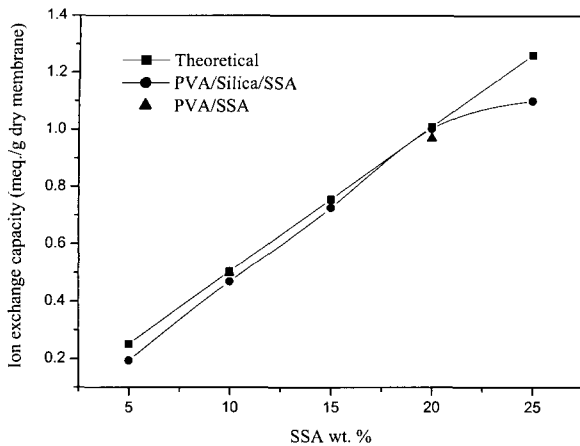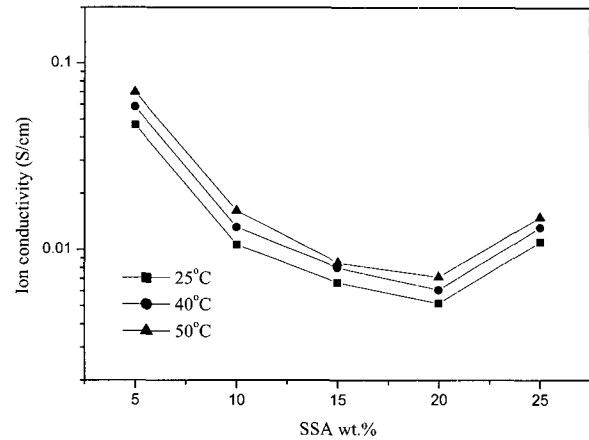
Fig. 5. Ion exchange capacity versus SSA wt%.

Table 2. The IEC and the State of Water Content

Sample	Theoretical IEC (meq./g)	IEC by titration (meq./g)	Water content (%)
PVTS 5	0.25	0.2	60.6
PVTS 10	0.51	0.47	46.5
PVTS 15	0.75	0.73	42.3
PVTS 20	1	1	33.5
PVTS 25	1.26	1.1	49.9

with the SSA concentration to its maximum value at 25 wt% SSA.

The total water content decreased until SSA content was 20 wt%, indicating an increase in the crosslinking density of the membranes to makes the polymer structure more compact and rigid and decrease free volume. However, above 20 wt% SSA content, total water content of the hybrid membranes increased slightly, owing to the increase of hydrophilic group (-SO₃H) in the polymer. This result suggest that the water content more depend on crosslinking density rather than SO₃H content up to 20 wt% SSA. But, above 20 wt%, the water content depend on SO₃H content.
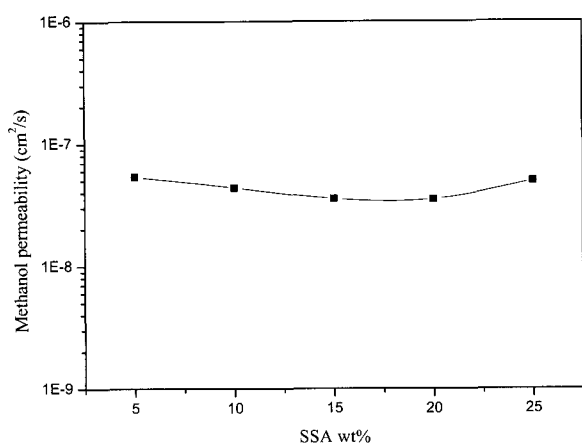
3.5. Proton Conductivity

Fig. 6 is plot of the proton conductivities as a function of the SSA concentration and temperature and the measured data were summarized in Table 3. The proton conductivity of hybrid membranes measured at 25, 40 and 50°C are in the range between 10^{-3} and

Fig. 6. Proton conductivity versus SSA concentration.

10^{-2} S/cm. As shown in Fig. 6, the conductivity decreased up to 20 wt% SSA content and above this content increase. This behavior shows the same tendency of water content (Table. 2). Although IEC increased with SSA concentration, ion conductivity decreased. Before a trial for the conductivity measurement, we expected that increase of SSA content in PVA matrix might lead to the improvement of the proton conductivity because the amount of sulfonic groups (-SO₃H) in PVA matrix was increased. In addition, these expectations were based on IEC values of membranes measured before the conductivity measurement. However, the crosslinking degree of SSA in PVA matrix turned out quite insensitive to the proton conductivity. That was controlled by reacting PVA with different amounts of SSA. As shown in Fig. 6, the membranes containing SSA up to 20 wt% were considered to be partially crosslinked when compared to membrane containing above this SSA content. Here we can say that only increase of IEC values by introduction of sulfonic acid group in these proton exchange membranes is not primary factor to increase the proton conductivities. That is, free volume being capable of containing water molecules in the polymeric structure should be seriously considered in the polymer design. From the results of water content and proton conductivity, increase of crosslinking density in membranes leads to reduction of free volume being able to associate water molecules and thus is followed

Table 3. Ion Conductivity and Methanol Permeability

Sample	Ion conductivity (x 10^{-2} S/cm)			Methanol permeability (x 10^{-8} cm^2/s) at 25°C
	25°C	40°C	50°C	
PVTS 5	4.67	5.83	7.0	5.36
PVTS 10	1.06	1.32	1.61	4.37
PVTS 15	0.67	0.8	0.85	3.54
PVTS 20	0.52	0.61	0.71	3.52
PVTS 25	1.1	1.31	1.49	4.95

Fig. 7. Methanol permeability of membranes measured at 25°C as a function of SSA content (wt%).

by decrease of proton conductivity. This result suggests that amount of crosslinking density with appropriate IEC values should be optimized in order to obtain the desirable proton conductivity.

3.6. Methanol Permeability

The methanol permeabilities through membranes were calculated using the eq(5), and the results were illustrated as a function of SSA content and with/without silica in Fig. 7 and listed in Table 3. As shown Fig. 7, the methanol permeabilities through hybrid membranes decreased up to 20 wt% SSA content and above 20 wt% SSA increased. Uphill and downhill trends of methanol permeabilities as a function of crosslinking agent (SSA) might be considered as two factors. Those are the effects of crosslinking by SSA and hydrophilic groups (-SO3H) involved in SSA. The effect of crosslinking dominates the methanol transport behavior until 20 wt% SSA content. Above 20 wt% SSA content, however, the effect of hydrop-

hilic SO3H groups contained in SSA exceeds the effect of crosslinking. This result suggest that the silica particle precipitate in the organic polymer matrix, and the strong interaction between the organic polymer and silica could be result in a hybrid of markedly reduced methanol permeability. The methanol permeability behavior of hybrid membrane is very similar to proton conductivity of PVA/SSA membranes.

3. Conclusion

Organic-inorganic hybrids, based on PVA/SiO2 hybrid membranes containing sulfonic acid groups, were successfully prepared via polymerization of PVA, sulfosuccinic acid (SSA), and TEOS using the sol-gel process.

The PVA/SSA/Silica hybrid membranes were investigated in relation to proton conductivity and methanol permeability. It was found that both these properties were very dependent on the effect of SSA content as a crosslinking agent and as a donor of hydrophilic SO3H group, respectively. Both these properties decrease up to SSA concentration of about 20 wt% and above this concentration increase with SSA content. The methanol permeabilities through PVA/SSA/Silica membranes were linearly proportional to the proton conductivities. The silica particle precipitate in the organic polymer matrix, and the strong interaction between the organic polymer and silica could be result in a hybrid of markedly reduced methanol permeability.

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