

설펜산기를 함유한 PVA막의 직접 메탄올 연료전지 응용

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Poly(vinyl alcohol) Membranes Containing Sulfonic Acid Groups for Direct Methanol Fuel Cell Application

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요 약: 본 연구에서는 polyvinylalcohol(PVA)의 hydroxyl 작용기와 sulfosuccinic acid (SSA)의 carboxylic acid 작용기의 반응을 통하여 열가교된 PVA막을 제조하였다. 설펜산기를 함유한 SSA는 PVA 매트릭스에 대한 가교제의 역할뿐만 아니라 수소이온의 전도도를 높이는 역할 모두를 수행하였다. PVA의 가교도(degree of crosslinking)는 SSA의 함량으로 조절하였고 가교밀도(crosslinking density)는 극성 및 비극성 용매를 이용하여 계산하였다. Xylene 및 benzene과 같은 비극성 용매를 사용한 경우 가교밀도는 SSA 함량에 따라 증가하였다. 그러나, 물과 methanol과 같은 극성 용매를 사용한 경우 가교밀도는 SSA 함량 20%까지 증가하다가 그 이상의 함량에서는 설펜산기의 영향으로 감소하였다. 가교도와 확산계수, 기계적 물성 및 전도도, 메탄올 투과도 등에 대한 PVA막의 특성을 평가하였고 이들 특성은 SSA 함량에 의존하였다.

Abstract: Crosslinked PVA membranes were achieved by esterification between the hydroxyl groups of PVA and carboxyl group of sulfosuccinic acid (SSA). SSA containing sulfonic group was used as a chemical crosslinking agent as well as a donor of fixed anionic group ($-SO_3H$). The crosslinking density of membranes was controlled by SSA content and calculated using polar and non-polar solvent. The crosslinking density measured by using non-polar solvent such as xylene and benzene increases with SSA content. However, using the polar solvent such as water and methanol, the crosslinking density increases up to SSA content of 20 wt% and above the content decrease due to sulfonic acid groups. The crosslinked PVA membranes were studied in relation with water diffusion coefficient and mechanical property as well as proton conductivity and methanol permeability as a function of crosslinking density. These properties were all dependent on the effect of SSA content.

Keywords: proton conductivity, methanol permeability, crosslinked poly(vinyl alcohol) membranes, direct methanol fuel cell, crosslinking density

1. Introduction

The fuel cells have been paid much attention as the promising alternative power sources due to lots of advantages such as high power density and low emis-

sion[1,2]. Among several types of fuel cells, direct methanol fuel cell (DMFC), using the liquid methanol directly as a fuel feed, has been interested as an alternative power source[3]. However, a methanol transport across the membrane has been observed, that is, methanol crossover, consequently, a decrease in cell performance[4,5] In general, the proton conductivity of

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membrane occurs by two mechanisms. Firstly, Grotthus mechanism can be idealized as a proton being passed down a chain of water molecules. The second mechanism is vehicle mechanism, assumes a proton combined with solvent molecules, yielding a complex like H_3O^+ or $CH_3OH_2^+$. It is believed that the proton conductivity and methanol permeability occur through the same pathway, because the behavior of both properties is appeared as the same trend[6]. The smaller size of water cluster in a polymer matrix decreases the methanol permeability and the proton conductivity[6,7]. Therefore, if water clusters in a polymer matrix are controlled by the crosslinking reactions between polymer chains, the methanol permeability can be reduced without much loss of proton conductivity. The morphological stabilization of acidic polymers by either acid/base blending or covalent cross-linking[8,9] appears to reduce swelling and water and methanol crossover. The blending or crosslinking may provide space for the adaptation of the polymer properties to particular fuel cell applications.

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[10-12]. 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[13-16]. PVA is water-soluble polymer that readily reacts with different crosslinking agents, that is, all multi-functional compounds are capable of reacting with the hydroxyl groups of PVA[17]. Therefore, in our previous study[18], we prepared the crosslinked PVA membrane having sulfonic acid group by the modifications of PVA chemical structure through esterification with sulfosuccinic acid (SSA) having carboxylic group. These crosslinked membranes are desirable in applications related with proton exchange membrane for DMFC. In this paper, we focused on the calculation of the crosslinking density of membrane using the polar and/or non-polar solvent and the proton

conductivity and the methanol permeability are investigated as a function of the crosslinking density of membrane.

2. Experimental

2.1. Materials

Fully hydrolyzed PVA with a molecular weight of 89,000-98,000 and sulfur succinic acid (SSA, 70 wt% solution in water) as a crosslinking agent was purchased from Aldrich Co. (Milwaukee, USA). All other chemicals: xylene, toluene, benzene, chlorobenzene, dichloromethane, dioxane and methanol (MeOH) were analytical grade from Aldrich Co. and the distilled and deionized water was used in this study.

2.2. Membrane Preparation

Crosslinked PVA membrane was prepared in the same manner as reported in our previous study[18]. Aqueous 10 wt% PVA solutions were prepared by dissolving preweighed quantities of dry PVA in deionized and distilled water and heating at 90°C for at least 6 h. Then the PVA solutions were mixed together with the SSA solution to form a homogeneous solution for at least 1 day at room temperature. The percentage of SSA was 5, 10, 15, 20, and 25 by weight relative to PVA. Homogeneous solutions were cast onto a Plexiglas plate using a Gardner knife with predetermined draw-down thickness. The membranes were allowed to dry in air at room temperature, and completely dried membranes were heated in a thermoset oven at 120°C for 1 hr to induce crosslinking. The resulting membranes (PS-xx: xx: percentage of SSA) were then stored in water solution to be separated for further use.

2.3. Swelling Measurement

To measure solubility parameter, the degree of swelling was measured using following method. The crosslinked membrane (sample PS 15) was immersed in the selected solvents at 25°C. After being wiped with the cleansing tissue, the membranes were weighed as quickly as possible. This procedure was repeated about 10 times

Table 1. The Molar Volume, Cohesive Energy Densities and Swelling Coefficient of the Used Solvent

Solvent	Molar volume (cm ³ /mol)	δ (cal/cm ³) ^{1/2}	Swelling coefficient (α)
Xylene	123.3	8.8	0.0951
Toluene	106.8	8.9	0.163
Benzene	89.4	9.2	0.079
Chlorobenzene	101.79	9.5	0.067
Dichloromethane	64.02	9.7	0.035
Dioxane	85.2	10	0.009
Methanol	41	14.5	0.171
H ₂ O	18	23.2	0.418

until satisfactory reproducibility was obtained. Then the samples were dried in a vacuum oven to a constant weight. The swelling coefficient (α) was calculated by using the equation[19];

$$\alpha = \frac{M_s}{M_p^* \rho_s} \quad (1)$$

where M_s is the mass of the solvent at equilibrium, ρ_s is density of the solvent and M_p is the initial mass of the membrane sample; α is indicative of the volume of solvent per unit mass of the membrane. The molar volume, cohesive energy densities and swelling coefficient of the solvents used in this study were listed in Table 1.

2.4 Water Vapor Sorption and IEC

To measure water diffusion coefficient, the water vapor sorption experiments were carried out using a dynamic vapor sorption apparatus (DVS-1000, Surface Measurement Systems Ltd., London, UK) at RH 95%.

The Ion-exchange capacity (IEC) was determined by titration. The sulfonic acid group was brought in the proton form by immersion of the membrane in a 0.1 M HCl solution for 24 hr. The membrane was washed thoroughly with water until pH neutral and then immersed into a 0.01 M NaCl solution to replace the H⁺ by Na⁺ ions. The remaining liquid was titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The IEC was expressed as meq.(-SO₃H)/g dry polymer.

2.5. Mechanical Properties

Mechanical properties of the membranes were eval-

uated using an Instron testing machine (Model 4465 with 1 kN load cell, MA, USA) and analyzed in accordance with ASTM D882-91 standard test protocol for thin film tensile tests. All the tests were conducted at a crosshead speed of 10 mm/min. Ten specimens of each tensile sample were tested to provide assurance of good data reproducibility. The percentage strain (λ) was calculated as follows:

$$\lambda = [(L - L_0)/L_0] \times 100\% \quad (2)$$

where L is the total extension measured from the grip displacement and L_0 is the grip distance (20 mm). The initial Young's modulus (E) was calculated from the initial slope of the stress-strain curve obtained. The tensile strength was recorded as stress at ultimate fracture[20]

2.6. Proton Conductivity and Methanol Permeability

Proton conductivity in hydrated PVA/SSA membranes was normally measured with a four-point probe technique. The impedance of membrane was determined by Full Material Impedance System 12608W consisted of a Frequency Response Analyzer 1260 and Electrochemical Interface 1287 (Solatron analytical). Each hydrated membrane for the measurement was prepared with the surface area of 4 cm \times 1 cm and the membrane thickness of 100 to 150 μ m.

Methanol permeability of the membranes was determined using a diffusion cell[18]. This cell consisted of two reservoirs each approximately 80 mL, separated by a vertical membrane. Prior to the test, the mem-

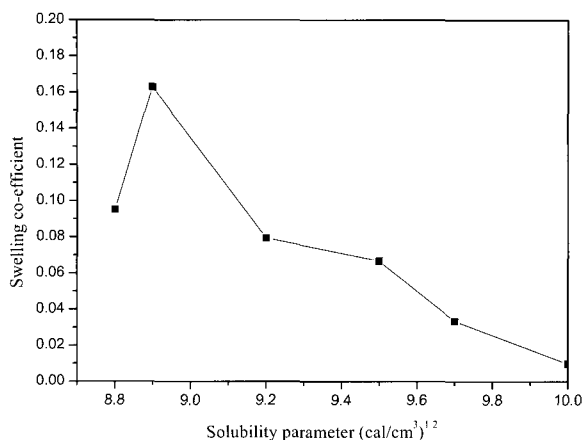


Fig. 1. Swelling coefficient versus solubility parameters of solvent.

branes were equilibrated in deionized water for at least 12 h. Initially, one reservoir contained 2 M methanol-water solutions and the other reservoir contained only pure ionized water. Concentration of methanol in the initially pure water reservoir was measured versus time using gas chromatography. For gas chromatography, 11 samples were analyzed using a Shimadzu GC-14B gas chromatograph. During permeability tests the temperature was controlled by means of a thermostatic water bath. Finally, permeability of methanol was obtained by analyzing the methanol flux with time.

3. Results and Discussion

3.1. Solubility Parameter of Polymer

As a measure of intermolecular interaction use is often made of Hilderband's parameter δ , which is connected with the cohesive energy density (CED, solubility parameter) of a liquid. According to the 'like dissolves like' theory, maximum swelling of a cross-linked polymer can take place in the solvent whose solubility parameter (CED) is similar to that of the polymer[21].

After experimentally determining the swelling coefficient of all samples used in different solvent having different δ (Table 1), the equilibrium swelling coefficient was plotted against the solubility parameter of the solvents as shown Fig. 1 and was listed Table 1. As

shown in Fig. 1, maximum swelling takes place in toluene (non polar solvent, $\delta = 8.9$). However, in polar solvents such as water and methanol, the swelling coefficient is the higher than non polar solvent due to hydrogen bonding between polymer (-OH group of PVA and -SO₃H group of SSA) and water. Therefore, the crosslinking density of membranes was calculated as two directions: (1) In case of non-polar solvent, the solubility parameter of membrane was considered to be 8.9. (2) In case of polar solvent, the solubility parameter of membrane was considered to be 23.2.

3.2. Crosslinking Density

In order to calculate the crosslinking density and molecular weight between crosslinks the polymer-solvent interaction parameter x was calculated using the solubility parameter obtained and the equation[21]:

$$x = \beta + V_s \left\{ \frac{(\delta_p - \delta_s)^2}{RT} \right\} \quad (3)$$

where β is the lattice constant whose value is about 0.34, V_s is the molar volume of the solvent, R is the universal gas constant (1.99 cal/mol K), T is thermodynamic temperature (in kelvins). The δ_p and δ_s are the solubility parameter of polymer and solvent, respectively. The polymer solvent interaction parameter (x) values for xylene, benzene, methanol and water were calculated to be 0.342, 0.355, 5.45, and 0.34, respectively. This result shows that lower x indicates higher interaction of the polymer with xylene in the non polar and water in the polar solvent, respectively, resulting in greater sorption as observed in the swelling studies.

The volume fraction of a polymer (ϕ) in the solvent swollen sample was calculated by using equation:

$$\phi = \frac{M_p / \rho_p}{M_s / \rho_s + M_p / \rho_p} \quad (4)$$

where M_p is the initial weight of the polymer sample, ρ_p is its density, M_s the weight of the solvent in the fully swollen sample, and ρ_s is the density of the

Table 2. Volume Fraction of Polymer (ϕ)

Sample	Xylene	Benzene	Methanol	H ₂ O
PS 5	0.808	0.842	0.680	0.610
PS 10	0.82	0.875	0.766	0.715
PS 15	0.851	0.906	0.790	0.746
PS 20	0.876	0.936	0.867	0.776
PS 25	0.901	0.961	0.758	0.657

Table 3. Volume Equilibrium Degree of Swelling (q)

Sample	Xylene	Benzene	Methanol	H ₂ O
PS 5	1.237	1.188	1.470	1.638
PS 10	1.219	1.143	1.306	1.399
PS 15	1.174	1.104	1.264	1.339
PS 20	1.141	1.069	1.151	1.287
PS 25	1.110	1.040	1.318	1.522

Table 4. Molecular Weight Between Crosslinks (M_c)

Sample	Xylene	Benzene	Methanol	H ₂ O
PS 5	167.61	101.29	15.73	67.25
PS 10	164.85	86.89	14.13	41.87
PS 15	137.99	70.41	13.64	35.71
PS 20	127.30	59.71	13.51	29.61
PS 25	122.11	52.12	17.48	68.46

solvent. The values of ϕ were listed in Table 2. From the results it was observed that volume fraction ϕ of the polymer was directly proportional to the crosslinked density of the polymer and inversely proportional to the sorption extent of the solvent.

As shown Table 2, in the case of non polar solvent (xylene, benzene) the ϕ increased with SSA content. Otherwise, in the methanol and water, the ϕ increased until SSA content was 20 wt%, however, above 20 wt%, the ϕ decreased slightly.

The volume equilibrium degree of swelling ratio (q) is equal to $1/\phi$ and the results were given in Table 3.

One of the most important structural parameters characterizing a crosslinked polymer is M_c , the average molecular weight between crosslinks that is directly related to the crosslinking density. When the polymer sample is immersed in a solvent medium its molecules diffuse into the polymer until the elastic retraction of the network balances the osmotic pressure driving the solvent into the swollen polymer. Equilibrium swelling

is widely used to determine M_c . Early research by Flory and Rehner laid the foundations for the analysis of equilibrium swelling. M_c was calculated from the Flory-Rehner equation[22]

$$M_c = \frac{\rho_p V_s \phi^{1/3}}{\ln(1 - \phi) + \phi + x \phi^2} \quad (5)$$

Here, the crosslink density, is inversely proportional to the molecular weight between crosslinks and is given by the equation[23]

$$v = \frac{1}{2M_c} \quad (6)$$

Substituting the value of x for all samples in equation (5) one can calculate the value of M_c for each sample and using equation (6) the crosslinking density is deduced. The Tables 4, 5 show the values for M_c and v .

As shown Table 5, in the case of non polar solvent

Table 5. Crosslinking Density (ν) of PVA Membranes

Sample	$\nu \times 10^{-3}$			
	Xylene	Benzene	Methanol	H ₂ O
PS 5	2.983	4.937	31.79	7.43
PS 10	3.033	5.754	35.39	11.94
PS 15	3.623	7.101	36.65	14.00
PS 20	3.928	8.374	37.02	16.88
PS 25	4.095	9.593	28.59	7.30

Table 6. Physical Properties of the Crosslinked PVA with Different SSA Content

Sample	SSA content wt%	Modulus ^a (MPa)	Ultimate strength ^b (MPa)	Ultimate elongation ^c (%)
PS 5	5	227	9.7	40.4
PS 10	10	466	10.0	3.12
PS 15	15	714	13.3	2.6
PS 20	20	1171	14.7	1.8
PS 25	25	1266	15.7	1.4

^a Initial slope of the stress-strain curve, ^b stress at break, ^c elongation at break

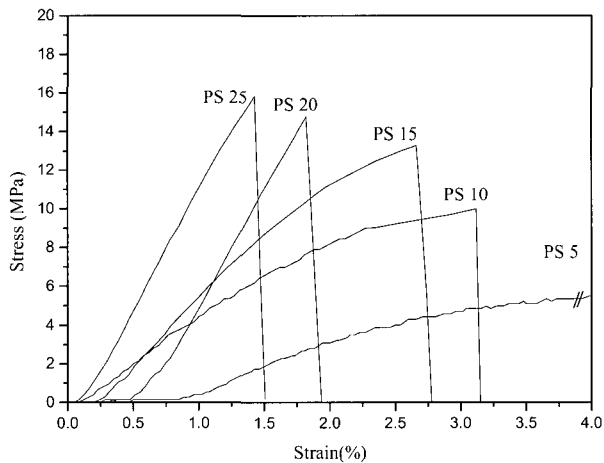


Fig. 2. Stress-strain curves for crosslinked PVA membranes.

(xylene, benzene) the ν increased with SSA content. Otherwise, in the methanol and water, the ν increased until SSA content was 20 wt%, however, above 20 wt%, the decreased slightly. Therefore, if the effect of hydrogen bonding is ignored, the degree of crosslinking between PVA and SSA is increased with SSA content.

3.3. Mechanical Properties of Crosslinked PVA

Tensile properties of crosslinked PVA membranes were studied by Instron mechanical testing machine,

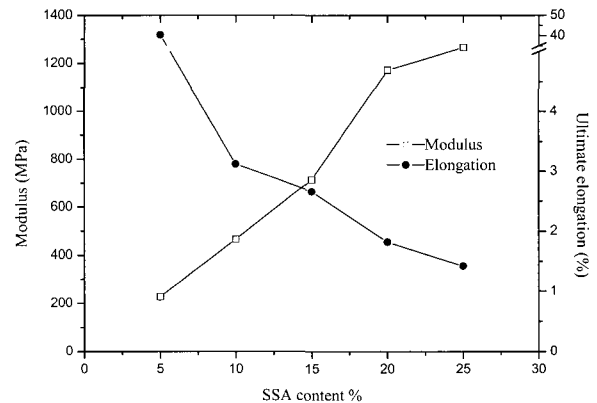


Fig. 3. Effect of crosslinking density upon modulus and elongation at break of crosslinked PVA membranes.

and stress-strain curves of membranes were shown in Fig. 2. The crosslinked PVA exhibited the brittle fracture before the yielding behavior took place. Specific values of the ultimate properties and the modulus of these membranes were shown in Fig. 3 and Table 6. The elongation at break decreased by the addition of crosslinking agent (SSA) in PVA, but ultimate strength and initial modulus increased with SSA content due to crosslinking by in the introduction of SSA.

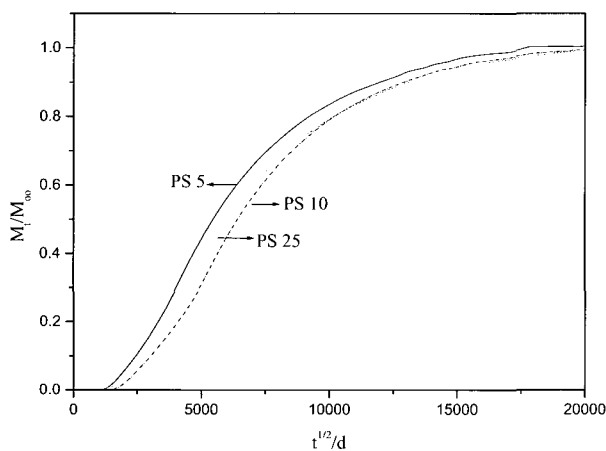
3.4. Water Vapor Sorption Kinetics

The interaction of water molecules and a crosslinked PVA membrane was investigated as a function of the

Table 7. Water Sorption Content, Proton Conductivity and Methanol Permeability of Crosslinked PVA Membranes

Sample	IEC (meq./g)	^a Water content (%)	^b $D \times 10^{-9}$ cm ² /s at 25°C	Proton conductivity ($\times 10^{-2}$ S/cm)			Methanol permeability ($\times 10^{-7}$ cm ² /s at 25°C)
				25°C	40°C	50°C	
PS 5	0.2	58.9	4.84	1.1	1.22	1.63	3.34
PS 10	0.46	42.5	3.35	0.64	0.67	0.73	2.64
PS 15	0.7	39.8	3.01	0.6	0.63	0.69	2.45
PS 20	0.9	34.5	2.41	0.56	0.6	0.64	2.2
PS 25	1.1	48.5	4.04	0.8	1.1	1.22	3.03

^awater sorption content (%) at RH 95, ^b D is water diffusion coefficient at RH 95

**Fig. 4.** Sorption curves of crosslinked PVA membranes at RH 95%.

crosslinking density. The variations of the mass of sorption water versus time at RH 95% were measured. A representative reduced sorption rate curves, as plot of M_t/M_∞ versus $(t^{1/2}/d)$ were given in Fig. 4. M_t is the mass of water sorption at time and M_∞ is the mass of water sorption at $t = \infty$ in an equilibrium state, d is the thickness of the dry membrane.

The apparent diffusion coefficient (D) were calculated from the linear part of curve in the region were $M_t / M_\infty < 0.5$ using the Fick's second law[24]

$$D = \frac{\pi}{16} \left[\frac{d(M_t/M_\infty)}{d(\sqrt{t}/d)} \right]^2 \quad (7)$$

D (cm²/s) is the diffusion co-efficient of water and polymer systems. The diffusion coefficient and water sorption content are obtained by simulating the normalized experimental data to Equation (7). Table 7 shows the water sorption content and diffusion coeffi-

cient. Here, water sorption content means the amount of sorption water/unit mass of dried membrane in equilibrium state. With SSA content, we expected two effects. (1) The number of hydroxyl group of PVA decreases as the amount of crosslinking agent increase due to esterification with carboxylic acid group of SSA. (2) Sulfonic group of SSA was increased in the membrane, indicating an increase of site that absorbs the water molecules. As shown in Table 7, the water sorption content decreased until SSA content was 20 wt%, indicating an increase in the crosslinking density to make the PVA/SSA structure more rigid and compact. However, above 20 wt% SSA content, water sorption content of the PVA/SSA 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 depends on -SO₃H content. This same type of diffusion coefficient behavior is typically interpreted in terms of plasticization of the polymer by water molecules and is common in hydrophilic polymers[17]. Plasticization results in an increase in the diffusion coefficient with concentration due to increased segmental polymer mobility caused by penetrant molecules[24]. In our case, segmental polymer chain mobility decreases but bulk side chain mobility increase with SSA content because the number of hydroxyl group per unit mass of the membrane decrease and hydrophilic group (-SO₃H) increase as the amount of crosslinking agent increases. The diffusion coefficient decreased until SSA content was 20 wt%, indicating a decrease in the segmental polymer chain mobility of the membranes. However,

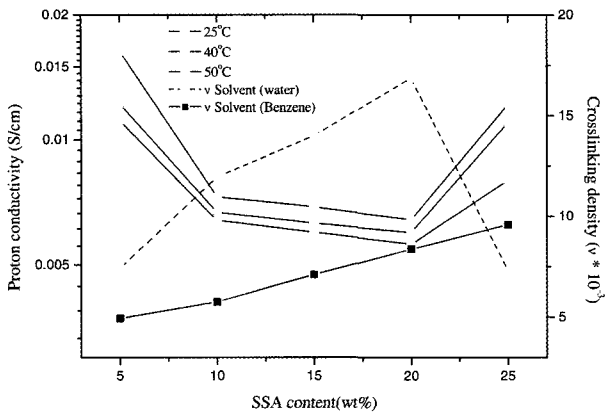


Fig. 5. Proton conductivities and crosslinking densities of PVA/SSA membranes as a function of SSA content (wt%).

above 20 wt% SSA content, the diffusion coefficient increased slightly, owing to the increase of bulk side chain mobility in the polymer, indicating that the effect of bulk side chain mobility prevails the segmental polymer chain mobility.

3.5. Proton Conductivity and Methanol Permeability

The proton conductivity of the membrane was measured by four-point-probe method and was calculated by a following equation.

$$\sigma = l / (R \times S) \tag{8}$$

where σ is proton conductivity (S/cm), l is the distance between the electrodes to measure the potential (cm), R is the impedance of the membrane (Ω), and S is surface area for proton to penetrate through membrane (cm^2).

Methanol permeability was calculated by

$$c_B(t) = \frac{A}{V_B} \frac{DK}{L} c_A(t - t_0) \tag{9}$$

where C is methanol 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

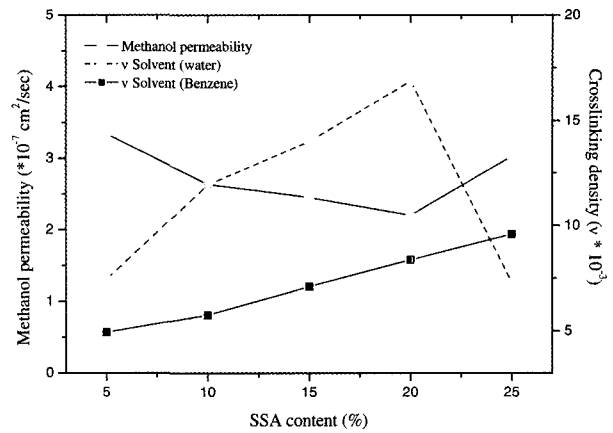


Fig. 6. Methanol permeabilities and crosslinking densities of PVA/SSA membranes as a function of SSA content (wt%).

membrane is constant and K does not depend on concentration. The product DK is the membrane permeability ($P(\text{cm}^2/\text{s})$).

Figs. 5 and 6 are plot of the proton conductivities, methanol permeability and crosslinking density as a function of the SSA concentration and the measured data were summarized in Table 7. The proton conductivities of the membranes were in the range of 10^{-3} and 10^{-2} S/cm and the methanol permeabilities ranged 10^{-7} cm^2/s .

As shown in Figs. 5 and 6, the conductivity and methanol permeability decreased with increasing crosslinking density up to 20 wt.% SSA content and above this content increase. The result was somewhat different when compared to the IEC value that increases with sulfonic group of SSA content. The behavior of proton conductivity shows the same tendency of water sorption content.

From the these results, we can say that increase of crosslinking density (SSA contents) in membranes leads to reduction of room being able to associate water molecules and thus is followed by decrease of proton conductivity and methanol permeability. The other hand, increase of crosslinking density (SSA content) leads to increase the number of hydrophilic group ($-\text{SO}_3\text{H}$) and the water cluster begins to be close so as to give rise to increase both the proton conductivity and the methanol

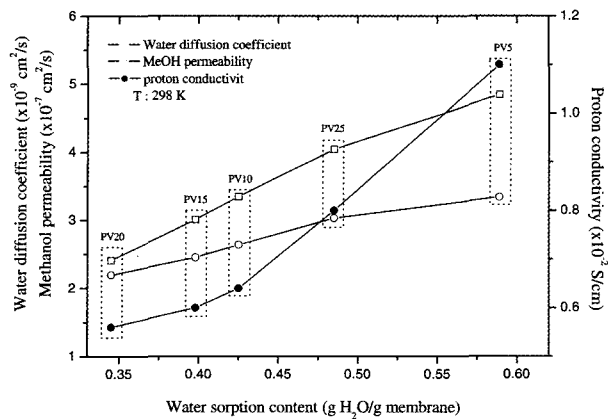


Fig. 7. Proton conductivities, methanol permeabilities and crosslinking densities as a water sorption content.

permeability. Therefore, we suppose that the proton conductivity depend on water content as well as sulfonic group in our system.

Fig. 7 shows the water diffusion coefficient, proton conductivity and methanol permeability as a function of the water sorption content with increasing water sorption content, the water diffusion coefficient increases. The proton conductivity and methanol permeability show a similar behavior since this is related to the water diffusion coefficient. It is believed that the proton conductivity and methanol permeability occur through the same pathway, because the behavior of both properties is appeared as the same trend[7].

4. Conclusions

In this work, the crosslinking density of prepared PVA membrane for direct methanol fuel cell (DMFC) was calculated using polar and non-polar solvent. The effect of crosslinking density on the proton conductivity, methanol permeability and water diffusion coefficient was investigated. The degree of crosslinking of membranes was controlled by SSA content. The crosslinking density used non-polar solvent such as xylene and benzene increases with SSA content. However, using the polar solvent such as water and methanol, the crosslinking density increases up to SSA content of 20 wt% and above the content decrease due to sulfonic

acid group. The behavior of proton conductivity and methanol permeability shows the same tendency of crosslinking density obtained using polar solvent. However, the ultimate strength and initial modulus increased with SSA content. From this result, we support that the crosslinking density increase with the amount of SSA although the somewhat different result was shown in the crosslinking density obtained using polar solvent.

Many polymer electrolyte membranes swell or become soluble in water or other strongly polar solvents. Therefore, the polymer should be crosslinked to prevent extensive swelling or methanol permeability. At this time, amount of crosslinking density with appropriate IEC value should be optimized to obtain the desirable proton conductivity.

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References

1. J. Larminie and A. Dicks, Fuel cell systems explained, Wiley, New York (2000).
2. K. Strasser, Mobile fuel cell development at Siemens, *J. Power Sources*. **37**, 209 (1992).
3. S. Surampudi, S. R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G. Prakash, and G. A. Olah, Advances in direct oxidation methanol fuel cells, *J. Power Sources*. **47**, 377 (1994).
4. C. Pu, W. Huang, K. L. Ley, and E. S. Smotkin, A methanol impermeable proton conducting composite electrolyte system, *J. Electrochem. Soc.* **142**, 119 (1995).
5. G. T. Burstein, C. J. Barnett, A. R. Kucernak, and K. R. Williams, Aspects of the anodic oxidation of methanol, *Catal. Today* **38**, 425 (1998).
6. Y. Woo, S. Y. Oh, Y. S. Kang, and B. Jung,

- Synthesis and characterization of sulfonated polyimide membranes for direct methanol fuel cell *J. Membr. Sci.* **220**, 31-45 (2003).
7. B. S. Pivovar, Y. Wang, and E. L. Cussler, Pervaporation membranes in direct methanol fuel cells, *J. Membr. Sci.* **154**, 155-162 (1999).
 8. J. Kerres, A. Ullrich, F. Meier, and T. Haring, Synthesis and characterization of novel acid-base polymer blends for application in membrane fuel cell, *Solid State Ionics* **125**, 243 (1999).
 9. W. Zhang, G. Dai, and J. Kerres, Synthesis of cross-linked poly(sulfone) ion exchange membranes, *Acta Polym. Sin.* **5**, 608 (1998).
 10. CA. Finch, Poly(vinyl alcohol), 2nd ed. New York: Wiley (1992).
 11. NA. Peppas, Hydrogel in medicine and pharmacy, vol.1. Boca Raton, FL: CRC Press (1986).
 12. W. Y. Chuang, T. H. Young, W. Y. Chiu, and C. Y. Lin, The effect of polymeric additives on the structure and permeability of poly(vinyl alcohol) asymmetric membranes, *Polymer*. **41**, 5633-5641 (2000).
 13. M. Nagura, T. Hamano, and H. Ishikawa, Structure of poly(vinyl alcohol) hydrogen prepared by repeated freezing and melting, *Polymer* **30**, 762-765 (1989).
 14. J. W. Rhim, S. W. Lee, and Y. K. Kim, Pervaporation separation of water-ethanol mixtures using metal-ion-exchanged poly(vinyl alcohol) (PVA)/ sulfosuccinic acid (SSA) membranes, *J. Appl. Polym. Sci.* **85**, 1867-1873 (2002).
 15. J. W. Rhim, C. K. Yeom, and S. W. Kim, Modification of poly(vinyl alcohol) membranes using sulfur-succinic acid and its application to pervaporation separation of water-alcohol mixtures, *J. Appl. Polym. Sci.* **68**, 1717-1723 (1998).
 16. J. W. Rhim and Y. K. Kim, Pervaporation separation of MTBE-methanol mixtures using cross-linked PVA membranes, *J. Appl. Polym.* **75**, 1699-1707 (2000).
 17. E. El. Shafee and H. F. Naguib, Water sorption in cross-linked poly(vinyl alcohol) networks, *Polymer*. **44**, 1647-1653 (2003).
 18. J. W. Rhim, H. B. Park, C. S. Lee, J. H. Jun, D. S. Kim, and Y. M. Lee, Crosslinked poly(vinyl alcohol) membranes containing sulfonic acid group: Proton and methanol transport through membranes, *J. Membr. Sci.* **238**, 143-151 (2004).
 19. S. Desai, I. M. Thakore, and S. Devi, Effect of crosslink density on transport of industrial solvents through polyether based polyurethanes, *Polymer Inter.* **47**, 172-178 (1998).
 20. C. Genies, R. Mercier, B. Sillion, P. Petiaud, N. Cornet, G. Gebel, and M. Pineri, Stability study of sulfonated phthalic and naphthalenic polyimide structures in aqueous medium, *Polymr.* **42**, 5097-5105 (2001).
 21. A. Tager, Physical chemistry of polymers, Mir, Moscow (1972).
 22. J. Brandrup and E. H. Immerjat (Eds.), Polymer Handbook, Wiley, New York, p. 1175 (Section VII) (1989).
 23. R. F. Fedors, Absorption of liquids by rubber vulcanizates, *Polymer*, **20**, 1087-1090 (1979).
 24. C. E. Bogers. In: Comyn, J, editor. Polymer permeability. London: Elsevier Applied Science Publishers p. 11 (1985).