이온전도성 가교 PVA/PAA/silica막의 제조 및 특성

신광호, 김대식, 박호범, 임지원[1], 이영무

한양대학교 공과대학 응용화학공학부
[1]한남대학교 공과대학 화학공학과

Crosslinked PVA/PAA/Silica Hybrid Membranes: Preparation, Characterization, and Proton and Methanol Transport

Kwang Ho Shin, Dae Sik Kim, Ho Bum Park,
Ji-Won Rhim[1], Young Moo Lee

National Research Laboratory for Membranes, School of Chemical Engineering, College of Engineering,
Hanyang University, Seoul 133-791, Korea
[1]Department of Chemical Engineering Hannam University, 133 Ojung-Dong, Daeduk-Gu, Daejon 306-791, Korea

1. Introduction

Crosslinked poly(vinyl alcohol) (PVA)/poly acrylic acid (PAA)/silica hybrid membranes were prepared using sulfosuccinic acid (SSA) containing sulfonic acid group (SO_3H), and they were considered as a proton exchange membrane for direct methanol fuel cell (DMFC). The dispersed silica particles were introduced into polymer matrices *via* sol-gel reaction. Proton conductivity and methanol permeability through membrane were investigated as not only the SSA content at fixed mixing ratio of PVA/PAA but also the different mixing ratio of PVA/PAA. It was found that the SSA content affected severely these properties because the SSA was used not only as a chemical crosslinking agent but also as a donor of fixed anionic group ($-SO_3-H^+$). In addition, the mixing ratio of PVA/PAA content affected the transport properties of crosslinked membranes. The proton conductivities of

these membranes was of the order of magnitude of 10^{-3} and 10^{-2} S/cm and the methanol permeabilities was of the order of magnitude of 10^{-8} and 10^{-7} cm^2/sec. The silica particle embedded in crosslinked polymer matrix was act as a methanol barrier by hindering pathway to pass methanol molecules. Consequently, methanol permeability reduced without lost proton conductivity. These characteristics of hybrid membranes are desirable in applications related to proton exchange membrane for DMFC.

2. Experimental

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 6 h. A definite amount of PAA was dissolved in pure water. Then the PVA solutions were mixed together with the SSA solution to form a homogeneous solution for at least 2 h at 50 °C.

A homogeneous tetraethyl orthosilicate (TEOS) mixture was prepared using hydrochloric acid, sulfosuccinic acid (SSA) and TEOS. TEOS solution was dropped to PVA/PAA solution while stirring to homogeneous mixtures. 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 heated in a thermostated oven at 120 °C for 1 h.

3. Results and discussion

Organic-inorganic hybrids, based on PVA/PAA/Silica hybrid membranes containing sulfonic acid groups, were successfully prepared *via* the sol-gel process. Amongst membranes prepared in this study, the total IEC value of 6/4 ratio membranes was higher than that of 8/2. However, the water contents were the reversed order of the total IEC value. Compared to the 6/4 mixing ratio membranes, the 8/2 mixing ratio membranes is higher amount of water. This result indicates that the degree of crosslinking of 6/4 ratio membranes is higher than that of 8/2 ratio membranes and the residue of hydroxyl group of 8/2 ratio membranes after crosslinking reaction is higher than that of 6/4 ratio membranes. Also, the total water content

increases with the SSA contentat fixed mixing ratio. The 8/2 mixing ratio membranes show higher proton conductivity than 6/4 mixing ratio membranes as shown Table 1.

Table 1 . Ion conductivity, Methanol permeability, IEC value and water content

Sample	Ion conductivity (* 10^{-2} S/cm)			Methanol permeability (* 10^{-8} cm^2/s) at 25 °C	IEC by titration (meq./g)	Water content (%)
	25	50	80 °C			
A1	0.14	0.26	0.8	10.5	0.54	30.7
A2	0.34	0.43	1.41	13.7	1.11	34.2
A3	1.1	1.35	2.67	15.7	1.58	42.9
V1	0.24	0.33	0.92	13.8	0.49	44.0
V2	0.58	0.84	2.0	18.1	0.92	50.6
V3	1.46	1.79	5.38	20.3	1.35	55.2
AT1	0.2	0.39	0.71	1.65	0.51	30.4
AT2	0.23	0.53	1.27	2.5	1.0	32.2
AT3	0.52	0.91	3.18	3.8	1.47	34.2
VT1	0.24	0.5	1.1	4.6	0.46	35.1
VT2	0.42	0.71	1.81	5.1	0.91	37.7
VT3	0.78	1.21	4.77	5.65	1.33	46.0

A-, AT- : PVA/PAA mixing ratio 6/4, V-,VT- : PVA/PAA mixing ratio 8:2

A1-A3: SSA 10 ~ 30 wt%, AT-, VT- : contain Silica

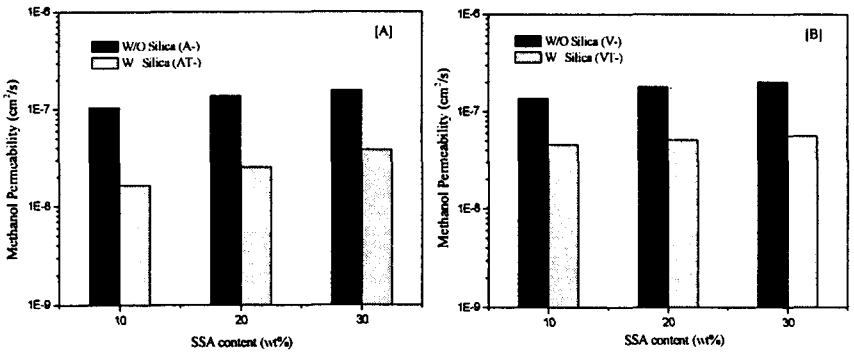

Fig.1. Methanol Permeability

[A] PVA/PAA mixing ratio = 6 / 4) [B] PVA/PAA mixing ratio = 8 / 2)

Only increase of IEC values by introduction of sulfonic acid and carboxylic acid group in these proton exchange membranes is not primary factor to

increase the proton conductivities. The relatively more crosslinked 6/4 membranes have a lower the channel, which methanol molecules can penetrate. Therefore, blocking the methanol transport through the channel may be sufficient to solve the methanol crossover problem. Especially, the 6/4 mixing ratio membranes having silica show the lowest methanol permeability due to the effect of silica particles and crosslinking (Fig. 1). From the results of proton conductivity and methanol permeability, it is suggests that silica in crosslinked membrane was act as a methanol barrier by reducing chain mobility and hydrophilic channel to pass methanol molecules without sacrificing significant proton conductivity.

References

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