

## Influence of Silica Content in Crosslinked PVA/PSSA<sub>MA</sub>/Silica Hybrid Membrane for Direct Methanol Fuel Cell (DMFC)

Dae Sik Kim and Michael D. Guiver

*Institute for Chemical Process and Environmental Technology, National Research Council,  
1200 Montreal Road, Ottawa, Ontario, K1A 0R6, Canada*

Mu Young Seo, Hyun Il Cho, Dae Hoon Kim, and Ji Won Rhim\*

*Department of Chemical Engineering, Hannam University, Daeduk Valley Campus, Daejeon 305-811, Korea*

Go Young Moon

*CRD, Research Park, LG Chem., Daejeon 305-380, Korea*

Sang Yong Nam

*Department of Polymer Science and Engineering, Engineering Research Institute, i-Cube Center,  
Gyeongsang National University, Jinju 660-701, Korea*

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**Abstract:** In the present study, crosslinked poly(vinyl alcohol) (PVA) membranes were prepared at different temperatures using poly(styrene sulfonic acid-co-maleic acid) (PSSA<sub>MA</sub>) (PVA:PSSA<sub>MA</sub> = 1:9). The hybrid membranes were prepared by varying the TEOS content between 5 and 30 wt%. The PSSA<sub>MA</sub> was used both as a crosslinking agent and the hydrophilic group donor (-SO<sub>3</sub>H and/or -COOH). The proton conductivity increased with up to 20 wt% TEOS, but decreased above this level, although the water content decreased with increasing TEOS content. This result suggests that the silica doped into the membrane improved the formation of proton-conduction pathways due to the absorption of molecular water. The PVA/PSSA<sub>MA</sub>/Silica containing TEOS 20% showed both high proton conductivity (0.026 S/cm at 90 °C) and low methanol permeability ( $5.55 \times 10^{-7}$  cm<sup>2</sup>/s).

**Keywords:** hybrid membranes, proton conductivity, methanol permeability, crosslinked poly(vinyl alcohol) membranes, poly(styrene sulfonic acid-co-maleic acid), direct methanol fuel cell.

### Introduction

The current popular method for polymer electrolyte membrane fuel cells is to use a perfluorosulfonic acid copolymer produced by DuPont called Nafion<sup>®</sup>.<sup>1</sup> Although Nafion<sup>®</sup> has good chemical and physical properties for use in fuel cell applications, it has three technical limitations: its high cost, its low conductivity at low humidity or high temperature, and its high methanol permeability that reduces the cell efficiency.<sup>2</sup>

There has been considerable effort spent trying to reduce methanol crossover and to reach high proton conductivity. Membranes containing metallic blocking layers have been proposed,<sup>3</sup> and organic-inorganic composite membranes containing Zr phosphonates,<sup>4</sup> Sn-doped mordenites,<sup>5</sup> zeo-

lites,<sup>6</sup> and silica<sup>7</sup> have been investigated. Hybrids are usually prepared using the sol-gel process by incorporating organic polymers containing alkoxy silanes (usually tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS)).<sup>8</sup> The starting materials for the sol-gel process are the corresponding metal alkoxides, along with a small concentration of acid or base as a catalyst.

Poly(vinyl alcohol) (PVA) appears to be very attractive material for preparing proton exchange membrane (PEM) because this polymer can function as an excellent methanol barrier.<sup>9</sup> PVA also has both very good mechanical properties and chemical stability, which are adequate for preparing PEMs.<sup>10</sup> Although PVA itself does not have fixed charges, several organic groups like hydroxyl, amine, carboxylate, sulfonate, and quaternary ammonium can be incorporated to impart hydrophilicity and/or ionic group.<sup>11,12</sup> As reported earlier,<sup>13,14</sup> it was assumed that the crosslinking of the com-

\*Corresponding Author. E-mail: jwrhim@hannam.ac.kr

pletely miscible blend system occurs *via* dehydration between carboxylic acid and hydroxyl group, that is, esterification and bond formation during thermal activated reaction.

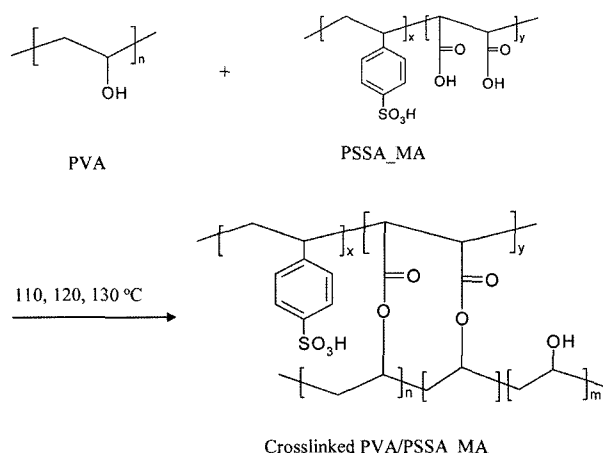
In our previous study,<sup>15-17,27</sup> we reported the preparation of crosslinked membranes employing PVA as a base materials and sulfosuccinic acid (SSA) or poly(acrylic acid-*co*-maleic acid) (PAM) or poly(styrene sulfonic acid-*co*-maleic acid) as both a crosslinking agent and as a donor of the hydrophilic group (-SO<sub>3</sub>H) and/or carboxylic group (-COOH). Recently, Kang *et al.* reported the preparation of PVA based (i.e. PVA/poly(styrene sulfonic acid-*co*-maleic acid, PSSA\_MA) PEM.<sup>18,19</sup> Since a maleic acid group has two ion-exchangeable sites in its molecular structure<sup>19</sup> and also could be crosslinked with -OH group of PVA, the introduction of PSSA\_MA into the PVA polymer matrix can control the membrane charge density and also prevent excessive swelling.

The aim of this study was to prepare membranes for possible use in a DMFC. To do this, PVA/PSSA\_MA/silica hybrid membranes containing sulfonic acid and carboxylic acid groups were synthesized using the sol-gel process. Sulfonic acid groups were introduced into the PVA matrix by esterification with poly(styrene sulfonic acid-*co*-maleic acid) (PSSA\_MA). In addition, silica particles were dispersed into the polymer matrix via the sol-gel reaction. We expected that the crosslinked PVA hybrid membranes would lead to high proton conductivity due to the addition of the sulfonic acid, and a low methanol permeability due to the crosslinking between the PVA and PSSA\_MA, with the silica domains providing a barrier to methanol. The crosslinking temperature and the content of silica were controlled to seek the best performance in terms of methanol permeability and proton conductivity measurements.

## Experimental

**Materials.** Fully hydrolyzed PVA (99% hydrolyzed, average Mw=89,000-98,000) and the PSSA\_MA (sodium salt, styrene (Sty)-sulfonic acid: maleic acid=3:1, average Mw=20,000 g/mol) as a crosslinking agent and as a donor of the hydrophilic -SO<sub>3</sub>H and -COOH group were purchased from the Aldrich Chemical Co., Milwaukee, WI, USA. The tetraethyl orthosilicate (TEOS) and methanol were analytical grade from Aldrich, and were of analytical grade. The water used was the ultrapure water produced from Younglin Pure Water System (Seoul, Korea).

**Membrane Preparation.** Aqueous 10 wt% PVA solutions were prepared by dissolving dry PVA in water and then refluxing at 90 °C for 6 h, and aqueous 20 wt% PSSA\_MA solutions were prepared. Inorganic-organic hybrids using the PVA and sol-gel derived silica were prepared by mixing PVA solution and TEOS mixture. The TEOS mixture was prepared by mixing H<sub>2</sub>O, HCl, and TEOS in the molar ratio of 4:0.1:1, which was stirred at room temperature for 2 h.



**Figure 1.** Possible reaction mechanism of PVA and PSSA\_MA.

The amount of TEOS was 5-30% by weight to PVA weight. Then, the PVA/TEOS solutions were mixed together along with PSSA\_MA solutions in the weight ratio of 1:9 (PVA: PSSA\_MA), and the mixture was stirred at room temperature for 12 h. The solutions were then poured onto a plexi-glass plate, and cast using the doctor blade process. The cast solutions were allowed to dry in air at room temperature. The fully dried membranes were peeled away from the glass plate, and then heated in a thermosetting oven. The prepared membranes were annealed at different temperature for 1 h to induce crosslinking reaction. The selected crosslinking temperatures were 110, 120, and 130 °C. The thickness of the membranes showed 100-150 μm. Figure 1 shows the reaction mechanism of PVA and PSSA\_MA.

**Membrane Characterization.** The FT-IR spectra of the membranes were measured using a Nicolet IR 860 spectrometer (Thermo Nicolet, Madison, WI, USA) operating in the wavenumber range 4000-500 cm<sup>-1</sup>. The degradation process and the thermal stability of the membranes were investigated using thermogravimetry (TGA) (TA Instruments TGA 2050, New Castle, DE, USA). The TGA measurements were carried out under a nitrogen atmosphere using a heating rate of 10 °C/min from 50-700 °C.

**Measurement of the Water Content and IEC Value.** The water content was measured by soaking the samples in distilled water for more than 24 h. After this period, they were wiped with a filter paper and then weighed immediately. The samples were then dried under vacuum until a constant weight was obtained. The water content (g H<sub>2</sub>O/g membrane) is the ratio of the hydrated membrane to the dried membrane.

The ion exchange capacity (also known as the IEC value) was measured using the classical titration technique (ASTM D2187) with 0.01 M NaOH and phenolphthalein as an indicator. To confirm the stability of membrane in hydrolytic condition, the membranes were immersed in boiling water for 3 days. The IEC value of the membrane was measured

after boiling water test.

**Proton Conductivity.** The proton conductivity of the membranes was measured using the normal four-point probe technique at RH (relative humidity)=100%. The impedance of the membranes was determined using a Solatron Analytical Full Material Impedance System 12608 W consisting of a Frequency Response Analyzer 1260 and Electrochemical Interface 1287 unit. Each sample was cut into sections  $4 \times 1 \text{ cm}^2$  prior to being mounted on the cell. The proton conductivity ( $\sigma$ ) was obtained using the following equation:

$$\sigma = \frac{l}{R \cdot S} \quad (1)$$

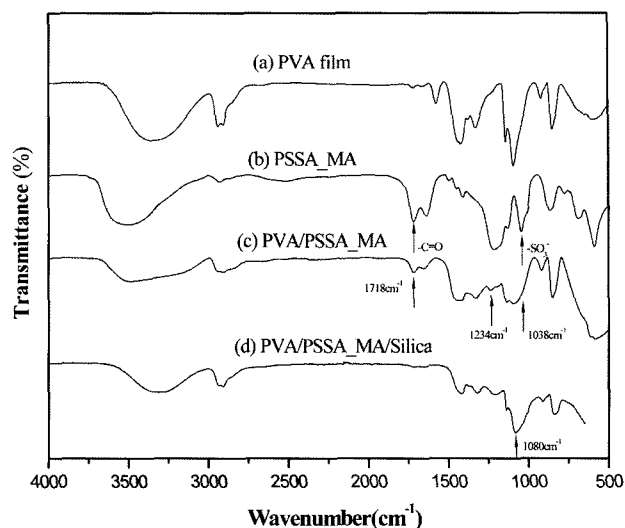
where  $\sigma$  is the proton conductivity (in S/cm), and  $l$  is the distance between the electrodes used to measure the potential (1 cm).  $R$  is the impedance of membrane (in  $\Omega$ ).  $S$  is the surface area required for a proton to penetrate the membrane (in  $\text{cm}^2$ ). The impedance of each sample was measured five times to ensure good data reproducibility.

**Methanol Permeability.** The methanol permeability of the membranes was determined using a diaphragm diffusion cell.<sup>12</sup> This cell consisted of two reservoirs, each with a capacity of approximately 60 mL, separated by a vertical membrane. The membrane was clamped between the two reservoirs, the contents of which were stirred during the experiments. Prior to the test, the membranes were equilibrated in deionized water for at least 12 h. Initially, one reservoir ( $V_A$ ) contained a 2 M methanol-water solution, and the other reservoir ( $V_B$ ) contained pure deionized water. The increase in concentration of methanol in the initially pure water reservoir was measured against time using gas chromatography. In the gas chromatography measurements,  $1\text{-}\mu\text{L}$  samples were analyzed using a Shimadzu GC-14B gas chromatograph. The methanol permeability was calculated.<sup>12</sup> In the permeability tests, the temperature was controlled using a thermostatic water bath at  $30^\circ\text{C}$ .

## Results and Discussion

**FT-IR Spectroscopy.** Figure 2 shows the FT-IR spectra of pure PVA, crosslinked PVA/PSSA\_MA and PVA/PSSA\_MA/silica membrane. The broad bands occurring at around  $3600\text{-}3200 \text{ cm}^{-1}$  (characteristic of O-H stretching vibration) are observed due to hydrogen bonding and OH single vibration. The absorption band at  $1718 \text{ cm}^{-1}$  (characteristic of C=O vibration, maleic acid) and at  $1038 \text{ cm}^{-1}$  (characteristic of  $\text{-SO}_3^-$ , PSSA) are observed in PVA/PSSA\_MA membrane. In addition, the absorption band at  $1234 \text{ cm}^{-1}$  is observed in the crosslinked membrane, indicating the formation of ether bonds (C-O-C) between -OH of PVA and -COOH of maleic acid.

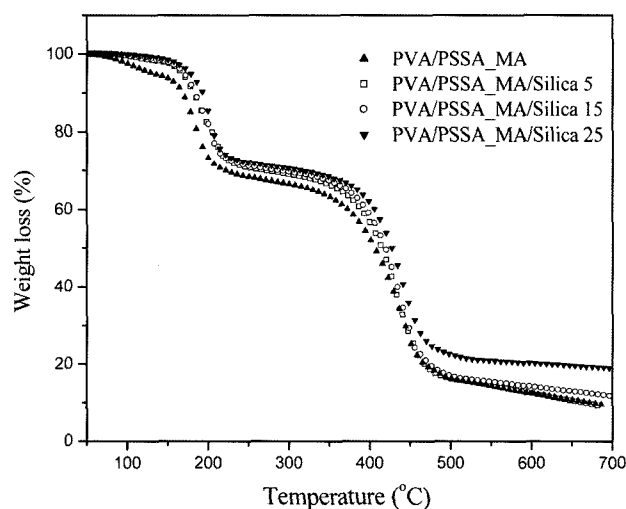
In addition, the bands occurring at around  $1080 \text{ cm}^{-1}$  (characteristic of Si-O-Si asymmetric stretching) were observed in the spectra of the PVA/PSSA\_MA/silica hybrid mem-



**Figure 2.** FT-IR spectra of (a) PVA, (b) PSSA\_MA, (c) crosslinked PVA/PSSA\_MA, and (d) PVA/PSSA\_MA/silica membrane.

brane. The broad absorption peak at around  $3400 \text{ cm}^{-1}$  in the PVA/PSSA\_MA/silica membrane indicates that there were a number of -OH groups due to non-condensed  $\equiv\text{SiOH}$  and/or unreacted -OH groups of the PVA.<sup>15</sup>

**Thermal Analysis.** The TGA curves measured under flowing nitrogen are shown in Figure 3. As shown in Figure 3, the TGA curve of the membranes was fitted using three main degradation stages arising from the processes of thermal solvation, thermal desulfonation, and thermooxidation of the polymer matrix. The first weight loss up to  $150^\circ\text{C}$  is closely associated with the loss of absorbed water molecules. The weight loss (%) of hybrid membranes (PVA/PSSA\_MA/silica 5-30) is lower than that of PVA/PSSA\_MA membrane. Most of these absorbed water molecules are



**Figure 3.** TGA curve (crosslinking temperature:  $130^\circ\text{C}$ ).

**Table I. Ion Exchange Capacities before and after Boiling Water Test and Thermal Property**

TEOS Content	IEC (meq/g)		$T_{d5\%}$ (°C) <sup>a</sup>	Ash <sup>b</sup>
	Before Boiling Water Test	After Boiling Water Test		
TEOS 0	0.95	0.93	130.8	9.1
TEOS 5	0.95	0.93	168.0	9.3
TEOS 10	0.94	0.93	169.2	10.4
TEOS 15	0.94	0.92	170.2	11.5
TEOS 20	0.93	0.91	174.5	17.8
TEOS 25	0.93	0.92	178.2	18.8
TEOS 30	0.92	0.91	180.1	20.6

<sup>a</sup>5% weight loss temperature of the membrane crosslinked at 130 °C.

<sup>b</sup>Residual ash is the char yield (wt%) at 700 °C.

supposed to exist in a bound state, rather than in the free molecular state,<sup>20</sup> and seem to be bound directly to the polymer chains, the -SO<sub>3</sub>H groups, and/or ≡SiOH groups via hydrogen bonds. The  $T_{d5\%}$  of membranes increases with increasing the silica content as shown in Table I. The second weight loss region (occurring between temperatures of  $T=150-300$  °C) corresponds to the loss of sulfonic acid group by the desulfonation. In the third weight loss region (at temperatures >400 °C), the polymer residues were further degraded at  $T=450$  °C, which corresponds to the decomposition of the main chains of the PVA. In the case of the hybrid membranes, the weight remaining after the polymer decomposition depended on the content of the silica content. As shown in Table I, the weight residues of the hybrid membranes containing silica at  $T=700$  °C were higher than that of unfilled PVA/PSSA\_MA membrane. These results suggest that the introduction of silica into the PVA chains enhance the thermal stability of the given hybrid materials.

**Ion Exchange Capacity and Hydrolytic Stability.** The IEC of PVA/PSSA\_MA membrane crosslinked at 130 °C is 0.95 meq/g dry membrane. The prepared hybrid membranes indicated the IEC of 0.92-0.95 meq/g dry membranes. The ionic site would be decreased with increasing silica content.

As shown in Table II, the EW increased at higher crosslinking temperature due to the more reaction of -SO<sub>3</sub>H and/or -COOH group in repeating units of PSSA\_MA with -OH of PVA. The numbers of molecules per sulfonic acid ( $\lambda$ ) were listed in Table II and Figure 4(b). The PVA/PSSA\_MA/silica 25 membrane crosslinked at 130 °C shows the similar value ( $\lambda=25$ ) of Nafion.<sup>21</sup>

We have also performed the hydrolytic stability test (i.e. boiling water test for 1 week) for PVA/PSSA\_MA membranes crosslinked at 130 °C. Before and after boiling water test, the IEC values were listed in Table I. Although the IEC value somewhat decrease due to partially decomposition during boiling water test, the membranes maintain the proper IEC value after boiling water test. Therefore, it is believed that the crosslinked PVA/PSSA\_MA/silica membrane has moderate hydrolytic stability.

**Water Content.** The water contents of membranes are plotted as functions of the TEOS content and crosslinking temperature in Figure 4(a).

As the crosslinking temperature increases, i.e. the esterification reaction between -OH of PVA and -COOH of PSSA\_MA as well as -OH of PVA and -SO<sub>3</sub>H of PSSA\_MA precedes more to make the membranes more rigid and compact, the water content decreases.<sup>22</sup> The water contents of the membrane crosslinked at 120 and 130 °C are lower than that of the membrane crosslinked at 110 °C. As shown in Figure 4(a), the water content of the membranes decreases with increasing silica content. For the membranes crosslinked at 130 °C, it is ranged from 30-105% for different silica content membranes. Nafion membranes have the water contents ranging from 24-33% depending on the content of sulfonic group; typically Nafion 117 indicates 24-26%.<sup>23</sup> The membrane containing 30 wt% TEOS crosslinked at 130 °C show the similar water content with Nafion membranes.

**Proton Conductivity and Methanol Permeability.** The proton conductivity measurements of the membrane were run at RH 100% as a function of silica content and temperature in the longitudinal direction by AC impedance spectroscopy and the results are shown in Figure 5. The proton

**Table II. Number of Water Molecules Per Ionic Site (-SO<sub>3</sub>H and -COOH)**

TEOS Content	110 °C			120 °C			130 °C		
	WC	EW	$\lambda^a$	WC	EW	$\lambda$	WC	EW	$\lambda$
TEOS 0	1.92	909	97.0	1.76	1,000	97.8	1.05	1,042	60.8
TEOS 5	1.86	909	93.9	1.50	1,000	83.3	0.95	1,042	55.0
TEOS 10	1.68	952	88.9	1.20	1,010	67.3	0.72	1,053	42.1
TEOS 15	1.52	952	80.4	1.08	1,020	61.2	0.65	1,053	38.0
TEOS 20	1.43	1,000	79.2	0.91	1,042	52.9	0.55	1,064	32.5
TEOS 25	1.22	1,020	69.2	0.74	1,064	43.7	0.43	1,064	25.4
TEOS 30	0.95	1,031	54.4	0.64	1,075	38.2	0.30	1,075	17.9

<sup>a</sup>Calculated by  $\lambda=(WC \times EW)/M_o$ , WC is the water content, EW is the equivalent weight (g/eq), and  $M_o$  is the molecular weight of water (18 g/mol).

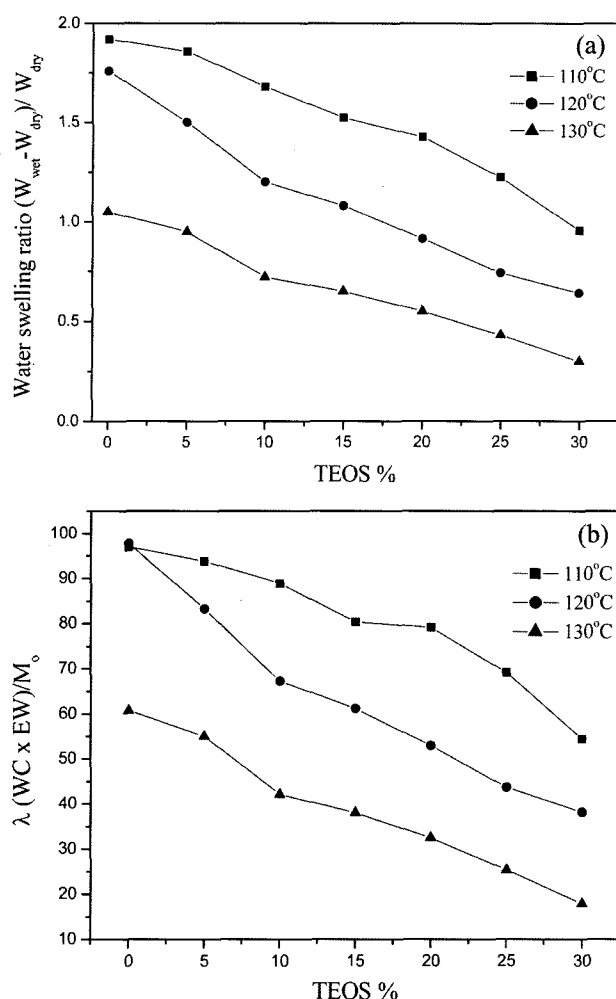


Figure 4. (a) Water content and (b)  $\lambda$  vs TEOS content %.

conductivities of the hybrid membranes measured at  $T=30^\circ\text{C}$  were in the range  $>10^{-2}$  S/cm.

Increasing of TEOS content lead to reduction of free volume being able to associate water molecules, thus are followed by decrease in size of interconnecting channels for protons. Therefore, we expected that an increase in TEOS content in the polymer matrix would lead to decrease proton conductivity before attempting the conductivity measurements. However, although the water content decreases by increasing TEOS content, the proton conductivity increase by up to 20 wt% TEOS, and above this level the proton conductivity decreased. The contents of TEOS turned out quite sensitive to the proton conductivity. This result suggests that the silica doped in the membrane has an effect on improving the formation of proton-conduction pathways due to molecular water absorption. In our previous report,<sup>24</sup> the introduction of silica enhanced the membrane hydrophilicity due to the presence of numerous  $\equiv\text{SiOH}$  groups. These  $\equiv\text{SiOH}$  groups, which can hydrogen bond, have strong bonding with  $\text{H}_2\text{O}$  molecules. Although these water molecules bond-

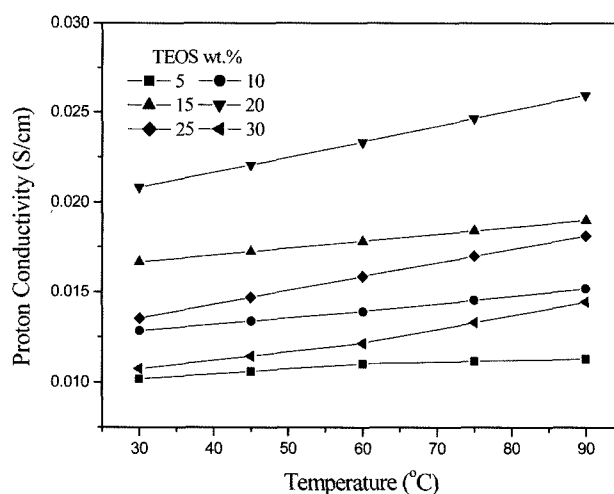
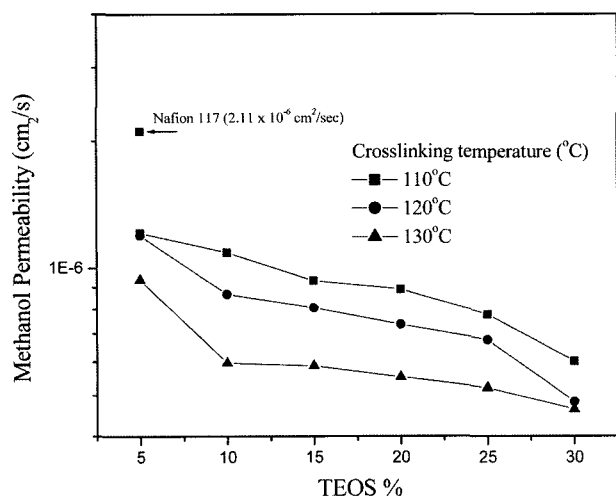


Figure 5. Proton conductivity of the hybrid membranes crosslinked at  $130^\circ\text{C}$  as a function of temperature.

ing with  $\equiv\text{SiOH}$  in the PVA/PSSA\_MA/silica membrane could not increase the total water content, it is enough to increase the proton conductivity. That is, new proton conduction due to the silica particles has a probable mechanism associated with proton hopping between  $\text{SiOH}$  and water molecules.<sup>25</sup> The dissociated proton moves to a water molecule bound with the  $\text{SiOH}$  bond, forming the activated  $\text{H}_2\text{O}:\text{H}^+$  state ( $\text{SiOH}\text{H}_2\text{O} \rightarrow \text{SiO}^-\text{H}^+:\text{H}_2\text{O}$ ).<sup>25</sup> The proton from the activated  $\text{H}_2\text{O}:\text{H}^+$  state dissociates to form a new activated state with a neighboring  $\text{H}_2\text{O}$ . Therefore, the proton conductivity increases due to the synergistic effect between the hydrated sulfonic group and the hydrated silica particle-absorbed water molecules.

Figure 5 shows the effect of operating temperatures raised from 30 to  $90^\circ\text{C}$  on the proton conductivities of the hybrid membranes crosslinked at  $130^\circ\text{C}$ . The degree of hydration of sulfonic and carboxylic group would increase with increasing temperature. In addition, as the proton conductivity of an electrolyte is generally thermally stimulated, it is not surprising to expect a rise in proton conductivity with temperature.<sup>26</sup>

Figure 6 shows the methanol permeability of the PVA/PSSA\_MA/silica membrane crosslinked at 110, 120, and  $130^\circ\text{C}$ . Compared with Nafion 117, most membranes show lower methanol permeability. As can be seen, the methanol permeability decreases with increasing TEOS contents and crosslinking temperature. It is known that methanol permeates through hydrophilic ionic channels; especially free water molecules and that proton are transported by hopping between ionic sites due to hydrogen bonding between bound water molecules as well as through ionic channels. Therefore, it is expected that the methanol permeability should be decreased due to the silica particles acted as materials for blocking the methanol transport and/or for reducing free water.



**Figure 6.** Methanol permeability of the hybrid membranes measured at 30 °C.

## Conclusions

In our previous study,<sup>22</sup> we reported the preparation of the crosslinked membranes employing PVA as the polymer matrix and poly(styrene sulfonic acid-*co*-maleic acid, PSSA\_MA) as both a crosslinking agent and as a donor of the hydrophilic group. This work is a continuation of our study on crosslinked PVA membranes. In the present work, crosslinked poly(vinyl alcohol) (PVA) membranes were prepared at various crosslinking temperatures using poly(styrene sulfonic acid-*co*-maleic acid, PSSA\_MA). The PSSA\_MA was used both as a crosslinking agent and as a donor of the hydrophilic -SO<sub>3</sub>H and/or -COOH group. From PVA/PSSA\_MA membranes, a series of hybrid membranes incorporating different amounts of silica nanoparticles were prepared using the sol-gel reaction with tetraethyl orthosilicate (TEOS) under acid conditions. The proton conductivity increase by up to 20 wt% TEOS, and above this level the proton conductivity decreased, although the water content decreases by increasing TEOS content. This result suggests that the silica doped in the membrane has an effect on improving the formation of proton-conduction pathways due to molecular water absorption.

Although the PVA/PSSA\_MA/silica containing TEOS 25% shows the similar value ( $\lambda=25$ ) of Nafion, the PVA/PSSA\_MA/silica containing TEOS 20% shows both high proton conductivity (0.026 S/cm at 90 °C) and low methanol permeability ( $5.55 \times 10^{-7}$  cm<sup>2</sup>/s). Although the PVA/PSSA\_MA (1:9) membrane maintained an adequate IEC value after boiling water test, more detailed analyses such as long-term and thermal stabilities of these type membranes may be needed for DMFC applications.

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