

# Sorption and Transport Properties of the Semi-Interpenetrating Network Based on Crosslinked Poly(vinyl alcohol) and Poly(styrene sulfonic acid-co-maleic anhydride) as Proton-Conducting Membranes

Y. F. Huang,<sup>1</sup> B. J. Hwang,<sup>2</sup> C. W. Lin<sup>1</sup>

<sup>1</sup>Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology, Yunlin 640, Taiwan

<sup>2</sup>Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

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**ABSTRACT:** This study investigates the sorption and transport properties of hydrocarbon membranes based on poly(vinyl alcohol) network and poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA). The water and methanol self-diffusion coefficients through an 80 wt % PSSA-MA interpenetrating SIPN-80 membrane measured  $3.75 \times 10^{-6}$  and  $5.47 \times 10^{-7}$  cm<sup>2</sup>/s, respectively. These results are lower than the corresponding values of Nafion<sup>®</sup> 115 ( $8.89 \times 10^{-6}$  cm<sup>2</sup>/s for water and  $8.63 \times 10^{-6}$  cm<sup>2</sup>/s for methanol). The methanol permeability of SIPN-80 membrane is  $4.1 \times 10^{-7}$  cm<sup>2</sup>/s, or about one-fourth that of Nafion<sup>®</sup> 115. The difference in self-diffusion behaviors of Nafion<sup>®</sup> 115 and SIPN-80 membranes is well correlated with their sorption characteristics. The solvent uptake of Nafion<sup>®</sup> 115 increased as the

methanol concentration increased up to a methanol mole fraction of 0.63, and then decreased. However, the solvent uptake of the SIPN-80 membranes decreased sluggishly as the methanol concentration increased. The  $\lambda$  values of water and methanol (i.e.,  $\lambda_{\text{H}_2\text{O}}$  and  $\lambda_{\text{CH}_3\text{OH}}$ ) in Nafion<sup>®</sup> 115 are quite close, indicating no sorption preference between water and methanol. In contrast, the  $\lambda_{\text{CH}_3\text{OH}}$  value is only one-third  $\lambda_{\text{H}_2\text{O}}$  for a SIPN-80 membrane. Accordingly, the SIPN membranes are regarded as candidates for direct methanol fuel cell applications. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 342–350, 2009

**Key words:** self-diffusion coefficient solvent uptake; poly(vinyl alcohol); polymer electrolyte membranes; DMFC

## INTRODUCTION

Polymer electrolytes play an important role in fuel cell technology because they are useful as separators and proton conductors. The current commercially used perfluorosulfonic acid membrane, Nafion<sup>®</sup>, is a well-known cluster structure with phase separation performed by its hydrophobic fluorocarbon and pendent sulfonic acid groups.<sup>1</sup> Although Nafion<sup>®</sup> membrane shows good stability and high proton conductivity, some serious drawbacks exclude it from placement in direct methanol fuel cells (DMFCs). The major drawback is its unacceptably high methanol permeability, which not only wastes fuel but also causes performance loss at the cathode due to oxygen consumption and catalyst poisoning.<sup>2,3</sup> Therefore,

proton exchange membrane (PEM) materials with decreased methanol permeability and high proton conductivity are especially desired for early commercialization of DMFC. In principle, a logical way to develop PEM materials will not only facilitate the passage of water but also restrict the movement of methanol. Ren et al.<sup>4</sup> have reported that the water/methanol uptake per sulfonic acid group in Nafion<sup>®</sup> is the same for membranes equilibrated in pure water or pure methanol. Hietala et al.<sup>5</sup> reported that there was no significant difference between the water and methanol self-diffusion coefficients either in Nafion<sup>®</sup> membrane or in solutions.

Water in a membrane plays a critical role in proton conduction because it is the major carrier of protons. A proton conduction mechanism is generally believed to be controlled by the proton diffusion through different states of water in membranes.<sup>6</sup> Two different states of water in Nafion<sup>®</sup> membrane have been distinguished, namely bound and unbound waters.<sup>7</sup> The mobility of protons through unbound water is fast. However, proton mobility through bound water, which refers to the water strongly bound to sulfonic

Correspondence to: C. W. Lin (lincw@yuntech.edu.tw).

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acid groups, is considerably smaller than that in the unbound water. Previous reports interpreted the correlation between the proton transport behavior and the state of water in membranes.<sup>8,9</sup> On the other hand, the self-diffusion rate of water in membranes may also have a significant effect on the transport properties of protons because the hydrated environment in a proton-conducting membrane acts as a solvent for the diffusion of the hydronium and dimer ions.<sup>10</sup> Specifically, water at different states was also reported to have different mobility in membranes.<sup>11</sup> Accordingly, interpreting the correlation between the transport behavior and the state of water in membranes is helpful to develop new proton exchange membranes with controlled transport properties. In addition, the methanol crossover was found to correlate well to the self-diffusion rates of water and methanol in membranes.<sup>12,13</sup> Several works<sup>5,12–18</sup> have investigated the relationship between the sorption behaviors and transport characteristics of water and methanol within proton-conducting membranes.

The microstructure of proton exchange membranes has a significant effect on their solvent sorption and transport characteristics. Proton exchange membranes with smaller hydrophilic domain structures show reduced water uptake.<sup>19</sup> McGrath et al.<sup>20</sup> indicated that connectivity between the hydrophilic domains is another important factor in the transport characteristics of membranes. A membrane with well-connected hydrophilic domains has higher proton conductivity and lower transport activation energy.<sup>21,22</sup> Recently, Zawadzonski et al.<sup>12</sup> reported that the larger hydrophilic domain structures in sulfonated poly(arylene ether sulfone) copolymer membranes may cause significantly higher methanol diffusion coefficients than Nafion<sup>®</sup> at low methanol concentrations. Therefore, analyzing these microstructures and correlating them to the sorption and transportation properties of membranes is helpful in developing novel proton exchange membranes.

This study reports the synthesis of a series of semi-interpenetrating network (SIPN) membranes using poly(vinyl alcohol) with sulfosuccinic acid (SSA) as a crosslinking agent and poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA) as a proton source. These SIPN membranes showed excellent polarization performances regardless of whether hydrogen or methanol was used as the fuel in our previous study.<sup>23,24</sup> A power density value of over 100 mW/cm<sup>2</sup> at 80°C from a direct methanol fuel cell consisting of such a SIPN membrane and commercial binary alloy anode catalysts was obtained.<sup>23</sup> This study systematically investigated the transport characteristics of the SIPN membranes in terms of self-diffusion coefficients and sorption behaviors in terms of  $\lambda$  value and methanol permeability. Specifically, these transport properties correlate well with

the morphology and sorption behaviors of the membranes.

## EXPERIMENTAL

### Materials

Poly(vinyl alcohol) (PVA, average MW: 89,000–98,000 g/mol), sulfosuccinic acid as a crosslinking agent (SSA, 70 wt % solution in water), and poly(styrene sulfonic acid-co-maleic acid) (sodium salt, the ratio of styrene sulfonic acid to maleic acid is 3 : 1, average MW = 20,000 g/mol) as proton sources were purchased from Aldrich. All chemicals were used without further purification.

### Membrane preparation

The PVA/SSA/PSSA-MA solution was prepared by mixing the PVA/SSA and PSSA-MA aqueous solutions with a continuous stirring at 60°C until a homogeneous solution was obtained. The resulting solution was poured into plastic Petri dishes, and water evaporated at 60°C for 1 day. After drying, membranes were peeled off from the dishes and then heated in an oven at 120°C for 1 h. The amounts (%) of SSA and PSSA-MA were determined by the weight basis of PVA (i.e., a PVA/SSA20/PSSA-MA80 membrane consisted of 1 g PVA, 0.2 g SSA, and 0.8 g PSSA-MA). The details of the membrane preparation procedures and conditions were according to our previous work.<sup>24</sup>

The Nafion<sup>®</sup> 115 membrane was pretreated according to a standard procedure: (i) boiling in 3% hydrogen peroxide solution for 1 h to oxidize organic impurities; (ii) boiling in water for 1 h; (iii) boiling in 1M H<sub>2</sub>SO<sub>4</sub> for 1 h to remove any metallic impurities and protonate the membrane; and (iv) boiling in water for 1 h to remove excess acid.

### Surface morphology by atomic force microscopy

Tapping mode atomic force microscopy (AFM, SPI3800N, Seiko Instruments, Chiba, Japan) was performed. All membranes were exposed to room temperature humidity during measurement.

### Ion exchange capacity, water uptake, and lambda value

A titration method was used to determine the ion exchange capacity (IEC). Each membrane was soaked in 1M sodium chloride aqueous solution for 1 day to exchange protons with sodium ions. The ion-exchanged solution was then titrated with a 0.005M sodium hydroxide solution, using phenolphthalein as an indicator. The IEC was calculated using the following equation:

$$\text{IEC} = \frac{M_{i,\text{NaOH}} - M_{f,\text{NaOH}}}{W_{\text{dry}}} = \frac{H^+(\text{mmol})}{W_{\text{dry}}}$$

where  $M_{i,\text{NaOH}}$  is the initial mmol of NaOH of titration and  $M_{f,\text{NaOH}}$  is the mmol ( $m_{\text{eq}}$ ) of NaOH after equilibrium.  $H^+$  is the molar number of proton sites presented in the membrane, and  $W_{\text{dry}}$  is the weight (g) of the dry membrane.

The water/methanol uptakes of the membranes were determined by measuring the membrane weight difference before and after immersion in water for 24 h. The surface of the membrane sample was quickly wiped with a filter paper to remove the excess of water. The wetted membrane weight ( $W_{\text{wet}}$ ) was then measured as quickly as possible. The weight of the dry membrane ( $W_{\text{dry}}$ ) was determined after drying it in a vacuum at 60°C for 1 day. The water/methanol uptake (%) was calculated using the following equation:

$$\text{Water/methanol uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

The lambda value ( $\lambda$ ) representing the number of water or methanol molecules per acid site can be calculated from the water or methanol uptake and IEC values using following equation:

$$\begin{aligned} \lambda_{\text{H}_2\text{O}} &= \frac{(W_{\text{wet}} - W_{\text{dry}})/\text{MW}_{\text{H}_2\text{O}}}{\text{IEC} \times W_{\text{dry}}} \times 1000 \\ &= \frac{n(\text{H}_2\text{O})}{n(\text{acid groups})} \end{aligned}$$

where  $\text{MW}_{\text{H}_2\text{O}}$  is the molecular weight of water (18.01 g/mol), and IEC is the ion exchange capacity (mmol/g) of the membrane.

### Water states in membrane

The freezing water (unbound water) and nonfreezing water (bound water) in fully hydrated membranes were determined using a differential scanning calorimeter (DSC 2010, TA Instruments, New Castle, DE) equipped with a rapid cooling system (RCS). The samples were loaded into aluminum pans and then heated at a rate of 3°C/min with a nitrogen gas flow rate of 50 mL/min. The freezing water content was then determined using following equation:

$$m_{\text{free}} = \frac{\Delta H_{\text{free}}}{Q_{\text{melting}}} \times m_{\text{total}}$$

where  $Q_{\text{melting}}$  is the melting enthalpy of pristine water at 0°C,  $\Delta H_{\text{free}}$  is the heat of melting around 0°C, and  $m_{\text{total}}$  is the total uptake water.

### Water and methanol self-diffusion coefficients in the membrane

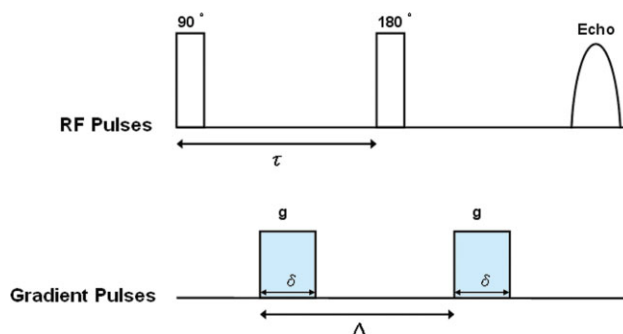
Before testing, membranes were soaked in water or methanol for at least 1 day. After the surface solvent was removed, the membrane was quickly placed in an NMR tube and sealed. The self-diffusion coefficient was measured using a Varian Infinityplus-500 NMR spectrometer (Varian, Inc., Palo Alto, CA). The pulsed gradient spin-echo (PGSE) pulse sequence began with a 90° pulse followed by two identical gradient pulses, separated by a 180° pulse. These pulses attenuate the echo when there are diffusing nuclei, as Figure 1 shows. Experiments were carried out with a decreasing gradient strength from 250 to 25 G/cm for a total of 10 points. The signal intensity ( $A$ ) as a function of the gradient strength ( $g$ ) was recorded. Stejskal and Tanner<sup>25</sup> reported that the predicted dependence of signal attenuation on gradient strength is

$$\ln \frac{A(2\tau)}{A_0(2\tau)} = - \left[ (\gamma_H G \delta)^2 \left\langle \Delta - \frac{\delta}{3} \right\rangle \right] D$$

where  $A(g)$  is the signal intensity as a function of the applied gradient  $g$ ,  $A(0)$  is the signal intensity observed in the absence of an applied gradient,  $\gamma$  is the nuclear gyromagnetic ratio,  $D$  is the diffusion coefficient,  $\delta$  is the length of the gradient pulse, and  $\Delta$  is the diffusion time between gradient pulses.

### Methanol permeability through membranes

The methanol permeability of membranes was determined using a home-made side-by-side glass diffusion cell. This cell consisted of two compartments, each approximately 80 mL, separated by a test membrane with a membrane cross-sectional area of 3.19 cm<sup>2</sup>. The membranes were placed between the two compartments by a screw clamp. Prior to all experiments, the membranes were equilibrated in water for 1 day. The receptor compartment was initially filled with water, whereas the donor



**Figure 1** Pulse field gradient spin-echo sequence. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



compartment was filled with a 3 wt % methanol solution. The concentration of methanol in the receptor compartment was measured using gas chromatography (GC, China Chromatography 9800, Taipei County, Taiwan) at regular intervals. Methanol permeability was determined from the slope of the plot of methanol concentration in the receptor compartment versus time, as described elsewhere.<sup>26</sup>

## RESULTS AND DISCUSSION

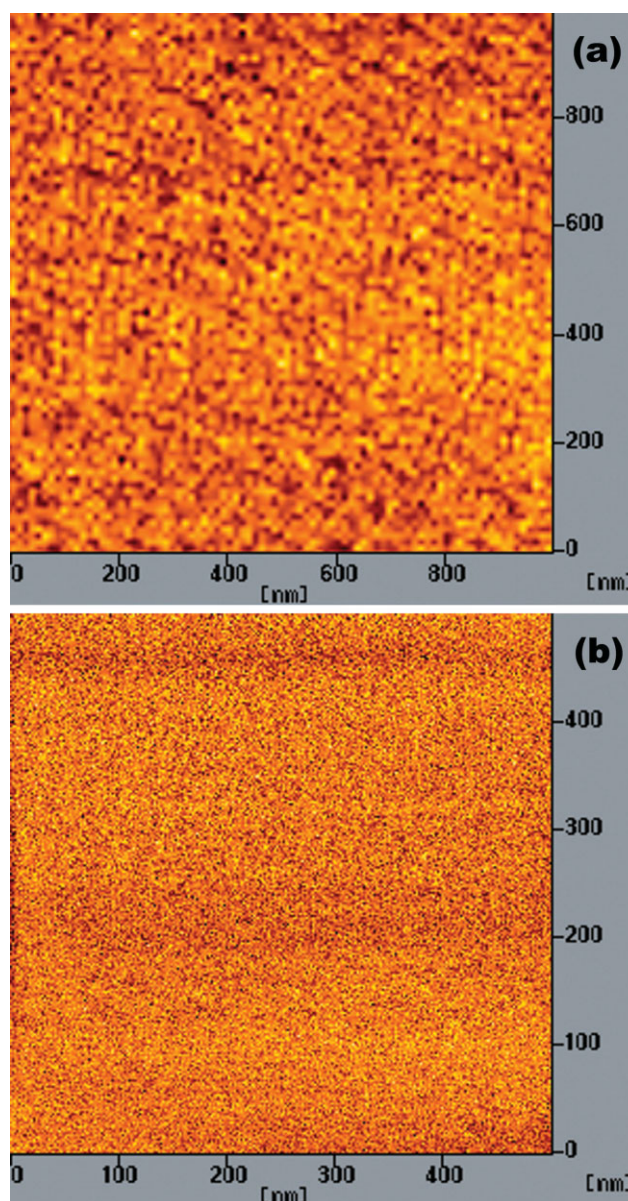
Our previous study<sup>24</sup> found that the SIPN-60 and SIPN-80 membranes have higher proton conductivity than Nafion<sup>®</sup> 115. Accordingly, we selected the SIPN-60 and SIPN-80 membranes and Nafion<sup>®</sup> 115 to further investigate their water and methanol transport properties and to establish the correlation between the transport properties and sorption behaviors in these membranes.

### Surface morphology of the membranes

Figure 2 shows the tapping mode AFM (TM-AFM) phase images of the surface morphology of Nafion<sup>®</sup> 115 and SIPN-80 membranes. The hydrophilic groups on Nafion<sup>®</sup> 115 aggregated as isolated domains, forming a well-defined phase separation morphology. In contrast, the SIPN-80 membrane exhibited a relatively homogeneous morphology without apparent phase separation between the hydrophilic and hydrophobic domains. The difference in chemical structure between Nafion<sup>®</sup> 115 and the SIPN-80 membranes with a semi-interpenetrating network is responsible for this result. Our previous study also confirmed that hydrogen bonds form between PVA and PSSA-MA.<sup>24</sup> These interactions enhance the formation of homogeneous microstructures.<sup>27</sup> Recently, Smith et al.<sup>28</sup> reported that the existence of interpolymer interactions between PVA and chitosan forms a homogeneous and dense PVA/chitosan membrane. Similarly, the contrast between the relatively homogeneous morphology of the SIPN-80 membrane and Nafion<sup>®</sup> 115 could be ascribed to the reason that the semi-interpenetrating network structure and the strong interaction between PVA and PSSA-MA enhanced the formation of homogeneous microstructures.

### Solvent sorption behaviors of the membranes

Table I shows the measured IEC values, water uptake values, and  $\lambda$  values of Nafion<sup>®</sup> 115 and the SIPN membranes. The IEC value, water uptake, and  $\lambda_{\text{H}_2\text{O}}$  of the SIPN-80 membrane are all greater than that of the SIPN-60, respectively. This difference can be ascribed to higher contents of sulfonic and maleic acid in the former membrane. The  $\lambda_{\text{H}_2\text{O}}$  values of the SIPN membranes are all lower than that of Nafion<sup>®</sup>



**Figure 2** TM-AFM phase images (a) Nafion<sup>®</sup> 115, (b) SIPN-80 membrane. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

115. The  $\lambda_{\text{H}_2\text{O}}$  value of Nafion<sup>®</sup> 115 was also measured under the same condition as 22.9, which is in good agreement with the literature.<sup>4,29</sup> This result seems to imply different water sorption behaviors of Nafion<sup>®</sup> 115 and the SIPN-80 membranes. The solvent uptake levels of the associated membranes in various methanol concentrations were measured to further investigate the sorption behavior of the SIPN and Nafion<sup>®</sup> 115.

Figure 3 shows that the water/methanol solvent uptake characteristics of Nafion<sup>®</sup> 115 and SIPN membranes were clearly distinguishable. The SIPN-80 membrane swelled in pure water and had a higher water uptake than did Nafion<sup>®</sup> 115. This can

TABLE I  
IEC, Solvent Uptakes, and Lambda Values of Water and Methanol in SIPN and Nafion<sup>®</sup> 115 Membranes

Sample	IEC (mmol/g)	Water uptake (wt %)	Methanol uptake (wt %)	$\lambda_{\text{H}_2\text{O}}$	$\lambda_{\text{CH}_3\text{OH}}$	$\lambda_{\text{CH}_3\text{OH}}/\lambda_{\text{H}_2\text{O}}$
SIPN-60	1.63	52.1	32.2	17.8	6.2	0.35
SIPN-80	1.86	62.9	35.8	18.8	6.0	0.32
Nafion <sup>®</sup> 115	0.9	37.0	62.6	22.9	21.7	0.95

be related to the higher IEC value of SIPN-80 membranes, as shown in Table I. As the methanol concentration increased, Nafion<sup>®</sup> 115 membrane exhibited a nearly linear increase in solvent uptake through a maximum value at a methanol mole fraction of 0.63. This trend is in good agreement with the literature,<sup>30</sup> which also reported that water and methanol have very similar behavior in Nafion<sup>®</sup> membranes. Methanol went into the Nafion<sup>®</sup> membrane in addition to water and increased with the increase of methanol concentration at low methanol concentrations; consequently, water became excluded at high methanol concentrations. Similar results have been found in previous studies.<sup>4</sup> Contrarily, SIPN-80 showed a decreasing trend of solvent uptake with the increase of methanol concentration, and the methanol uptake of the SIPN membrane was about half that of Nafion<sup>®</sup> 115. These different sorption behaviors may be ascribed to the discrepancy between the chemical crosslinking structure of the SIPN membranes versus the physical crosslinking structure of Nafion<sup>®</sup> 115. Our previous study<sup>24</sup> identified the chemical crosslinking structure between PVA and SSA.

The chemical crosslinking structure of a proton exchange membrane may result in a favorable morphology, inhibiting excess swelling of the membrane in the fully hydrated state.<sup>31</sup> We believe that the chemical crosslinking structure can help stabilize the

microdomain structure of the SIPN membranes, regardless of whether the membrane was immersed in what concentration of methanol solutions. Contrarily, Villaluenga et al.<sup>32</sup> reported that the porosity of Nafion<sup>®</sup> increased with the increase of methanol concentration, indicating the increase of the dimensions of the channels connecting the swollen ionic cluster in Nafion<sup>®</sup> membrane. In addition, the size of the clusters for a water-swollen Nafion<sup>®</sup> membrane was reported to be smaller than that of a methanol-swollen membrane,<sup>33</sup> manifesting the dependence of the microstructure of Nafion<sup>®</sup> on the concentration of methanol solutions.

Comparison of sorption preference between methanol and water in Nafion<sup>®</sup> 115 and SIPN-80 membranes can be identified extensively by comparing the ratio of  $\lambda_{\text{CH}_3\text{OH}}$  to  $\lambda_{\text{H}_2\text{O}}$  in those membranes. Table I shows the  $\lambda$  ratios for SIPN-60, SIPN-80, and Nafion<sup>®</sup> 115 membranes. For Nafion<sup>®</sup> 115, the  $\lambda$  values of water and methanol are very close (22.9 for water and 21.7 for methanol). This result indicates equal sorption preference for water or methanol and agrees well with the literature.<sup>4,30</sup> In contrast, the values of  $\lambda_{\text{H}_2\text{O}}$  and  $\lambda_{\text{CH}_3\text{OH}}$  in SIPN membranes differ greatly. For both SIPN-60 and SIPN-80 membranes, the values of  $\lambda_{\text{CH}_3\text{OH}}$  are only one-third those of  $\lambda_{\text{H}_2\text{O}}$ . These results indicate that SIPN membranes have higher selectivity in sorption of water over methanol.

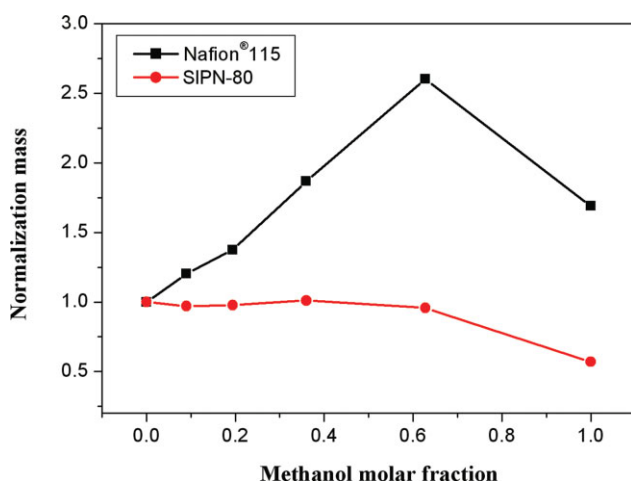


Figure 3 Solvent uptakes of Nafion<sup>®</sup> 115 and SIPN-80 membranes as a function of methanol concentration. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

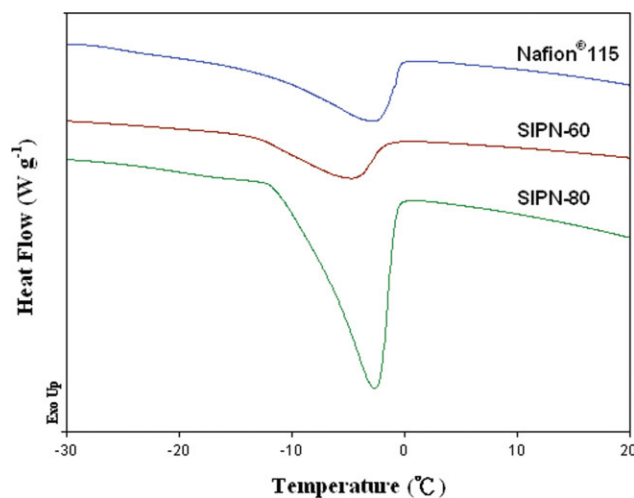


Figure 4 DSC heating curves of the fully hydrated SIPN and Nafion<sup>®</sup> 115 membranes. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE II  
Distributions of Water States in SIPN and Nafion® 115 Membranes

Sample	Water uptake (wt %)	Unbound water (%)	Bound water (%)	Unbound water/total water (%)	Bound water/total water (%)
SIPN-60	52.1	3.5	48.6	6.7	93.3
SIPN-80	62.9	13.3	49.6	21.1	78.9
Nafion® 115	37.0	8.4	28.6	22.8	77.2

### Water states in the membranes

This study categorizes water in different states in polymers as free water, freezable bound water, and nonfreezing water. These terms refer to water that is strongly bound to sulfonic acid groups (nonfreezing water), weakly bound to polymer chains (freezable bound water), and water that has the same properties as bulk water (free water), respectively.<sup>34</sup> Recently, Hickner and coworkers<sup>29</sup> indicated that the transport of proton and methanol in proton exchange membranes occurs through hydrated regions containing unbound or loosely bound water. Therefore, this study uses a DSC to determine the distributions of bound and unbound water existing in the associate membranes.

Figure 4 shows the DSC curves of fully hydrated SIPN and Nafion® 115 membranes. As can be seen, the SIPN-80 holds more unbound water than the SIPN-60, primarily due to the influence of higher acidic groups in the former membrane. Table II summarizes the distribution of water states in these membranes in terms of bound and unbound water. Note that the water state distributions in the SIPN-80 and Nafion® 115 membranes are similar. Therefore, it is worthy to investigate the transport properties of SIPN-80 and Nafion® 115 membranes to further determine the effect of microstructure and morphology on the transport of water and methanol.

### Self-diffusion characteristics

The self-diffusion coefficients in Nafion® 115 and the SIPN-80 membranes were studied using the pulsed field-gradient nuclear magnetic resonance (PFG-NMR) method. Figure 5 indicates the resulting linear relationship between  $\ln A(2\tau)/A_0(2\tau)$  and  $(\gamma_H G \delta)^2 \langle \Delta - \delta/3 \rangle$  of Nafion® 115 and the SIPN membranes. The self-diffusion coefficients in the associated membranes can be determined from this slope. Table III shows water and methanol self-diffusion coefficients in Nafion® 115 and the SIPN-80 membranes at 30°C. The water self-diffusion coefficient of fully hydrated Nafion® 115 is  $8.89 \times 10^{-6}$  cm<sup>2</sup>/s, which agrees well with previous studies.<sup>5,14</sup> On the other hand, water self-diffusion coefficients in the SIPN membranes increased as the PSSA-MA content increased. This result correlates with the fact that unbound water was

higher within the SIPN-80 membrane than that within the SIPN-60 membrane.

Considering that the water state distribution in SIPN-80 is similar to that in Nafion® 115, the effects of membrane morphology on water transport can be identified by comparing the difference of water self-diffusion coefficients between SIPN-80 and Nafion® 115 membranes. For the SIPN-80 membrane, the water self-diffusion coefficient measures  $3.75 \times 10^{-6}$  cm<sup>2</sup>/s, or about one third of that in Nafion® 115. This difference is caused by the different chemical environments and morphologies of the SIPN-80 and Nafion® 115 membranes. The following section describes the effect of chemical environment and morphology on the transport of water through membranes.

The great polymer chain segmental mobility, highly fluorinated backbone, and strongly acidic sulfonic acid groups of Nafion® appear to be helpful in transporting water.<sup>35</sup> In contrast to Nafion®, PVA-based semi-interpenetration network membranes have chemical crosslinking networks and specific acid-base interactions between the penetrating PSSA-MA molecular chains and the PVA network. This chemical cross-linking can help stabilize the microdomain structure,<sup>31</sup> and the acid-base interactions between polymers can help form a dense membrane.<sup>28</sup>

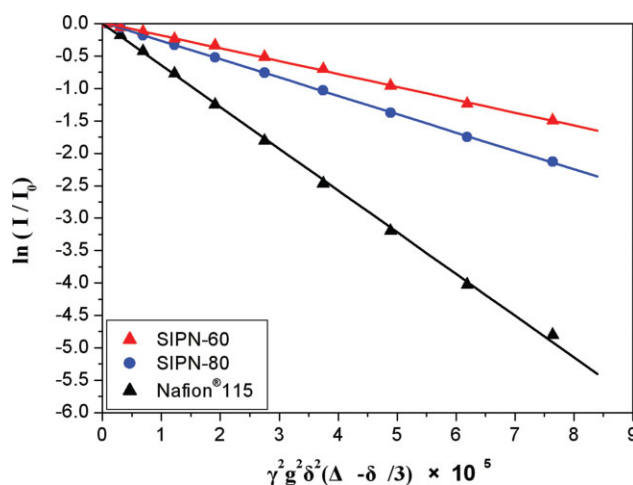


Figure 5 Plot of  $\ln(I/I_0)$  vs.  $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$  of SIPN and Nafion® 115 membranes in the fully hydrated state. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**TABLE III**  
**Water and Methanol Self-Diffusion Coefficients**  
**in SIPN and Nafion® 115 Membranes**

Sample	$D_{\text{H}_2\text{O}}$ ( $\text{cm}^2/\text{s}$ )	$D_{\text{CH}_3\text{OH}}$ ( $\text{cm}^2/\text{s}$ )	$D_{\text{CH}_3\text{OH}}/D_{\text{H}_2\text{O}}$	Methanol permeability ( $\text{cm}^2/\text{s}$ )
Water <sup>a</sup>	$2.3 \times 10^{-5}$	N/A	N/A	N/A
Methanol <sup>a</sup>	N/A	$2.4 \times 10^{-5}$	N/A	N/A
SIPN-60	$2.57 \times 10^{-6}$	N/A	N/A	$2.96 \times 10^{-7}$
SIPN-80	$3.75 \times 10^{-6}$	$5.47 \times 10^{-7}$	0.146	$4.10 \times 10^{-7}$
Nafion® 115	$8.89 \times 10^{-6}$	$8.63 \times 10^{-6}$	0.97	$1.8 \times 10^{-6}$

<sup>a</sup> Data obtained from Ref. 5.

Therefore, we would deduce that the semi-interpenetrating network structure and specific acid–base interactions can lead to distinguishable water mobility behavior in the SIPN membranes out of Nafion®.

Table III shows the methanol self-diffusion coefficients in SIPN and Nafion® 115 membranes. The methanol self-diffusion coefficient of Nafion® 115 measures  $8.63 \times 10^{-6} \text{ cm}^2/\text{s}$ , very close to its water self-diffusion coefficient. This result is consistent with the fact that Nafion® 115 shows no preference in the sorption of water or methanol. Accordingly, it can be concluded that Nafion® 115 has no specific selectivity in either sorption or transport of water and methanol. On the other hand, the methanol self-diffusion of SIPN membranes exhibits remarkably different behavior. The methanol self-diffusion coefficient of SIPN-80 membrane measures  $5.47 \times 10^{-7} \text{ cm}^2/\text{s}$ , an order of magnitude lower than that of Nafion® 115 ( $8.63 \times 10^{-6} \text{ cm}^2/\text{s}$ ). This value is also much lower than the water self-diffusion coefficient ( $3.75 \times 10^{-6} \text{ cm}^2/\text{s}$ ) in the same membrane.

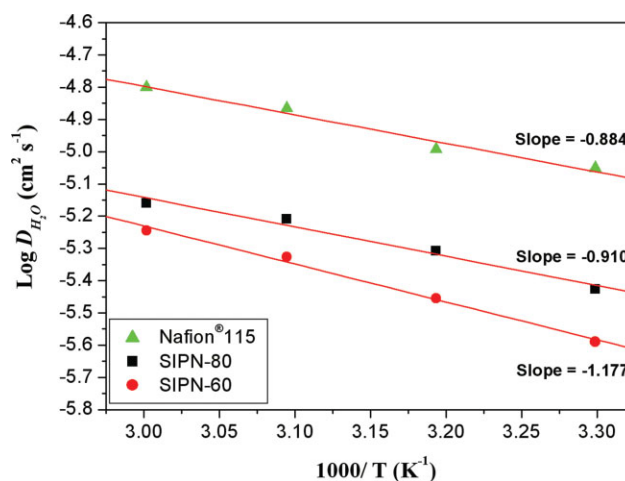
A comparison of the self-diffusion coefficient ratio of water to methanol, expressed as  $D_{\text{CH}_3\text{OH}}/D_{\text{H}_2\text{O}}$ , is shown in Table III. The ratio of the SIPN-80 membrane is approximately one-seventh that of Nafion® 115 (0.146 for SIPN-80 and 0.97 for Nafion® 115). This result indicates that the SIPN-80 membranes have higher selectivity in water transport over methanol transport. The results of diffusion behavior are strongly correlated to the sorption behaviors of the corresponding membranes.

#### Temperature dependence of self-diffusion coefficients

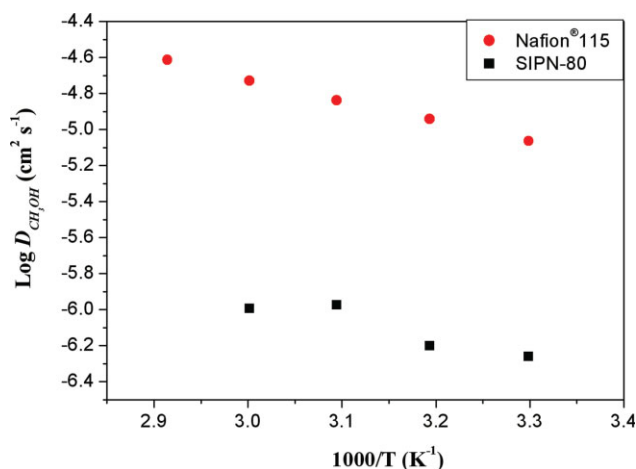
Figure 6 shows the Arrhenius plot of the water self-diffusion coefficients for Nafion® 115 and SIPN membranes in a fully hydrated state. All membranes exhibited positive temperature dependence of self-diffusion coefficient. The slopes of the SIPN-80 and Nafion® 115 membranes are quite close and are slightly higher than that of the SIPN-60 membrane. This result can be explained by the distribution of water states in these membranes as follows.

The evaporation of free water occurs faster than bound water in a vaporized measuring condition.<sup>36</sup> This means that membranes with a higher content of free water will exhibit greater degrees of dehydration at higher temperatures. It can be seen from Table II that SIPN-80 and Nafion® 115 have close values of ratio of unbound water/total water in membranes, and SIPN-60 has a much lower value. This means that the former two membranes have higher free water content than the latter under the fully hydrated state. This explains why the SIPN-60 membrane shows a lower slope than Nafion® 115 and SIPN-80 membranes.

Figure 7 shows the Arrhenius plot of the methanol self-diffusion coefficients for SIPN-80 and Nafion® 115 membranes under a fully methanol uptake state at different temperatures. Note that the methanol self-diffusion coefficient in SIPN-80 sluggishly decreased when the temperature is over  $50^\circ\text{C}$ . However, it still linearly increased in Nafion® 115 during the measured temperature range, even up to  $70^\circ\text{C}$ . This result implies that methanol is well retained in



**Figure 6** Comparison of water self-diffusion coefficients between Nafion® 115 and SIPN membranes as a function of temperature. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 7** Comparison of methanol self-diffusion coefficients between Nafion® 115 and SIPN-80 membranes as a function of temperature. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Nafion® 115 at temperatures up to 70°C.<sup>16</sup> This result corresponds well to the observations in sorption behaviors such as the solvent uptake and  $\lambda$  values of the membranes as discussed in previous sections.

### Methanol permeabilities of the membranes

Table III presents the measurements of methanol permeability of SIPN membranes and Nafion® 115. SIPN-80 exhibits higher methanol permeability than SIPN-60. Similar trends in the effect of PSSA-MA content in SIPN membranes on solvent uptake were also observed, as shown in Table II. For comparison, this study also measured the methanol permeability of Nafion® 115 under similar experimental conditions. The value for Nafion® 115 is  $1.8 \times 10^{-6}$  cm<sup>2</sup>/s, which agrees well with the literature.<sup>37</sup> Both SIPN membranes have lower values of methanol permeability than Nafion® 115. The methanol permeability of the SIPN-80 membrane ( $4.1 \times 10^{-7}$  cm<sup>2</sup>/s) is only about one fourth that of Nafion® 115. The methanol permeability of a membrane is highly related to its methanol uptake and self-diffusion behavior. The lower methanol permeability of the SIPN-80 membrane is strongly correlated to its lower methanol uptake and lower self-diffusion coefficient of methanol. These results indicate that SIPN membranes have better methanol resistance than Nafion® 115 and may therefore be suitable to be used as proton-conducting membranes in DMFCs.

### CONCLUSIONS

This study systematically investigated the sorption and transport properties of PVA-based SIPN mem-

branes and compared them with Nafion® 115. A significant difference in the sorption behavior of Nafion® 115 and SIPN-80 membranes was identified by solvent uptake and  $\lambda$  values. Nafion® 115 showed no preference in sorption of water and methanol. In contrast, SIPN membranes exhibited excellent selectivity of sorption of water over methanol. The solvent uptake of Nafion® 115 increased as the methanol concentration increased, up to a methanol mole fraction of 0.63, and then decreased. On the other hand, the solvent uptake of the SIPN-80 membrane decreased sluggishly as the methanol concentration increased. Moreover, the ratios of  $\lambda_{\text{CH}_3\text{OH}}/\lambda_{\text{H}_2\text{O}}$  for SIPN membranes were only about one-third that of Nafion® 115. The transport properties of the SIPN and Nafion® 115 membranes were also identified by water and methanol self-diffusion coefficients. Compared with Nafion® 115, SIPN membranes showed lower water and methanol self-diffusion coefficients. Moreover, the ratio of  $D_{\text{CH}_3\text{OH}}/D_{\text{H}_2\text{O}}$  for SIPN-80 was approximately only one-seventh that of Nafion® 115. Evidently, there is a good correlation between the sorption behavior and transport behavior for Nafion® 115 and SIPN-80 membranes. The SIPN-80 membrane exhibited excellent selectivity of water over methanol in both sorption and transport properties. With a methanol permeability of  $4.1 \times 10^{-7}$  cm<sup>2</sup>/s, the SIPN-80 membrane promises to be a good candidate as a proton-conducting membrane in DMFCs.

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