

Nafion/PTFE/silicate composite membranes for direct methanol fuel cells

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Abstract

Poly(tetrafluoro ethylene) (PTFE)/Nafion composite membranes (PN composite membranes) were prepared by impregnating micro-porous PTFE membranes in Nafion/2-propanol/water solutions. The PN composite membranes were then further impregnated with tetraethoxysilane (TEOS) solutions to prepare PTFE/Nafion/silicate (PNS) composite membranes. The influence of hybridizing silicate into the PN membranes on their direct methanol fuel cell (DMFC) performance and methanol crossover was investigated. Silicate in PN membranes causes reduction both in proton conductivity and methanol crossover of membranes. Thus PNS had a higher voltage than PN at low current densities due to the lower methanol crossover of PNS. However, at high current densities, PNS had a lower voltage than PN due to the higher resistance to proton transference of PNS. The range of lower current densities where PNS had a higher voltage than PN was $i = 0\text{--}120\text{ mA cm}^{-2}$ when the methanol feed concentration was 2 M. This lower current density range became broader as the methanol feed concentration was increased, and it was broadened to $i = 0\text{--}190\text{ mA cm}^{-2}$ as the methanol feed concentration was increased to 5 M. A comparison of the methanol crossover on the DMFC performance of PN and PNS with Nafion-112 was also studied. We showed that Nafion-112 exhibits higher methanol electro-osmosis than PN and PNS. Thus at a high current density, the higher methanol crossover via electro-osmosis caused Nafion-112 to have a lower voltage than PN and PNS. © 2006 Elsevier B.V. All rights reserved.

Keywords: Nafion; Poly(tetrafluoro ethylene); Tetraethoxysilane; Composite membrane; Direct methanol fuel cell

1. Introduction

Perfluorosulfonated ionomer (Nafion, a registered trademark of DuPont Co.) membrane is successfully used as the proton exchange membrane (PEM) a fuel cell using H₂ as the fuel and O₂ (or air) as the oxidant. It is generally accepted that PEM fuel cells present an attractive alternative to traditional power sources, due to their high efficiency and lack of pollution. However, it is known that the application of Nafion membranes to direct methanol fuel cells (DMFC), causes the problem of *methanol crossover* and lowers the DMFC performance [1,2]. The methanol crossover results in depolarization losses at the cathode and efficiency losses due to lost fuel. Researchers have made efforts to reduce *methanol crossover* by modifying the Nafion membranes via hybridizing Nafion with inorganic

nano-particles, such as silicone oxide [3–6], tetraethoxysilane (TEOS) [7–9], zirconium oxide [10–12] and phosphotungstic acid [13–15], etc. It had been reported that the methanol crosses over either by diffusion or by electro-osmosis through the ionic clusters of Nafion membranes. Mixing inorganic nano-particles into Nafion membranes and leading the nano-particles to locate inside the ionic clusters of Nafion membranes could reduce methanol crossover [3–15].

In the literature, it has been reported that composite membranes can be prepared by impregnating a low cost micro-porous support material, such as poly(tetrafluoro ethylene) (PTFE) membranes, with a Nafion solution [16–22]. The advantages of the composite membranes are: low cost, good mechanical strength in both swollen and un-swollen states, good thermal stability, and a potentially thinner membrane (the thickness of composite membranes, prepared in our lab, is around 20 μm, the thicknesses of Nafion-117 and Nafion-112 membrane are around 175 and 50 μm, respectively), thus lowering the ionic resistance of the membranes. It had also been reported that a PTFE/Nafion (PN) composite membrane has a better H₂/O₂ polymer electrolyte membrane fuel cell (PEMFC) [19–22] and

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DMFC [23] performance than DuPont Nafion-series membranes (i.e., Nafion-117, Nafion-115 and Nafion-112). These experimental results indicated that inserting porous PTFE into the Nafion polymer caused reduction in the methanol crossover, and the lower thickness of the PN composite membrane led to a lower proton resistance. Thus a PN composite membrane has a better DMFC performance than a Nafion-117 membrane. Modification of pure Nafion membranes by TEOS via the sol–gel process has been reported by Mauritz and co-workers [7–9]. It was shown that methanol crossover of the Nafion membrane could be reduced by hybridizing the membranes with TEOS. In this paper, we have tried to reduce the methanol crossover of PN composite membranes by hybridizing TEOS solutions into the PN composite membranes via sol–gel processing. The influence of hybridizing silicate into PN composite membranes on DMFC performance was investigated.

2. Experimental

2.1. Materials

The Nafion solution (DuPont Co.) was a 5 wt% of 1100 EW Nafion diluted in a mixture solvent containing water, 2-propanol, methanol and unspecified ethers [24]. The porous poly(tetrafluoro ethylene) membrane (PTFE membrane, Yue-Ming-Tai Chemical Ind. Co., Taichung, Taiwan) with thickness of $18 \pm 3 \mu\text{m}$, pore sizes of $0.5 \pm 0.1 \mu\text{m}$, and porosity of $52 \pm 5\%$ was used as a supporting material of composite membranes. Tetraethoxysilane (TEOS, Aldrich Chemical Co.) with a purity of 98% was used without any purification.

2.2. Preparation of PTFE/Nafion (PN) composite membranes

Porous PTFE membranes were mounted on a steel frames and boiled in acetone at 55°C for 1 h. The pretreated PTFE membranes were impregnated with a 5 wt% Nafion/2-propanol/water (with 2-propanol/water = 4/1, w/w) solution for 24 h and then annealed at 120°C for 1 h. The weight ratio of Nafion/PTFE of composite membranes without swelling with water was around 53.8/46.2. After annealing, these membranes were then swollen with distilled water for 24 h, and then swollen with 1N sulfuric acid solution for another 4 h. The thickness of the composite membrane was around $20 \pm 3 \mu\text{m}$.

2.3. Preparation of PTFE/Nafion/silicate (PNS) composite membranes

The procedures for preparing silicate modified PN composite membranes were similar to that of preparing TEOS modified Nafion membranes, reported by Mauritz et al. [7–9]. (1) The TEOS/water/HCl (1/4/0.5 in mole ratio) solution was prepared with continuous stirring at room temperature for 5 h. The TEOS/water/HCl solution was then mixed with methanol to prepare TEOS/water/HCl/methanol solutions, which contained 50 and 80 vol% of TEOS/water/HCl solution for preparing PNS-3 and PNS-4 membranes, respectively. (2) The PN composite

membranes, which were prepared as described in Section 2.2 above but without swelling with sulphuric acid, were impregnated in a methanol/water (2/1, v/v) mixture solvent for 10 min at room temperature. The membranes were then impregnated into TEOS/water/HCl/methanol solutions for another 10 min. The surfaces of the membranes were then washed with distilled water to clean out the TEOS covered on the surfaces of the membranes. Only the TEOS molecules in the ionic clusters of Nafion were left inside the membranes. The membranes were then kept at 100°C for 1 h to promote TEOS crosslinking reactions inside the membranes, and then swollen with 1N sulfuric acid for another 4 h. Table 1 shows the compositions of dried PN and PNS membranes without swelling with water. The thickness of composite membranes was around $\sim 20 \pm 3 \mu\text{m}$.

2.4. Characterizations of the PN and PNS composite membranes

2.4.1. Scanning electron microscopy (SEM) study

The morphology of surfaces of composite membranes were investigated using a scanning electron microscope (SEM, model JSM-5600, Jeol Co., Japan). The samples surfaces were coated with gold powder under vacuum before SEM observations were carried out.

2.4.2. Thermogravimetric analysis (TGA) study

Thermogravimetric analyses of composite membranes were carried out using a Perkin-Elmer model Pyris-1 TGA with a heating rate of $10^\circ\text{C}/\text{min}$ and a nitrogen flow rate of 145 ml/min. The samples weights for analyses were around 10 mg.

2.4.3. Conductivity measurement

The ionic conductivity (σ) was calculated from the measured current resistance (R) using Eq. (1):

$$\sigma = \frac{l}{A \times R} \quad (1)$$

where A is the cross section area of a membrane for resistance measurement and l is the thickness of a membrane. R was measured using an ac impedance system (model SA1125B, Solartron Co., UK). A device capable of holding a membrane for R measurement was located between probes. The testing device with a membrane was kept in a thermo-state under a relative humidity of 95% and a temperature of 70°C . The membrane area A for R measurement was 3.14 cm^2 . The proton resistance r per unit area of a membrane was obtained from Eq. (2):

$$r = \frac{l}{\sigma} = AR \quad (2)$$

Table 1
Compositions of dried PNS membranes (wt ratio)

Membrane	Nafion	PTFE	Silicate
PN	59.40	40.60	0.0
PNS-3	57.80	40.26	1.94
PNS-4	56.84	40.37	2.79

2.4.4. Methanol crossover measurement

Methanol crossover of membranes was investigated using an apparatus designed in our lab. A device for holding a membrane was located in the middle, to separate a container (204 ml) into two vessels, with each vessel having a volume of 102 ml. The cross section of the membrane for methanol crossover measurement was a round shape with a diameter of 2.6 cm (i.e., the cross section area was 5.31 cm²). At the beginning of the methanol crossover test, vessel-1 was filled with 13 wt% methanol/water solution and vessel-2 was filled with pure water. The whole apparatus was kept at a temperature of 25 °C. The methanol across the membrane was characterized by measuring the methanol concentration of vessel-2 (C_2) versus testing time using a gas chromatography (GC, HP Co model 8590A) with a capillary column (Agilent Co., 30 m × 0.53 mm × 20 μm) and a TCD detector. The carrier gas of GC was helium and the injection sample size was 0.2 μl. The injector, oven and detector temperatures of GC were 120, 100 and 130 °C, respectively. Six standard methanol aqueous solutions with known methanol concentrations were prepared to run GC calibration curves. The methanol concentration C_2 of each methanol crossover measurement was calculated from GC data using a standard calibration curve.

2.5. Direct methanol fuel cell (DMFC) performance test

2.5.1. Preparation of the membrane electrode assembly (MEA)

The Nafion membranes purchased from DuPont Co., i.e., Nafion-112, PN, PNS-3 and PNS-4 composite membranes prepared in this work were used for MEAs (area = 5 cm × 5 cm) preparation. The gas diffusion layer of MEA was a carbon paper (E-TEK Co.) pre-treated with FEP (fluoroethylene polymer) resin (DuPont Co.). The Pt-Ru catalyst (E-TEK Pt-Ru/C catalyst with 40 wt% Pt-Ru) content of anode was 4.0 mg cm⁻² and the Pt catalyst (E-TEK Pt/C catalyst with 40 wt% Pt) content of cathode was 2.0 mg cm⁻².

2.5.2. DMFC performance test

The performance of DMFC single cells prepared from Nafion-112, PN, PNS-3 and PNS-4 membranes were tested at 70 °C using a Globe Tech Computer Cell GT testing system (Electrochem Inc.). The anode input methanol flow rate was 5 ml min⁻¹ with various methanol concentrations, i.e., 2, 3, 4 and 5 M, and the cathode input O₂ flow rate was 150 ml min⁻¹. Before i - V data was collected, the cell was activated for 3 h to enhance the humidification and activation of MEA. i - V curves were obtained by measuring the current density i with stepwise decrements of voltage of 0.05 V and held for 20 s for each measurement.

3. Results and discussion

3.1. SEM study of the morphology of PNS composite membranes

PN composite membranes were prepared following the procedures described in Section 2.2. The PN composite membrane

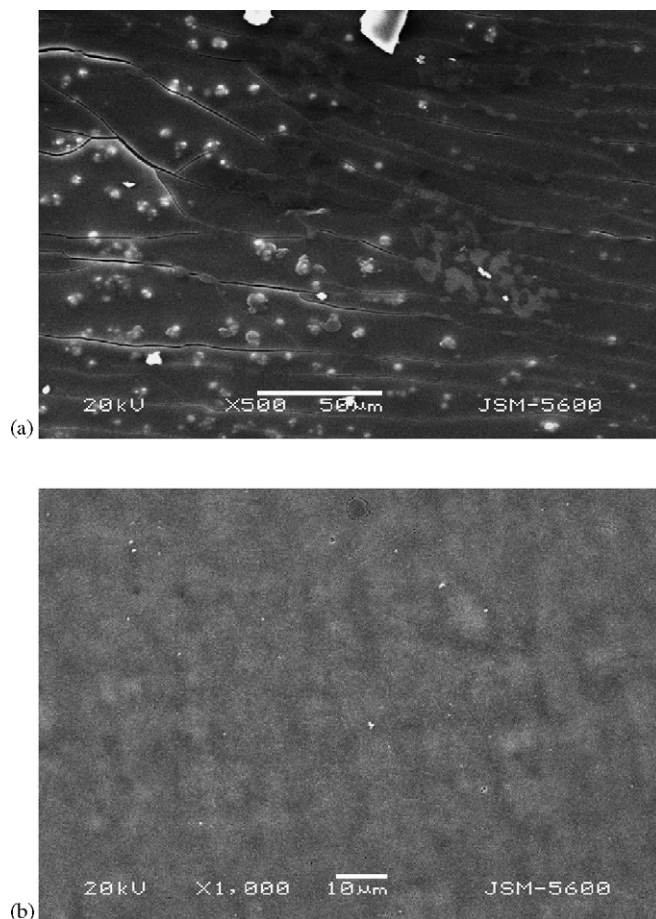


Fig. 1. SEM micrographs of the surface of PNS composite membrane. (a) (Top) PNS-3n membrane, a PN composite membrane with silicate on its surface (×500); (b) (bottom) PNS-3 membrane, which is same as that of (a), but TEOS covered on the surface of membrane was cleaned out with distilled water before heating at 100 °C to promote silicate crosslinking.

was then treated with TEOS/water/HCl/methanol solutions and then heated at 100 °C for 1 h to promote TEOS silicate crosslinking as described in Section 2.3. Fig. 1a shows the SEM micrograph of a PNS composite membrane without cleaning the surface of the membrane (designated as sample PNS-3n). Fig. 1b shows the same membrane as that shown in Fig. 1a, but the membrane had been washed with distilled water to clean out TEOS covered on the surface of the membrane before heating at 100 °C to promote silicate crosslinking (designated as sample PNS-3). As shown in Fig. 1a and b, the surfaces of PTFE membranes were completely covered and filled with Nafion resin and no micro-pores of PTFE membranes were observed in the micrograph, indicating the porous PTFE membranes were well impregnated with Nafion resin. Fig. 1a shows that the surface of the PTFE/Nafion composite membrane was covered with a thin film of crosslinked silicate with small crosslinked silicate particles (diameter 1–2 μm) dispersed on its surface. The crosslinked silicate thin film seems to be rigid and cracking can be clearly seen in the SEM micrograph. However, no crosslinked silicate particle was observed on the surface of the PNS-3 membrane (Fig. 1b), indicating that TEOS thin film covered on the surface of PN composite membrane had been washed

out. Only the TEOS molecules inserted into ionic clusters of Nafion remained in the PN membranes. It is noticed that the silicate content (1.9–2.8 wt%) in the present PTFE/Nafion/silicate composite membranes is much lower than the silicate content (6.4–21.2 wt%) of Nafion/silicate hybrid membranes reported by Jung et al. [25]. Jung prepared Nafion/silicate hybrid membranes using a higher thickness Nafion-115 membrane (thickness 125 μm) without washing out the silicate covered on the surfaces of membranes. The presence of PTFE and the lower thickness of PN composite membranes caused much less TEOS molecules inserted into Nafion ionic clusters of Nafion in PN membranes than in Nafion-115 membranes.

3.2. Thermogravimetric analysis (TGA) study

Fig. 2 shows the TGA curves of PTFE, Nafion, PN, PNS-3 and PNS-4 membranes. As temperature increases, the weight loss of Nafion, PN and PNS rises slowly at the beginning, followed by a plateau, and then the weight loss increases sharply above 300 $^{\circ}\text{C}$. No decomposition took place in membranes below 250 $^{\circ}\text{C}$. It is believed that weight loss of membranes below 250 $^{\circ}\text{C}$ is due to the evaporation of water from the membranes. The residual weights appearing above 600 $^{\circ}\text{C}$ in the TGA curves of PNS-3 and PNS-4 membranes can be attributed to the non-decomposed inorganic silicate. Fig. 2 shows that at temperatures above 600 $^{\circ}\text{C}$, PNS-4 has a larger content of non-decomposed residual than PNS-3, indicating a higher silicate content of PNS-4 than PNS-3. For pure Nafion membrane, the first decomposition temperature region (from ~ 298 to 420 $^{\circ}\text{C}$), as shown in Fig. 2, can be attributed to the decomposition of Nafion side chains $-\text{OCF}_2\text{CF}_2-\text{SO}_3\text{H}$ [26]. The weight loss of pure Nafion at temperatures higher than 420 $^{\circ}\text{C}$ can be attributed to the decom-

position of Nafion- CF_2-CF_2 main chains [26]. Fig. 2 shows that the initial decomposition temperature of PN and PNS was around 3–5 $^{\circ}\text{C}$ higher than that of pure Nafion (the starting decomposition temperature of pure Nafion was ~ 298 $^{\circ}\text{C}$) as silicate and PTFE were hybridized in the membranes. As the temperature was below ~ 370 $^{\circ}\text{C}$, the thermal decomposition weight loss of PNS-3 was lower than Nafion and PN membranes, indicating that the inserted silicates in the ionic clusters reduced the Nafion side chain decomposition as the temperature was below 370 $^{\circ}\text{C}$. However, as temperature was raised from 370 to 460 $^{\circ}\text{C}$, the weight loss for PNS-3 was larger than Nafion and PN membranes, suggesting the acceleration of Nafion side chain decomposition. The decomposition mechanism is still not clear to us. But, the TGA results of Nafion, PN and PNS-3 are very similar to the TGA data of pure Nafion and Nafion–silicate hybrid membranes reported by Deng et al. [26]. Deng et al. suggested immobilization of Nafion side chains within the crosslinked silicone oxide network retarded degradation of the Nafion side chains $-\text{SO}_3\text{H}$ groups as temperature was raised from 298 to 370 $^{\circ}\text{C}$. As the temperature was raised from 370 to 460 $^{\circ}\text{C}$, Deng et al. suggested HF, which was a product of decomposition of Nafion, caused degradation of the $(\text{SiO}_2)_x$ network via the reaction: $4\text{HF} + (\text{SiO}_2)_x \rightarrow 4\text{SiF} + (\text{SiO}_2)_{x-4} + 2\text{H}_2\text{O}$, which led to a larger weight loss of PNS-3 than Nafion and PN. The silicate/Nafion weight ratios of PNS-3 and PNS-4 were 3.36 and 4.91 (calculated from Table 1), respectively. The number of TEOS molecules inside the Nafion ionic clusters of PNS-4 was around 1.6 times larger than that of PNS-3. It could be the higher TEOS molecular density inside the Nafion ionic clusters caused TEOS molecules to have a better chance to proceed in a crosslinking reaction and form larger silicate network particles in PNS-4 than in PNS-3. The larger crosslinked silicate particles inside the ionic clusters of Nafion caused less mobility of the Nafion side chains and thus less decomposition of $-\text{OCF}_2\text{CF}_2-\text{SO}_3\text{H}$ side chains. Also the larger and higher crosslinked silicate particles had smaller surface area and less uncrosslinked $-\text{SiOH}$ groups left on the surface of the silicate particles, thus less degradation of $(\text{SiO}_2)_x$ at high temperature. Thus the TGA thermal decomposition curve of PNS-4 was different from that of PNS-3.

3.3. Conductivity measurements

The conductivities, σ , of commercial Nafion-117 and Nafion-112, and PN, PNS-3, and PNS-4 membranes prepared in our lab after swelling with 1N sulfuric acid for 4 h, were measured using an ac impedance system at 70 $^{\circ}\text{C}$ with a relative humidity of 95%. The σ values and the proton resistances r values ($r = l/\sigma$, where l is the thickness of a membrane) of these membranes are listed in Table 2. These data were the average of five measurements with standard deviations of around +5%. The σ values of PN and PNS were lower than those of Nafion-117 and Nafion-112, due to the poor conductivity of PTFE membrane. However, due to lower thickness of composite membranes, the r values of PN and PNS were lower than that of Nafion-117. As shown in Table 2, σ value of PN membranes was lowered while TEOS was inserted into the ionic clusters and formed crosslinked silicate particles in Nafion ionic clusters. σ value decreased with

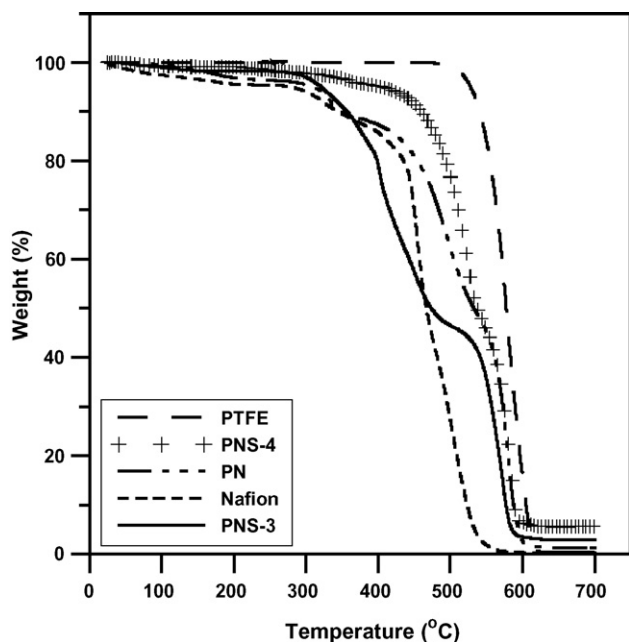


Fig. 2. TGA curves of PTFE, Nafion-112, PN, PNS-3 and PNS-4 membranes, which had been swollen with water. Membranes: (---) PTFE; (++++) PNS-4; (-.-.-) PN; (.....) Nafion; (—) PNS-3.

Table 2
Conductivities and resistances of membranes at 70 °C and relative humidity of 95% (Eq. (1))

Membrane	l (cm)	σ (S cm ⁻¹)	$r = l/\sigma$ (cm ² S ⁻¹)
Nafion-117	0.0175	1.01×10^{-2}	1.730
Nafion-112	0.0050	9.82×10^{-3}	0.509
PN	0.0020	3.91×10^{-3}	0.512
PNS-3	0.0020	3.25×10^{-3}	0.615
PNS-4	0.0020	2.07×10^{-3}	0.966

increasing TEOS concentration of TEOS/water/HCl/methanol solutions, which were used for preparing PNS membranes.

3.4. Methanol crossover measurements

The methanol crossover tests of Nafion-112, PN, PNS-3 and PNS-4 membranes after swelling with water were performed at 25 °C with vessel-1 feed 3 M methanol aqueous solution and vessel-2 feed pure water, as described in Section 2.4.4. Fig. 3 shows methanol concentration in vessel-2, which was separated from vessel-1 by a membrane, versus measuring time. We found that at beginning of measurements, i.e., at a measuring time $t \leq 1$ h, the quantity of methanol crossover increased in the sequence of: Nafion-112 \leq PNS-4 $<$ PNS-3 $<$ PN. However at a measuring time longer than 3 h, the quantity of methanol crossover increased in the sequence of: PNS-4 $<$ PNS-3 $<$ Nafion-112 $<$ PN. The reason for the lower methanol crossover of Nafion-112 than PNS and PN at early stage of methanol crossover measurements can be attributed to the greater thickness of Nafion-112 (thickness ~ 50 μ m) compared with PNS and PN membranes (thickness ~ 20 μ m).

The reason for the larger increment of methanol crossover for Nafion-112 at a longer time of methanol crossover measurement can be attributed to the larger amount of methanol

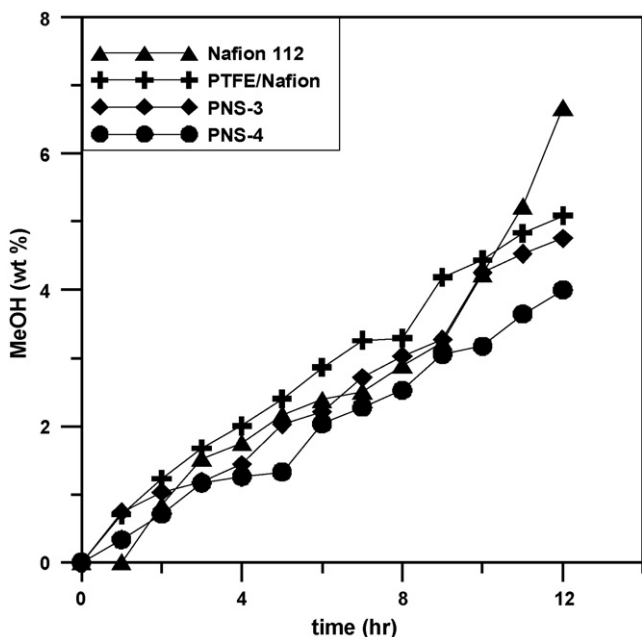


Fig. 3. Concentration of methanol crossover the membranes vs. measuring time. Membranes: (▲) Nafion-112; (+) PN; (◆) PNS-3; (●) PNS-4.

swollen in Nafion-112 membrane than in PN and PNS membranes, which contain PTFE. It is known that the morphology of Nafion membranes is composed of: (1) amorphous perfluorocarbon backbone aggregation regions; (2) crystalline perfluorocarbon backbone aggregation regions; and (3) hydrophilic ionic cluster regions, and phase separation happens between the hydrophobic perfluorocarbon backbones and the hydrophilic ionic side chains in Nafion membranes [27]. Depending on solvents and temperatures for membranes preparation, different degrees of phase separation with some of the sulfonated side chains mixing into the amorphous regions of membranes may be obtained [28]. Yeo [29] had reported dual solubility parameters for Nafion, i.e., 9.7 and 17.3 (cal cm⁻³)^{0.5} for perfluorocarbon backbone and ionic side chains, respectively. From the solubility parameters of solvents and Nafion, we know that methanol (solubility parameter is 14.5 (cal cm⁻³)^{0.5}) has a better compatibility with Nafion perfluorocarbon backbone (solubility parameter is 9.7 (cal cm⁻³)^{0.5}) than water (solubility parameter is 23.4 (cal cm⁻³)^{0.5}), the swelling of methanol in Nafion membrane may cause dissociation of perfluorocarbon backbone aggregations and lead to a higher methanol crossover rate at a longer time of methanol crossover measurement. Since PTFE is an excellent barrier for methanol, and PN, PNS-3, and PNS-4 composite membranes contain much less Nafion resin than pure Nafion-112 membrane, thus less methanol is in PN and PNS than in Nafion-112. Though PN and PNS membranes were thinner than Nafion-112 membrane, the methanol crossover rates of PN and PNS were similar to that of pure Nafion-112 at a longer time of methanol crossover measurement, due to larger amount of methanol in Nafion-112 than in PN and PNS.

3.5. DMFC performance test

The proton resistance of the Nafion-112 (thickness 50 μ m) membrane, compared with Nafion-117 (thickness 175 μ m), is close to that of a PN composite membrane. In previous work [22], we studied a PEMFC (H₂/O₂) performance of a MEA prepared from Nafion-117, Nafion-112 and PN membranes, and found that the PEMFC performance of PN was similar to that of Nafion-112 but better than that of Nafion-117. In order to reduce the overvoltage difference caused by the difference in membrane resistance to proton transfer, we used an MEA prepared from Nafion-112, rather than from Nafion-117, and MEAs prepared from PN, PNS-3 and PNS-4 composite membranes to investigate the influence of hybridizing silicate into PN composite membrane on DMFC performance and methanol crossover via electro-osmosis, will be discussed in Section 3.6.

Figs. 4–7 show data of the single cell potential V and power density versus current density i for these DMFCs operated at 70 °C, with methanol feed concentrations of 2, 3, 4 and 5 M.

The cell voltage at open circuit, i.e., the open circuit voltage (OCV), usually does not reach the theoretical value of the overall reversible cathode and anode potentials at the given pressure and temperature. The lowering of the OCV from the theoretical voltage has been attributed to the penetration of fuel across the membrane [30], and the OCV is an indicator of the degree of methanol crossover via diffusion. Table 3 summarizes

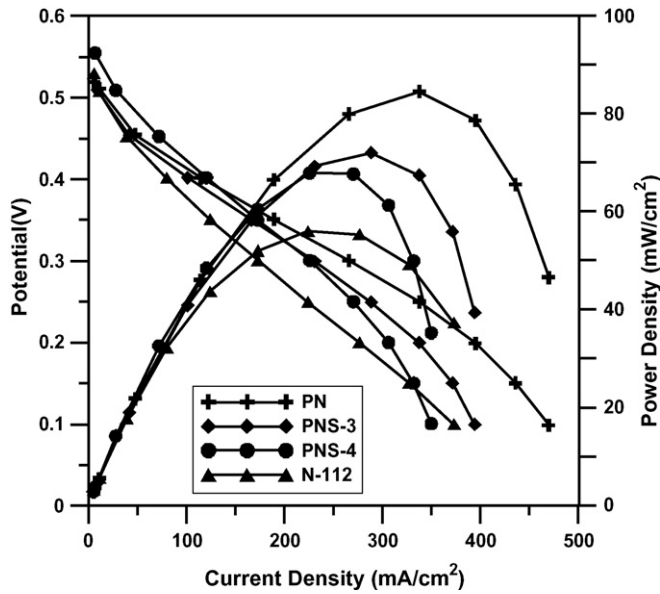


Fig. 4. DMFC single cell performance test at 70 °C, the concentration of feeding methanol is 2 M. The MEAs were prepared from: (▲) Nafion-112; (+) PN; (◆) PNS-3; (●) PNS-4.

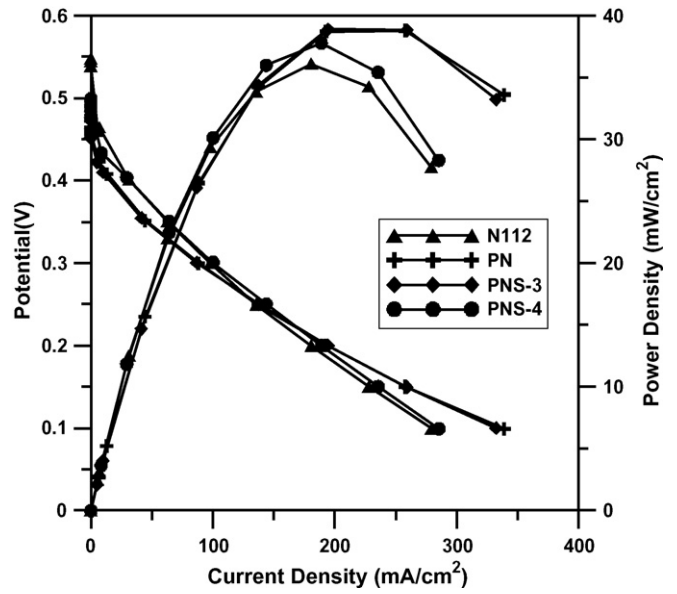


Fig. 6. DMFC single cell performance test at 70 °C, the concentration of feeding methanol is 4 M. The MEAs were prepared from: (▲) Nafion-112; (+) PN; (◆) PNS-3; (●) PNS-4.

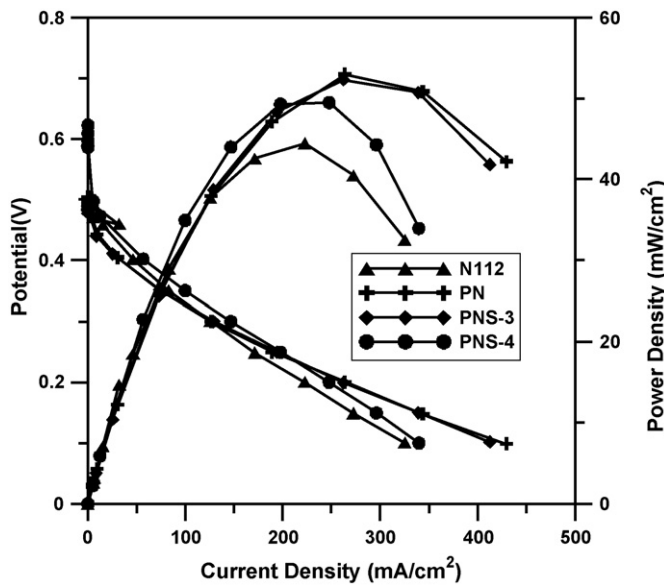


Fig. 5. DMFC single cell performance test at 70 °C, the concentration of feeding methanol is 3 M. The MEAs were prepared from: (▲) Nafion-112; (+) PN; (◆) PNS-3; (●) PNS-4.

the DMFC OCV values of MEAs prepared from Nafion-112, PN, PNS-3 and PNS-4 membranes with methanol feed concentrations of 2, 3, 4 and 5 M and an operating temperature of 70 °C. Table 3 shows that OCV value decreased with increas-

Table 3
Open circuit voltage at 70 °C (V)

Methanol feed concentration (M)	Nafion-112	PN	PNS-3	PNS-4
2	0.591	0.560	0.556	0.564
3	0.568	0.490	0.484	0.503
4	0.508	0.456	0.462	0.490
5	0.468	0.444	0.450	0.464

ing methanol feed concentration for MEAs prepared from the same membrane. However at a fixed methanol feed concentration, OCV values of MEAs decreased in the sequence of: Nafion-112 > PNS-4 > PN ~ PNS-3. At zero current density, the methanol crossover the membrane totally comes from the diffusion of methanol across the membrane, where the membrane is not swollen with methanol. The OCV values were quite consistent with the methanol crossover data obtained at early stage of methanol crossover measurements (Fig. 3). In Fig. 3, we found that at methanol crossover measuring time $t \leq 1$ h, the quantity of methanol crossing over the membrane increased in the sequence of: Nafion-112 < PNS-4 < PNS-3 < PN.

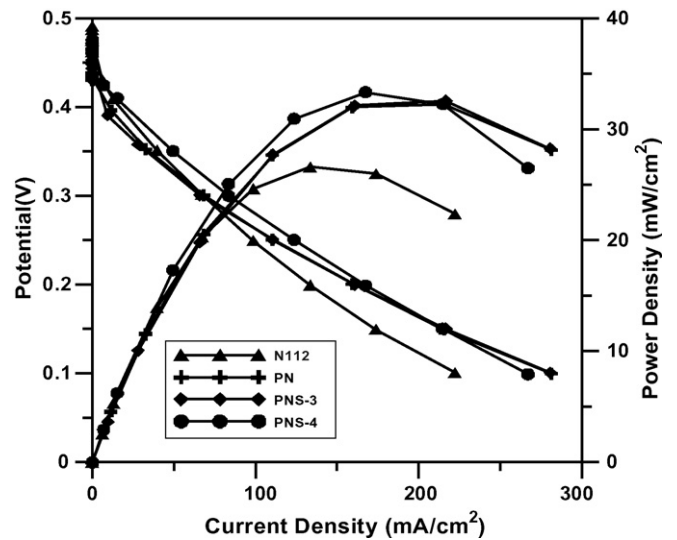


Fig. 7. DMFC single cell performance test at 70 °C, the concentration of feeding methanol is 5 M. The MEAs were prepared from: (▲) Nafion112; (+) PN; (◆) PNS-3; (●) PNS-4.

By careful investigation of the potential V versus current density i curves (i - V curves shown in Figs. 4–7), we found that at low currents, PNS-4 and Nafion-112 had higher voltage than PN and PNS-3. However at high i , PN and PNS-3 had higher voltages than PNS-4 and Nafion-112. The reasons for the reduction of cell potential with increasing i in the middle current density region of the i - V curves (i.e., region-II, where the current density i is between 80 and 300 mA cm⁻² with a linear negative slope) can be attributed to the resistance to proton transfer and methanol crossover of the membrane [31–32]. As shown in Fig. 3, at the beginning of the methanol crossover measurement, the Nafion membrane was not swollen with methanol, Nafion-112 had a lower methanol crossover than PN and PNS composite membranes (methanol crossover rate: Nafion-112 < PNS-4 < PNS-3 < PN), because of higher thickness of Nafion-112. However, at a methanol crossover measuring time $t \geq 3$ h, where the Nafion membrane was swollen with methanol, the methanol crossover rate of Nafion-112 was similar to those PN and PNS membranes. It is obvious that the lower methanol crossover of PNS-4 (because of high silicate content) and Nafion-112 (because of high membrane thickness) causes these two membranes to have higher voltages than PN and PNS-3 at low i . However at higher current densities, methanol crosses over the membrane not only via diffusion, which is caused by methanol concentration differential across the membrane, but also via electro-osmosis. The higher electro-osmosis at high i in region-II of i - V curves may cause higher swelling of the membrane with methanol. Thus the mechanism of methanol crossover in region-II of i - V curves is quite different from that at zero i , where the membrane is less swollen with methanol and most of methanol crossover is via diffusion. The presence of PTFE in composite membranes causes less methanol in PN and PNS membranes than in Nafion-112 membrane via electro-osmosis. The higher swelling of methanol via electro-osmosis in Nafion-112 than in other membranes may cause Nafion-112 to have higher methanol crossover via diffusion than PN and PNS at high current density. In Section 3.6, we will show that Nafion-112 had a higher methanol electro-osmosis than PN and PNS membranes. Thus at high i , the higher methanol crossover of Nafion-112 and higher proton resistance of PNS-4 caused them to have lower voltage than PN and PNS-3 membranes.

The maximum power density (PD_{\max}) is located in region-II of the i - V curves, as shown in Figs. 4–7. In region-II of the i - V curves, methanol crosses the membrane via both diffusion and electro-osmosis processes. In Fig. 8, we plot PD_{\max} of MEAs prepared from various membranes versus methanol feed concentration. Comparing the PD_{\max} of various MEAs, we found that PN had the highest PD_{\max} when methanol feed concentration was 2 M, PD_{\max} decreased in the sequence of PN > PNS-3 > PNS-4 > Nafion-112 at a methanol feed concentration of 2 M. The lower PD_{\max} of Nafion-112 than those of PN and PNS can be attributed to the higher electro-osmosis of methanol crossover Nafion-112 membrane at high i . The lower PD_{\max} s of PNS-3 and PNS-4 than that of PN can be attributed to the higher proton resistance, while silicate was hybridized into Nafion of PN membranes. As the methanol feed concentration was increased from 2 to 5 M, the PD_{\max} s of all MEAs decreased

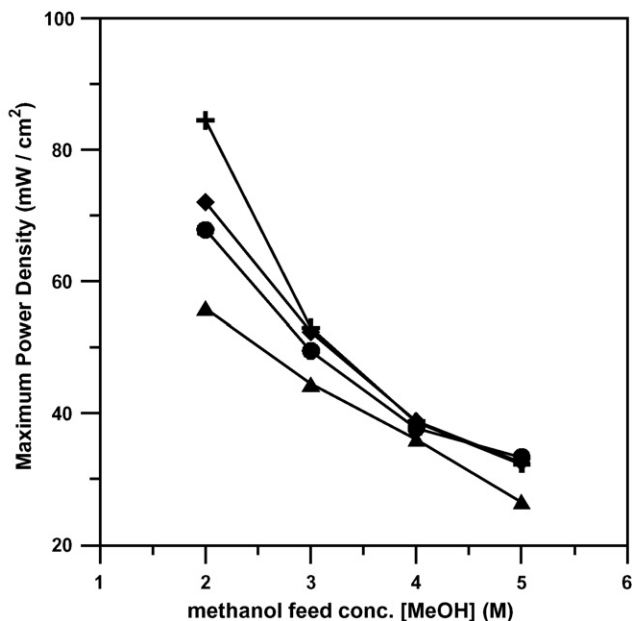


Fig. 8. Plots of maximum power density vs. methanol feed concentration for MEAs prepared from: (+) PN; (◆) PNS-3; (●) PNS-4; (▲) Nafion-112.

with increasing methanol feed concentration, due to the increase of methanol crossover. The higher methanol crossover of PN than PNS caused PN to have a larger PD_{\max} decrement than PNS-3 and PNS-4, when the methanol feed concentration was increased from 2 to 5 M. As methanol feed concentration was higher than 4 M, the PD_{\max} of PN was close to those of PNS-3 and PNS-4, though PNS-3 and PNS-4 had a higher proton resistance than PN.

We took the i - V curve of PN as a reference, and from Figs. 4–7 we calculated the intercept voltage V_{int} and intercept current density i_{int} values of i - V curve of Nafion-112 with i - V curve of PN and the V_{int} and i_{int} values of i - V curve of PNS-4 with i - V curve of PN. The results show that V_{int} of PNS-4 with PN decreased from 0.39 to 0.17 V and i_{int} of PNS-4 with PN increased from 120 to 190 mA cm⁻² as the methanol feed concentration was increased from 2 to 5 M. The voltage of PNS-4 was larger than that of PN when for current densities $i < i_{\text{int}}$, and the voltage of PNS-4 was smaller than that of PN when $i > i_{\text{int}}$. The behaviour of increment of i_{int} and decrement of V_{int} of PNS-4 versus PN with increasing methanol feed concentration suggests that the low i range for PNS-4 having a higher voltage than PN became broader while the methanol feed concentration was increased. These results suggest that hybridizing silicate into PN composite membranes improve DMFC performance at low i with a high methanol feed concentration. Similarly, the voltage of Nafion-112 was higher than that of PN when $i < i_{\text{int}}$, and the voltage of Nafion-112 was lower than that of PN when $i > i_{\text{int}}$. The V_{int} of the intercept of Nafion-112 with PN decreased from 0.55 to 0.25 V and i_{int} of the intercept of Nafion-112 with PN increased from 10 to 138 mA cm⁻² as the methanol feed concentration was increased from 2 to 4 M, then V_{int} increased from 0.25 to 0.30 V and i_{int} decreased from 138 to 70 mA cm⁻² as the methanol feed concentration was increased from 4 to 5 M. For membranes with the same thickness, PTFE was a better methanol barrier than

Nafion. However, the higher thickness of Nafion-112 (~50 μm) caused Nafion-112 to have a lower methanol crossover than PN membrane (~20 μm) at low current density i . The decrement of V_{int} and the increment of i_{int} for the intercept of Nafion-112 with PN suggested the range of low i for Nafion-112 having a higher voltage than PN became broader as methanol feed concentration was increased from 2 to 4 M. When the methanol feed concentration was increased from 4 to 5 M, the high methanol in Nafion-112 caused an increment of V_{int} and a decrement of i_{int} of the intercept of Nafion-112 with PN, and the range of low current density for Nafion-112 having a higher voltage than PN became narrower as methanol feed concentration was increased from 4 to 5 M.

3.6. Influence of silicate in PNS composite membranes on electro-osmosis of methanol across the membranes

In this section, we study the influence of silicate on the electro-osmosis of methanol crossover the PNS composite membranes. The cell voltage of a DMFC can be written as [30]:

$$\begin{aligned} V &= E - \eta_{\text{an}} - \eta_{\text{cat}} - \eta_{\text{ohm}} - \eta_{\text{xov}} \\ &= E - A_1 \ln \left[\frac{i}{i_0} \right] - \eta_{\text{ohm}} - \eta_{\text{xov}} \end{aligned} \quad (3)$$

where V is the cell voltage, E the reversible open circuit voltage, η_{an} the overvoltage of anode, η_{cat} the overvoltage of cathode, i the current density, i_0 the current density at which the overvoltage begins to move from zero, A_1 the sum of slope of the polarization curves for anode and cathode, η_{ohm} the ohmic overpotential, η_{xov} is the overpotential produced by methanol crossover.

The ohmic overpotential η_{ohm} for a membrane can be calculated from the resistance of the membrane, i.e., Eq. (4).

$$\eta_{\text{ohm}} = i \frac{l}{\sigma} \quad (4)$$

where l and σ are thickness and conductivity of a membrane, respectively.

The methanol crossover causes depolarization losses at the cathode and losses of fuel. It is expected that as the methanol feed concentration at the anode is higher than a critical concentration, it will cause a decrease in the cell voltage as a result of potentially higher rates of methanol transport through the membrane. Permeation of water and/or methanol through an electrolyte membrane will take place under: (1) the driving force of concentration differential (ΔC) across the membrane; (2) the pressure differential ΔP across the membrane acting on permeate at the membrane-permeate interface; and (3) electro-osmotic flux of methanol, which is accompanied with the electro-osmotic flux of water caused by proton dragging solvating water molecules through membrane. Assume: (1) a Fick diffusion and a linear concentration gradient through the thickness of the membrane, i.e., the methanol diffusivity D is independent of the concentration differential $\Delta C = C_{\text{cat}} - C_{\text{an}}$, where C_{an} and C_{cat} are concentrations of methanol, which are not catalytically oxidized at the anode and cathode sides, respectively; and (2) the

methanol molecules permeating from anode to cathode are either catalytically oxidized or entrained in the carrier gas flow at a rate proportional to the un-oxidized methanol concentration at cathode C_{cat} , the overvoltage η_{xov} due to methanol crossover can be calculated using Eq. (5) [31]:

$$\eta_{\text{xov}} = \chi J_{\text{MeOH}} = \chi \frac{DC_{\text{an}}/l + \lambda i/nF}{1 + D/kl + K_p \Delta P/kl} \quad (5)$$

where χ is a constant and J_{MeOH} the flux of methanol crossover, D the diffusion coefficient of methanol across the membrane, λ the number of moles of methanol per mole proton transferred by electro-osmosis, n the number of electrons involved in the reaction, F the Faraday constant, k a mass transfer coefficient for the cathode backing layer and flow channel, K_p a constant related to the hydraulic permeability across the membrane and ΔP is the pressure differential across the membrane.

The model in Eq. (5) predicts that the flux of methanol crossover the membrane J_{MeOH} has a current i -independent term but affected by unoxidized methanol concentration C_{an} at anode, and a current i -dependent term due to electro-osmosis of methanol.

Substituting Eqs. (4) and (5) into Eq. (3), we obtain:

$$V = E - A_1 \ln \left[\frac{i}{i_0} \right] - \frac{il}{\sigma} - \chi \frac{DC_{\text{an}}/l + \lambda i/nF}{1 + D/kl + K_p \Delta P/kl} \quad (6)$$

Rearranging Eq. (6) and separating the C_{an} -dependent and i -dependent terms, we obtain Eq. (7):

$$V(i, C_{\text{an}}) = E - A_1 \ln \left[\frac{i}{i_0} \right] - A_2 C_{\text{an}} - A_3 i \quad (7)$$

with

$$A_2 = \frac{\chi D}{l + D/k + K_p \Delta P/k} \quad (8)$$

$$A_3 = \frac{l}{\sigma} + \frac{\chi \lambda}{nF(1 + D/kl + K_p \Delta P/kl)} = \frac{l}{\sigma} + A_{\text{eos}}(\text{MeOH}) \quad (9)$$

where A_2 is a term relating the overvoltage to the methanol crossover via diffusion, A_3 a term relating the overvoltage to the sum of resistance to proton transference and electro-osmosis of methanol crossover, and $A_{\text{eos}}(\text{MeOH}) = \chi \lambda / [nF(1 + D/kl + K_p \Delta P/kl)]$ a term relating the overvoltage to the electro-osmosis of methanol crossover the membrane. The term “ $1 + D/kl + K_p \Delta P/kl$ ” in the denominator of A_2 , A_3 and $A_{\text{eos}}(\text{MeOH})$ relates backward methanol crossover from cathode to anode via diffusion and hydraulic permeation. The equations describing A_2 and A_3 are valid only in region-II of i - V curves, i.e., $100 \text{ mA cm}^{-2} < i < 300 \text{ mA cm}^{-2}$ in the present work [30–32], and a large overflow of water from cathode to anode may happen at $i > 300 \text{ mA cm}^{-2}$ due to the high production of water from the electrochemical reaction at cathode. A_2 can be obtained from the slope of the plot of $V(i, C_{\text{an}})$ versus C_{an} at a fixed current density i with

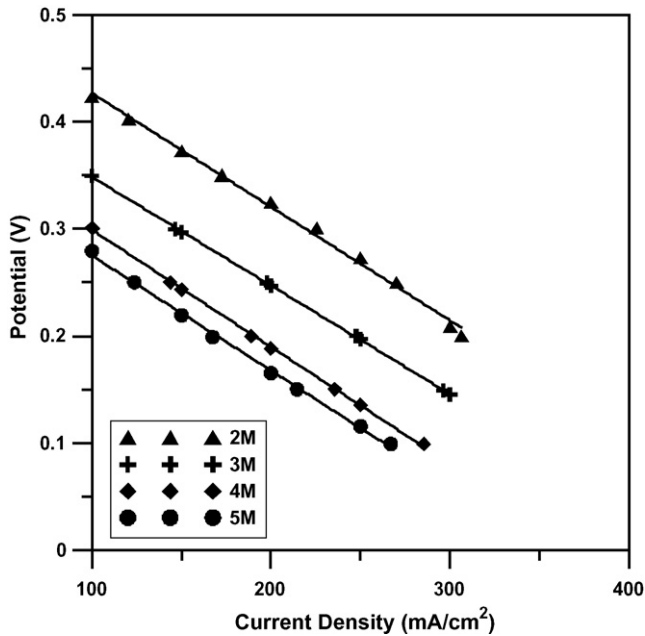


Fig. 9. Plots of $V(i, C_{an})$ vs. i for MEA made from PNS-4 composite membrane with $350 \text{ mA cm}^{-2} > i > 100 \text{ mA cm}^{-2}$ and methanol feed concentrations are: (\blacktriangle) 2 M, ($+$) 3 M, (\blacklozenge) 4 M and (\bullet) 5 M.

$100 \text{ mA cm}^{-2} < i < 300 \text{ mA cm}^{-2}$. The derivative of $V(i, C_{an})$ versus i derived from Eq. (7) is:

$$\frac{dV(i, C_{an})}{di} = -\frac{A_1}{i} - A_3 \quad (10)$$

At current densities $i > 100 \text{ mA cm}^{-2}$, $A_1/i < A_1/100 \ll A_3$. Thus A_3 can be obtained from the slope of the plot of $V(i, C_{an})$ versus i at a fixed methanol feed concentration C_{an} and at $i > 100 \text{ mA cm}^{-2}$.

Fig. 9 shows the region-II single cell voltage $V(i, C_{an})$ versus i data with $300 \text{ mA cm}^{-2} > i > 100 \text{ mA cm}^{-2}$ for PNS-4 MEA operated at 70°C with methanol feed concentrations of 2, 3, 4 and 5 M. Similar $V(i, C_{an})$ versus i plots were also obtained for Nafion-112, PN, and PNS-3 and are not shown in the present paper. A_3 parameters of Nafion-112, PN, PNS-3 and PNS-4 can be obtained from the slopes of $V(i, C_{an})$ versus i plots and are summarized in Table 4. A_3 is a parameter relating the over voltage to a combination of proton resistance, l/σ , and electro-osmosis of methanol, $A_{eos}(\text{MeOH})$, in the membrane. $A_{eos}(\text{MeOH})$ can be obtained by subtracting l/σ (listed in Table 2) from A_3 . Table 5 summarizes $A_{eos}(\text{MeOH})$ data of the membranes. From Table 5, we found that $A_{eos}(\text{MeOH})$ decreased in the sequence of Nafion-112 > PN > PNS-3 > PNS-4, and the ratio of $A_{eos}(\text{MeOH})$ s of four membranes at a methanol

Table 4
Parameter A_3 ($\text{V cm}^2 \text{ mA}^{-1}$) of Eqs. (7) and (9)

[MeOH]	2 M	3 M	4 M	5 M
Nafion-112	1.010×10^{-3}	1.015×10^{-3}	1.087×10^{-3}	1.150×10^{-3}
PN	6.860×10^{-4}	7.073×10^{-4}	8.188×10^{-4}	9.230×10^{-4}
PNS-3	7.308×10^{-4}	7.282×10^{-4}	8.008×10^{-4}	8.986×10^{-4}
PNS-4	1.061×10^{-3}	1.013×10^{-3}	1.073×10^{-3}	1.072×10^{-3}

Table 5
Parameter $A_{eos}(\text{MeOH})$ ($\text{V cm}^2 \text{ mA}^{-1}$) of Eqs. (9) and (10)

[MeOH]	2 M	3 M	4 M	5 M
Nafion-112	5.01×10^{-4}	5.06×10^{-4}	5.78×10^{-4}	6.41×10^{-4}
PN	1.74×10^{-4}	1.95×10^{-4}	3.07×10^{-4}	4.11×10^{-4}
PNS-3	1.16×10^{-4}	1.13×10^{-4}	1.86×10^{-4}	2.84×10^{-4}
PNS-4	9.50×10^{-5}	4.70×10^{-5}	1.07×10^{-4}	1.06×10^{-4}

feed concentration of 2.0 M was: Nafion-112/PN/PNS-3/PNS-4 = 5.27/1.83/1.22/1.00. The term " D/kl " in the denominator of $A_{eos}(\text{MeOH}) = \chi\lambda/[nF(1 + D/kl + K_p \Delta P/kl)]$ is a term describing methanol backward crossover from cathode to anode via diffusion. D/l is proportional to the quantity of methanol crossover the membrane with a thickness of l per unit time, and can be estimated from Fig. 3. We take the methanol crossover quantity data of Fig. 3 at a measuring time of 4 h and obtain the ratio of the methanol crossover quantity of four membranes: Nafion-112/PN/PNS-3/PNS-4 = 1.36/1.65/1.17/1.00. Comparing the ratio of $A_{eos}(\text{MeOH})$ with the ratio of methanol crossover rate quantity of four membranes, we may conclude that Nafion-112 could have a highest λ value in these four membranes in spite of its highest membrane thickness. The overvoltage caused from electro-osmosis of methanol crossover membranes decreased in the sequence of Nafion-112 > PN > PNS-3 > PNS-4. The phenomenon that PNS-3 and PNS-4 had lower $A_{eos}(\text{MeOH})$ values than PN and Nafion-112 suggests that introducing silicate into PN composite membranes causes reduction not only in methanol diffusion across the membrane but also in electro-osmosis of methanol across the membrane. The reason for Nafion-112 having a lower DMFC operating voltage than PN and PNS-3 at high i can be attributed to higher methanol crossover Nafion-112 membrane via electro-osmosis processes. The reason for PNS-4 having a lower DMFC operating voltage than PN and PNS-3 at high i can be attributed to a higher proton resistance in PNS-4 than in PN and PN-3.

4. Conclusion

Hybridizing silicate in PN composite membranes caused reductions in methanol diffusion and methanol electro-osmosis crossing the membranes. Hybridization of silicate in PN composite membranes also caused reduction in proton conductivity. Thus the PNS membranes, which are hybridized with silicate, have a higher voltage than PN at a low current density, due to the lower methanol crossover of PNS than PN. But at high current densities, PNS membranes have a lower voltage than PN, due to the higher proton resistance of PNS than PN. The range of lower current density for PNS having a higher voltage than PN increases with increasing methanol feed concentration at anode.

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