



Nafion/sulfated β -cyclodextrin composite membranes for direct methanol fuel cells

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ARTICLE INFO

Article history:

Received 1 May 2008

Received in revised form 27 May 2008

Accepted 23 June 2008

Available online 17 July 2008

Keywords:

Nafion

Sulfated β -cyclodextrin

Composite membrane

Direct methanol fuel cell

Proton diffusion coefficient

ABSTRACT

Proton-conducting composite membranes based on H^+ -form sulfated β -cyclodextrin (sb-CD) in a Nafion matrix are prepared via the solution-casting method and their methanol permeabilities, proton conductivities, proton diffusion coefficients and cell performances are measured. The methanol permeabilities of the composite membranes increase very slightly with increases in their sb-CD content. As a result of adding sb-CD with its many sulfonic acid groups into the Nafion matrix, the proton conductivities of the composite membranes increase with increases in their sb-CD content. The methanol permeability and proton conductivity results are used to show that the best selectivity of the membranes is that of the NC5 membrane ('NCx' denotes a Nafion/sb-CD composite membrane containing x wt.% sb-CD). The proton diffusion coefficients are measured with 1H pulsed field gradient nuclear magnetic resonance (PFG-NMR) and found to increase with increase in the sb-CD content in the order $NC5 > NC3 > NC1 > NC0$. Thus the presence of sb-CD in the Nafion membranes increases the proton diffusion coefficients as well as the proton conductivities, ionic cluster size, water uptakes and the ion-exchange capacities (IECs). A maximum power density of 58 mW cm^{-2} is obtained for the NC5 membrane. The combination of these effects should lead to an improvement in the performance of direct methanol fuel cells prepared with Nafion/sb-CD composite membranes.

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1. Introduction

One of the most important current environmental issues is the pollution level due to internal combustion motor vehicles. Fuel cells with near-zero pollutant emission levels are a promising alternative for on-board power generation [1,2]. Of the various fuel cells under development, direct methanol fuel cells (DMFCs) are suitable for portable devices or transportation applications because of their high specific energy at low operating temperatures and the ease of handling liquid methanol fuel. DMFCs utilize proton-conducting polymer membranes, of which Nafion is by far the most studied because of its high proton conductivity and excellent chemical/electrochemical stability; it is also used in polymer electrolyte membrane fuel cells (PEMFCs). It has been widely reported that the material in Nafion membranes self-organizes to form hydrophobic and hydrophilic domains. The hydrophobic region consists primarily of poly(tetrafluoroethylene) (PTFE), which ensures the long-term chemical stability of such membranes in both reducing and oxidizing environments, and the hydrophilic region contains a

mixture of sulfonic acid groups, protons, water and methanol [3]. The microstructures of the hydrophilic domains of Nafion membranes can be understood in terms of "reverse-micelle-like" ionic clusters [4]. The proton conductivity of these membranes is due to these networked ionic clusters. On the other hand, Nafion exhibits high methanol permeability, commonly referred to as methanol crossover, which results in a lower selectivity (i.e., proton conductivity/methanol permeability). Methanol crossover through the membrane occurs as a result of electro-osmotic drag and a concentration gradient, and decreases the performance of fuel cells because of the resulting mixed potential [5].

Recent literature describes modifications of Nafion membranes with a variety of organic and inorganic materials such as montmorillonite [6,7], palladium [8,9], zeolite [10,11], polyvinyl alcohol [12], polypyrrole [13], titania [14,15], silicon oxide [16,17], alumina [18] and zirconium phosphates [19,20]. Nafion-organic/inorganic composite membranes have mainly been prepared via two distinct methods: (i) mixing Nafion solutions with organic/inorganic materials or their precursors by solution casting; (ii) infiltration of commercial Nafion membranes with precursors of organic/inorganic materials. These composite membranes do indeed exhibit reduced methanol permeability, but this does not always lead to the desired improvement in the perfor-

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mance of the DMFCs, mainly because the proton conductivity of the composite membranes that contain less proton-conductive materials is often markedly lower than that of pristine Nafion membranes.

We recently reported the fabrication of Nafion-based composite membranes that contain sulfated β -cyclodextrin (sb-CD) with many sulfonic acid groups [21]. It was found that the water uptakes and ion-exchange capacities (IECs) of such composite membranes gradually increase with increases in their sb-CD content. In addition, ^1H nuclear magnetic resonance (NMR) cryoporometry measurements showed that the ionic cluster size distributions of the water-swollen composite membranes become slightly broader with increases in their sb-CD content. In that study, however, no measurements were made of the proton conductivities, methanol permeabilities, proton diffusion coefficients, or single-cell performances of these composite membranes.

Cyclodextrins (CDs) are cyclic oligosaccharides with six (α -), seven (β -) or eight (γ -) glucose units linked by 1,4- α -glucosidic bonds [22]. The CDs have a shallow truncated cone shape and a hydrophobic cavity that is apolar relative to the outer surface. β -CD is the most readily available, lowest-priced and generally the most useful CD, and is used in this study. sb-CD is very hydrophilic because its external surface has many reactive sites, i.e., sulfonic acid groups. Therefore, the addition of hydrophilic sb-CD into Nafion membranes assists the transport of protons, since the number of reactive ionic cluster sites is increased. In addition, the presence of sb-CD inside the ionic clusters of the membranes means that the methanol transport pathway is tortuous. In this study, the proton conductivities, the methanol permeabilities, the proton diffusion coefficients, and the single-cell performances of Nafion/sb-CD composite membranes are studied and compared with those of a pristine Nafion membrane.

2. Experimental

2.1. Preparation of the composite membranes

Nafion perfluorinated ion-exchange resin (5 wt.% solution in a mixture of lower aliphatic alcohols and water) was purchased from Aldrich Chemicals and used as the membrane material; it has an equivalent weight (EW) of 1100 g for each sulfonic acid group. The Na^+ -form sb-CD (typical substitution: 7–10 mol mol $^{-1}$ β -CD) was purchased from Aldrich Chemicals. The H^+ -form sb-CD was obtained by recrystallization after adjusting the pH of the Na^+ -form sb-CD solution.

The Nafion/sb-CD composite membranes were prepared via the solution-casting method. The desired amount of sb-CD was added to the 5 wt.% Nafion solution, and then stirred at room temperature. The sb-CD contents of the mixtures were 1, 3 or 5 wt.% with respect to Nafion. Composite membranes with sb-CD contents greater than 5 wt.% were found to be plagued by defects such as cracks, which meant that they could not be used. The resulting mixture in each case was slowly poured into a glass dish. The mixture was evaporated at 40 °C for 2 days and then annealed at 120 °C in a convection oven for 2 h. After cooling, the membrane was peeled off the glass dish after the addition of water. The membrane thickness was maintained at approximately 80 μm by employing the same total amount of Nafion and sb-CD in each case. The membranes were stored in deionized water so that they were water-saturated. In this paper, NCx denotes a Nafion/sb-CD composite membrane containing x wt.% of sb-CD.

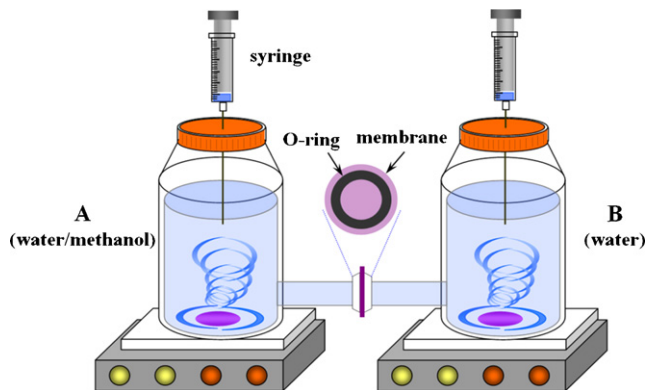


Fig. 1. Schematic representation of methanol glass diffusion cell.

2.2. Membrane characterization

Methanol permeabilities were determined at 20 °C using a home-made glass diffusion cell consisting of two cylindrical glass compartments (A and B) separated by a composite membrane with an effective area of 3.8 cm 2 , as shown in Fig. 1. The A and B vessels were filled with 15 wt.% methanol ($V_A = 300 \text{ cm}^3$) and deionized water ($V_B = 300 \text{ cm}^3$), respectively. Magnetic stirrers were used in each vessel to ensure uniformity. In order to determine the methanol permeability of each membrane, 1 cm 3 liquid samples were taken from the A and B vessels using a syringe at prescribed time intervals (20, 40, 60, 80, 100 and 120 min). The methanol concentrations were analyzed using a HP 5890 Hewlett Packard gas chromatograph (GC) equipped with a capillary column (14% cyano propyl phenyl methyl polysiloxane) and a flame ionization detector (FID).

Proton conductivity measurements were carried out on fully hydrated membrane samples with the cell immersed in liquid water. The installed cell was placed in a chamber with a controlled temperature. The conductivity, σ , was calculated from the bulk resistance, R , which was obtained from the intercept of the impedance curve with the real axis at the high-frequency end according to

$$\sigma = \frac{L}{RA} \quad (1)$$

where L is the thickness of the membranes and A is the membrane cross-sectional surface area. The impedance measurements were carried out in the frequency region 1–10 5 Hz with an ac current amplitude of 1 mA by using a Solartron 1255 electrochemical impedance analyzer with ZPLOT software.

In order to perform pulsed field gradient nuclear magnetic resonance (PFG-NMR) measurements, each membrane was immersed in deionized water (as a diffusant) for a week, and its surface was wiped to remove excess water before the membrane was packed into a NMR tube with a 5 mm outer diameter and then sealed. The sample height was restricted to approximately 15 mm to ensure that the sample located within the transmitter/receiver coil was homogeneously irradiated. In order to prevent the evaporation and desorption of water from the samples, the spaces above the samples in the NMR tube were filled with hydrophobic perfluorooctane (C $_8$ F $_{18}$, Aldrich Chemicals). The temperature was maintained at 25 °C and all PFG-NMR measurements were conducted with a Bruker DMX 600 spectrometer and a Bruker BGU II pulse 50 G cm $^{-1}$ gradient generator. The well-known spin echo sequence was used to measure the proton diffusion coefficient and the stimulated echo sequence was used when diffusion was slow and long times between gradient pulses were required. The strength of the mag-

Table 1
Physical properties of Nafion/sb-CD composite membranes

Membrane	Water uptake ^a (%)	λ value (H ₂ O/SO ₃ H)	Ion-exchange capacity ^a (mequiv. g ⁻¹)	Cluster size distribution ^a (nm)	Methanol permeability ($\times 10^{-6}$ cm ² s ⁻¹)
NC0	21.4	13.4	0.89	1.2–2.4	1.065
NC1	22.1	13.5	0.91	1.2–2.7	1.071
NC3	23.3	13.8	0.94	1.4–3.4	1.086
NC5	24.4	14.1	0.96	1.6–3.9	1.093

^a Previously reported data [21].

netic field gradient was varied from 0 to 50 G cm⁻¹. The pulse length of the magnetic field gradient, δ , was in the range 1–5 ms and the time interval, Δ , between two gradient pulses was between 40 and 500 ms. The gradient was calibrated by observing the profile of a calibrated water phantom in the presence of gradients covering the range used experimentally. To extract the diffusion coefficient from the raw experimental data, the observed signal intensities for eight incremented field gradient strengths were fitted to the predicted decay curve using a non-linear least-squares procedure.

Testing of the membrane-electrode assemblies (MEAs) was performed using a 4 cm² single cell. Anode and cathode electrodes were purchased from E-TEK and the catalyst loading on each was 5 mg cm⁻². The catalyst used in the anode was Pt–Ru on carbon and Pt black was used as the cathode catalyst. The MEAs were fabricated via hot pressing at 140 °C and 3000 psi for 5 min. The performance of each single cell was evaluated at 25 °C with 2 M aqueous methanol anode feed at 2 cm³ min⁻¹ and air feed to the cathode at 100 cm³ min⁻¹.

3. Results and discussion

3.1. Lambda values, methanol permeabilities, proton conductivities, and selectivities

The number of water molecules per sulfonic acid site, i.e., the lambda value, λ (H₂O/SO₃H), was calculated using the IEC data for the composite membranes with the following equation, in which, MW_{H₂O} is the molecular weight of water (18.01 g mol⁻¹) and IEC is the value of the milliequivalents of acid groups per gram of membrane:

$$\lambda = \frac{(M_{\text{wet}} - M_{\text{dry}})/MW_{\text{H}_2\text{O}}}{\text{IEC} \times M_{\text{dry}}} \quad (2)$$

where M_{wet} and M_{dry} are the weights of the wet and dried membranes, respectively. The λ of the composite membranes increases very slightly with increases in the sb-CD content; the results are listed in Table 1.

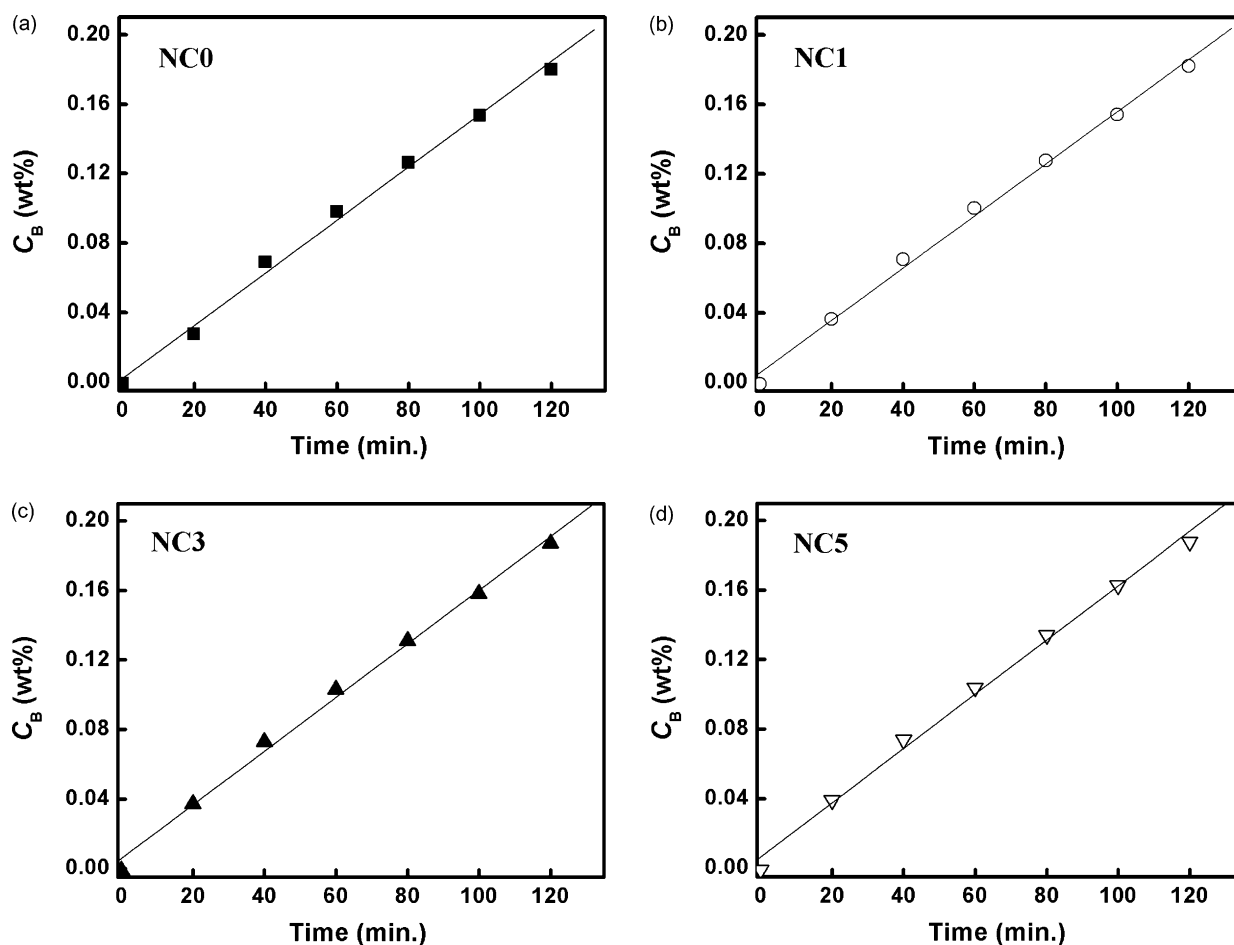


Fig. 2. Methanol concentration in water compartment at various times for Nafion/sb-CD composite membranes: (a) NC0, (b) NC1, (c) NC3 and (d) NC5.

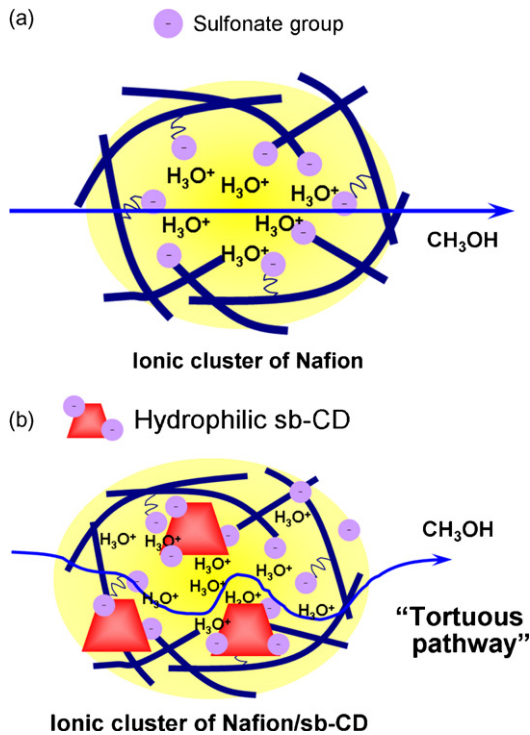


Fig. 3. Transport in (a) pristine Nafion membrane and (b) Nafion/sb-CD composite membrane.

The methanol permeability, P , of each sample was determined as follows [23,24]. The concentration of methanol in the deionized water cell is given by

$$\frac{V_B dC_B}{dt} = A \times \frac{DK}{L} C_A \quad (3)$$

where C_A and C_B are the concentrations of methanol in the feed compartment and in the permeate (water) compartment, respectively, A is the membrane area, L is the membrane thickness, V_B is the volume of the water compartment, D is the methanol diffusivity and K is the partition coefficient. Eq. (3) can be solved to give

$$C_B(t) = \frac{A}{V_B} \times \frac{P}{L} C_A (t - t_0) \quad (4)$$

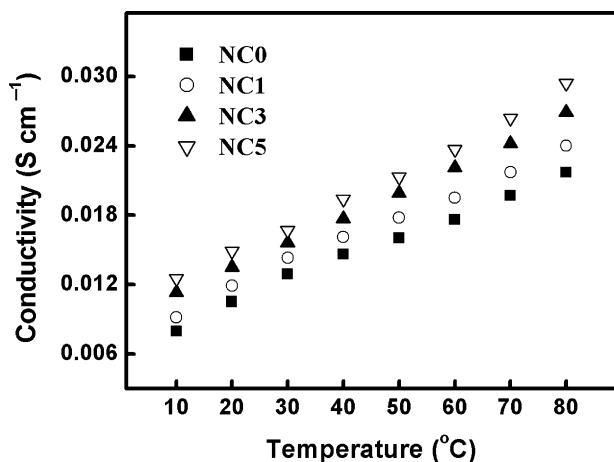


Fig. 4. Proton conductivities of Nafion/sb-CD composite membranes. All composite membranes have same membrane thickness, approximately 80 μm .

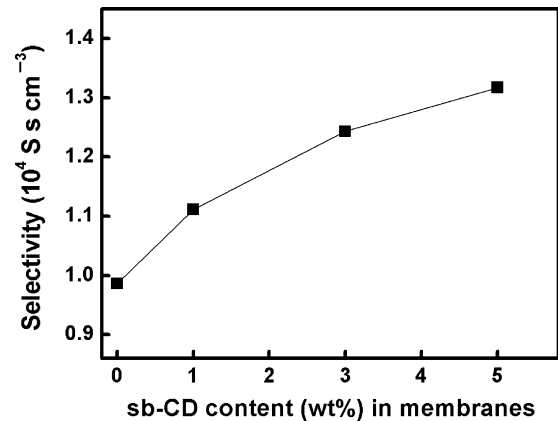


Fig. 5. Selectivities of Nafion/sb-CD composite membranes determined at 20 °C.

where P is the membrane permeability, defined as the product DK ; t_0 , also termed the time lag, is explicitly related to the diffusivity ($t_0 = L^2/6D$). C_B was measured several times during each experiment, and the methanol permeability was then calculated from the slope of the straight line.

The methanol concentration in the permeate compartment of the diffusion cell is shown in Fig. 2 as a function of time for Nafion/sb-CD composite membranes with various sb-CD contents. The linear behaviour predicted by Eq. (4) is present for all membranes, so their methanol permeabilities can be calculated from the slopes of the straight lines. The results are listed in Table 1. The methanol permeabilities of the composite membranes increase slightly in the range $(1.065\text{--}1.093) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 20 °C with increases in the sb-CD content. The increase in the methanol permeability is very small, however, when compared with the large increases in water uptake and ionic cluster size distribution observed in our previous study [21]. This small increase in the methanol permeability can be explained in terms of the internal changes in the Nafion structures that result from increasing the sb-CD content: the path of the methanol molecules around sb-CD in the ionic clusters of the composite membranes becomes more tortuous, as shown in Fig. 3. Similar trends have been reported for other membranes such as Nafion/polypyrrole composites [13]. It has also been reported that the methanol permeabilities of Nafion/polypyrrole composite membranes prepared with chemical in situ polymerization decrease with increase in polypyrrole content because increases in the numbers of the nano-sized polypyrrole particles in the ionic clusters make transport paths longer or increase their tortuosity.

The proton conductivities of composite membranes with various sb-CD contents are shown in Fig. 4. In general, the proton conductivities of composite membranes decrease with increases in the inorganic filler content with respect to that of pristine Nafion membrane. The proton conductivities of the Nafion/sb-CD composite membranes increase with increases in the sb-CD content. Thus the introduction of sb-CD with its many reactive sulfonic acid sites into the membranes contributes to an increase in their ion-exchange capacities, thereby resulting in an increase in their proton conductivities. For example, composite membranes with sb-CD contents of 0, 1, 3 and 5 wt.% have proton conductivities of 10.5, 11.9, 13.5 and 14.4 mS cm^{-1} at 20 °C, respectively. All the composite membranes exhibit increases in proton conductivity with increases in the temperature, implying that temperature plays a significant role in the kinetics of proton motion in the polymer membrane and in the mobility of the polymer chains.

The efficiency of separating two components in membrane separation processes is usually evaluated in terms of a selectivity that

is defined as the ratio of the permeation flux of the two components. In DMFC applications, the proton/methanol selectivity, Φ ($S\text{ s cm}^{-3}$), can be expressed in the form $\Phi = \sigma/P$, i.e., the ratio of proton conductivity to methanol permeability [25]. In general, for DMFCs, membranes with a higher selectivity are more desirable. Fig. 5 shows the selectivities of the composite membranes as a function of the sb-CD content, as based on their proton conductivities and methanol permeabilities measured at 20 °C. The selectivities of the composite membranes increase with increases in their sb-CD content. This trend arises because the increases in the proton conductivity are larger than the increases in the methanol permeability. In the case of the NC5 membrane, its selectivity is $1.32 \times 10^4 S\text{ s cm}^{-3}$, which is an improvement of 34% relative to that of the pristine Nafion membrane (i.e., NC0).

3.2. Proton diffusion coefficients

PFG-NMR experiments were used to provide a measure of the translation motion of protons in the membranes. In the most common PFG-NMR diffusion experiments, a spin echo sequence and stimulated echo sequence with pulse magnetic field gradient are used. Monitoring the proton diffusion in a sample is accomplished during the application of a magnetic field gradient in de-phasing and re-phasing periods. Between the two rf pulses and after a 180° or 90° pulse, pulse length of a field gradient, δ , and strength, g , is applied. This gradient causes the spin in different positions in the sample to precess differently, thereby enhancing the de-phasing process. That is, if the spins change positions during the experiment, their precession rates will also change, and the refocusing will be incomplete and result in a decrease in the intensity of the spin echo. The predicted dependence of signal attenuation on gradient strength is given by [26]:

$$\ln \left[\frac{A(g)}{A(0)} \right] = -\gamma^2 D g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \quad (5)$$

where $A(g)$ is the signal intensity observed for an applied gradient, g ; $A(0)$ is the signal intensity observed in the absence of an applied gradient; γ is the nuclear gyromagnetic ratio; δ is the pulse length of the magnetic field gradient; D is the self-diffusion coefficient; Δ is the time interval between the two gradient pulses. In this study, a series of spectra are obtained at increasing gradient strengths while holding all other parameters constant. The diffusion coefficients are obtained by fitting the variation in the peak intensity with the applied gradient strength.

A fundamental requirement of the PFG-NMR technique is that the diffusional attenuation must be significant relative to the attenuation caused by the relaxation of the nuclei. If the relaxation is too rapid, determination of diffusion coefficients with PFG-NMR measurements is difficult. In order to measure the spin–lattice relaxation times, T_1 , and spin–spin relaxation times, T_2 , of the Nafion/sb-CD composite membranes, NMR experiments were carried out using a Bruker mq20 spectrometer at 0.47 T. T_1 and T_2 were measured by using inversion recovery and spin echo sequences, respectively. It is found that T_1 and T_2 of NC0 (i.e., the pristine Nafion membrane) are approximately 133 and 71 ms at 25 °C, respectively. Thus, there is an ample time window for the PFG-NMR measurements. Zawodzinski et al. [26] have reported that T_1 of water in acid-form Nafion membranes varies with water concentration over an approximate range of 80–200 ms; less water in the membrane results in a shorter T_1 , and the T_2 values are generally about half as long.

The proton diffusion coefficients were determined by increasing the gradient strengths for Nafion/sb-CD composite membranes with various sb-CD contents. A typical plot of the observed signal

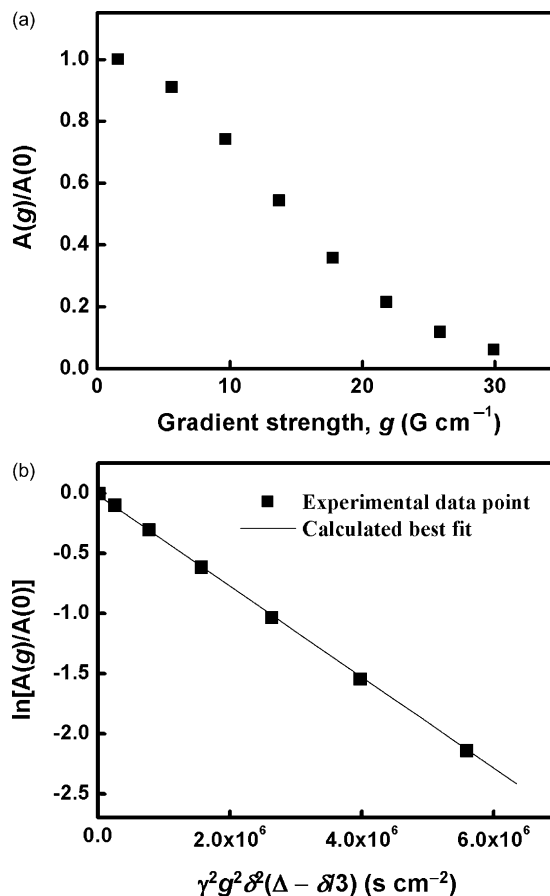


Fig. 6. Plots of (a) $A(g)/A(0)$ versus g and (b) $\ln[A(g)/A(0)]$ versus $\gamma^2 g^2 \delta^2 (\Delta - (\delta/3))$ for NC0 at $\delta = 2$ ms and $\Delta = 120$ ms. Calculated diffusion coefficient is $3.87 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C.

attenuation versus gradient strength for NC0 is given in Fig. 6(a). A typical plot of $\ln[A(g)/A(0)]$ versus $\gamma^2 g^2 \delta^2 (\Delta - (\delta/3))$ for NC0 is presented in Fig. 6(b). A linear relationship is confirmed in each case and the proton diffusion coefficient is determined from the slope. Plots of the proton diffusion coefficients as a function of the time interval Δ between the gradient pulses for the composite membranes are shown in Fig. 7. The diffusion coefficients are much smaller than that for pure bulk water ($2.11 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and increase with increases in the sb-CD content in the order $\text{NC5} > \text{NC3} > \text{NC1} > \text{NC0}$. The differences between the proton diffu-

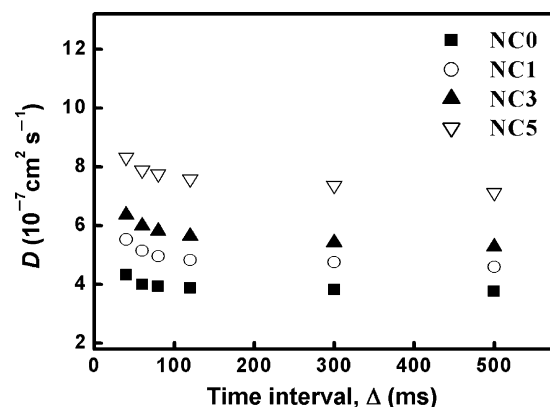


Fig. 7. Proton diffusion coefficients of Nafion/sb-CD composite membranes as function of time interval between two gradient pulses.

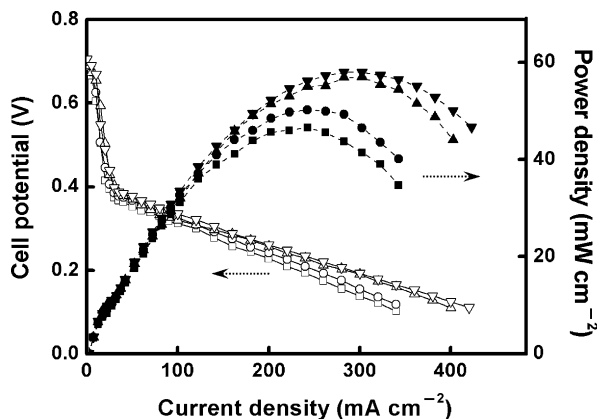


Fig. 8. Polarization curves for MEAs fabricated with Nafion/sb-CD composite membranes operated at 25 °C with 2 M methanol and air: (■) NC0, (●) NC1, (▲) NC3 and (▼) NC5. Open versions of same symbols denote cell potentials for corresponding samples.

sion coefficients of the composite membranes can be explained in terms of their different water uptakes and ion-exchange capacities. The addition of sb-CD with its many reactive sulfonic acid sites into a membrane results in an increase in both water uptake and ion-exchange capacity, thereby resulting in an increase in the proton diffusion coefficient. Zawodzinski et al. [26] reported that the proton diffusion coefficients range from 6.0×10^{-7} to $5.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for a Nafion117 membrane with λ ($\text{H}_2\text{O}/\text{SO}_3\text{H}$) in the range 2–14. By contrast, the proton diffusion coefficients for hydrated Nafion/sb-CD composite membranes are in the range of $(3.8\text{--}8.3) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ when λ is between 13.4 and 14.1. Nitta et al. [27] have reported that the proton diffusion coefficient depends on the pore size and thickness of the membrane matrix. All composite membranes investigated in this study have the same membrane thickness of approximately 80 μm . Thus the addition of sb-CD in the membranes contributes to increases in their ionic cluster size as well as water uptake and ion-exchange capacity and thereby results in increases in their proton diffusion coefficients.

3.3. Single-cell performances

The performance of the Nafion/sb-CD composite membranes was evaluated in a single cell. Fig. 8 shows the plots of cell voltage versus current density (polarization curves) and power density versus current density for the MEAs prepared with the Nafion/sb-CD composite membranes. The current densities for the NC0, NC1, NC3, and NC5 composite membranes are 232, 250, 282 and 291 mA cm^{-2} , respectively, at a potential of 0.2 V. Thus, the performance of the MEAs improves with increase in the sb-CD content. As mentioned above, methanol permeability increase very slightly with increase in the sb-CD content of the membranes. This behaviour is not, however, directly translated into improved performance of the MEAs in cells. This result may be due to increased proton conductivity and selectivity. The maximum power density of 58 mW cm^{-2} is obtained with NC5. It is concluded that a loading of 5 wt.% (i.e., the NC5 composite membrane) is the optimum sb-CD content of the Nafion matrix. Composite membranes with sb-CD contents above 5 wt.% may exhibit better performance than the NC5 composite membrane. Unfortunately, as mentioned in the experimental section, composite membranes with sb-CD contents above 5 wt.% suffer from defects such as cracks and gaps, which means that they cannot be used.

4. Conclusions

Nafion/sb-CD composite membranes with sb-CD contents of 0, 1, 3 and 5 wt.% have been prepared via the solution-casting method. The lambda values, water uptakes and ion-exchange capacities of the composite membranes increase gradually with increases in their sb-CD content. The methanol permeabilities of the composite membranes increase very slightly with increase in their sb-CD content. The proton conductivities increase with increases in the sb-CD content at all temperatures examined. These results for the composite membranes are used to show that the selectivity of the NC5 membrane is the highest ($1.32 \times 10^4 \text{ S s cm}^{-3}$). The proton diffusion coefficients obtained with ^1H PFG-NMR are much smaller than that of pure bulk water, and increase with increases in the sb-CD content of the membrane in the order $\text{NC5} > \text{NC3} > \text{NC1} > \text{NC0}$. The addition of sb-CD with its many reactive sulfonic acid sites into the membranes contributes to increases in their proton conductivities, ionic cluster size, water uptakes and IECs, that thereby results in increases in their proton diffusion coefficients. The performances of the MEAs fabricated with the Nafion/sb-CD composite membranes improve with increase in the sb-CD content, which is in good agreement with the selectivity results. The maximum power density of 58 mW cm^{-2} is obtained for the NC5 composite membrane. Thus a loading of 5 wt.% (i.e., the NC5 composite membrane) is the optimum sb-CD content of the Nafion matrix for use in DMFCs.

Acknowledgement

The authors thank the Korea Science and Engineering Foundation (KOSEF) for sponsoring this research through the SRC/ERC Program of MOST/KOSEF (R11-2005-065).

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