

# Determination of Pore Size Distribution of Nafion/Sulfated $\beta$ -Cyclodextrin Composite Membranes as Studied by $^1\text{H}$ Solid-State NMR Cryoporometry

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## ABSTRACT

Nafion/sb-CD membranes were prepared by mixing 5 wt% Nafion solution with  $\text{H}^+$ -form sulfated  $\beta$ -cyclodextrin (sb-CD), and their water uptake, ion exchange capacity (IEC), and ionic cluster size distribution were measured. The water uptake and IEC of the membrane increased with an increase in the sb-CD content. The SAXS experiments confirmed that an increase in the sb-CD content of the membranes shifted the maximum SAXS peaks to lower angles, indicating an increase in the cluster correlation peak. NMR cryoporometry is based on the theory of the melting point depression of a liquid confined within a pore, which is dependent on the pore diameter. The intensity-temperature (*IT*) curves showed that the cluster size distribution gradually became broader with an increase in the sb-CD content due to the increased water content, indicating an increase in the ionic cluster size. This result indicates that the presence of sb-CD results in increases in the cluster size as well as in the water uptake and the IEC.

**Keywords:** Nafion, sulfated  $\beta$ -cyclodextrin, pore size distribution, cryoporometry, fuel cell

## 1 INTRODUCTION

Direct methanol fuel cells (DMFCs) are promising candidates for portable power sources and transport applications because they do not require the fuel processing equipment that is essential for polymer electrolyte membrane fuel cells (PEMFCs) [1]. One of the critical problems hindering the commercialization of DMFCs is high methanol permeation rate across proton-exchange membranes [2]. Methanol permeates into the membranes primarily through the ionic clusters, and thus the size distribution of these clusters determines the methanol permeability. Therefore, an improved understanding of the cluster size distribution might help improve the performances of fuel cell membranes.

To our knowledge, there has been no previous direct and precise characterization of the cluster size distribution of Nafion-based membranes using  $^1\text{H}$  NMR cryoporometry. In this study, we report the ionic cluster size distribution of Nafion-based membranes, which are determined using NMR cryoporometry. In order to reduce the methanol permeability of the Nafion membranes while minimizing

the loss of proton conductivity, we add sulfated  $\beta$ -cyclodextrin (sb-CD) into the membranes. Cyclodextrins have a shallow truncated cone shape and a hydrophobic cavity that is apolar relative to the outer surface. Among them,  $\beta$ -CD is the most accessible, lowest-priced and generally the most useful CD, and is used in this study. Sulfated  $\beta$ -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 the Nafion membranes assists the transport of protons, since the number of reactive ionic cluster sites is increased. In addition, the presence of sb-CD nanoparticles inside the ionic clusters in the membranes means that the methanol transport pathway is tortuous, resulting in a decrease in the methanol permeability.

The objective of this study is to prepare Nafion/sb-CD composite membranes with various sb-CD contents and to probe the ionic cluster size distributions for the swollen membranes with NMR cryoporometry. The detailed results of this experimental approach are presented and discussed. In the near future, we plan to report the performance, i.e., the proton conductivity and methanol permeability, of these composite membranes in DMFCs.

## 2 EXPERIMENTAL

### 2.1 Materials

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  $\text{Na}^+$ -form sulfated  $\beta$ -CD (typical substitution: 7 – 11 moles/mol  $\beta$ -CD) was purchased from Aldrich Chemicals. The  $\text{H}^+$ -form sulfated  $\beta$ -CD (denoted hereafter as sb-CD) was obtained by recrystallization after adjusting the pH of the  $\text{Na}^+$ -form sulfated  $\beta$ -CD solution.

### 2.2 Fabrication of Composite Membranes

The composite membranes were prepared by the solution casting method. The desired amount of sb-CD was added into 5 wt% Nafion solution, and then stirred at room temperature and degassed by ultrasonication. The sb-CD content of the mixture was 1, 3, or 5 wt% with respect to

Nafion. The resulting mixture was slowly poured into a glass dish in an amount that would produce a formed membrane thickness of approximately 100  $\mu\text{m}$ . The filled glass dish was evaporated at 40  $^{\circ}\text{C}$  for 2 days and then annealed at 120  $^{\circ}\text{C}$  in a convection oven for 2 h. After cooling, the membrane was peeled off the glass dish by the addition of water. The membranes were stored in deionized water so that they were water-saturated. In this study, NCx denotes a Nafion/sb-CD composite membrane containing x wt% of sb-CD.

### 2.3 Characterization

The swelling characteristics of the membranes were determined with water uptake measurements. The samples were completely dried under vacuum for 3 days at 30  $^{\circ}\text{C}$  and then weighed. They were then placed in deionized water for a week at 25  $^{\circ}\text{C}$ . Water on the surfaces of the wet samples was removed with filter paper, and then the samples were immediately transferred to a weighing dish and weighed. The water uptake was calculated according to the equation

$$\text{water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the wet and dried membranes, respectively.

The ion exchange capacity (IEC) indicates the number of milliequivalents of ions in 1 g of the dry polymer.  $\text{H}^+$ -form samples of similar weight were soaked in 50 mL of 0.1 N NaCl solution for 24 h at 25  $^{\circ}\text{C}$  in order to achieve complete  $\text{H}^+$  to  $\text{Na}^+$  ion exchange. 10 mL of the released  $\text{H}^+$  was then titrated with 0.1 N NaOH solution, in which phenolphthalein was used as an indicator. The IEC was calculated from the titration data with the following equation:

$$\text{IEC (mequiv/g)} = \frac{V_{\text{NaOH}} \times N_{\text{NaOH}} \times 5}{W_{\text{dry}}} \quad (2)$$

where  $V_{\text{NaOH}}$  is the amount of NaOH required to neutralize a blank sample,  $N_{\text{NaOH}}$  is the normality of the NaOH solution, 5 is the ratio of the amount of NaOH required to dissolve the sample to the amount used for titration, and  $W_{\text{dry}}$  is the weight of the dried sample.

Small-angle X-ray scattering was carried out on a Bruker AXS Nanostar. In the experiments, the X-ray beam was produced with a rotating-anode X-ray generator operated at 40 kV and 35 mA, of which X-ray source was a monochromatized Cu  $K\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation. The samples were immersed in deionized water for a week and then three swollen pieces were placed within a Mylar bag under wet conditions.

In order to carry out the  $^1\text{H}$  NMR cryoporometry, each sample was immersed in deionized water for a week, and its surface was wiped to remove excess water before the sample was packed into a 10 mm outer diameter NMR tube and sealed. 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. The NMR cryoporometry measurements were carried out with a Bruker mq20 spectrometer at 0.47 Tesla and a resonance frequency of 19.95 MHz. The spin-echo amplitude from  $90^{\circ}-\tau-180^{\circ}-\tau$ -echo pulse sequence was measured with a pulse separation time,  $\tau$ , of 10 ms to ensure that the signal was entirely from the liquid present. Since the spin-spin relaxation time of solid ice confined within pores of NCx membranes was very short, whereas the corresponding relaxation time of mobile water was long, the mobile water could be detected during 20 ms of total echo time. The signal amplitude was measured as a function of temperature ranging from 210 to 277 K with an interval of 1 K using a Bruker BVT-3000 temperature control unit. All measurements were obtained by increasing the temperature after initially cooling the samples to a low temperature (i.e., 190 K) in order to prevent the complications of supercooling or hysteresis. The warming rate was low enough to achieve equilibrium, which was controlled by waiting above 10 min at each temperature step for NMR signal to stop changing. The signal intensity was corrected for temperature by implementing the Curie law, i.e., the observed signal intensity was multiplied by the factor  $T/T_0$  ( $T_0 = 273 \text{ K}$  and  $T$  defining actual temperature).

## 3 RESULTS AND DISCUSSION

### 3.1 Water Uptake and Ion Exchange Capacity (IEC)

Figure 1 shows the equilibrium percentage sorption of water, obtained by soaking the membranes in water at 25  $^{\circ}\text{C}$ . The water uptake of the membranes was found to increase from 21.4 for NC0 to 24.4% for NC5 with the increase in the sb-CD content. In order to validate whether or not there was any loss of sb-CD during swelling, the weight of the dried membranes before and after water uptake (i.e., swelling) experiments was measured. As a result, there was no significant difference in membrane weight between before and after the experiments, implying that loss of sb-CD did not occur during swelling. This result shows that the water uptake of the membranes can be controlled by varying their sb-CD content.

The ion exchange capacity (IEC) provides an indication of the number of ion-exchangeable groups present in an ion-conducting polymer membrane; these groups are responsible for the conduction of protons and thus the IEC is a reliable measure of the proton conductivity. The IEC of each membrane was determined by using the acid-base titration method. The results are shown in Figure 1 and demonstrate that the IECs of the membranes increase from 0.89 to 0.96 mequiv/g with increase in the water uptake. Thus the introduction of sb-CD with its many reactive sulfonic acid sites into the membranes contributes to an increase in the IEC.

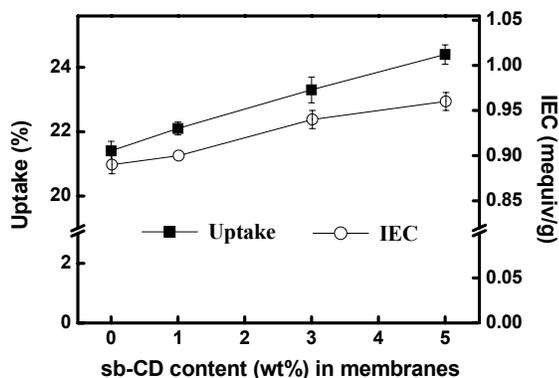


Figure 1: Water uptake and IEC for the composite membranes as functions of sb-CD content.

### 3.2 Cluster Correlation Peak: SAXS

Under wet conditions, the SAXS results indicate that there are significant changes in the properties of the membranes with variation in the sb-CD content, i.e., with variation in the water content. Figure 2 shows the relative scattering intensity as a function of scattering vector,  $S$ , for the hydrated Nafion membrane (NC0) and the hydrated Nafion/sb-CD composite membranes (NC1, NC3, and NC5). The scattering vector,  $S$ , is defined by  $S = 2\sin\theta/\lambda$ . The scattering intensity increased with increase in the water content. This is due to the enhancement of the difference in the electron density by decreasing the electron density of the ionic clusters containing more water content relative to the backbone [3]. It can be also seen that the maximum SAXS peak shifts to lower scattering vector (i.e., scattering angle) as the sb-CD content (i.e., water content) increases. This maximum peak position is inversely proportional to the cluster correlation peak. Therefore, these decreases in scattering angle indicate the expansion of the hydrophilic ionic clusters due to the increased cluster correlation peak. In addition, by revealing these changes in the cluster correlation peak, the SAXS data confirmed the presence of sb-CD particles in the ionic clusters. It has previously been reported that the increase in the cluster correlation peak for Nafion membranes is directly proportional to the volume of absorbed water [4].

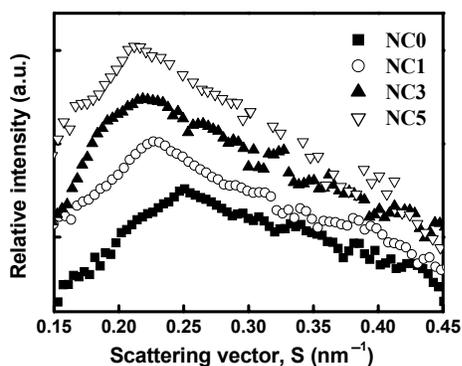


Figure 2: SAXS curves for swollen composite membranes.

### 3.3 Cluster Size Distribution: NMR Cryoporometry

The theoretical basis for this NMR application is the well-known Gibbs-Thompson equation [5–7], which relates the melting point depression,  $\Delta T_m$ , of a confined liquid to the pore diameter,  $D$ :

$$\Delta T_m(D) = K \frac{1}{D} \quad (3)$$

where  $K$  is a constant depending solely on the physical properties of the liquid confined within the porous material. Measurement of the amount of liquid confined within the pores as a function of temperature enables the pore size,  $D$ , and its distribution to be estimated when  $K$  is known. In this study, water was used as the probe liquid, for which  $K$  is approximately 62 K nm. This equation indicates that the difference between the normal and depressed melting temperatures is inversely proportional to a linear dimension of the liquid confined within the pores. The spin-echo signal intensity,  $V$ , indicates the amount of liquid water confined within the pores at a particular temperature,  $T$ , and thus the volume of the pores with linear dimensions equal to the corresponding the pore diameter,  $D$ , can be calculated.

$$\frac{dV}{D} = \frac{K}{D^2} \frac{dV}{dT_m(D)} \quad (4)$$

Therefore, the measurement of  $dV/dT_m(D)$  enables the pore size distribution of the samples to be determined, provided  $K$  is known.

Figure 3 shows the intensity-temperature ( $IT$ ) curves of water confined within the ionic cluster pores of the Nafion/sb-CD composite membranes. In the case of the solid phase, the relative signal intensities were denoted as 0, corresponding to totally frozen water. The relative signal intensities from the liquid phase of totally molten water were denoted as 1. These curves show that the signal intensities increase gradually with increasing temperature (below 273 K) due to the gradual melting of the frozen water confined within the ionic cluster pores in the membranes. The abrupt increase in intensity at the melting point of bulk water, 273 K, is due to the melting of the bulk supernatant water.

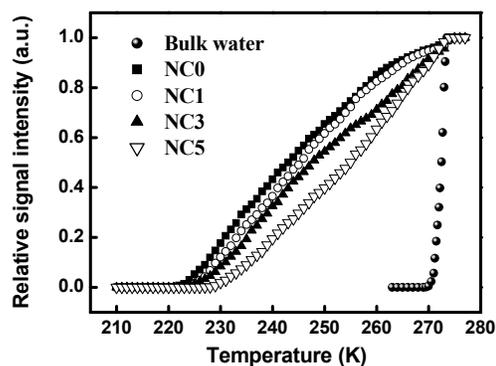


Figure 3: Relative signal intensities versus temperature (*IT* curves) of water confined within the ionic cluster pores of the Nafion/sb-CD composite membranes.

If the amount of liquid confined within the pores of the membranes and  $K$  are known, their cluster size distribution can be estimated using equation (4). It has generally been reported that  $K$  is in the range 41 – 73 K nm, when water is used as the probe liquid. We assumed that  $K = 62$  K nm to obtain the cluster size distributions. These data were used in equation (4) to obtain the relative pore volume as a function of pore diameter, as shown in Figures 4(a) to (d).

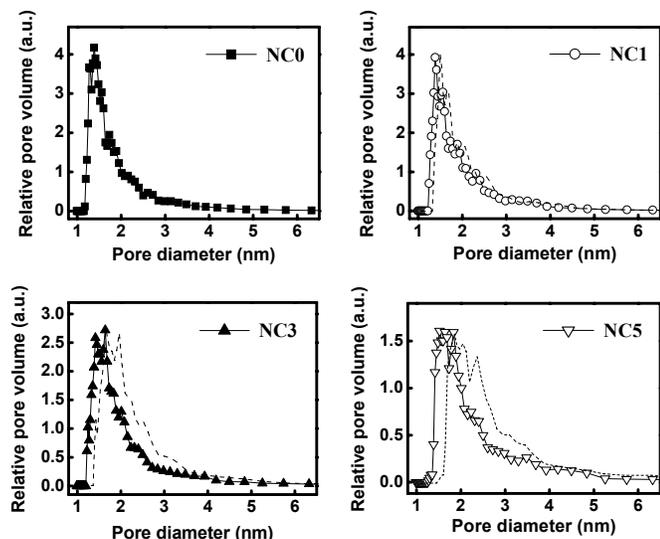


Figure 4: Pore size distribution curves of the Nafion/sb-CD composite membranes. The dashed lines of NC1, NC3, and NC5 are corrected by the melting point depressions, which are caused by colligative effect.

On the other hand, colligative effect will also affect the *IT* curves due to the addition of different sb-CD content. This effect is a phenomenon by which the freezing/melting point of a solution is lowered when more solute is dissolved in the solution. In order to validate the colligative effect of water/sb-CD solutions confined within ionic clusters of composite membranes, the melting point of water/sb-CD solutions was measured by using the NMR spin-echo method. The water/sb-CD solutions confined within ionic clusters of NC1, NC3, and NC5 composite membranes had various sb-CD concentrations of 4, 11, and 17 wt%, respectively. These concentrations were determined by assuming that water (the amount of water measured by the gravimetric method) and sb-CD particles were confined within only ionic clusters of composite membranes. As a result, the melting point depressions of the water/sb-CD solutions with 4, 11, and 17 wt% concentrations compared to pure water were found to be 2, 6, and 8 K, respectively. Therefore, the original *IT* curves of the composite membranes were corrected by adding their melting point

depressions to original temperature. In Figure 4, it is clear that the cluster size distribution of the composite membranes broadens gradually with an increase in their sb-CD content, i.e., there is an increase in the ionic cluster pore size. This is probably due to the expansion of the hydrophilic ionic clusters due to the increased water content, which is caused by the addition of sb-CD with its many sulfonic acid groups into the hydrophilic ionic clusters. This increase in cluster size is in agreement with the trend in the results obtained from the SAXS measurements. Overall, these results show that NMR cryoporometry can be used to determine the ionic cluster size distributions of Nafion-based membranes and that this method provides a means with which to determine pore sizes on the nanometer scale.

## 4 CONCLUSIONS

Nafion/sb-CD composite membranes were prepared with the solution casting method. The water uptake values were found to increase with an increase in their sb-CD content. The acid-base titration results show that the IEC of the membranes increases from 0.89 to 0.96 mequiv/g with an increase in their sb-CD content, indicating that the introduction of sb-CD with its many reactive sites (sulfonic acid groups) into the membranes results in an increase in IEC. SAXS and  $^1\text{H}$  solid-state NMR cryoporometry results were obtained to determine the cluster correlation peak and ionic cluster size distributions of the membranes, respectively. The SAXS results show that the cluster correlation peak increases with an increase in the sb-CD content. From the *IT* curves by NMR cryoporometry, it was determined that the cluster sizes of the membranes increase with an increase in their sb-CD content due to their increased water content, i.e., there is an increase in the ionic cluster pore size. Thus the presence of sb-CD with its many sulfonic acid groups in the Nafion membranes leads to increases in their water uptake, IEC, and ionic cluster size. In conclusion,  $^1\text{H}$  solid-state NMR cryoporometry was found to be a very effective method for characterizing the ionic cluster size distribution of Nafion-based membranes, which is strongly correlated with the performance of membranes for polymer electrolyte fuel cells (PEMFCs).

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