



Quantification of Methanol Concentration in the Polymer Electrolyte Membrane of Direct Methanol Fuel Cell by Solid-state NMR

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Abstract: Direct quantification of methanol in polymer electrolyte membrane (PEM) by solid-state nuclear magnetic resonance (NMR) spectroscopy was studied and the methanol concentrations in PEM produced by crossover and diffusion were compared. The error range of the quantification was not smaller than $\pm 15\%$ and the amount of the methanol crossed over in our direct methanol fuel cells (DMFCs) was less than the methanol diffused to PEM. The methanol concentration in the PEM of the DMFC operated at different current densities were equivalent.

Keywords: Methanol Crossover, Nuclear Magnetic Resonance, Direct Methanol Fuel Cell, Permeation, Diffusion

INTRODUCTION

Methanol crossover is one of the several barriers to overcome for the direct methanol fuel cells (DMFCs) to be commercialized.¹ Various methods have been used to detect the methanol crossed over from an anode to a cathode in a DMFC.¹⁻⁷ However, most of the detection methods measure the chemical species in the exhaust gas at the cathode side.¹⁻⁷ Carbon dioxide (CO₂) sensors detect CO₂ (final electrochemical oxidation product) only in the cathode exhaust gas assuming that CO (intermediate), other possible intermediates or methanol (fuel) are present in negligible amounts.² Alternatively, the intermediates and methanol were converted to CO₂ before sensing with the CO₂ sensors.^{3,4} However, CO₂

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produced at the anode was reported to crossover to the cathode.^{3,4} Thus, the CO₂ observed at the cathode side includes not only the ones produced by the electrochemical reaction of the crossed-over methanol at the cathode but also the ones generated at the anode. Consequently, sensing CO₂ at the cathode side cannot measure the crossover rate accurately although real time measurements are possible.²⁻⁴ Mass spectroscopy,⁵ gas chromatography,^{6,7} and gas analyzers¹ also have been employed to detect the methanol crossover by identifying and quantifying the chemical species in the exhaust gas at the cathode side. In contrast, direct detection of the chemical species present in a polymer electrolyte membrane (PEM) in a DMFC was only recently reported.⁸

In this work, the direct quantification method of methanol concentration in PEM by solid-state nuclear magnetic resonance (NMR) spectroscopy was studied and the methanol concentrations in PEM produced by crossover and diffusion were compared.

EXPERIMENTALS

Preparation of PEM for NMR experiments

For PEM, Nafion 117 was purchased from Ion Power Inc. (U.S.A.). Pretreated PEM⁸ was soaked in 2 M ¹³CH₃OH aqueous solution for 24 hours and the surfaces were wiped off prior to powdering at liquid nitrogen temperature with a Spex 6700 freezer mill (Spex CertiPrep Group, U. S. A.). Empty rotors were weighed before placing any powdered PEM in a rotor and then the rotor filled with powdered PEM and a known amount of 1.8 M ¹³CH₃CH₂OH aqueous solution was weighed again to measure the weight of powdered PEM in the rotor. Carbon-13 enriched ethanol (¹³CH₃CH₂OH) was used as a standard material to calibrate the amount of methanol in the weighed PEM sample.

To measure the methanol traveling through PEM in a real operating DMFC, a DMFC with a triple-layer PEM was prepared as previously reported.⁸ The DMFCs were operated in a constant voltage mode at 250 mV but at different current densities such as 730 and 350 mA/cm² and then the methanol amounts in the middle-layer PEM of the DMFCs were determined by NMR spectroscopy were compared.

Solid-state NMR Spectroscopy

All ^{13}C magic-angle spinning (MAS) NMR experiments were carried out on a Bruker Avance II 400 MHz spectrometer using a double-resonance (^1H -X) MAS probe equipped with a 4 mm rotor spinning module at room temperature. Samples were spun at a relatively slow spinning rate of 2.3 kHz to minimize a centrifugal force on the wet samples. The excitation pulse length for 90° flip was $3.0\ \mu\text{s}$ and pulse repetition delay of 3 s was used. Proton decoupling was applied during the ^{13}C NMR experiments. No change in the sample mass was observed during the MAS NMR experiments. All the chemical shifts in ppm were referenced to external neat tetramethylsilane.

RESULTS and DISCUSSION

Possibility to quantify the amount of methanol in PEM by ^{13}C MAS NMR spectroscopy was tested first by repeating the measurement with the PEM soaked in the methanol solution. The sampling procedure was schematically summarized in Fig. 1(b). It was noticed that water in air was frozen on the PEM powder as soon as the sample holder for the freezer mill was open if the sample holder was not warmed up to room temperature prior to the opening. In this case, consequently, the measured weight of PEM included the weight of water. Thus, in order to reduce the error in the measured weight of the PEM powder sample, the PEM powder was transferred to a rotor after the sample holder for a freezer mill was warmed up to room temperature.

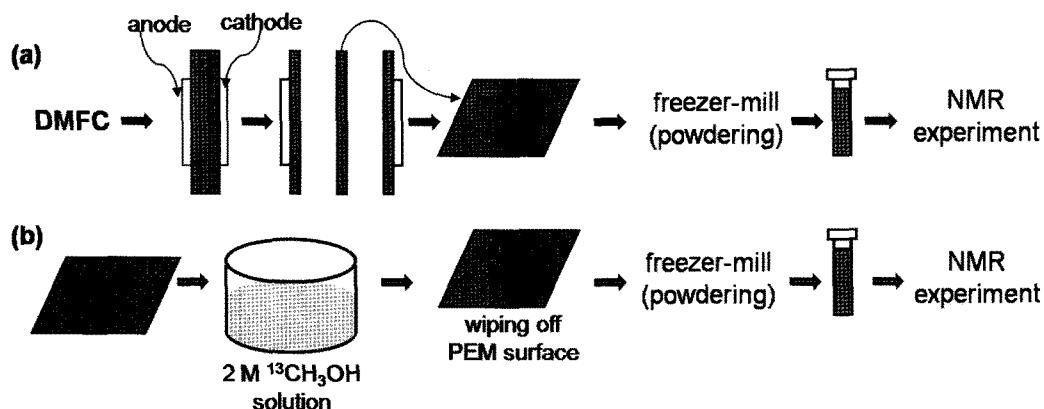


Fig. 1. Schematic diagram of the sampling procedure for quantitative NMR studies of methanol contents in PEM: (a) by operation of DMFCs in a constant voltage mode but at different current densities prior to the NMR experiments and (b) by soaking PEM in 2 M ^{13}C CH₃OH aqueous solution for 24 hours prior to the NMR experiments.

From the ^{13}C MAS NMR spectrum as shown in Fig. 2, the peak areas of individual resonance signals were obtained. The peak at 49.4 and 16.7 ppm is for methyl carbons of methanol and of ethanol, respectively, and the known amount of ethanol was added to the rotor. Thus, the mole ratios of methanol and ethanol could be calculated. Then, with the measured weight of PEM powder in the rotor, the amount of methanol per weight of PEM was calculated in $\mu\text{mol/g}$. Quick evaporation of methanol requires careful and skillful handling of the samples in order to minimize the experimental error. However, even with the skillful handling the error in the repeated measurement of the methanol amounts in PEM was not smaller than about $\pm 15\%$.

The middle-layer PEM of a triple-layer PEM in a DMFC was taken for NMR experiments after the fuel cell operation with 2 M ^{13}C CH₃OH aqueous solution for about 15 min as described in the experimental section and sampling was carried out as schematically summarized in Fig. 1(a). The methanol amount in the middle-layer PEM taken after the operation at two different current densities in a constant voltage mode was compared. As summarized in Table 1, the methanol concentrations in the PEM taken from a DMFC were smaller than that in the PEM soaked in the methanol solution. Another observation is that

the methanol concentration in the PEM in a DMFC did not differ even when the current densities were almost two times higher as shown in Table 1.

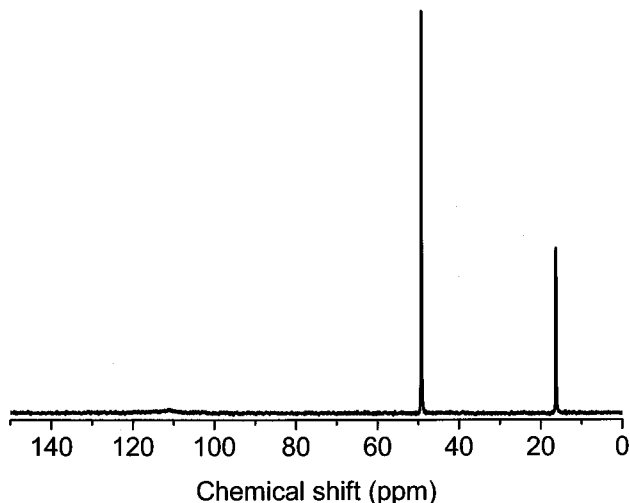


Fig. 2. Representative ^{13}C MAS NMR spectrum of the PEM prepared by soaking in 2 M $^{13}\text{CH}_3\text{OH}$ aqueous solution for 24 hours. A known amount of $^{13}\text{CH}_3\text{CH}_2\text{OH}$ (1.8 M, 7 μL) was added for the quantitative analysis. The spectrum was acquired at sample spinning of 2.3 kHz under proton decoupling. The peak at 49.4 and 16.7 ppm is for methyl carbons of methanol and of ethanol, respectively. The broad signal near 115 ppm is from PEM.

Table 1. Quantification data of methanol in PEM

Sample*	PEM in a rotor (mg)	Ethanol added (mg)	Calculated mole ratio of ethanol: methanol	Calculated methanol/PEM ($\mu\text{mol/g}$)
A	24.2	7.0	1 : 1.4 ± 0.2	740 ± 110
B	8.2	6.8	1 : 0.17 ± 0.03	286 ± 52
C	11.9	6.9	1 : 0.26 ± 0.04	271 ± 42

* Sample A was prepared by soaking PEM in 2 M $^{13}\text{CH}_3\text{OH}$ aqueous solution while Sample B and C was prepared by operating a DMFC at the current density of 730 and 350 mA/cm^2 in a constant voltage (250 mV) mode.

Our results confirm that diffusion or permeation of methanol to Nafion results in much higher methanol concentration in PEM than methanol crossover in a real DMFC. Not only diffusion but also electroosmotic drag of methanol to cathodes, both of which can increase net methanol crossover, occurs in a DMFC. On the other hand, electroosmotic drag of water to cathodes and diffusion of water produced at cathodes dilute the methanol concentrations in PEM. In general, the PEM in a DMFC is under a constant pressure to hold the DMFC. As a result, the PEM cannot swell freely in contrast to the PEM soaked in the methanol solution. It has been reported that methanol crossover rates depend on various operation conditions of DMFCs such as methanol solution concentration^{1,2,6} and flow rate,^{2,7} current density,^{1,2,5,6} temperature,^{2,6,7} thickness of PEM,¹ and air humidification temperature.² Typically, the methanol crossover rate increased for higher methanol concentration solutions. In contrast, the reports on the dependence of the crossover rate on current density and temperature were not consistent.^{1,2,5-7} Our independence of the crossover rate on current density is not consistent with none of the previous reports in which methanol crossover rates increased^{2,5} or decreased^{1,6} at higher current density. However, further experiments are required for the systematic data.

CONCLUSION

Quantification of methanol in a PEM was possible by ¹³C MAS NMR spectroscopy. However, the error range was not smaller than ± 15 %. The comparison of the methanol contents in the PEM prepared by soaking a PEM in a methanol aqueous solution was much higher than those in a DMFC in operation. The NMR data indicate that permeation of methanol to PEM results in higher concentration of methanol in the PEM than the methanol crossover in a DMFC. The DMFCs operated at the two different current densities in a constant voltage mode had equivalent methanol concentrations in the PEMs in the DMFCs. Further experiments are in progress to confirm the results and to obtain systematic data of methanol crossover under various conditions.

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