Fuel Cells

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Methanol Behavior in Direct Methanol Fuel Cells**

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The direct methanol fuel cell (DMFC) is a promising alternative power source[1] that combines the merits of direct hydrogen/air fuel cells with the advantages of a liquid fuel, such as convenient handling and high energy density. DMFCs that operate at temperatures between 110 and 130 °C are designed for transportation, whereas those operating at lower temperatures (≤ 60 °C) are intended for use in portable devices.[2] DMFC development is presently focused on optimizing the operating conditions. Nevertheless, a few technical barriers remain to be overcome before successful commercial applications can be achieved.[3] One such barrier is methanol crossover from the anode to the cathode, which not only causes a decrease in the energy efficiency as a result of fuel loss but also affects the fuel cell performance as a consequence of the development of a mixed potential at the cathode. However, information about methanol crossover and the related phenomena occurring in the polymer electrolyte membranes (PEMs) of operating DMFCs is scarce, which can be mainly attributed to the difficulty of directly studying the methanol behavior. Recently, nuclear magnetic resonance (NMR) techniques were successfully employed to probe water production and distribution in PEM fuel cells (PEMFC)[4] as well as water and methanol transport in DMFCs.[5] Herein, we present a new type of membrane electrode assembly (MEA) from which a PEM can be extracted free from electrode components, such as catalysts, carbon black, and carbon cloth. Solid-state magic-angle spinning NMR (MAS NMR) studies of this PEM allowed—for the first time—the direct detection of methanol and the reaction intermediates traveling through the PEM during fuel-cell operation.

An MEA consisting of a triple-layer PEM (Nafion 117) was prepared for the DMFC by using PtRu/C and Pt/C as the anode and cathode catalysts, respectively. The MEA configuration and the sampling procedure for the MAS NMR experiments are shown schematically in Figure 1. The procedure is described in the Experimental Section, and more details are available in the Supporting Information. The triple-layer PEM DMFC exhibited a current density that was about 80 % of that of a standard cell (operating with 2 M methanol and a single-layer PEM), and the maximum potential of the triple-layer cell was about 100 mV lower than that of the standard cell (Figure 2). This reduction in current density and potential can be ascribed to the increased resistance of the triple-layer PEM, which is three times thicker (0.54 mm) than a single-layer membrane (0.18 mm).

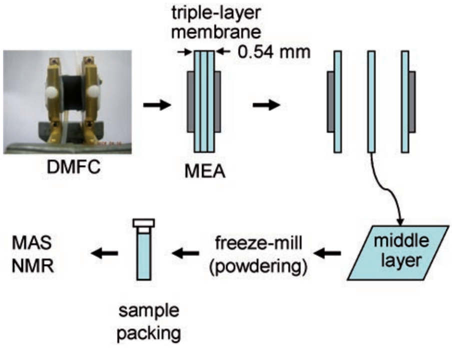

Figure 1. Diagram of the sampling procedure for solid-state MAS NMR studies of MEAs containing triple-layer PEMs operated in DMFCs.

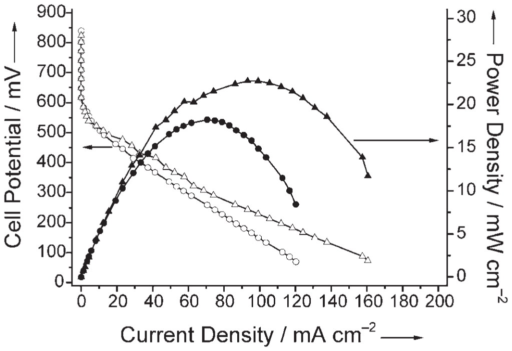

Figure 2. Comparison of the fuel-cell performances (at room temperature) of DMFCs containing a standard MEA with a single-layer PEM (triangles) and a MEA with a triple-layer PEM (circles).

Figure 3 shows the ^{13}C MAS NMR spectrum of the middle PEM layer of a DMFC, which was extracted after operation of the fuel cell using a 2 M aqueous solution of $^{13}CH_3OH$ (for at least 15 min). Previous to this operation, the fuel cell was run for 2 days (using 2 M CH_3OH) at 350 mV, thereby achieving a current density of about 50 mA cm^{-2}. The dominant ^{13}C signal (observed at $\delta = 49$ ppm) corresponds to methanol species in the PEM, which are crossing over to the cathode. Several reaction intermediates involved in methanol oxidation were also detected. The ^{13}C signals observed at $\delta = 166$ and 163 ppm are attributed to the formic groups (HCOO−) of formic acid and methyl formate, respectively, and their intensities are only about 2 % of the

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

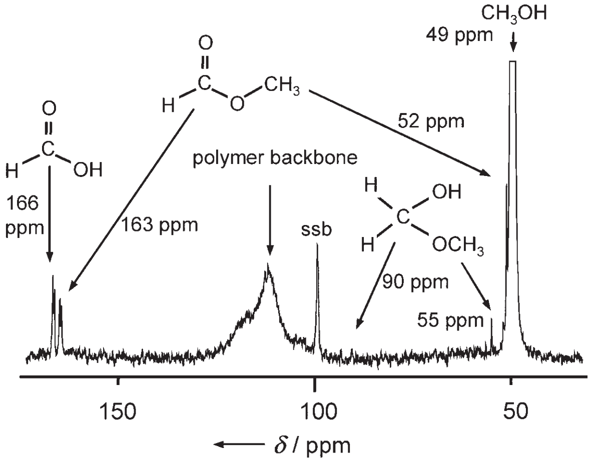

Figure 3. ^{13}C MAS NMR spectrum of the middle PEM layer extracted (using 2 M ^{13}CH$_3$OH) from the MEA of a DMFC after operation. The species assigned to the peaks are shown in the spectrum (see text for more details). Only 10% of the methanol peak (at $\delta = 49$ ppm) is shown to achieve an appropriate display of all peaks. The sample was spun in a 4-mm rotor (at 5 kHz), and the spinning sideband (ssb) is marked in the spectrum.

methanol signal. These species were possibly produced in the reactions shown in Equations (1) and (2).[6]

$$CH_3OH + H_2O \rightarrow HCOOH + 4\,H^+ + 4\,e^- \quad (1)$$

$$HCOOH + CH_3OH \rightarrow HCOOCH_3 + H_2O \quad (2)$$

The methyl ($-$CH$_3$) signal of methyl formate can be clearly observed at $\delta = 52$ ppm, whereas the broad band found in the region $\delta = 100$–125 ppm can be attributed to the backbone carbon centers of Nafion.[7] Formaldehyde is a well-known by-product of methanol oxidation. However, no formaldehyde signal was detected at the expected position, namely, at $\delta = 82$ ppm, in the ^{13}C spectrum. Instead, methoxyhydroxymethane (H$_2$C(OH)OCH$_3$)—a hemiacetal formed between formaldehyde and methanol at a 1:1 ratio—produced acetal and methyl carbon signals at $\delta = 90$ and 55 ppm, respectively, whereas no ^{13}C signal was observed for dimethoxymethane (H$_2$C(OCH$_3$)$_2$)—an acetal formed between formaldehyde and methanol at a 1:2 ratio—which has been reported as the major intermediate of methanol oxidation when neat methanol is fed into the DMFC anode.[6] All these observations on formaldehyde-related species suggest that formaldehyde is, in fact, formed during DMFC operation but reacts readily with methanol to produce methoxyhydroxymethane. The concentration of methanol (relative to that of formaldehyde) must be high enough to produce methoxyhydroxymethane but not sufficient to generate dimethoxymethane. The ^{13}C peaks were assigned based on literature data[8] and on ^{13}C MAS NMR spectra obtained from PEMs soaked in aqueous solutions of reference compounds, such as methanol, formaldehyde, formic acid, and their mixtures. These spectra and the ^{13}C peak assignments are presented in the Supporting Information.

The identified reaction intermediates were the same, even in the case of a DMFC comprising an anode and a cathode both made of Pt/C catalysts (see the Supporting Information). A closer inspection of both ^{13}C MAS spectra (Figure 3 and Supporting Information) revealed that the Pt/C catalyst at the anode produced three times more formic acid than PtRu/C, which is possibly a result of its lower activity toward methanol oxidation.[9]

Figure 4 shows the ^{2}D MAS NMR spectrum of the middle PEM layer extracted from the MEA of a DMFC after operation for 30 min using a 2 M aqueous solution of CD$_3$OH. Previous to this operation, the DMFC was run for 2 days (using 2 M CH$_3$OH) at 350 mV, thereby achieving a current density of approximately 50 mA cm^{-2}. The peaks were assigned based on the ^{2}D MAS spectra of the PEM absorbed in the reference solutions and of the solutions themselves (see the Supporting Information). The dominant deuterium signals observed at $\delta = 3.3$ and 5.6 ppm in Figure 4 are attributed, respectively, to CD$_3$OH molecules crossing over to the cathode and to D$_2$O or HOD species, which are a product of the methanol oxidation reaction shown in Equation (3).[6]

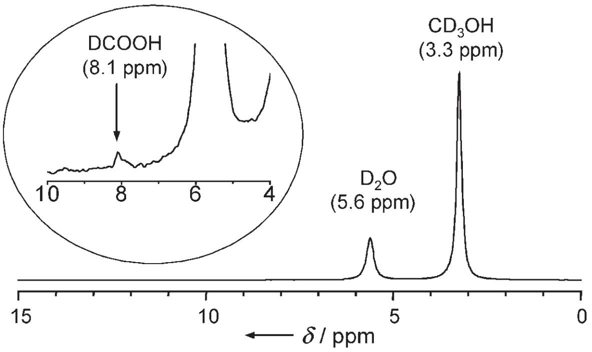

Figure 4. ^{2}D MAS NMR spectrum of the middle PEM layer extracted (using 2 M CD$_3$OH) from the MEA of a DMFC after operation. The inset shows an enlargement of the spectrum in the y scale. The sample was spun in a 4-mm rotor (at 5 kHz).

$$CD_3OH + 3/2\,O_2 \rightarrow CO_2 + D_2O + HOD \quad (3)$$

The deuteroxy group (D$_2$O and HOD) of a water sample absorbed in a PEM afforded a ^{2}D signal at $\delta = 5.6$ ppm (see the Supporting Information). This chemical shift was higher than that observed for pure water (at $\delta = 4.8$ ppm), thus indicating that the deuteroxy groups reflect the acidic environments of the ion pores in Nafion. The water molecules in the ion pores of the membrane share the acidic protons of the sulfonyl groups ($-$SO$_3$H) located at the end of the side chains of the polymer matrix.[10] On the other hand, the ^{2}D chemical shift of the deuterated methyl group of a methanol sample absorbed in a PEM was the same as that observed for methanol in solution, that is, $\delta = 3.3$ ppm (see the Supporting Information). This result indicates that the hydrophobic methyl groups do not interact directly with the sulfonyl protons of the Nafion side chains and are instead surrounded by water molecules, even inside the ion pores.[10] The inset of

Figure 4 shows a quite small deuterium peak at $\delta = 8.1$ ppm, which can be assigned to DCOO−. However, no ^{2}D signals are observed in the spectrum for formaldehyde or its acetals. In contrast, Figure S3c of the Supporting Information does show a deuterium signal at $\delta = 4.8$ ppm—attributed to formaldehyde and its acetals—both in solution and in PEM. Thus, it is possible that the ^{2}D peaks from formaldehyde and its related compounds are hidden under the strong signals produced by D_2O and CD_3OH in Figure 4. The power density of a single-cell DMFC was reduced by about 10% when deuterated methanol was used because of the deuterium isotope effect observed during catalytic cleavage of methanol on the anode.[11]

In conclusion, we have designed an MEA composed of a triple-layer PEM, thus facilitating the sampling procedure for NMR studies of methanol crossover and methanol reaction intermediates in a DMFC. High-resolution ^{2}D and ^{13}C MAS NMR spectra were obtained from the middle PEM layer of a fuel cell after operation (for 15–30 min) using ^{2}D or ^{13}C enriched methanol solutions. The MAS NMR spectra enabled the unambiguous and quantitative detection of methanol and several reaction intermediates traveling through the PEM during DMFC operation. Research is presently being conducted to study the effects of the operating conditions, such as fuel concentration and temperature, on the reaction intermediates, the methanol crossover, and their correlations to the DMFC performances. Our approach can be readily extended to other direct alcohol fuel cells to investigate fuel crossover, fuel oxidation mechanisms, and the functions of novel catalysts. In addition, the methodology may be applied to study the migration of soluble Pt^{2+} species in the polymer electrolyte, which is a proposed pathway of Pt-cathode degradation in H_2/O_2 PEMFCs.[12]

Experimental Section

Please refer to the Supporting Information for a more detailed description.

Preparation of the MEAs: Standard MEAs were prepared by hot-pressing an anode, a Nafion 117 electrolyte membrane layer, and a cathode at 135 °C for 3 min under a pressure of 100 kg cm^{-2}. MEAs containing triple-layer PEMs were prepared in the same way, except that three PEM layers were used.

Electrochemical tests of DMFCs: The experimental DMFC assembly consisted of an MEA and two rectangular blocks of graphite with serpentine flow fields machined on the inner surface to a depth and width of 1 mm. The assembly was held together by two home-built stainless-steel clamps. An aqueous methanol solution (2 M) was fed to the anode (at a rate of 0.8 cm^3 min^{-1}) while oxygen gas was fed to the cathode (at a rate of 1000 cm^3 min^{-1}). The DMFCs were operated, intermittently, for 2–3 days on an electronic analyzer at a constant voltage (of about 350 mV) previous to the measurements at ambient temperature.

Sample preparation and solid-state NMR experiments: The middle PEM layer of a DMFC was removed after operation of the fuel cell (for 15–30 min) using either CD_3OH (2 M) or $^{13}CH_3OH$ (2 M). The layer was then freeze-milled at liquid-nitrogen temperature to obtain a powder and packed into a 4-mm rotor for the MAS NMR experiments. The sample was exposed to air (at room temperature) during sample packing. This occurred for less than 2 min during which the evaporation of organic components or water in the PEM was confirmed to be less than 10%. NMR experiments were carried out on a Bruker Avance II 400 MHz spectrometer using a double-resonance (^{1}H-X) MAS probe equipped with a 4-mm rotor spinning module. Samples were spun at 5 kHz (unless otherwise stated). The excitation pulse length for 90° flip was 3.0 μs for both ^{2}D and ^{13}C NMR, and a three-second pulse-repetition delay was used. Proton decoupling was applied during the ^{13}C NMR experiments.

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