Fuel Cells

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Observation of Methanol Behavior in Fuel Cells In Situ by NMR Spectroscopy**

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Fuel cells are power sources with much potential for mobile electronic devices, automobiles, and electrical use in remote locations.[1,2] Direct methanol fuel cells are more convenient than hydrogen fuel cells owing to more facile fuel storage and handling.[2,3] However, their advancement and commercialization requires less expensive catalysts with higher activities and cheaper electrolyte membranes with lower methanol crossover.[3,4] Chemical reactions in fuel cells must be comprehensively understood to allow better materials to be engineered. Herein, methanol oxidation in direct methanol fuel cells was directly observed in situ by NMR spectroscopy. Deuterium (^{2}D) NMR spectra showed the chemical conversion of deuterated methanol (CD_3OH) during methanol oxidation. Comparing the NMR spectra of the methanol oxidation on Pt and PtRu anode catalysts demonstrated that the role of Ru could be studied by the in situ NMR probe that we developed and that both Faradaic and non-Faradaic reactions could be investigated. The spatial distributions of chemicals could also be detected by the in situ NMR probe. The observation of fuel oxidation in various fuel cells under various operating conditions is possible using this in situ NMR technique, making it useful for the development of inexpensive and improved functional materials for fuel cells.

It is important to understand the functions of each fuel-cell component and the mechanisms of the electrochemical reactions and degradation. However, most fundamental studies of fuel cells have been carried out on model systems or half cells, while full fuel cells have been monitored without simultaneous observation of their electrochemical reactions or chemical changes of their components. The working electrodes of half cells are typically made by depositing catalyst powder on conducting materials, such as glassy graphite,[5] polished gold,[6] Pt gauze,[7] or a Pt boat,[8] with immersion in an electrolyte containing fuel solution. Protons generated during fuel oxidation at the working electrode travel through the solution. In contrast, in full fuel cells, protons produced at the anode catalyst travel through the polymer electrolyte membrane to the cathode. The anode and cathode catalysts are attached as thin layers on opposite sides of the membrane and are covered with gas diffusion layers. These structural and chemical differences between half cells and full fuel cells affect the spatial distributions and diffusion of species involved in the fuel-cell reactions and thus influence the efficiency of the reactions.

Herein, in situ NMR studies were carried out on an operational direct methanol fuel cell (DMFC) placed inside a customized NMR probe.[9] The probe (Figure 1) was equipped with a toroidal cavity detector (TCD)[9–11] of gold-coated copper. The central conductor acted as a current collector at the anode. A membrane–electrode assembly (MEA) was located inside the outer conductor and the gas diffusion layer on the anode side contacted the surface of the central conductor (Figure 1a). To measure the current and voltage of the DMFC in the TCD, the central conductor was connected to the common ground and the current collector on the cathode side was connected to the loader. During NMR experiments, radio frequency pulses were applied to the TCD

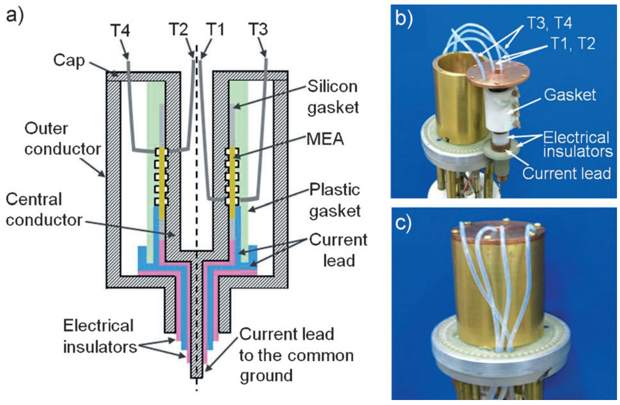

Figure 1. The toroid cavity detector (TCD) probe used herein. a) Sliced view. b) Photograph of the probe before complete assembly; c) after the probe was assembled by inserting the central conductor wrapped in a membrane–electrode assembly into the outer conductor. T1 and T2 denote fuel inlet and exhaust outlet tubes, respectively. T3 and T4 denote oxygen inlet and exhaust tubes, respectively.

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through the LC circuit in the NMR probe completed by connecting the central conductor to the common ground and the outer conductor to the capacitors (Figure 1 a). Deuterium NMR spectra (Figure 2), which lacked background signals, were better than ^{13}C or ^{1}H spectra, which showed intense background signals. Aqueous CD$_3$OH (2 M, 3.3 mL) was kept in circulation through the DMFC in the TCD and a constant current was allowed to pass for a given duration and voltage was monitored prior to recording each spectrum. The electrical connection to the loader was disconnected during NMR acquisition to avoid noise.

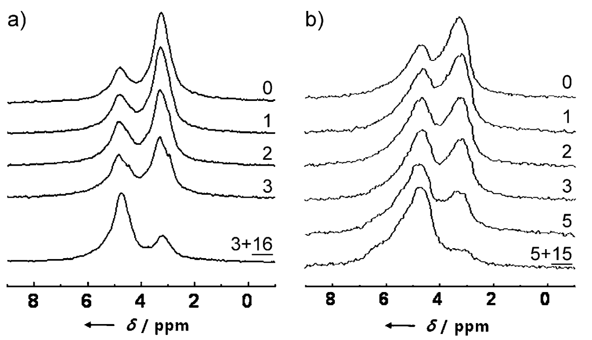

Figure 2. ^{2}D NMR spectra obtained with the in situ toroid cavity detector probe for DMFCs with a) PtRu/C and b) Pt/C anode catalysts. Cumulative fuel-cell operation hours are labeled; the underlined numbers denote hours in open-circuit condition.

The complete oxidation of a single CD$_3$OH molecule produces six electrons: $CD_3OH + H_2O \rightarrow CO_2 + 3D^+ + 3H^+ + 6e^-$.[12,13] However, the reaction can be halted during one of its intermediate steps, including dehydrogenation, such as $CD_3OH \rightarrow M\text{-}CD_3OH \rightarrow M\text{-}CD_2OH + D_{ads} \rightarrow (MM){=}CDOH + 2D_{ads} \rightarrow (MMM){\equiv}COH + 3D_{ads}$ and subsequent reactions with adsorbed OH$_{ads}$ on the catalysts, as described below, where M is a surface metal atom of the catalysts and D$_{ads}$ is an adsorbed deuterium atom on the surface of the catalyst.[12,13]

$$(MMM){\equiv}COH + OH_{ads} \rightarrow (MM){=}CO + H_2O \tag{1}$$

$$(MM){=}CO + OH_{ads} \rightarrow M\text{-}C{=}O(OH) \tag{2}$$

$$M\text{-}C{=}O(OH) + OH_{ads} \rightarrow CO_2 + H_2O \tag{3}$$

Other reaction pathways and intermediates have been also reported.[14,15] However, discussion with respect to the simplified methanol oxidation pathways is desirable providing the main concepts are not distorted. The reactions $D_{ads} \leftrightarrow D^+ + e^-$ and $D_{ads} + OH^- \leftrightarrow DOH + e^-$ occur in acidic and alkaline solutions, respectively.[12] Similarly, OH$_{ads}$ radicals are formed from the reactions $H_2O \leftrightarrow OH_{ads} + H^+ + e^-$ and $OH^- \leftrightarrow OH_{ads} + e^-$ in acidic and alkaline solutions, respectively.[12] The produced D$^+$ quickly exchanges with the hydroxy protons of CD$_3$OH, H$_2$O, or any intermediates, including the adsorbed species, to produce deuterated hydroxy groups, OD. Consequently, deuterated hydroxy groups of all the species appeared as a single peak in the ^{2}D NMR spectra. However, the intensity of the −CD$_3$ peak would decrease even when CD$_3$OH adsorbed onto the catalyst and a D atom was detached. Line broadening in NMR spectra occurs owing to the reduced mobility of the reaction intermediates, such as M−CD$_3$OH, M−CD$_2$OH, and (MM)=CDOH, which hinders their signal detection. Therefore, if the reduction of the CD$_3$ peak area and the electric power generated were measured simultaneously, performance differences between the fuel cells could in principle be correlated with each electrochemical reaction. To test this proposition, a DMFC was prepared with Pt/C replacing the PtRu/C anode catalysts.

As methanol oxidation progressed, the OD peak at about 4.8 ppm increased in size and the CD$_3$ peaks at about 3.3 ppm decreased regardless of the anode catalyst composition (Figure 2). No other reaction intermediates were observed, possibly because of the relatively low sensitivity and spectral resolution of the TCD. The DMFC with Pt/C anode catalyst produced a 90 C electric charge (detected with an electric loader) with a 34 % reduction of methanol concentration (calculated from the reduction of the area of the CD$_3$ NMR peak in Figure 2). The DMFC with PtRu/C anode catalyst produced 252 C with a 28 % reduction of methanol concentration (Supporting Information, Table S1). Consequently, methanol concentration decreased about 3.8 and about 1.1 % per 10 C charge produced by the DMFCs with Pt/C and PtRu/C anode catalysts, respectively. The higher methanol consumption per given charge generation suggests more incomplete methanol oxidation on the Pt/C anode catalyst, as the methanol depletion observed by in situ NMR spectroscopy is related to the total amount of all of the generated intermediates and to the charge generated during their production, and not necessarily to the generated amount of complete oxidation product, CO$_2$.

NMR spectra obtained after maintaining the DMFCs for 15 or 16 h under open-circuit conditions (Figure 2) clearly show decreasing methanol concentrations, even under open-circuit conditions. This is the direct in situ NMR observation of non-Faradaic and spontaneous methanol oxidation. The appearance of OD peaks in the spectra at the commencement of fuel-cell operation also indicates that non-Faradaic and spontaneous methanol oxidation occurred during the setting up of the NMR experiments before the cells' operation. The rate of non-Faradaic oxidation on the Pt/C catalyst, 1.3 %/hour, was slower than that on PtRu/C, 1.9 %/hour, calculated from the reduction of CD$_3$ peak area under open circuit conditions. Therefore methanol oxidation on Pt/C was 30–70 % less efficient and slower than on PtRu/C, through both non-Faradaic and Faradaic routes, indicating more complete methanol oxidation on the PtRu/C. Therefore, the data observed in situ are consistent with previous observations of half cells that showed the Ru of PtRu/C better facilitating methanol oxidation than the Pt of Pt/C through the generation of more OH$_{ads}$ from H$_2$O near the dehydrogenated methanol species.[16,17] These results are the first direct evidence of the role of Ru in the reaction of methanol gathered in situ from an operating DMFC.

As the radial distance from the TCD center increases, radio-frequency field strength decreases.[10,11] Consequently, an effective 90° pulse length, which determines the nutation frequency, becomes longer with increasing radial distance. This variation of effective nutation frequency with radial distances in the TCD allowed the recording of spatially resolved NMR spectra of samples at different radial distances from its center[10,11] with three layers of Teflon tubes filled with solutions of D_2O, CD_3OH and DCOOD in D_2O (Figure 3a). However, the individual samples in Figure 3a were much thicker than the components in DMFCs. Therefore, 0.1 mm liquid layers of each of D_2O and CD_3OH, separated by a 0.1 mm thick plastic film, were tested (Figure 3b). Spatially and spectroscopically separated signals were observed. This shows that in principle individual NMR spectra of chemicals at a fuel-cell anode, polymer electrolyte membrane, and cathode could be separated using the TCD. For spectra with better spatial resolution, it is necessary to increase radio-frequency field gradient strength and to improve radio-frequency field homogeneity at a given radial distance.

In situ NMR can unambiguously identify and quantify chemicals, including fuel, intermediates, products, and water in fuel cells in conjunction with electrical measurements. It can also analyze two-dimensional spatial distributions of chemicals without NMR imaging (MRI) instruments.[9–11] Therefore, it has potential to analyze the progress of chemical reactions and the distributions of chemicals in operating fuel cells, complementing other in situ spectroscopic techniques, such as neutron scattering imaging[18,19] and MRI[20–23] of water for water management in polymer electrolyte membrane fuel cells, X-ray absorption measurements of charge, and coordination variation of surface metal atoms of catalysts, including coordination with adsorbed species,[24,25] fluorescence imaging of oxygen-distribution in flow channels,[26] and FTIR spectroscopy for the detection of adsorbed species on catalysts and gas-phase products in DMFCs.[27]

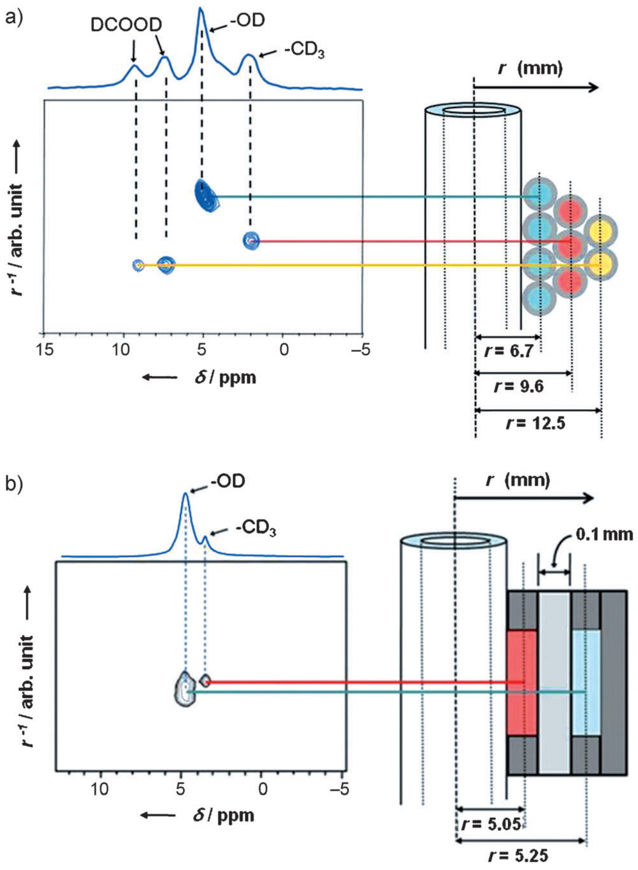

Figure 3. Spatially resolved two-dimensional ^2D NMR spectra obtained with the TCD probe from the phantoms consisting of a) Teflon tubes filled with neat D_2O, neat CD_3OH, and DCOOD solution in D_2O at different radial distances from the central conductor, and b) 0.1 mm thin layers of neat D_2O and CD_3OH. The diagram on the right of (a) depicts the central conductor wrapped in Teflon tubes filled with three different samples; that in (b) shows the central conductor wrapped in thin layers of two different samples.

In summary, in situ NMR spectroscopy successfully analyzed operational DMFCs with anode catalysts of PtRu/C and Pt/C. The results clearly demonstrated that non-Faradaic and Faradaic chemical reactions occurring in DMFCs can be directly detected by in situ NMR methods. Oxidation on the Pt/C anode catalyst was less efficient and slower than on PtRu/C, resulting in less complete methanol oxidation. Thus the results suggest that ruthenium facilitated the oxidation of methanol through the generation of more OH_{ads} from H_2O near dehydrogenated methanol species. The technique is also expected to be useful to analyze fuel oxidation and crossover mechanisms in other fuel cells with different compositions and operating conditions. It has potential advantages over other in situ methods in that it could allow unambiguous identification of chemicals and their spatial distribution without MRI equipment. Further work for improving the spatial resolution and the sensitivity of the TCD probe and for improving fuel-cell performance in the TCD probe is currently underway. Furthermore, to obtain not only in situ but also real-time NMR spectra of fuel cells, separation of the fuel-cell circuit and the NMR circuit using an active switch synchronized with radio frequency pulses is currently being tested. NMR spectra of nuclei other than ^2D will provide further chemical information and expand the application of this in situ method to other chemical reactions.

Experimental Section

NMR experiments: All of the in situ ^2D NMR spectra were acquired at 25 °C using a Varian 200 MHz Unity INFINITYplus system with an excitation pulse length of 50 μs, a pulse repetition delay of 1.5 s, and 512 scans for each spectrum when the empirical pulse length for the maximum signal intensity[10,11] was 50 μs for D_2O. Chemical shifts were calibrated with D_2O at 4.8 ppm. For the two-dimensional spatially resolved spectra, 64 files with different pulse lengths were obtained at pulse length increments of 30 μs with an initial pulse length of 50 μs. For each file, 64 free induction decay signals were accumulated. All of the deuterated compounds were obtained from Cambridge Isotope Laboratories, Inc.: CD_3OH (99.8 %), DCOOD (98 %; $\leq$ 5 % D_2O), and D_2O (99.9 %).

MEA preparation: The pretreatment of Nafion 117 and the general preparation of MEAs were carried out as described elsewhere,[28] but the size of the MEA was modified to 2.5 cm × 1.5 cm. Both electrodes consisted of metal particles supported on Vulcan XC-72 carbon (60 % metal/C, E-TEK, U.S.A.). PtRu/C was loaded at 5 mg cm^{-2} for the anode and Pt/C was loaded at 3 mg cm^{-2} for the cathode. MEAs with Pt/C anode catalysts were prepared by loading Pt/C at 5 mg cm^{-2} for the anode and at 3 mg cm^{-2} for the cathode.

DMFC performance: 2 M aqueous CD_3OH and oxygen gas were supplied at flow rates of 0.2 mL min^{-1} and 200 mL min^{-1}, respectively. The DMFCs were operated at 25 °C. The power of the DMFC in the TCD, measured with the electric loader, PRODIGIT 3351D (Prodigit Electronics, Taiwan), was about 30 % lower than that of an ordinary flat type DMFC under similar operating conditions (Supporting Information, Figure S1).

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