Short Communication

Electrochemical phenomena in direct methanol fuel cells investigated by multiple NMR analyses of cathode and anode exhausts

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ARTICLE INFO

ABSTRACT

Taking advantage of nuclear magnetic resonance (NMR) spectroscopy to easily identify and quantify chemicals, electrochemical reactions in direct methanol fuel cells (DMFCs) are investigated here by NMR analyses of cathode and anode exhausts. Deuterium (^{2}H) NMR spectroscopy directly detects CD_3OH unreacted and D^+ produced during CD_3OH oxidation in the DMFC prepared with PtRu/C or Pt/C anode catalysts and operated at different voltages. The data indicate more CD_3OH oxidation for PtRu/C anode catalysts, confirming methanol oxidation activity of PtRu/C to be higher than that of Pt/C. However, CD_3OH populations at the cathode side, which reflects the amount of methanol crossed over to the cathode but not oxidized, are similar, and D^+ detected at the cathode is primarily from CD_3OH oxidation at the cathode. Our results support the Grotthuss mechanism contribution in the proton transfer and demonstrate an advantage in investigating electrochemical phenomena of the DMFCs by directly detecting methanol and protons electrochemically generated at the anode and cathode side.

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1. Introduction

Transport of chemical species in fuel cells—for example, water, methanol, and electrochemical intermediates in the case of a direct methanol fuel cell (DMFC)—through constituents of fuel cells such as gas diffusion layers and polymer electrolyte membrane (PEM) has been known to significantly influence fuel cell performance [1–3]. For example, too much water flux to a cathode electrode, thereby filling the porous structure at the cathode side with water (so-called flooding) can inhibit gaseous oxygen reaching the active oxygen-reduction sites. However, too low water content and inhomogeneous water distribution over constituents of low temperature fuel cells degrade the performance of fuel cells by low and inhomogeneous proton conduction. Some fuel moves to the cathode side, which is referred to as fuel crossover, and oxidized at the cathode, resulting in cell voltage reduction and fuel loss. Methanol crossover is especially severe because behavior of methanol molecules is similar to that of water in proton exchange and hydrogen bonding. Therefore, optimizing water content and distribution, and reducing methanol crossover have been regarded as essential

factors in improving performance of DMFCs. Consequently, identification and quantification of chemicals at different parts of DMFCs operated at different conditions may provide clues to improve DMFC performance.

Recently, the chemical species present in a polymer electrolyte membrane (PEM) of DMFC [4] and those in PEM of direct ethanol fuel cells (DEFCs) [5] have been investigated to directly detect chemicals crossing over through PEM from anode to cathode by ^{2}H and ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, respectively. Anode liquid exhausts of DEFCs were also analyzed to compare ethanol oxidation mechanisms on different anode catalysts using ^{13}C NMR spectroscopy [5,6]. Even in situ ^{2}H NMR detection of the anode side of DMFC placed in a toroid cavity detector [7] and in situ ^{13}C NMR detection of ethanol oxidation using a commercial NMR tube for the electrochemical NMR cell [8] have been reported. However, these NMR spectroscopic methods could not provide the whole picture of electrochemical reactions and distribution of chemicals in DMFC, since they did not simultaneously analyze chemicals at various places in the fuel cells.

Analytical techniques other than NMR spectroscopy have been also used to identify and quantify chemical species in fuel cells prepared with different materials and operated at different conditions as summarized in section 2.5 of reference 9. Popular analytical methods have been

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various mass spectrometry and infrared spectroscopy. Different methods were also employed together complimentarily [9,10], as in the case in which methanol crossover and oxidation on the cathode were investigated using attenuated total reflection infrared spectroscopy detecting intermediates on the cathode catalysts and using real time mass spectrometry observing chemicals in the cathode exhaust [10]. The adsorbed species on the anode and cathode catalytic surfaces, as well as desorbed species, were investigated by in situ Fourier transform infrared-diffuse-reflectance spectroscopy [11]. Cathode gas exhaust was also analyzed by Fourier transform infrared spectroscopy for studying water and methanol flux and their mutual dependence [12].

This work reports identification and quantification of chemicals in anode and cathode exhaust of the DMFCs prepared with different anode catalysts and operated at various voltages by ^{2}H NMR spectroscopy for comparing the activities of the catalysts and investigating proton transfer mechanisms. This is the first report on analyses of both the anode and cathode liquid exhaust of DMFC by NMR spectroscopy, to the present authors' knowledge.

2. Experimental

2.1. Preparation of membrane electrode assembly

Preparation of membrane electrode assembly (MEA) was done as described elsewhere [4], though the size of MEA was changed to 2.5 cm × 1.8 cm. By spraying the catalyst slurry on the carbon-cloth gas diffusion layer, PtRu/C (60 wt% 1:1 alloy of Pt and Ru on Vulcan XC-72) was loaded at 5.0 ± 0.2 mg cm^{-2} for the anode and Pt/C (60 wt% Pt on Vulcan XC-72) was loaded at 3.0 ± 0.2 mg cm^{-2} for the cathode. For the comparison study, some DMFCs were prepared with Pt/C loaded at 5.0 ± 0.2 mg cm^{-2} for the anode. DMFCs without catalysts were also prepared to estimate the methanol crossover amounts. The Nafion 117 membrane was pre-treated by sequentially boiling in 3% H$_2$O$_2$, deionized water, 0.5 M H$_2$SO$_4$ and again in deionized water, for 1 h per step. The MEA was prepared by hot-pressing the sandwich of an anode, Nafion 117, and a cathode at 135 °C for 3 min under pressure of 100 kg cm^{-2}.

2.2. Electrochemical test of DMFC

The electrochemical test of DMFC was done as described elsewhere [6]. The experimental unit cell of the DMFC consisted of an MEA and two rectangular blocks of graphite with serpentine flow fields that were machined on the inner surfaces with a depth and width of 0.6 mm. Each graphite block worked as a current collector and was electrically connected to an electronic analyzer, PRODIGIT 3351D (Prodigit Electronics, Taiwan). The assembly was held together with two stainless-steel end-plates. The temperature of the cell was controlled by two heating rods (one threaded into each of the end-plates) and monitored using a thermocouple placed in the middle of the graphite block on the anode side. A 2 M methanol solution was fed to the anode at a rate of 0.4 cm^3 min^{-1} with a peristaltic pump 323 S/D (Watson-Marlow, UK), and oxygen gas was fed to the cathode at a rate of 45 cm^3 min^{-1}. The unit cell temperature was maintained at 80 °C. In order to take current–voltage curves the voltage values were determined by an electronic analyzer at a constant-current mode when the cell current values were increased from zero at intervals of 20 mA.

2.3. NMR experiments

For the NMR investigation of the liquid exhaust from the anode and cathode, the DMFC was operated with 2 M CD$_3$OH solution at constant-voltage mode and activated for 10 min at each voltage using the electronic analyzer before the respective NMR samplings. The anode liquid exhausts were collected for 30 min at each voltage into fifteen vials that were sealed with para-film in order to prevent evaporation. The

cathode exhausts were collected only into two vials during the same period. The cell current remained steady during the NMR sampling at each voltage: 782 ± 2, 671 ± 2, 510 ± 2, 304 ± 2, 190 ± 2, 39 ± 2, and 8 ± 7 mA at 0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 V, respectively for the DMFC with PtRu/C anode catalysts and 584 ± 2, 417 ± 2, 267 ± 2, 139 ± 2, and 41 ± 2 mA at 0, 0.1, 0.2, 0.3, and 0.4 V, respectively for the DMFC with Pt/C anode catalysts. The NMR sampling method is schematically summarized in Fig. 1. For the quantification of each chemical, an 80-μL liquid exhaust was placed in a 4-mm outer-diameter zirconia rotor for a double-channel MAS probe. The NMR peak areas were calibrated with 2 M CD$_3$OH solution. The chemical population in each 80-μL cathode exhaust was calibrated using the volume ratio of anode and cathode exhausts collected for a given time. The ^{2}H NMR spectra were acquired using an Avance II$^+$ NMR system at 9.4 T (Bruker BioSpin GmbH, Germany) with a pulse length of 3 μs corresponding to 30° flip angle, 3-s pulse repetition delay time, and 4 scans. The chemical shift was calibrated with external neat D$_2$O at 4.8 ppm. Neat D$_2$O (99.9%) and CD$_3$OH (99.5%) were purchased from Sigma-Aldrich Inc. and Cambridge Isotope Laboratories, Inc., respectively.

3. Results and discussion

Fig. 2 shows the representative ^{2}H NMR spectra of the anode (Fig. 2(a)) and cathode (Fig. 2(b)) exhausts collected simultaneously from the DMFC prepared with PtRu/C anode catalyst and operated at different potentials. In all of the spectra, the dominant signals are observed at 3.3 and 4.8 ppm for deuterated methyl (CD$_3$) and deuterated hydroxyl (OD) groups, respectively, and no other species are observed. This contrasts with the recently reported solid-state MAS NMR spectrum, where a small but definite deuterated formic acid (DCOOH) peak, at 8.9 ppm, was detected [4]. The hydroxyl signals of formic acid and formaldehyde in aqueous solutions appeared at 4.8 ppm in ^{2}H NMR spectra, which were not distinguishable from water signal [4]. No detection of formic acid or formaldehyde in the ^{2}H NMR spectra means they are absent or present below 5 mM in the liquid exhaust since our ^{2}H NMR methods have a detection limit of ~5 mM. The lack of detection of formic acid in this work must be due to media difference (liquid exhaust versus Nafion membrane) [5] and a performance difference between DMFCs in this work and previous work; that is, less production of the electrochemical reaction intermediates such as formic acid, results in better DMFC performance. The CD$_3$ signal at 3.3 ppm of anode exhaust represents the unreacted CD$_3$OH. The OD peaks at 4.8 ppm are from D$^+$ produced during electrochemical oxidation of CD$_3$OH. These D$^+$ ions, produced at the anode, exchange with protons of water according to Eq. (1) below.

$$H_2O + D^+ \leftrightarrow HDO + H^+. \tag{1}$$

Likewise, these D$^+$ ions can exchange with protons with proton-exchanging functional groups such as hydroxyl groups of CD$_3$OH, or any intermediates with hydroxyl groups, producing OD groups. However, because of the large excess ($\geq$~25 times) of water over CD$_3$OH, the dominant reaction must be the one in Eq. (1). NMR peak areas are linearly proportional to the amount of chemical species. Consequently, the OD peak area is linearly proportional to the produced D$^+$ ions. The OD groups for all of the species with hydroxyl groups appear as a single peak in a ^{2}H NMR spectrum, the chemical shift of which is not different from that of either water or methanol. This manifests negligible contribution of the other proton-exchanging chemical species in DMFCs to the observed OD peaks. The spectra for the cathode exhaust clearly show CD$_3$ signals from CD$_3$OH on the cathode side (Fig. 2(b)), reflecting the CD$_3$OH crossed over from the anode to cathode side. Some of the methanol crossed over was oxidized at the cathode electrode, producing D$^+$/ H$^+$ ions. The peak areas of CD$_3$ signals at the cathode side are much smaller than those at the anode side (Figs. 2 and 3), indicating that the amount of CD$_3$OH crossed over and unreacted at the cathode