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Electrochemical and infrared study of electro-oxidation of dimethyl ether (DME) on platinum polycrystalline electrode in acid solutions

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Abstract

Electro-oxidation of dimethyl ether (CH_3OCH_3, denoted as DME below) on Pt polycrystalline electrode has been investigated by electrochemical and *in situ* infrared (IR) measurements in acid solutions. A reaction intermediate species, $(CH_3OCH_2–)_{ad}$, has been observed in the low potential region as an initial product for dehydrogenation process of DME on Pt electrode surface. This species is subsequently decomposed to adsorbed carbon monoxide (CO) and finally oxidized to carbon dioxide (CO_2) in higher potential region. The time-resolved IR measurement is employed to follow the transient process of the formation and decomposition of the intermediate on Pt electrode surface. Based on these electrochemical and IR spectroscopic results, a reaction scheme for DME electro-oxidation process is proposed.

Keywords: Electro-oxidation; Dimethyl ether (DME); Fuel cell; Platinum electrode; *In situ* IR spectroscopy; Flow-cell

1. Introduction

Fuel cells are promising alternative power generation devices that generate electricity with higher efficiency and lower pollution than traditional fuel combustion based power systems. As a direct-fed liquid fuel with high energy density, methanol has been paid much attention in the past decades. However, the application of methanol in proton exchange membrane fuel cell (PEMFC) system still suffers from some barriers, such as degradation of electrode catalysts, fuel loss due to the methanol crossover to cathode as well as safety problem by high toxicity of methanol.

Dimethyl ether (DME, CH_3–O–CH_3) presents some interesting options for electrochemical power generation acting as fuel in PEMFC [1–10]. As the simplest ether, DME contains two C–O bonds but no C–C bond and is expected to show high electro-oxidation activity. DME can be stored in liquid state under a modest pressure (ca. 5 atm). This combines the advantages of high energy density and easy introduction into fuel cell in gas phase without pumping system. Furthermore, DME is safe in handling due to its low toxicity in comparison with methanol.

The performance of the direct DME fuel cell has been evaluated in the past few years. Müller et al. reported that high Faradic efficiency for the fuel cell was obtained at relatively high temperature (130 °C) [1]. Although part of DME molecules crossed over to the cathode side, no oxidation occurred there. They found that DME was mainly oxidized to CO_2 with trace quantities of methanol as by-product. They proposed that the electro-oxidation of DME is initiated from the hydrolysis of one methyl group followed by cleaving the C–O–C bond. Tsutsumi et al. reported that formic acid was the main by-product in the DME electro-oxidation [10]. They suggested that DME initially decomposes through the two methyl groups, which are hydrolyzed simultaneously on the Pt surface. Further oxidation involves the cleavage of the C–O–C bond. Recently, Mizutani et al. observed a small amount of methyl formate and methanol in the anode exhaust of the direct DME fuel cell [6]. Most of these works showed that main product in the DME electro-oxidation process is CO_2 while reaction intermediates are quite different.

In situ IR vibrational spectroscopy combined with the electrochemical characterization is a powerful probe to clarify the reaction scheme in electrocatalytic reaction, including molecu-

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lar information about the reaction intermediate. By using *in situ* IR reflectance absorption spectroscopy (IRRAS) in a thin-layer cell, Kerangueven et al. reported that the intermediates of DME electro-oxidation on a Pt electrode in H_2SO_4 solutions are linearly bonded carbon monoxide (CO_L), bridge bonded CO (CO_B), and adsorbed COOH species. They proposed that DME was hydrolyzed and partially oxidized to CH_3OH, HCOOH and CO_2 [11]. Shao et al. investigated the electro-oxidation process of DME on a Pt thin film electrode in 0.1 M $HClO_4$ solutions by ATR-IR measurement [12]. They reported a number of reaction intermediates for DME decomposition near the hydrogen adsorption region and found that reaction intermediates and products are dependent on the DME concentration. Recently, Liu et al. investigated electrochemical behavior of DME on a sputtered Pt electrode by ATR-IR measurement [13] and reported a number of reaction intermediates such as adsorbed CO, –COOH and –CHO.

Although these measurements were carried out in acid solutions under similar conditions, most of the *in situ* IR characterization results are quite different. Apparently, this is not due to the different kinds of electrolyte used ($HClO_4$ or H_2SO_4) in these works. One of possible reasons is considered to be the diffusion problem for these measurements, which may change the IR spectral features. It is well known that the concentration of reactant and products as well as soluble intermediates can be easily changed during electrochemical reaction in an environment where diffusion process is restricted. As discussed previously [14], this is considered as main reason that formate, which is observed as a reaction intermediate for many C_1 molecules, such as methanol [15] and formic acid [16], could not be observed by *in situ* IR measurement using the traditional thin-layer geometry. Normally, *in situ* IR measurement using Kretschmann ATR configuration can greatly improve the diffusion and mass transport processes but may also suffer from it if the cell volume is too small for long-time electrolysis in a high current density. Recently, Chen et al. reported a kinetic study for electro-oxidation of formic acid by *in situ* ATR-IR spectroscopy using a flow-cell [17].

In the present study, we aim to clarify the reaction scheme of DME electro-oxidation on Pt electrode in acid solutions, by using electrochemical and *in situ* IR methods under more reliable and reproducible conditions. The potential dependence of DME decomposition has been electrochemically evaluated. In order to avoid the influence from diffusion and accumulation problems from soluble species, a spectroscopic flow-cell with Kretschmann ATR configuration is newly designed and employed in the *in situ* IR measurement in comparison with conventional one used in our group. Supply of reactant with constant concentration and quick removal of soluble products in solution side will enable us to exactly investigate the species on the electrode surface. Through this *in situ* IR measurement, the transient processes of DME decomposition process at different potentials are clearly observed. Based on these experimental results, the reaction mechanism of DME on Pt electrode is discussed. We expect that the present research can provide a clue for designing new electro-catalysts for direct DME fuel cells.

2. Experimental

The details of the *in situ* IR measurements with the Kretschmann ATR configuration have been described elsewhere [14–16]. A Pt thin film was chemically deposited on a hemi-cylindrical silicon (Si) prism surface as a working electrode. The fabrication procedure is briefly described as follows. Si surface was firstly activated by contacting with 0.5% HF containing 1 mM $PdCl_2$, which can improve the adhesion of the deposited metal film to the Si substrate. Then, 50-nm thick Pt thin film was deposited with a commercially available plating solution (LECTROLESS PT100, Electroplating Engineering of Japan) at 60 °C. The surface morphology and thickness of the Pt thin film are critical to get a reproducible high-quality IR spectrum. For example, Shao et al. investigated DME electro-oxidation on the Pt film electrode by ATR-IR spectroscopy, however, their *in situ* IR spectra for adsorbed CO show a unusual bipolar band shape making further analysis difficult [12].

Potentials were controlled by a potentiostat (EG&G PARC model 263A) and presented with respect to the reversible hydrogen electrode (RHE). The *in situ* IR measurements were carried out using a BioRad FTIR-575C spectrometer equipped with a MCT detector. The IR spectra were recorded in the dynamitic mode with a spectral resolution of 4 cm^{-1}. Five interferograms were co-added to each spectrum. It takes 0.98 s to get one spectrum in present work. All IR spectra shown were normalized to the spectrum taken at 0.05 V in electrolyte solution without DME.

A spectroscopic flow-cell for *in situ* IR measurements was newly made to remove the possible influence from accumulation of reaction intermediates and products dissolved in the electrolyte. Fig. 1 shows its schematic structure for the flow-cell with three-electrode design. The flow of solution in the cell is driven by pressure of Ar or DME gas through a three-way stopcock. The cell volume is ca. 4 ml and solution can be exchanged as fast as 20 ml min^{-1}, i.e., the solution inside could be exchanged by more than five times per minute. A conventional static spectroscopic cell [15] with a cell volume of ca. 30 ml is also employed for a comparison in the experiment.

The supporting electrolyte solutions were prepared from Milli-Q water (>18 MΩ) and analytical grade $HClO_4$ or H_2SO_4. Electrolyte solutions were deaerated with Ar for 30 min prior to use. After electrochemically cleaning the electrode surface by successive potential cycles between 0.05 and 1.5 V in the blank electrolyte, an IR reference spectrum was recorded at 0.05 V. Then, the solution was saturated with DME (ca. 1.65 M)

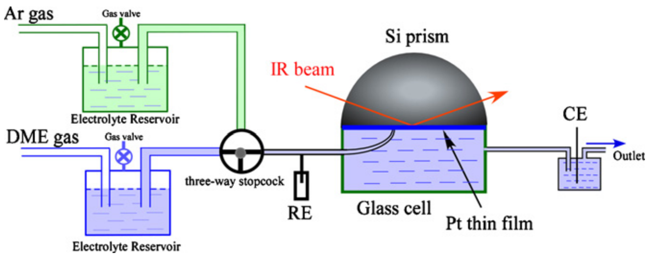

Fig. 1. A simplified scheme for the flow IR cell used in the work.