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In situ ATR-SEIRAS study of electrooxidation of dimethyl ether on a Pt electrode in acid solutions

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Abstract

The electrooxidation of dimethyl ether (DME) was studied on a Pt film electrode in $HClO_4$ solution using surface enhanced infrared absorption spectroscopy (SEIRAS) and cyclic voltammetry. $(CH_2OCH_3)_{ad}$ and $\eta^2(O,C)$-H_2CO are inferred as the adsorbed intermediates resulting from the dissociative adsorption of DME in the hydrogen adsorption region. Adsorbed CO was also found, with coverages increasing rapidly upon DME adsorption, probably due to the further dissociation of $(CH_2OCH_3)_{ad}$ and $\eta^2(O,C)$-H_2CO. In the main oxidation region no adsorbed species, excluding CO, were found. However, for low DME concentration (0.025 M), vibration bands associated with adsorbed CH_3COO or CH_3OCOO were observed between 0.3 and 0.95 V. These results lead to the conclusion that the reaction products could depend on the concentration of the fuel. Additional discussion of the reaction mechanism is also presented.

Keywords: Dimethyl ether; Electrooxidation; Surface enhanced infrared absorption spectroscopy; Platinum

1. Introduction

Direct oxidation fuel cells, especially direct methanol fuel cells (DMFCs), have recently attracted considerable attention [1,2]. Dimethyl ether (DME) appears to be a possible substitute for methanol, being the simplest ether which has no carbon–carbon bond. The overall reaction for the DME electrooxidation is

$$CH_3OCH_3 + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \quad (E^\circ = 0.03\,\mathrm{V\,vs\ SHE\,at}\,25\,^\circ\mathrm{C}) \tag{1}$$

It was found earlier that the performance of direct DME fuel cell (DDFC) was equivalent to that of DMFC if 1.5 times more fuel than that of methanol was fed to the anode [3]. It appears that DME has advantages compared with methanol and other fuel candidates for direct oxidation fuel cells, including: low toxicity, negligible crossover effect, high energy density, easy handling and high reactivity [3–7].

No spectroscopic or differential mass spectrometry studies on DME adsorption and oxidation on Pt electrode have been reported so far, thus no information about reaction intermediates is available. Surface enhanced infrared reflection absorption spectroscopy (SEIRAS) with attenuated total reflection (ATR) has been demonstrated as a powerful technique for studying the electrooxidation of small organic molecules [8–11].

In this work, the electrooxidation of DME on a Pt thin film electrode in 0.1 M $HClO_4$ solution was investigated by in situ ATR-SEIRAS with the aim of determining

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the adsorbed intermediates in this reaction and describing their behavior as a function of potential.

2. Experimental

A hemispherical Si crystal, 2.54 cm in diameter (ISP Optics, New York) was used as the internal reflection element and the substrate for a Pt film. The deposition of Pt on a Si was described elsewhere [11]. Briefly, the silicon oxide film was removed by dilute HF solution and then the fresh surface was exposed to plating solution containing 0.01 M K_2PtCl_6 + 10% HF for 30 min. The Pt thin film was rinsed and then attached to a three-electrode spectroelectrochemical cell with an ultra thin platinum foil connecting the Pt electrode to a CHI604A electrochemical analyzer (CH Instruments). A Pt ring and an Ag|AgCl, Cl^- electrode were used as the counter- and reference-electrode, respectively. The potentials in this paper are expressed with respect to this reference electrode.

In the spectroelectrochemical cell, the 0.1 M $HClO_4$ solution was first purged with pure nitrogen gas and then DME (Aldrich) of 99% purity was bubbled through the solution from a compressed gas cylinder with a flow rate of 2.5×10^{-4} mol min^{-1} without further purification, while keeping the electrode potential at −0.2 V. The concentration of DME in the acid solution was calculated for a given dosing time and the volume of the electrolyte (5 ml). The saturation concentration of DME in 0.1 M HCO_4 solution was found to be 1.05 M at room temperature.

Rapid scan FT-IR experiments [11,12] were performed using a Nicolet Nexus 670 FT-IR spectrometer equipped with a MCT detector cooled with liquid nitrogen. No polarization discrimination was utilized. The spectral resolution was set to 4 cm^{-1} and 32 interferograms were co-added for every spectrum. Spectra are given in absorbance units defined as $A = -\log(R/R_0)$, where R and R_0 represent the reflected IR intensities corresponding to the sample- and reference-single beam spectrum, respectively. The reference spectrum was collected at −0.2 V in 0.1 M $HClO_4$ solution before DME was added. Thus, the spectra shown here demonstrate positive-going features due to DME adsorption and reaction as a gain of a particular species upon potential shift. All the experiments were carried out at room temperature (~20 °C).

3. Results and discussion

3.1. Electrooxidation of DME

Fig. 1(a) shows the first voltammogram for the Pt electrode in 0.1 M $HClO_4$ solution containing 0.025 M (dashed trace) and 0.1 M DME (solid trace); the voltammogram in supporting electrolyte is given by dotted line. As shown, there are two new positive current peaks related to the adsorption and/or oxidation of DME in the positive scan. For 0.1 M DME, the first oxidation peak (Peak I) is found at 0.0 V, i.e., in the H-adsorption region. The dissociative adsorption of DME occurs at potentials above −0.16 V, which is indicated by the positive currents that are larger than the background current (dotted line). This is supported by the in situ FT-IR results, which are discussed later. A large well-defined positive peak (Peak II) occurs at 0.42 V. During the negative scan, the current of DME oxidation is imposed on the current of Pt oxide reduction resulting in a bipolar current peak (Peak III), with a positive lobe at about 0.4 V and a negative lobe at 0.55 V, respectively. In the hydrogen adsorption region, the hydrogen peaks are largely suppressed implying that DME, or intermediates of its oxidation, is adsorbed on a Pt surface in that potential region.

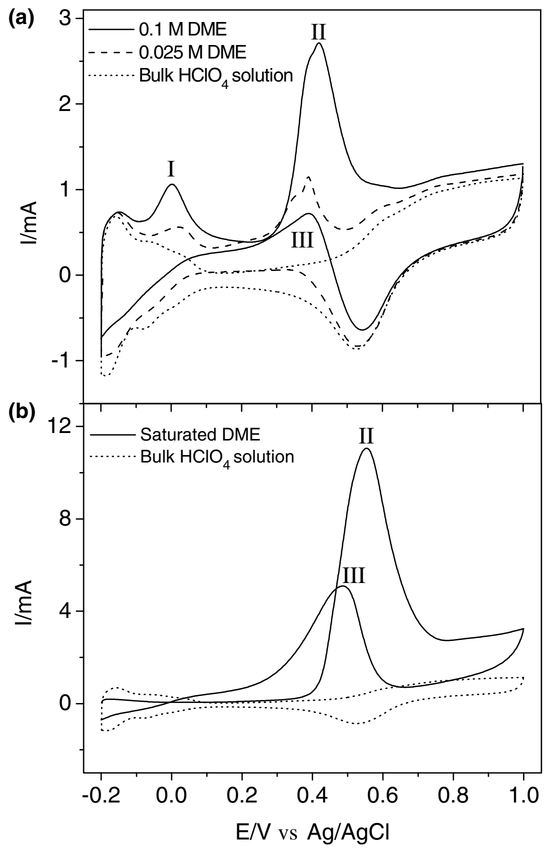

Fig. 1. The first potential sweep of the Pt electrode in 0.1 M $HClO_4$ solution with different DME concentration; sweep rate 10 mV s^{-1}.

In the case of 0.025 M DME, both oxidation currents of Peak I and II are smaller and Peak III is not as well pronounced due to the smaller concentration of DME. Peak I is shifted positively to 0.035 V. The dissociative adsorption of DME in the hydrogen region involves hydrogen abstraction and its oxidation