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Short communication

Study of adsorbed water on Pt during methanol oxidation by ATR-SEIRAS (surface-enhanced infrared absorption spectroscopy)

Hidenobu Shiroishi [1], Yusuke Ayato, Keiji Kunimatsu [2], Tatsuhiro Okada *

National Institute of Advanced Industrial Science and Technology, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

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Abstract

Potential dependence of adsorbed water, CO species, formate and perchlorate ions on polycrystalline Pt electrode chemically deposited on a Si substrate has been investigated by in situ ATR-SEIRAS (surface-enhanced infrared absorption spectroscopy) in 0.1 M $HClO_4$ in the presence of 0.1 M methanol. The newly appeared adsorbed water with O–H stretching vibration around 3658 cm^{-1} co-exists with adsorbed CO derived from methanol and its consumption during oxidation of the adsorbed CO and increase of formate species above ca. 0.6 V is demonstrated in a quantitative way by a linear relationship between the intensity of the adsorbed water and those of linear CO and formate. This can be interpreted as a strong proof that the water molecules which appeared upon methanol adsorption and co-exist with the resultant CO is in fact the species which react with the CO and promotes further methanol oxidation.

Keywords: ATR-SEIRAS; Methanol oxidation; Catalytic poison, Adsorbed water; Formate

1. Introduction

Direct methanol fuel cell (DMFC) is a potential candidate for the noteworthy power sources for mobile devices because of its energy density per unit volume and immediate use by refueling. A pioneering research on methanol oxidation reaction (MOR) on Pt and Pt alloys were carried out in the decade of 1960 [1–3], and there are several hundreds of reports on its mechanisms and applications [4–7]. According to the early proposed MOR mechanism based on electrochemical investigations, the first step of the reaction is adsorption of methanol on Pt or Pt alloys, which needs plural sites of Pt, and the second step is the dissociation of water to OH which reacts with the methanol adsorbate to produce CO_2.

In situ infrared spectroscopic method coupled with electrode potential modulation method, EMIRS, developed in 1980s enabled in situ investigations of the adsorbed species on electrode surfaces, and this led to the first detection and identification of the adsorbed CO derived from methanol, which works as a catalytic poison to inhibit further oxidation of methanol on platinum electrodes [8]. As the EMIRS being unable to give quantitative information on the methanol adsorbate, CO, in situ polarization modulated infrared measurements were conducted for both adsorbed CO on Pt produced by bubbling CO gas into the electrolyte solution and for the CO derived from methanol under controlled total adsorbate coverage [9]. It was shown that the CO derived from methanol occupies ca. 70% of the Pt surface and the methanol oxidation on Pt commences only after the CO is oxidized off the Pt surface around 0.6 V(RHE) [9].

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* Corresponding author. Tel.: +81 29 861 4464; fax: +81 29 861 4678.
E-mail address: okada.t@aist.go.jp (T. Okada).

[1] Present address: Department of Chemical Science and Engineering, Tokyo National College of Technology, Hachioji 193-0997, Japan.

[2] Present address: Clean Energy Research Center, University of Yamanashi, Kofu 400-8510, Japan.

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Although nature of the methanol adsorbate to act as the catalytic poison was elucidated, detection of the reactive intermediate had not been successful until Osawa et al. [10] conducted studies by surface-enhanced infrared absorption spectroscopy (SEIRAS). They detected unambiguously formate species, HCOO, giving rise to the asymmetric COO vibration around 1300 cm^{-1} which appeared and increased its intensity on Pt when the catalytic poison, CO, was oxidized leading to increase of methanol oxidation current. Based on the new finding they confirmed the dual path mechanism of methanol oxidation on Pt; the CO and non-CO paths as the reaction intermediates.

Oxygen donor related to MOR has not been elucidated in these in situ infrared spectroscopic methods [4,8,9], although Gillman [11] suggested that oxygen donor related to MOR on Pt was an adsorbed OH species derived from water dissociation, whereas Wieckowski et al. [12] postulated that oxygen donor is activated water molecules adsorbed on Pt. Recently, however, Yajima et al. [13,14] conducted in situ ATR-FTIR studies of methanol adsorption and oxidation on Pt, PtRu and Ru electrodes and detected water molecules adsorbed on the Ru sites giving rise to O–H stretching vibration at 3610 cm^{-1}. The water molecules were assigned as the oxygen donor to the methanol adsorbates which promotes the methanol oxidation. The detection of the water molecules on the Ru sites was considered as the direct support to the “bi-functional mechanism” for the MOR. On Pt, however, the water species similar to that observed on PtRu and Ru was not detected in these studies.

The present paper describes the potential dependence of infrared absorption band derived from water in the presence of methanol, to investigate the oxygen donor for MOR by in situ ATR-SEIRAS.

2. Experimental

2.1. Materials

Super special grade of perchloric acid (Kishida Chemical Co., Ltd.) and the HPLC grade methanol (Sigma–Aldrich Co., Ltd.) were used to make the electrolyte solutions together with the pure water generated by Milli-Q system (conductivity $<10^{-7}\ \Omega^{-1}\,cm^{-1}$, TOC <4 ppb). The Pt plating solution (LECTROLESS Pt 100, Electroplating Engineering of Japan Ltd.) was used for chemical deposition of a Pt thin layer on the Si prism as described below.

2.2. In situ surface-enhanced FT-IR spectroscopy

Details of ATR-SEIRA spectroscopy were described in the literature [10,15–20]. The following procedure was employed to fabricate a thin Pt film on the base plane of a hemicylindrical silicon prism (Nippon Pastec Co., Ltd., radius 12.5 mm, length 25 mm). Palladium was deposited on the base plane with 0.5 % HF – 1 mM $PdCl_2$ for 5 min at room temperature. After rinsing with water, platinum deposition was carried out by contacting with the Pt plating solution at 333 K for a few minutes. Osawa and co-workers [15] reported the structure of a chemically deposited Pt electrode fabricated in the similar way. The silicon prism was mounted in a spectro-electrochemical cell with a reversible hydrogen reference electrode and a spiral platinum wire counter electrode. The cell was then placed in a homemade reflection optics at an angle of incidence of 65° as shown in the literature [19,20].

A Fourier transform infrared spectrometer equipped with a MCT detector (Digilab FTS7000) was employed for in situ SEIRAS measurements. The homemade electrochemical measurement program was used to drive the electrochemical equipment. The cell was purged with N_2 gas for 30 min before the measurement. First, the platinum surface was cleaned by cycling the potential between 0.05 and 1.5 V before the measurements. After the spectrum was measured at each potential which served as the reference in the absence of methanol, methanol was added to the spectro-electrochemical cell. Potential of the working electrode was maintained at 0.1 V for 30 min after adding methanol before starting the FT-IR measurements, and was changed stepwise from 0.1 to 1.1 V after co-adding a 100 interferograms for each potential, to improve the signal/noise ratio. All potentials shown in this paper are quoted with respect to the reversible hydrogen electrode in the same solution (RHE). Note that a single beam spectrum at each potential before addition of methanol was selected as the reference to detect the adsorbed species produced from methanol on platinum at a given potential (Figs. 2, 4, 5, and 6), whereas spectra were referred to 0.1 V in Fig. 3 , at which no adsorption of the anions is expected, for the sake of monitoring adsorption of perchlorate ions on platinum.

3. Results and discussion

Fig. 1 depicts cyclic voltammograms of a chemically deposited platinum electrode in 0.1 M $HClO_4$. The roughness factor of the electrode was 5.4, which was estimated from a ratio of the real surface area determined from the hydrogen desorption charge (0.1–0.4 V), assuming $0.210\ mC\,cm^{-2}$ [21], to the geometrical surface area ($2.17\ cm^{-2}$).

Fig. 2 shows a series of ATR-SEIRA spectra for $\nu(OH)$ band (Fig. 2(a)) together with low wavenumber region for the perchlorate anions (Fig. 2(b)) and for the adsorbed CO species derived from methanol