Adsorbed water for the electro-oxidation of methanol at Pt–Ru alloy†

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Adsorbed water molecules which promote the methanol oxidation reaction (MOR) at Pt–Ru alloy electrode are clearly detected by *in-situ* **FTIR spectroscopy with the attenuated total reflection configuration, which directly supports the "bi-functional mechanism" for the MOR.**

Direct methanol fuel cells (DMFCs) have attracted great interest as a primary power source for electric vehicles and portable devices. In DMFCs, methanol aqueous solution is directly fed to the anode and electrochemically oxidized. At a Pt anode, an overpoteintial of a few hundred millivolts to the theoretical oxidation potential ($E° = 0.016$ V vs. SHE at 25 °C) is required to obtain reasonable current density, because the adsorbed intermediates such as CO are difficult to be oxidized.[1,2] It has been reported that the MOR rate is significantly enhanced when Pt is alloyed with Ru, Sn, Mo, etc.[3–5] So far, the enhanced activities of the alloy anodes were explained by the bi-functional mechanism[3] or a ligand (electronic) effect.[5] The mechanistic study is very important to design new electro-catalysts with higher activity.

In-situ IR spectroscopy can, in principle, identify the adsorbed species formed during the MOR. Linear bonded CO,[1,6,7] bridged CO,[6,7] HCHO,[7] and HCOOH[7] were observed at Pt-base electrodes by using infrared reflection absorption spectroscopy (IRAS). However, we have to notice that there is still much controversy about the mechanism of the MOR even at the Pt electrode resulting from the limitation of the configuration of IRAS.[8] Recently, Osawa *et al.* reported a series of IRAS obtained on Au or Pt electrode surfaces in aqueous electrolyte solution, utilizing the attenuated total reflection (ATR) configuration.[8,9] Using the ATR-IRAS, we have successfully observed the electro-oxidation of the CO ad-layer incorporating with adsorbed water at a pure Pt and a Pt-Fe alloy film electrode.[10] We have also reported a potential-induced conversion between the linear CO, the bridged CO and the formic acid-related species during the MOR at Pt electrode.[2]

Here, we, for the first time, report distinct IR spectra of the adsorbed water together with the reaction intermediates in the MOR at Pt–Ru alloy electrode using the ATR-IRAS technique. The role of the adsorbed water in the MOR at Pt–Ru alloy is elucidated. The present results give a clue for designing new electrocatalysts for DMFCs.

The configuration of the spectro-electrochemical cell used in the present work was similar to that described in our previous works.[2,10] The working electrode was a thin Pt–Ru film (about 10 nm thick and 1.77 cm² of geometrical surface area) prepared on the flat plane of a silicon hemi-cylindrical prism by simultaneous sputtering of Pt and Ru targets. The resulting alloy composition determined by a fluorescent X-ray analysis (EDX-800, Shimadzu) was Pt₅₀Ru₅₀. X-ray diffraction patterns of the Pt–Ru alloy indicated the formation of a solid solution with a face-centered cubic (fcc) crystal structure.

Solution of 0.1 M HClO₄ with and without 1 M CH₃OH was prepared from reagent grade chemicals (Kanto Chemical Co.

Japan) and Milli-Q water. The supporting electrolyte solution of 0.1 M HClO₄ was purified with conventional methods.[11] All electrode potentials are reported with respect to the reversible hydrogen electrode (RHE). Before the collection of spectro-electrochemical data, a cyclic voltammogram for Pt–Ru electrode in deaerated 0.1 M HClO₄ (methanol-free) was obtained. Then, methanol was added into the solution, keeping the electrode potential at 100 mV until a potential sweep and simultaneous spectra acquisitions were started. Fourier transform infrared (FTIR) spectra were taken with Bio-rad FTS-6000 spectrometer equipped with a linearized narrow-band MCT detector. The incident angle was 70°. Each spectrum was acquired by integrating 15 interferograms with a resolution of 8 cm⁻¹ during a potential sweep at 20 mV s⁻¹. Since the acquisition time was 2.5 s per spectrum, each spectrum is the averages of every 50 mV interval. The spectrum at each potential is shown as absorbance. The spectrum at 975 mV was chosen as the reference.

Figure 1 shows linear sweep voltammograms (LSVs) for the MOR at Pt₅₀Ru₅₀ (A) and a sputtered polycrystalline Pt (B) in 1 M CH₃OH + 0.1 M HClO₄ solution. The oxidation current commences to increase at about 400 mV *vs.* RHE at the Pt–Ru electrode, while the onset potential at Pt was *ca.* 600 mV. This indicates that Pt–Ru alloy has higher activity for the MOR at lower potential region, being consistent with many other studies so far.[3,12,13] In order to clarify the MOR further, the electro-oxidation of the CO ad-layer at the Pt–Ru and Pt electrodes was also investigated.[14] The anodic current for the CO oxidation commences to increase at about 400 mV at Pt–Ru (C in Fig. 1), which is almost the same onset as that for the MOR. Similar behavior is seen at Pt electrode (D in Fig. 1). Thus, it is indicated that the rapid increase in the MOR current strongly corresponds to the oxidation of the poisoning intermediate CO. Coupled with the voltammograms, *in-situ* FTIR measurement provides more detailed information about such surface process.

Figure 2 shows ATR-IRAS simultaneously acquired with the LSV for the MOR at the Pt–Ru electrode. At the low potential region less positive than the onset potential in Fig. 1, strong bipolar shaped bands and some positive bands are observed at 2050 to 1700 cm⁻¹, which can be assigned to the stretching
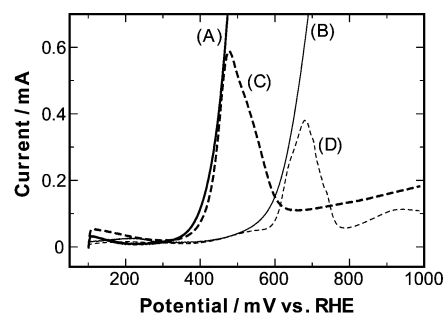

Fig. 1 Linear sweep voltammograms (LSVs) for the MOR in 1 M CH₃OH + 0.1 M HClO₄ at Pt–Ru (A) and Pt (B) electrodes. Dashed curves show LSVs for the oxidation of CO pre-adsorbed at Pt–Ru (C) and Pt (D) in 0.1 M HClO₄. Scan rate was 20 mV s⁻¹.

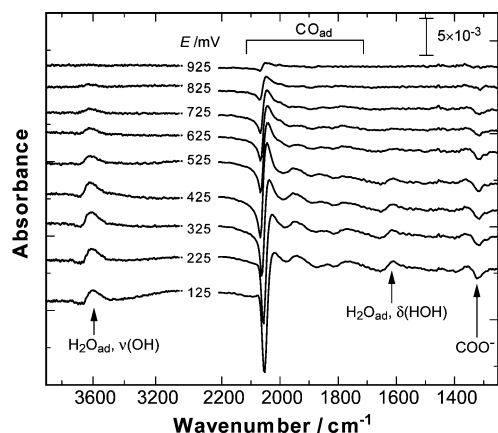† Electronic supplementary information (ESI) available: additional explanation for Figs. 2 and 3. See http://www.rsc.org/suppdata/cc/b2/b212197b/

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Fig. 2 *In-situ* ATR-IRA spectra for the MOR at Pt–Ru in 1 M CH₃OH + 0.1 M HClO₄, coupled with the LSV (A) in Fig. 1. The spectrum obtained at 975 mV was taken as the reference.

mode of linearly bonded CO (CO$_L$) at Pt site (2050 cm^{-1}),[2,6–8,10] CO$_L$ adsorbed at Ru sites (1940–2000 cm^{-1}),[15] and stretching mode of bridge-type CO (CO$_B$, 1700–1900 cm^{-1}),[2,10,13] respectively. These results indicate that methanol is dehydrogenated to CO dominantly during keeping the potential at 100 mV on Pt–Ru electrode. In addition, distinct positive-going bands around 3610 and 1610 cm^{-1} are clearly observed at the same potential region on the Pt–Ru alloy. These bands can be assigned to symmetric stretching mode and bending mode of adsorbed water, ν(OH) and δ(HOH), respectively.[16,17] Their wavenumbers are quite different from those of bulk water, but are rather similar to those of water monomer, *i.e.*, weakly hydrogen-bonded water molecules adsorb on Pt–Ru alloy surface. According to the surface selection rule,[8] the water is adsorbed on the surface with its C_2 axis perpendicular to the surface. Because such sharp bands have been also clearly observed at pure Ru electrode[18] but not at pure Pt,[2,9] water molecules probably adsorbed at Ru sites. The bands at 1315 cm^{-1} and 1390 cm^{-1} (very weak) are assigned to COO$^-$ and COOH, respectively.[2,6] Decrease of the height in the negative bands with increasing potential implies that the concentrations of these species increase with the potential, *i.e.*, they are the reaction intermediates generated at a high potential region.

Figure 3 shows the potential-dependence of the normalized IR-band intensity of each adsorbed species and the methanol oxidation current in the positive-going sweep at the Pt–Ru alloy electrode. It is striking that the band intensities of both CO$_L$ and adsorbed water commence to decrease together steeply at about 400 mV, *i.e.*, the onset potential of the MOR.[18] The similar behaviour was obtained at Pt–Ru alloy surface for the anodic stripping of CO pre-adsorbed in a CO saturated electrolyte solution.[18,19] This is a clear demonstration of that the adsorbed
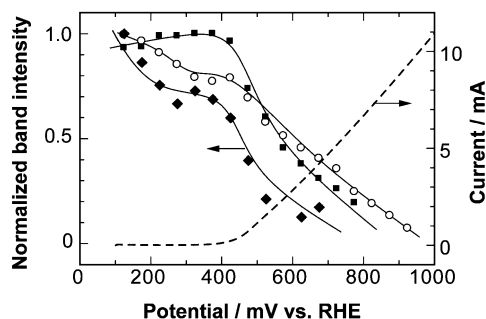
CO, which is the dominant reaction intermediate of the MOR, is oxidized by consuming the adsorbed water.

However, it must be noted that the electro-oxidation of adsorbed CO cannot occur at less positive potential than 400 mV even though such water molecules are already adsorbed together with CO at Pt–Ru surface. This indicates that adsorbed water molecules cannot directly oxidize CO molecules. As indicated by the reduction of ν(OH) and δ(HOH) bands, however, the water molecules adsorbed on Ru sites disappear presumably due to the discharge at relatively less positive potential (about 400 mV)[18] and form active species, *e.g.*, such a Ru–OH, as previously supposed in the literature.[3,12,13]

$$Ru–OH_2 \rightarrow Ru–OH + H^+ + e^- \qquad (1)$$

Once the Ru–OH is formed, the adsorbed CO (mainly at Pt sites) is easily oxidized to CO₂, as indicated by the simultaneous reduction of IR-bands both of the adsorbed water and CO.

$$Pt–CO + Ru–OH \rightarrow Pt + Ru + CO_2 + H^+ + e^- \qquad (2)$$

This is the reaction mechanism so-called ″bi-functional mechanism″, proposed by Watanabe and Motoo.[3] The present ATR-FTIR research is the first to show direct clear evidence for the mechanism at the MOR and CO oxidation on Pt–Ru electrode. We believe that this result accelerates the designing of new DMFC anode catalysts.

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14 Helium gas containing 1% CO was purged into 0.1 M HClO₄ solution at 100 mV for 30 min in order to obtain a pre-adsorbed CO layer on the electrode. Then CO in the bulk solution was removed by purging with N₂ while keeping the potential constant for 1 h.

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18 It is seen in Fig. 3 that the band intensities of CO$_L$ and δ(HOH) decrease gradually as the potential is increased up to 400 mV in spite of negligibly anodic current. However, we consider that such changes were ascribed to some artifacts yielded by background subtraction (see ESI† for details). The most important point is that the band intensities of both CO$_L$ and adsorbed water commence to decrease together steeply at about 400 mV at the Pt–Ru electrode.

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Fig. 3 Potential dependence of the normalized IR-band intensity of adsorbed species obtained from Fig. 2. (○) CO$_L$; (■) H₂O$_{ad}$, ν(OH); (◆) H₂O$_{ad}$, δ(HOH). Dashed curve shows the LSV cited from A in Fig. 1.