

## Formate, an Active Intermediate for Direct Oxidation of Methanol on Pt Electrode

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Because of the great potential of methanol (MeOH) as a fuel for low temperature fuel cells, the electro-oxidation of MeOH on Pt or Pt-based metal electrodes has been extensively studied in the past decades.<sup>1–5</sup> It is generally accepted that MeOH can be oxidized to CO<sub>2</sub> via a dual-path mechanism, that is, via adsorbed CO (CO<sub>ad</sub>) or non-CO reactive intermediates.<sup>1–6</sup> The formation of strongly adsorbed CO, which leads to the self-poisoning of electro-catalysts, has been well confirmed. However, no consensus on the nature of the reactive intermediates in the non-CO pathway has been reached so far.<sup>1–9</sup> By using in situ IR reflection–absorption spectroscopy (IRRAS), various adsorbates such as (CH<sub>x</sub>OH)<sub>ad</sub>,<sup>7</sup> (–COH)<sub>ad</sub>,<sup>7</sup> formyl (–HCO)<sub>ad</sub>,<sup>8</sup> carboxy (–COOH)<sub>ad</sub>,<sup>8</sup> or a dimer of formic acid (HCOOH)<sub>2ad</sub><sup>9</sup> have been claimed to be the reactive intermediates for MeOH electro-oxidation. However, the spectra of the “reaction intermediates” are not well reproduced by other groups.<sup>1–9</sup> To get a better understanding of the mechanism of MeOH electro-oxidation, it is highly desirable to identify the actual reactive intermediates and clarify their roles in the reaction process. In the present study, the electro-oxidation of MeOH on Pt in 0.1 M HClO<sub>4</sub> has been investigated by in situ surface-enhanced IR absorption spectroscopy (SEIRAS) with the Kretschmann ATR configuration.<sup>10</sup> Formate adsorbate has been undoubtedly identified for the first time and is proposed to be an active intermediate for the direct oxidation of MeOH to CO<sub>2</sub> on the Pt electrode.

As compared to IRRAS, SEIRAS has a higher surface selectivity and sensitivity; thus the interface can be selectively monitored with less interference from the bulk solution.<sup>10</sup> Furthermore, the use of the ATR configuration in SEIRAS surmounts the mass transfer limitation encountered in IRRAS with a thin-layer configuration.<sup>10</sup> The details of the SEIRAS measurements have been described elsewhere.<sup>10</sup> A 50-nm thick Pt film chemically deposited on a Si ATR prism was used as the working electrode. We have demonstrated that the chemically deposited Pt electrodes have a very high SEIRA-activity.<sup>11</sup> All potentials were presented with respect to the reversible hydrogen electrode (RHE). All IR spectra shown were obtained by integrating 50 interferograms at a resolution of 4 cm<sup>–1</sup> and normalized to the spectrum taken at 0.05 V in 0.1 M HClO<sub>4</sub>.

The cyclic voltammogram (CV) of the Pt thin film electrode in 0.1 M HClO<sub>4</sub> (Figure 1a, dotted line) shows the same behavior as that of polycrystalline Pt electrodes. In the solution containing 0.5 M MeOH, the oxidation of MeOH occurs at *E* > 0.5 V with a current peak around 1.0 V in the positive-going sweep (Figure 1b, solid line). While in the negative-going scan, the anodic current increases from ca. 0.95 V with a peak at 0.9 V, and then drops to nearly zero at *E* < 0.5 V.

Figure 2 shows the in situ SEIRA spectra recorded simultaneously with the CV (Figure 1b) in the solution containing MeOH. At 0.05 V, two bands are clearly observed at 2060 and 1860 cm<sup>–1</sup>,

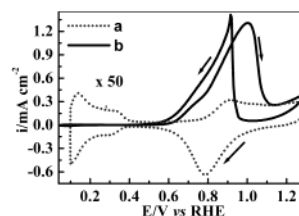


Figure 1. CVs of Pt in (a) 0.1 M HClO<sub>4</sub>; (b) 0.1 M HClO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH. Scan rate: 5 mV/s.

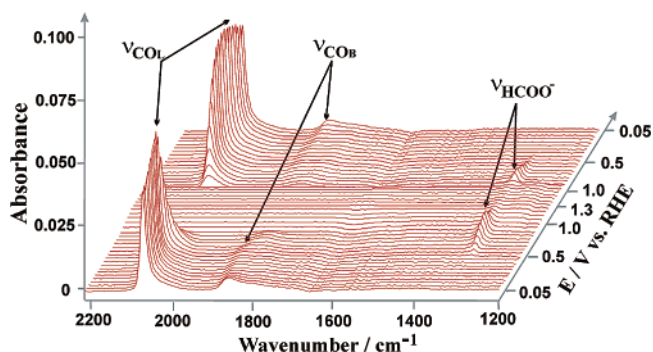


Figure 2. SEIRA spectra of the Pt/solution interface in the range from 1200 to 2200 cm<sup>–1</sup> during MeOH electro-oxidation on Pt. For the other conditions, see Figure 1b.

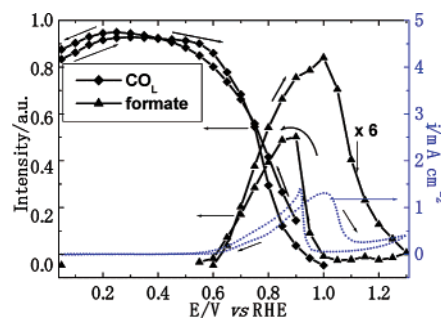


Figure 3. Dependence of IR intensity of linearly bonded CO, formate, and anodic current on the electrode potential; the other conditions are the same as those in Figure 2.

which are attributed to CO molecules linearly and bridge-bonded to the Pt electrode surface, respectively.<sup>3</sup> The intensities of these bands are almost constant in the potential range of 0.05–0.5 V and decrease rapidly at more positive potentials (Figure 3). Accompanying the decrease in the CO band intensities, a new band appears around 1320 cm<sup>–1</sup>. The intensity of this band increases with an increase of the potential and shows a maximum around 1.0 V, very similar to the potential dependence of the anodic current observed in the positive-going sweep (Figure 3). A similar potential dependence of the anodic current and the IR band intensity of the new peak is also observed in the negative-going scan (Figure 3).

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The correlation between the anodic current and IR band intensity implies that the species related to the new peak plays an important role in the electro-oxidation of MeOH on the Pt electrode.

Furthermore, the peak position of this band was found to shift with potential from  $1320\text{ cm}^{-1}$  (0.6 V) to  $1328\text{ cm}^{-1}$  (1.25 V), indicating that this band comes from the species adsorbed on the electrode. It was also found that this band shifts to  $1300\text{ cm}^{-1}$  when  $\text{CD}_3\text{OH}$  or  $^{13}\text{CH}_3\text{OH}$  are used instead of  $\text{CH}_3\text{OH}$ , indicating that the adsorbed species contains both H and C atoms. The similar band at  $1324\text{ cm}^{-1}$  was also observed during MeOH oxidation on Pt(111) by  $\text{O}_2$  under UHV<sup>12a</sup> or ambient pressure conditions.<sup>12b</sup> This band was assigned to the symmetric OCO stretching mode of adsorbed formate, which was attributed to be a reactive intermediate for complete oxidation of MeOH to  $\text{CO}_2$  on the Pt surface in the gas phase study.<sup>12</sup> We also assign the  $1320\text{ cm}^{-1}$  peak observed in the present study to formate ( $\text{HCOO}^-_{\text{ad}}$ ) adsorbed on the Pt electrode surface. The absence of the corresponding antisymmetric OCO mode of formate reveals that formate is adsorbed on the Pt surface with its  $\text{C}_2$  axis perpendicular to the surface, that is, with two oxygen atoms bonded to the surface, based on the surface selection rule of SEIRAS.<sup>10</sup> It should be mentioned that this is the first observation of formate on the Pt electrode during the MeOH oxidation in acidic solutions. Despite the very high sensitivity of SEIRAS we employed, no bands corresponding to other intermediates proposed previously based on the IRRAS studies<sup>1–9</sup> were detected, although great effort and care have been given.

For the electro-oxidation of  $\text{CO}_{\text{ad}}$  from dissolved CO in the solution, the formate band was not observed by SEIRAS, which indicates that formate is not derived from  $\text{CO}_{\text{ad}}$ . In this study, the formate can only be observed at  $E > 0.5\text{ V}$  in an intimate correlation between its band intensity and Faradaic current (Figure 3). It is known for the Pt(111)/0.1 M  $\text{HClO}_4$  system that the adsorption of OH from the dissociation of water, that is,  $\text{H}_2\text{O} + \text{Pt} \rightleftharpoons \text{Pt}-\text{OH}_{\text{ad}} + \text{H}^+ + \text{e}^-$ , occurs at  $0.6\text{ V} < E < 0.9\text{ V}$ .<sup>4</sup> On a roughened surface,  $\text{OH}_{\text{ad}}$  at defects sites can be formed even at much lower potentials.<sup>4</sup> It indicates that the presence of active oxygen sources (e.g.,  $\text{O}_{\text{ad}}$  and  $\text{OH}_{\text{ad}}$ ) on the surface is one of the prerequisites to oxidize MeOH to formate on the Pt surface. Studies of methanol oxidation at Pt surface in the gas phase also confirmed this.<sup>12</sup>

On the other hand, it is well known that formic acid and formaldehyde are formed and dissolved into the solution as byproducts in the MeOH electro-oxidation.<sup>13–15</sup> In a previous study, we showed that formic acid is adsorbed on Pt electrode as formate and is further oxidized to  $\text{CO}_2$ .<sup>11</sup> To check the effects of the byproducts on MeOH electro-oxidation, we carried out similar SEIRAS measurements using a flow-cell aiming to remove the soluble products from the electrode surface. For a flow rate from zero to a rate which can replace the solution in the cell twice per second, no decrease of the formate band intensity was observed. This result indicates that formate species are mainly formed on the Pt surface from the direct electro-oxidation of MeOH and the readsorption of formic acid gives a negligible contribution to the formate band observed in the present study. Furthermore, when 0.2 M  $\text{CH}_3\text{OH}$  was added into 0.1 M  $\text{HClO}_4 + 0.1\text{ M } ^{13}\text{CH}_3\text{OH}$  solution at +0.75 V (where MeOH oxidation takes place), a peak at  $1320\text{ cm}^{-1}$  corresponding to  $\text{H}^{12}\text{COO}^-_{\text{ad}}$  appeared immediately and grew in intensity on consumption of the band at  $1300\text{ cm}^{-1}$  related to  $\text{H}^{13}\text{COO}^-_{\text{ad}}$ . This result further proves that formate is formed directly from the oxidation of MeOH. The dynamic changes of formate formed on the surface during the electro-oxidation of MeOH are associated with the fact that the formate can be further oxidized to  $\text{CO}_2$ , or may desorb into the solution, and consequently free sites for the adsorption of newly produced formate from MeOH.

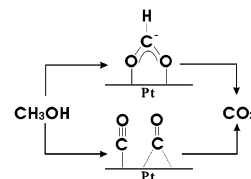


Figure 4. Reaction pathways of methanol oxidation at Pt electrode.

Recently, the differential electrochemical mass spectroscopic (DEMS) study using a thin layer flow-cell confirmed that the current efficiency for the complete oxidation of MeOH to  $\text{CO}_2$  increases with an increase of Faradaic current during the electro-oxidation of MeOH on Pt electrodes.<sup>14</sup> This result is well correlated with the increase in the formate band intensity with the Faradaic current found in this study (Figure 3). All of these facts suggest that at least a certain amount of formate formed from the electro-oxidation of MeOH on the Pt electrode surface is directly oxidized to  $\text{CO}_2$ .

In conclusion, results obtained in the present study strongly suggest that formate should be included as a reactive intermediate in the non-CO pathway of the reaction mechanism for MeOH electro-oxidation. A simplified scheme for the complete electro-oxidation of MeOH to  $\text{CO}_2$  on Pt in acidic solutions is proposed (Figure 4). For clarity, the pathways via byproducts dissolved in the solution are not shown. Besides the well-known CO path to  $\text{CO}_2$ , the non-CO pathway via formate as the reactive intermediate will be active, when free sites for adsorption of MeOH and oxygen donors at Pt surface are available. Note that this non-CO reaction pathway is new and largely different from those proposed previously.<sup>1–9</sup> The fact that many other reaction intermediates reported previously are not detected in the present study strongly suggests that many previous reaction mechanisms based on these so-called intermediates<sup>1–9</sup> should be reconsidered carefully. We believe that the clarification of the reaction pathway with formate as the active intermediate for the electro-oxidation of MeOH on the Pt will be of great help in designing anode catalysts with high catalytic activity for direct methanol fuel cells.

**Acknowledgment.** Financial support from the Ministry of Education, Culture, Sports, Science and Technology, Japan, RITE, and the Asahi Glass Foundation is acknowledged. Y.X.C. is grateful for a COE-fellowship from the Japanese government. S.Y. gratefully acknowledges the support from PRESTO, JST, and a grant from NOASTEC.

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JA029044T