Electrooxidation of Ethanol on Pt in the Absence of Water

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ABSTRACT

It is well accepted that the electrooxidation of ethanol on Pt in aqueous solution proceeds via two parallel pathways: C1-pathway, which is the complete oxidation of ethanol to CO2 via COad intermediate, and C2-pathway, which produces acetaldehyde and also acetic acid with further oxidation. Water plays important roles for the oxidation, i.e., for the oxidative removal of COad in the C1-pathway and for the oxidation of acetaldehyde to acetic acid in the C2-pathway. In the present work, however, we show that the ethanol oxidation proceeds in the absence of water. Detailed study using surface-enhanced infrared absorption spectroscopy and high-performance liquid chromatography reveals that COad reacts with ethanol to form ethyl formate, which is designated as C3-pathway, and also that the ethanol oxidation produces ethyl acetate, which is designated as C4-pathway.

1. Introduction

Direct alcohol fuel cells (DAFCs), which mostly use low-molecular weight alcohols such as methanol and ethanol as fuels, have attracted considerable interest in recent years because liquid fuels are suitable for portable applications compared with gas fuels, that is, liquid ones can be easily handled, stored, and transported. Methanol is recognized as a promising fuel for DAFCs, and the anode reaction in direct methanol fuel cells (DMFCs), or the electrooxidation of methanol, has been comprehensively studied in order to improve performance of DMFCs and also to achieve cost reduction.1 Furthermore, DMFCs have been widely studied for commercial purposes. However, methanol has shortcomings: it is toxic for human, and it is mostly produced from natural gas. On the other hand, ethanol is non-toxic, and it can be sustainably produced on a large scale from biomass. Furthermore, ethanol has a high theoretical energy density of 8.0 kWh kg⁻¹, which is higher than that of methanol (6.1 kWh kg⁻¹).1,2 In these regards, direct ethanol fuel cells (DEFCs) have a strong advantage over DMFCs.

1.1 Methanol oxidation at Pt electrodes

For decades, the methanol oxidation has been most extensively studied using Pt anode, which is an excellent electrocatalyst for the oxidation. The oxidation of methanol with water is written as follows:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad (1) \]

It is well accepted that the oxidation proceeds via a dual path mechanism (cf. reaction pathways to CO2 shown in Fig. 1a). One of the pathways involves adsorbed carbon monoxide (COad) as a poisoning intermediate, and the other pathway involves a non-CO intermediate as a reactive one. Water produces oxygenated species such as hydroxide and oxide, and it plays an important role in removal of COad. Thus, it seems that the oxidation does not proceed without water. However, as we have reported previously,3,4 the methanol oxidation produces current without water, and the current is of the same order of magnitude as that observed in the presence of water, e.g., 0.1 and 1 M methanol aqueous solutions (see Fig. 2).

A detailed study using surface-enhanced infrared absorption spectroscopy (SEIRAS) and high-performance liquid chromatography (HPLC) has revealed that COad reacts with methanol to form methyl formate (HCOOCHOH): 3

\[ \text{COad} + \text{CH}_3\text{OH} \rightarrow \text{HCOOCH}_3 \quad (2) \]

where * stands for an adsorption site. Here, we assume that the attack by CH3OH does not require adsorption sites. The detailed study has also revealed that the formation of formaldehyde (HCHO) occurs in the absence of water:

\[ \text{CH}_3\text{OH} \rightarrow \text{HCHO} + 2\text{H}^+ + 2\text{e}^- \quad (3) \]

Furthermore, it has concluded that the main current-producing reaction in the absence of water is the formation of HCOOCHOH via non-CO pathway:
This conclusion is in line with the methanol oxidation in aqueous solution: the oxidation leads to the production of HCOOCH₃, which is believed to occur via the nucleophilic attack of a methanol molecule to HCOₐd.⁵,⁶ When a H₂O molecule instead of methanol attacks to HCOₐd, HCOOH is produced resulting in the formation of CO₂ with its further oxidation (see Fig. 1a). Hence, the amount of produced HCOOCH₃ considerably increased as the methanol concentration increased. It should be noted that the HCOOCH₃ production is not attributed to a homogeneous reaction between HCOOH and CH₃OH in the aqueous solution (HCOOH + CH₃OH → HCOOCH₃ + H₂O).

**1.2 Ethanol oxidation at Pt electrodes**

Pt is also known to be active for the electrooxidation of ethanol in aqueous solution. The oxidation of ethanol produces CO₂ when ethanol is oxidized completely with water (or oxygenated species):

\[
\text{C}_2\text{H}_5\text{OH} + \text{3H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \quad (5)
\]

The mechanism of the oxidation, which has been investigated by many researchers,²⁴⁻²⁹ is quite complex compared to the methanol oxidation.
oxidation. The ethanol oxidation proceeds via parallel pathways in acid media (see Fig. 1b). The C1-pathway, which includes cleavage of C–C bond, is the complete oxidation of ethanol to CO2 via COad intermediate. The C2-pathway, in which the C–C bond remains intact, produces acetaldehyde (CH3CHO), and also acetic acid (CH3COOH) with further oxidation:

\[
\begin{align*}
C_2H_5OH & \rightarrow CH_2CHO + 2H^+ + 2e^- \\
CH_2CHO + H_2O & \rightarrow CH_3COOH + 2H^+ + 2e^- 
\end{align*}
\]

(6) (7)

The cleavage of C–C bond requires high activation energy, and thus most ethanol is partially oxidized via the C2-pathway.

1.3. Significance of this study
Water also plays important roles for the ethanol oxidation, i.e., for the oxidative removal of COad (the CO2 formation) in the C1-pathway and for the oxidation of CH3CHO to CH3COOH in the C2-pathway, which are indicated by the blue arrows in Fig. 1b. However, as demonstrated in this present study, ethanol is also oxidized at Pt electrodes in the absence of water. From the analogy of the methanol oxidation without water, we can propose that COad reacts with ethanol to form ethyl formate (HCOOC2H5) and also that ethyl acetate (CH3COOC2H5) is formed from ethanol:

\[
\begin{align*}
CO_{ad} + C_2H_5OH & \rightarrow HCOOC_2H_5 + + \\
2C_2H_5OH & \rightarrow CH_3COOC_2H_5 + 4H^+ + 4e^- 
\end{align*}
\]

(8) (9)

Let us designate the former reaction route as C3-pathway, and the latter one as C4-pathway. In this work, by using SEIRAS and HPLC, we provide direct evidence that the C3-pathway proceeds at high potentials, and confirm the existence of the C4-pathway.

Systematic investigations of the effect of ethanol concentration (up to 1 M) on its electrooxidation were conducted previously.2,20 They showed that the contributions of the C1-pathway and the C2-pathway strongly depend on ethanol concentration. Besides, the limiting current densities at relatively high ethanol concentrations were studied.21 However, in the previous study, the concentration range was limited up to 5 M. This present work is the first attempt to study the ethanol oxidation at the highest concentration (17 M). We, therefore, believe that this work contributes a deeper understanding of the parallel pathways.

2. Experimental
All chemicals used were purchased from FUJIFILM Wako Pure Chemical Corporation (Japan) and used as received. The electrolyte solutions were prepared with sulfuric acid (“Super Special Grade”, 96.7%), methanol (“Super Dehydrated Grade” with a water content of 0.0003%), ethanol (“Super Dehydrated Grade” with a water content of 0.0008%), and ultrapure water (resistivity: >18 MΩcm), the last of which was used to prepare aqueous solutions. To deoxygenate the solutions, nitrogen gas was bubbled through the solution before measurement and was passed over the solution during measurement to keep the solution deoxygenated.

In this report, 0.5 M H2SO4 + 24 M CH3OH and 0.5 M H2SO4 + 17 M C2H5OH solutions were used as electrolyte solutions. The alcohol solutions were prepared without using ultrapure water, that is, they were prepared by directly adding appropriate amounts of the sulfuric acid to the pure methanol and ethanol, respectively. Note that the concentration of the pure methanol is 24 M and that of pure ethanol is 17 M. The concentration of water in the solutions was at most 93 mM, as the sulfuric acid with a purity of 96.7% contained a little amount of water.

Details of experimental setup have been described elsewhere.3 In short, electrochemical experiments were conducted in a three-electrode configuration at room temperature (controlled at 25 ± 1°C with air conditioners). The values of electrode potential (E) and current (I) were stored in a personal computer equipped with a data acquisition system. The reference electrode was a reversible hydrogen electrode (RHE), which was immersed in a solution with the same composition as electrolyte solution. The counter electrode was a platinized Pt wire. The working electrodes was a thin (~50 nm) Pt film (real surface area: 12.4 cm²) deposited on a Si triangular prism (20 mm on a side and 25 mm long) by a procedure described in our previous paper.3

SEIRAS measurements were performed in the attenuated total reflection mode with a homemade single-reflection accessory. SEIRA spectra were recorded on an Agilent Technologies Varian 670-IR Fourier transform infrared spectrometer equipped with an MCT detector at a spectral resolution of 4 cm⁻¹. The reference spectrum was taken with a 0.5 M H2SO4 aqueous solution in the absence of alcohol at 0.05 V. Before taking it, N2 (purity: 99.9995%) gas was bubbled through the solution for 20 minutes.

In order to estimate the coverage of COad (θCO), the following procedure, which is essentially similar to that described in a paper,25 was carried out using 0.5 M H2SO4 solution. While E was kept at 0.05 V, CO gas (99.9%, GL Science Inc., Japan) was bubbled through the electrolyte solution for 20 minutes in order to form COad on the surface of Pt film. Afterwards, SEIRA spectra were corrected to obtain integrated band intensity of COad. Here, θCO after the CO bubbling is assumed to be 0.83, which was calculated from the charge for the complete oxidation of COad, i.e., from anode stripping voltammograms of COad as done previously.23 There are two types of COad, namely, linearly bonded CO (COB) and bridge-bonded CO (COH). Since the latter requires two Pt surface atoms, the coverages of COH and COB (θ continue L and θ continue B) after the CO bubbling are assumed to be respectively 0.66 and 0.17 (θCOB = 0.83 and θCOH + 2θCOB = 1). These values were used as references for estimating the coverages assuming linear relationships between them and the integrated band intensities for COH (~2060 cm⁻¹) and COB (~1830 cm⁻¹).

A HPLC system (Agilent, Infinity 1220) which is connected with a diode array detector (Agilent, Infinity 1260 II) was utilized to analyze ethyl acetate and acetaldehyde. The separation was achieved on an Agilent ZORBAX Eclipse C18 column (150 mm × 4.6 mm, i.d., 5 µm) by isocratic elution at a flow rate of 1 mL/min at room temperature (around 25°C). A binary mixture of phosphate buffer (pH 2.6) and methanol (60:40 by volume) was used as the isocratic mobile phase for ethyl acetate. A derivatization method using 2,4-dinitrophenylhydrazine (DNPH) was used to analyze acetaldehyde. A binary mixture of acetonitrile and water (50:50 by volume) was used as the isocratic mobile phase for acetaldehyde. The detection limits for ethyl acetate and acetaldehyde were 0.5 mM and 5 µM, respectively (see Fig. S1 in Supporting information).

3. Results and Discussion
3.1. Methanol oxidation
For purpose of comparison, let us here show some experimental results obtained for the methanol oxidation at the Pt film electrode.

3.1.1. Voltammetric behavior
For 1 M methanol aqueous solution (the left panels in Fig. 2), the cyclic voltammograms (CVs) showed dominant peaks which were closely related to θCO and the coverage of oxygenated species. As reported in the previous work,3 when the electrolyte solution was 0.5 M H2SO4 + 24 M methanol (the right panels in Fig. 2), that is, when the solution scarcely contained water, the CV showed peaks I and IV in the positive- and negative-going scans, respectively. The oxidation current at peak IV was 7.7 mA, which was a little smaller than half of the peak current for 1 M methanol (16.4 mA).

The SEIRA spectra taken simultaneously with the CVs are also shown in Fig. 2 (panels a2 and b2). They clearly indicate that adsorption bands of COH and COB were dependent on E. As seen in Fig. S2, peak frequencies of COH and COB bands increased with

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increasing $E$ (Stark effect). In the spectra taken for the 1 M methanol, a potential-dependent absorption band was observed at $\sim 1320 \text{ cm}^{-1}$ (Figs. 2(a2) and S2(a)). This is assigned to formate bonded via both oxygen atoms to two surface Pt atoms, i.e., adsorbed formate in a bridging configuration, which is denoted as HCOOH. On the other hand, for the 24 M solution, the band was not observed while some other bands ascribed to interfacial methanol were observed at 1447, 1415, 1103, and 1037 cm$^{-1}$ (Figs. 2(b2) and S2(b)). Incidentally, the band at $1238 \text{ cm}^{-1}$, which is assigned to sulfate or hydrogen sulfate, increased in its intensity with increasing $E$ because of the decrease in the amount of COad (Fig. S2(b)). These are in good agreements with the previous study.3

From the spectra, the dependences of $\theta_{\text{CO,L}}$ and $\theta_{\text{CO,B}}$ on $E$ were estimated (panels a3, a4, b3, and b4 of Fig. 2). In the positive-going scan, both $\theta_{\text{CO,L}}$ and $\theta_{\text{CO,B}}$ decreased with the increasing $E$ in the potential region above 0.5 V even when the solution scarcely contained water, i.e., when it was the 24 M methanol solution (b3 and b4). This is due to the reaction between COad and methanol.3 It should be noted that COad was still present even at 1.4 V because the rate of the reaction was slow. It is expected that COad would be significantly removed when scan rate was sufficiently slow (e.g., 1 mV/s). On the other hand, for the aqueous solution (a3 and a4), COad was completely removed by water (or oxygenated species) at 1.1 V in the positive-going scan (red curves). This indicates that the rate of the reaction between COad and methanol is slower than that of the reaction between COad and water.

Incidentally, in the potential region between 0.05 and 0.3 V, $\theta_{\text{CO,L}}$ increased while $\theta_{\text{CO,B}}$ decreased as $E$ increased, which was due to a site conversion between COad and COB.24,25

3.1.2 Reaction between COad and methanol

As shown above, COad was removed at high potentials even in the 24 M methanol solution. As mentioned in the experimental section, the solution contained a little amount of water (93 mM) originated from sulfuric acid, and thus it is most likely that the COad removal was partially due to water (COad + H2O $\rightarrow$ CO2 + 2H+] + 2e$^- + \text{H}_2$). In order to separate the removal by methanol from that by water, time-dependences of $\theta_{\text{CO}}$ were measured not only for the methanol solution but also for the solutions to which a small amount of water was intentionally added. The measurements were conducted using a locally weighted scatter plot smoothing (LOWESS) applied to the time-dependences to obtain the relationship among $\theta_{\text{CO}}$, the concentration of water ($C_{\text{H2O}}$), and time ($t$). From the relationship, the time-dependences of $\theta_{\text{CO}}$ that should be obtained if the solutions contained no water, or the variations of $\theta_{\text{CO}}$ in the absence of water, were estimated (see Figs. S3).

Figure 3 shows the variations of $\theta_{\text{CO,L}}$ and $\theta_{\text{CO,B}}$ that should be obtained if the solutions contained no water, or the variations of $\theta_{\text{CO}}$ in the absence of water, were estimated (see Figs. S3).

Figure 3 shows the variations of $\theta_{\text{CO,L}}$ and $\theta_{\text{CO,B}}$ that should be obtained if the solutions contained no water, or the variations of $\theta_{\text{CO}}$ in the absence of water, were estimated (see Figs. S3).

The appearance of the peaks was attributed to $\theta_{\text{CO}}$ and the coverage of oxygenated species, similarly to the peaks observed for 1 M methanol. The adsorption band of COB was clearly observed at low potentials whereas that of COad was slightly observed even at 0.05 V (panel a2). Besides, a band at $\sim 1404 \text{ cm}^{-1}$, which is assigned to the OCO stretching of adsorbed acetate ions,26 increased with the increasing potential (see Fig. S4(a)). This indicates that acetic acid was formed via the C2-pathway at high potentials.

In the positive-going scan, COB was oxidized by water (or oxygenated species) when $E > 0.6 \text{ V}$, and was completely oxidized at 1.2 V. In the similar manner as the 1 M methanol oxidation, site conversion between COad and COB occurred, that is, $\theta_{\text{CO,L}}$ increased while $\theta_{\text{CO,B}}$ decreased as $E$ increased, at $E < 0.6 \text{ V}$. In the negative-going scan, COB started to form at 0.8 V. When the ethanol concentration was 17 M (the right panels of Fig. 4), i.e., when the solution scarcely contained water, the ethanol oxidation produced current, which can be ascribed to the formation of acetaldehyde (reaction 6) and also to that of ethyl acetate (reaction 9) because acetaldehyde and ethyl acetate were both detected by HPLC as shown later. The SEIRA spectra were slightly dependent on $E$ (panel b2). The adsorption bands of COad and COB were observed even at 1.4 V. Some other bands were observed at 1447, 1383, 1093, and 1053 cm$^{-1}$ (see also Fig. S4(b)). They can be ascribed to interfacial ethanol. Note that the reference spectrum was taken with a 0.5 M H2SO4 aqueous solution in the absence of alcohol.

As $E$ increased, both $\theta_{\text{CO,L}}$ and $\theta_{\text{CO,B}}$ gradually decreased and the current increased monotonically in the potential region above ca. 0.4 V. Similarly to the methanol oxidation, we can thus conclude that the ethanol oxidation proceeds even in the absence of water. Incidentally, $\theta_{\text{CO,L}}$ decreased linearly with the increasing potential, that is, $d\theta_{\text{CO,L}}/dE$ is constant, in a wide potential range in contrast to the dependence of $\theta_{\text{CO,L}}$ on $E$ for the 24 M methanol solution, which will be studied in a future work.

Independently of alcohol concentration, both $\theta_{\text{CO,L}}$ and $\theta_{\text{CO,B}}$ are lower at low potentials (e.g., 0.5 V or lower) during the ethanol oxidation than during the methanol oxidation. This indicates that the rate of COad formation from ethanol is slower than that from methanol, which is consistent with the fact that the COad formation from ethanol requires the cleavage of C-C bond that has high
activation energy. It is reported\(^9\) that adsorbed CH\(_x\) species accumulate at low potentials during ethanol oxidation. Therefore, it is also possible that the CH\(_x\) accumulation might hinder the CO\(_{ad}\) formation from ethanol.

3.2.2 Is CO\(_{ad}\) removed by ethanol?

To answer this question, the variations of \(\theta_{CO,L}\) and \(\theta_{CO,B}\) in the absence of water were estimated using the same method as done in the subsection 3.1.2 with the exception that the solution used here was 0.5 M H\(_2\)SO\(_4\) + 17 M C\(_2\)H\(_5\)OH. As shown in Figs. 5 and S5, \(\theta_{CO,L}\) and \(\theta_{CO,B}\) were 0.26 and 0.066, respectively, at \(t = 0\) s, and they decreased with time after the potential step. This clearly indicates that CO\(_{ad}\) was removed by ethanol (reaction 8), leading to a conclusion that the C3-pathway was involved in the ethanol oxidation.

It is known that the reaction between CO\(_{ad}\) and water (or oxygenated species), i.e., the electrooxidation of CO\(_{ad}\) to CO\(_2\), includes an elementary step that proceeds by Langmuir-Hinshelwood (L-H) mechanism.\(^{27-32}\) In other words, the adsorption of water (or oxygenated species) is involved in the CO\(_{ad}\) oxidation. On the other hand, density functional studies show that ethanol binds on the on-top site of Pt surface through its oxygen atom.\(^{33,34}\) This configuration is highly favorable for the formation of a bond between the oxygen atom and a carbon atom of CO\(_{ad}\) which facilitates the formation of ethyl formate at the surface. Hence, we can suggest that the C3-pathway proceeds by L-H mechanism (CO\(_{ad}\) + C\(_2\)H\(_5\)OH\(_{ad}\) \(\rightarrow\) HCOOCC\(_2\)H\(_5\) + \(\text{H}_2\)). Further study is required for the clarification of the mechanism of the C3-pathway.

3.2.3 Qualitative analysis of reaction products

As clearly shown above, the ethanol oxidation proceeds even in the absence of water. Then, HPLC analysis was performed in order to identify reaction products. Figure 6 shows a chromatogram taken after the ethanol oxidation achieved by cycling the potential 3200
times between 0.05 V and 1.4 V at a sweep rate of 0.1 V/s. The chromatogram shows two dominant peaks at retention time of 1.6 and 4.0 min, which are respectively assigned to the electrolyte solution and ethyl acetate (see Fig. S1). The latter peak was not observed for the solution before the potential cycle, and hence we can conclude that ethyl acetate was formed during the potential cycles. Furthermore, ethyl acetate was detected after conducting the ethanol oxidation for 24 hours at a potential as high as 1.2 V. Since ethyl acetate is volatile, it was not detected after the oxidation was conducted at 1.0 V or lower. Acetaldehyde was also detected after potential cycles by HPLC analysis (Fig. 7), indicating that the ethanol oxidation also produced acetaldehyde without water due to the occurrence of reaction 6.

3.3 C4-pathway

As shown above, ethyl acetate was clearly detected after the ethanol oxidation in the absence of water. Therefore, we supposed that ethyl acetate was produced indirectly by esterification of acetic acid with ethanol (CH₃COOH + C₂H₅OH → CH₃COOC₂H₅ + H₂O) because we could confirm that the esterification occurred when a small amount of acetic acid was intentionally added into the 0.5 M H₂SO₄ + 17 M C₂H₅OH solution. However, the indirect production of ethyl acetate is thought to be negligible because acetic acid was not formed by the ethanol oxidation without water. Note that the acetic acid formation from acetaldehyde requires water (reaction 7). We can thus conclude that ethyl acetate was produced directly by reaction 9 and also that the current producing reaction during the ethanol oxidation without water is the C4-pathway (reaction 9) as well as the formation of acetaldehyde in the C2-pathway (reaction 6).

4. Conclusions

We studied the electrooxidation of ethanol on Pt in the absence of water, in order to confirm the newly proposed pathways (namely, the C3- and C4-pathways). The study, which was conducted by measuring CVs, SEIRA spectra, and chromatograms, revealed the following: (a) The ethanol oxidation occurred in the absence of water. (b) The adsorbed CO (COad) was removed by ethanol, that is, COad reacted with ethanol to form ethyl formate (HCOOC₂H₅), in the similar manner as the reaction between COad and methanol. In order to confirm the removals of COad by the alcohols, the variations of ¹CO in the absence of water were estimated from the time-dependences of ¹CO at various concentrations of water. (c) The oxidation produced ethyl acetate in the absence of water. These results strongly support the existence of the newly proposed pathways.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00056.

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