

Oxidation of formic acid and methanol and their potential oscillations under no or little water conditions



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ARTICLE INFO

Article history:

Received 20 April 2014

Received in revised form 23 May 2014

Accepted 23 May 2014

Available online 2 June 2014

Keywords:

Formic acid oxidation

Methanol oxidation

Potential oscillation

Anhydrous conditions

Effect of water

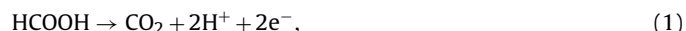
ABSTRACT

We have found that the formic acid oxidation on Pt does not produce current in the potential range between 0.05 and 1.4 V (vs. a hydrogen electrode) in the absence of water, while the methanol oxidation produces a large current in the absence of water. Investigations by surface-enhanced infrared absorption spectroscopy (SEIRAS) simultaneously with electrochemical measurement clarify that, for formic acid oxidation, adsorbed CO is not oxidized even at 1.4 V due to the absence of water, and thus practically no current is produced. On the other hand, for methanol oxidation, the amount of adsorbed CO decreases at a high potential, which leads us to think that adsorbed CO reacts with methanol to form methyl formate to produce vacant sites, where methanol is oxidized to form formaldehyde or methyl formate. With increasing water concentration for formic acid oxidation, the current in the negative-going potential sweep grows larger due to the increasing number of vacant sites produced by the oxidation of adsorbed CO with water, hydroxide or oxide, the last two are formed from water. Potential oscillations during oxidation of formic acid and methanol with no or low water concentrations have also been investigated.

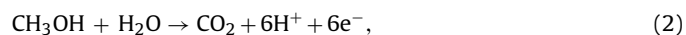
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1. Introduction

The reaction formula of electrochemical formic acid oxidation is



meaning that water is not required for production of current. On the other hand, that of methanol is



meaning that water is required for production of current. A question then arises that, under conditions without water but with sulfuric acid as an electrolyte, the methanol oxidation does not really produce current, while the formic acid oxidation does independently of the water concentration.

The question, however, is related not only to surface reactions but also to reactions in the bulk solution. It is well known that

formic acid is decomposed in two ways, dehydration and dehydrogenation, as



Since the standard Gibbs energies of reactions (3) and (4) are negative, -12.9 and $-33.1 \text{ kJ mol}^{-1}$, respectively, both reactions can proceed at room temperature with a catalyst like sulfuric acid. If sulfuric acid is present in excess, reaction (3) prevails over reaction (4) due to a strong dehydrating property of sulfuric acid, producing saturated CO in the solution together with water, causing the current to decrease due to the CO adsorption. However, with a low concentration of sulfuric acid, 0.5 mol dm^{-3} (M), reaction (4) may prevail due to a larger standard Gibbs energy decrease than that of reaction (3), producing H_2 and causing the current to increase. On the other hand, methanol is stable even with a little sulfuric acid at room temperature. That is, dehydration of methanol,



only proceeds when the solution is heated above 100°C and dehydrogenation,



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has a standard reaction Gibbs energy of approximately $+59 \text{ kJ mol}^{-1}$ and is difficult to proceed accordingly. In this sense, it is interesting to examine the electrochemical reactions of formic acid and methanol in the absence of water but with a small amount of sulfuric acid as an electrolyte.

The issue is also interesting with respect both to basic research on the reaction mechanism [1–6] and to application of low temperature fuel cells using formic acid and methanol as a fuel [7–11]. Although water adsorbs and produces hydroxide and oxide [12–16], playing an important role in oxidations, especially on Pt, very few studies have been carried out relating to controlled water content using a Pt electrode. Conway et al. [17] studied the effect of trace water on the oxidation of hydrogen using trifluoroacetic acid as a solvent. Camargo et al. [18] studied the effect of water concentration on the ethanol oxidation in concentrated phosphoric acid.

The dependence of the current on the concentration of formic acid or methanol has been studied [19,20] rather than that on the concentration of water. Although both dependences are the two sides of a relationship between current and solution composition, the studies up to now have been carried out for very high molar fractions of water, e.g., 0.76 (10 M methanol) and 0.97 (1 M methanol). Here, the methanol solutions contain 0.5 M H_2SO_4 . We therefore think that investigation on the oxidation of formic acid and methanol with no or little water is also important for obtaining an overall picture of the reaction.

It is almost established [1,2,21,22] that the electrochemical oxidation of formic acid and methanol on Pt in an acidic aqueous solution proceeds via a dual path mechanism, consisting of direct and indirect paths. It is also established [1,23–28] that the indirect path involves adsorbed CO, which requires water as an oxygen source to form CO_2 . Almost all the observed current in the voltammogram is produced through the direct path on vacant sites. For formic acid oxidation, the direct path produces only CO_2 , while for methanol oxidation, it produces formaldehyde and formic acid besides CO_2 [29–34]. Abd-El-Latif et al. [35] have recently argued that methyl formate, the amount of which has often been assumed to be an indirect measure of that of formic acid formed, is directly formed on the surface but not in the liquid phase by esterification. They and Nagao et al. [36] have reported that the product ratio of methyl formate to CO_2 increases with increasing methanol concentration, from 0.1 to 0.2 M [35] and from 0.5 to 2 M [36].

Oxidation of formic acid and methanol produce potential oscillation under constant current conditions [37–43]. It is well known [40–44] that a hidden negative differential resistance (hidden NDR) is required for the appearance of oscillation. The NDR is partially found on the positive potential side of a current peak at around 0.6 V, peak I, in the voltammogram. Several reasons for the appearance of the NDR have been proposed, such as formation of interfacial CO_2 [45] and adsorption of OH [44], formic acid (and/or formate anion) [46], and bridge-bonded formate [47,48]. Gojuki et al. have recently argued [49] that it is due to water adsorption, which increases in its amount with increasing potential due to the enhancement of water-surface interaction [50–52].

This paper describes oxidations of formic acid and methanol on Pt, with an emphasis on very low water concentrations, and potential oscillations during the oxidations under the same conditions.

2. Experimental Section

Details of experimental setup have been described elsewhere [50,53]. In short, experiments were conducted in a three-electrode cell isolated from the surrounding air. The reference electrode was a hydrogen electrode in an aqueous 0.5 M sulfuric acid solution. Although the reaction solution contained 0.5 M sulfuric acid, this is

Table 1

Conductivities, κ_{F} and κ_{M} , for formic acid and methanol solutions, respectively, containing 0.5 M H_2SO_4 . n : water concentration, m_{F} and m_{M} : formic acid and methanol concentrations, respectively.

n/M	m_{F}/M	$\kappa_{\text{F}}/\text{S m}^{-1}$	n/M	m_{M}/M	$\kappa_{\text{M}}/\text{S m}^{-1}$
0.0	26	1.5	0.0	24	3.3
1.0	25	1.5	1.0	24	2.7
3.0	24	1.9	3.0	23	2.8
10	21	3.3	10	20	4.4
17	17	5.2	17	17	6.1
33	10	9.6	32	10	10.0

not a reversible hydrogen electrode (RHE). This is because the activity of hydrogen ions is not the same as that in the reaction solution and a liquid junction potential is present when the reaction solution is formic acid (or methanol) containing 0.5 M H_2SO_4 with no or little water. However, we suppose that the potential measured is not so different from that with a correct RHE. The counter electrode was a platinized Pt wire. To avoid contamination of the reaction solution with water from the reference electrode, the hole of capillary end of the reference electrode was made extremely small by trial and error so that the hole could not be observed with a naked eye or a stereo microscope. The hole was small such that water with the surface level 5 cm higher than the position of the capillary end flowed into the reference electrode at a speed of less than 0.2 mm in height/day.

We used two different kinds of working electrodes: a Pt wire (purity: 99.99%, real surface area: 2.5 cm^2 , roughness factor: 1.16) for electrochemical measurement and a thin ($\sim 50 \text{ nm}$) Pt film (real surface area: 12.4 cm^2 , roughness factor: 6.9) for infrared spectroscopic and electrochemical measurements. The Pt film was deposited on one of the three rectangular faces of a triangular Si prism (20 mm on a side and 25 mm long) by a procedure similar to that described by Miki et al. [54]. The real surface area was determined by assuming a charge of 0.210 mC/cm^2 for a monolayer of adsorbed hydrogen on Pt.

The electrolyte solution without water was carefully prepared with sulfuric acid (0.5 M, “Super Special Grade”, 96–98%) and formic acid (“Special Grade”, 98–100%) or methanol (“Super Dehydrated”, water content: less than 0.001%) immediately after opening bottles. All chemicals were of Wako Pure Chemical Industries, Ltd., Japan. The water concentration, 0.001%, of the “Super Dehydrated” methanol corresponds to approximately 0.4 mM. The working and counter electrodes, and the glass cell and its components were all washed with formic acid or methanol for three times before use. To add water, 0.5 M sulfuric acid aqueous solution prepared with Millipore “Milli-Q” water, deoxygenated by bubbling with nitrogen gas in advance, was added into the cell to a desired water concentration. Solution conductivities were measured with an electric conductivity meter (Horiba, Ltd., Japan, F-55) and are shown in Table 1.

To deoxygenate the electrolyte solution, nitrogen gas was bubbled through the solution before measurement and was passed over the solution during the measurement to keep the solution

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