



Different behavior of adsorbed bridge-bonded formate from that of current in the oxidation of formic acid on platinum



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ABSTRACT

Clarification has been made whether or not adsorbed bridge-bonded formate (HCOO_B) is the reactive intermediate in the direct path during oxidation of formic acid, using surface-enhanced infrared absorption spectroscopy (SEIRAS) simultaneously with electrochemical measurement. With a decrease in the sweep rate of cyclic voltammetry, the potential of the maximum current in the positive-going sweep decreases from 0.9 to 0.6 V, while that of the maximum HCOO_B band intensity in the positive-going sweep is almost constant at approximately 0.9 V. When the potential is held at 0.7 V after a potential increase or decrease, the current monotonically decreases, while the HCOO_B band intensity keeps constant. In the absence of adsorbed CO, the current presents a maximum at approximately 0.5 V, while the HCOO_B band intensity does at approximately 0.9 V. All these results clearly show that HCOO_B is not the reactive intermediate. The second order kinetics for the decomposition of HCOO_B has also been discussed.

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1. Introduction

The electrochemical oxidation of formic acid on Pt in acidic media has been extensively investigated [1–6] as a model electrocatalytic reaction because it is the simplest electrocatalytic reaction involving an organic molecule. The application of the reaction includes low temperature direct formic acid fuel cells (DFAFCs) [7,8]. It has been widely accepted that the reaction proceeds via a dual path mechanism composed of a direct path and an indirect path [1–3]. The indirect path involves adsorbed CO [9–11], which is formed by dehydration of formic acid at potentials lower than approximately 0.6 V (vs. RHE). The adsorbed CO blocks the surface adsorption site at the stated potentials but is oxidized to CO_2 at potentials higher than 0.6 V.

The direct path proceeds via a reactive intermediate, producing most current observed in the voltammogram. Sun et al. [12] reported that the reactive intermediate was a carboxylic acid species adsorbed on the surface through the carbon atom ($-\text{COOH}$) by infrared reflection-absorption spectroscopy (IRRAS). The species, however, was not detected by surface-enhanced infrared absorption spectroscopy in the attenuated total reflection mode (ATR-SEIRAS) [13–20] developed by Osawa et al. [21–24]. Because IRRAS involves a thin electrolyte layer confined between

the electrode and an IR-transparent window, mass transport of reactants and products is suppressed and, hence, IRRAS is not pertinent to measure dynamical changes on the electrode. Such shortcomings have been overcome by SEIRAS, in which bulk solutions freely approach the electrode and, furthermore, a high surface selectivity and sensitivity is obtained [13–16].

Osawa et al. [13–16] have found that, other than adsorbed CO, the only formic acid-related surface species observed by SEIRAS is formate adsorbed on the surface in a bridging conformation, that is, bonded via both oxygen atoms to two surface Pt atoms. They argued that adsorbed bridge-bonded formate (HCOO_B) is the reactive intermediate in the direct path, based on the experimental fact of the close similarity of potential dependence of the current and HCOO_B band intensity [16]. The argument was also based on the ability to explain the mechanism of the appearance of a current peak at around 0.6 V (vs. RHE) during the positive-going potential sweep in the voltammogram [14,15,25,26]. The current peak produces, at the positive potential side of the peak, a negative differential resistance necessary for the appearance of potential oscillation [27–29]. Grozovski et al. [30] have supported the idea of HCOO_B as the reactive intermediate by use of Pt(111) and Cuesta et al. [31] have proposed that HCOO_B is an intermediate common to the direct and indirect paths.

On the other hand, Chen et al. [17,19,20,32] have thought differently that HCOO_B is not a reactive intermediate in the direct path and is rather a site-blocking spectator, based on the experimental data obtained mainly with a thin-layer electrochemical flow cell coupled to SEIRAS. Peng et al. [33] have suggested that HCOO_B is

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not a reactive intermediate in the main pathway on Sb-modified Pt electrodes, based on the fact that by electrodepositing Sb on Pt the formic oxidation current increased simultaneously with a decrease in the amount of HCOO_B . Joo et al. [34] have reported that the reactive intermediate in the direct path is not HCOO_B but is a weakly-adsorbed formate precursor, from experiments over a wide pH range.

The role of HCOO_B is, thus, controversial at the moment. To determine whether it is the reactive intermediate in the direct path or not, we have studied in detail the potential dependent behavior of HCOO_B on unmodified Pt, behavior which was a strong evidence for HCOO_B being the reaction intermediate in the direct path. In this paper, we clarify a distinctly different behavior between the current and HCOO_B , concluding that HCOO_B is not the reactive intermediate in the direct path.

2. Experimental Section

Experiments were conducted in a three-electrode cell isolated from the surrounding air. The reference electrode was a reversible hydrogen electrode (RHE) in the supporting electrolyte solution (0.5 M H_2SO_4 , M: mol dm^{-3}). The counter one was a platinized Pt wire in a glass tube with bubbling nitrogen gas (Nippon Sanso Corp., Japan, over 99.9999%), a tube which was separated by a glass frit from the reaction solution. The working electrode was a thin (~ 50 nm) Pt film deposited on one of the three rectangular faces of a triangular Si prism (20 mm on a side and 25 mm long, Pier Optics Co., Ltd., Japan, FZ) by the following procedure, which is similar to the one described by Miki et al. [13].

First, the Si substrate surface was made hydrophobic by placing droplets of a 40% NH_4F (Wako Pure Chemical Industries, Ltd., Japan, "First Grade") solution over it for 30–60 s. After rinsing with Millipore "Milli-Q" water and drying with a nitrogen gas blow, Pd was deposited on the hydrophobic Si substrate surface by placing droplets of a mixture of 1 wt% HF (Kanto Chemical Co., Inc., Japan, 50%, "Atomic Absorption Analysis Grade") and 0.17 wt% PdCl_2 (Kanto Chemical Co., Inc., "Special Grade") over it for 4 min to improve the adhesion of the Pt film to the substrate [35]. After rinsing with Millipore "Milli-Q" water and drying with a nitrogen gas blow, Pt was subsequently deposited on the Pd layer by placing droplets of a mixture of an ammonia solution (Wako Pure Chemical Industries, Ltd., 28–30%, "First Grade") and a plating solution (Tanaka Kinkinzoku, Japan, LECTROLESS Pt100) including a base solution and a reducing agent over it at 65–68 °C for approximately 3 min. Although the deposited Pt films were not analyzed, we suppose they were similar to those analyzed by Miki et al. [13]. Assuming a charge of 0.210 mC/cm^2 for the monolayer of adsorbed hydrogen on Pt [36], the true surface area was estimated to be 12.4 cm^2 , the roughness factor being 6.9 since the geometrical surface area was 1.8 cm^2 .

The electrolyte solution, containing 0.5 M sulfuric acid, was prepared by adding sulfuric acid (Wako Pure Chemical Industries, Ltd., "Super Special Grade") and, if necessary, formic acid (Wako Pure Chemical Industries, Ltd., "Special Grade") to Millipore "Milli-Q" water. 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 deoxygenated. The working electrode was pretreated by repeatedly applying a triangular potential sweep between 0.05 and 1.4 V before each run. The solution temperature was room temperature (24 ± 2 °C).

SEIRA spectra were recorded on an Agilent Technologies Varian 670-IR Fourier transform infrared spectrometer equipped with an MCT detector and a homemade single-reflection accessory. The spectrometer was operated with a spectral resolution of 4 cm^{-1}

either in the kinetic mode in which the time required for recording one interferogram was 0.066 and 0.24 s at 150 and 37.5 kHz, respectively, or in the rapid mode (37.5 kHz) involving an interval time. Specifically, the time resolution adopted for potential dynamic measurements was 0.066 s for the sweep rate of 1 V/s, 0.24 s for 0.1 V/s, and 2.4 s (ten interferograms co-added) for 0.01 V/s. Spectra are shown in the absorbance units defined as $A = -\log(R/R_0)$, where R_0 and R represent the reflectance at the reference potential, normally 1.4 V, and at the sample potential, respectively, both in the formic acid containing solution.

Using a function generator (Hokuto-Denko Co., Ltd., Japan, HB-105) and a potentiostat/galvanostat (Hokuto-Denko Co., Ltd., HA-501G), the time sequence of the potential or current values was acquired through an AD converter (National Instruments Corp., PCI-6034E) and saved in a personal computer after averaging 100 values acquired at a sampling rate of 100 kHz or slower. At the same time, it was recorded with an X-T or X-Y recorder.

3. Results

3.1. Behavior of current and HCOO_B with 0.1 M formic acid during potential sweep.

Fig. 1a shows a cyclic voltammogram (CV) for the oxidation of 0.1 M formic acid between 0.05 and 1.4 V at a sweep rate of 0.1 V/s at room temperature. In the positive-going potential sweep, the current shows two peaks, peak I at around 0.6 V and peak II at around 0.9 V. In the reverse negative-going potential sweep, two other current peaks are observed, peak IV at around 0.7 V, and peak V (a

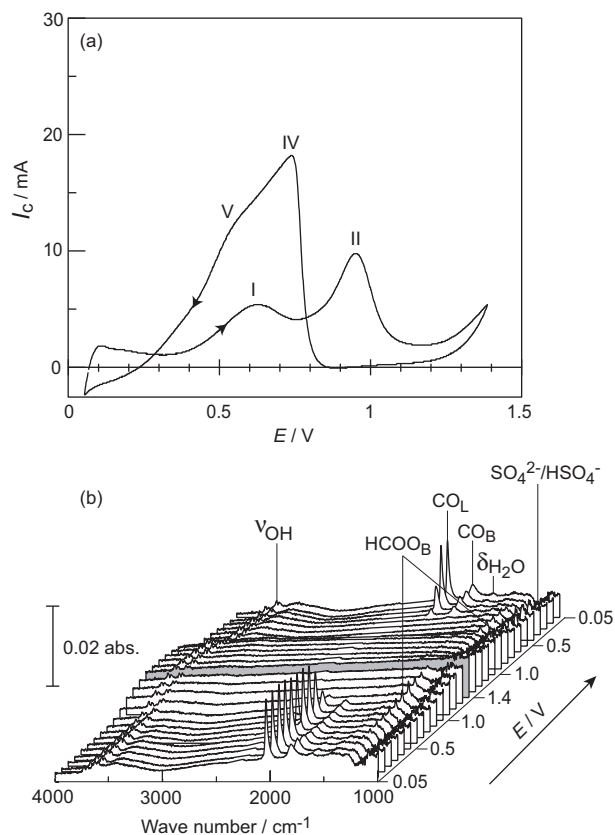


Fig. 1. A cyclic voltammogram, CV, (a) for 0.1 M formic acid oxidation at a sweep rate of 0.1 V/s and selected SEIRA spectra (b) of the Pt surface acquired simultaneously with the CV. The current shows two peaks, peaks I and II, in the positive-going potential sweep and two other peaks, peaks IV and V, in the negative-going potential sweep.

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