Hidden negative differential resistance in the oxidation of formic acid on platinum

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ARTICLE INFO

ABSTRACT

Clarification is reported of the mechanism for the appearance of hidden negative differential resistance, HNDR, in the oxidation of formic acid using surface-enhanced infrared absorption spectroscopy, SEIRAS, simultaneously with electrochemical measurements. The HNDR is necessary for the appearance of potential oscillation. After holding the potential at 0.7 V for 300 s, the voltammogram exhibits a long monotone current decrease, which means NDR and is named LCD, in a wide potential range between 0.5 and 0.8 V. In the LCD potential range, the voltammogram is reversible with regard to potential sweep directions and there is neither adsorbed CO nor adsorbed hydroxide. The latter information is obtained by the voltammogram in the absence of formic acid and by the change in the baseline of the SEIRA spectra. We hence think that the LCD appears due to the adsorption of water, which increases in residence time on the surface with potential due to the water-surface interaction. Based on this idea, we have been able to mathematically reproduce the experimentally observed oscillation pattern. Using a pseudo-stationary voltammogram and simultaneously measured SEIRA spectra, we conclude that the HNDR appears due to the formation of adsorbed CO, which hides the LCD between 0.5 and 0.7 V.

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1. Introduction

It is almost established that the electrochemical oxidation of formic acid on Pt in acidic media proceeds via a dual path mechanism [1–3], consisting of direct and indirect paths. Almost all the observed current in the voltammogram is produced through the direct path. It is also established that the indirect path involves adsorbed CO [4–6]. One of the important issues for the development of low temperature direct formic acid fuel cells (DFAFCs) [7,8] is to reduce poisonous adsorbed CO, which, however, plays an important role in the oscillation phenomena.

The electrochemical oscillation observed during oxidation of formic acid has long been studied since Müller and Hindesmith reported potential oscillation during oxidation of formic acid in sulfuric acid on Rh plated Pt in 1927 [9]. The oscillation phenomenon includes current oscillations under constant potential conditions and potential oscillations under constant current conditions. The former requires an ohmic resistance, sometimes an external series resistance in addition to the solution resistance, between working and reference electrodes [10–13] and therefore involves changes both in the current and interfacial potential difference, a potential difference across the double layer. On the other hand, the latter does not require an ohmic resistance and involves a change only in the interfacial potential difference, which is the same as the outer potential except for a constant difference, which is proportional to an ohmic resistance and applied current. Since the latter shows a pure potential behavior with a constant current, we have been studying galvanostatic potential oscillations during formic acid oxidation [14–17].

The potential oscillation during formic acid oxidation has been studied by various methods other than electrochemical ones, such as differential electrochemical mass spectroscopy, DEMS, [18], surface-enhanced infrared spectroscopy, SEIRAS, [19], methods using an electrochemical quartz crystal microbalance (nanobalance), EQCM (EQCN), [20–22], probe beam deflection [23], surface stress [21,24], and ultrasound [25]. Incidentally, to our knowledge, the potential oscillation has not been reported on low-index Pt single crystals, whereas the current oscillation has been reported [13,26–28].

It is often said that during the potential oscillation under constant current conditions, the potential increases to a high value due to surface deactivation caused by the formation of adsorbed CO, a surface poison, and there and then decreases to a low value

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due to surface activation caused by the oxidation of adsorbed CO. However, this is not all for the appearance of oscillation because the potential, also adsorbed CO coverage, stops oscillating and approaches a constant value only by the mechanism of formation and oxidation of adsorbed CO.

To sustain oscillation, it is well known [13,29–32] that the negative differential resistance (NDR) is required. The NDR is partially found on the positive potential side of a current peak at around 0.6 V, peak I, in the voltammogram. The reason for the current decrease with potential has been proposed to be the presence of interfacial CO_2 [33] or adsorption of some species such as water [14,34,35], OH [13], formic acid (and/or formate anion) [36], and bridge-bonded formate [19,37]. For the appearance of potential oscillation, the NDR should be hidden [13,29–32,38] by a slow process which provides a positive slope, a positive resistance, in the stationary voltammogram, whereas a hiding process is not required for the appearance of current oscillations. The hidden NDR, HNDR, is necessary for the appearance of potential oscillations. This paper clarifies electrochemically and spectroscopically what causes the NDR and what is a slow hiding process.

2. Experimental Section

Experimental details have been described elsewhere [17]. In short, experiments were conducted in a three-electrode cell isolated from the surrounding air, with a reversible hydrogen electrode (RHE, 0.5 M H_2SO_4, M: mol dm^{-3}) as the reference electrode and a platinized Pt wire as the counter electrode. The working electrode was a thin ($\sim$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) by a procedure similar to that described by Miki et al. [39]. Assuming a charge of 0.210 mC/cm^2 for the monolayer of adsorbed hydrogen on Pt [40], 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 and 0.1 or 1 M formic acid, was prepared with Millipore "Milli-Q" water and special or higher grade chemicals. 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).

Spectra were taken by surface-enhanced infrared absorption spectroscopy, SEIRAS, [39] in the attenuated total reflection mode. They 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 spectral and time resolutions were 4 cm^{-1} and 0.24 s, respectively. Spectra are shown in the absorbance units defined as $A = -\log(R/R_0)$, where R_0 and R represent the reflectance at a reference potential, normally 1.4 V, and at a sample potential, respectively, both in a formic acid containing solution. 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.

3. Results

3.1. SEIRA spectra during potential oscillation.

Fig. 1(a) shows a typical potential oscillation pattern generated by the oxidation of 1 M formic acid on polycrystalline platinum at a constant applied current of 7 mA at room temperature. We can see that the potential increases slowly from a lower limit potential, 0.52 V, to around 0.6 V, where it begins to increase rapidly to
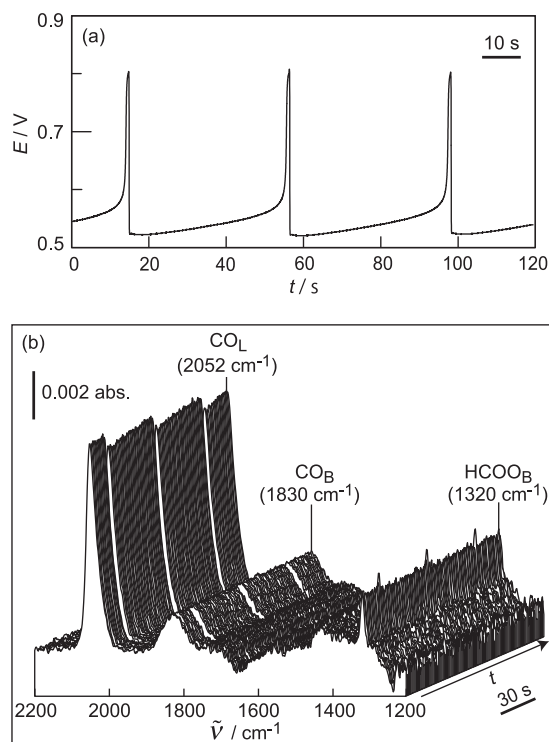

Fig. 1. A typical potential oscillation pattern (a) and selected simultaneously-measured SEIRA spectra (b) during oxidation of 1 M formic acid at a current of 7 mA. $\tilde{\nu}$ is wavenumber.

a higher limit potential, approximately 0.8 V, and then decreases steeply to the lower limit potential.

A series of selected SEIRA spectra recorded simultaneously with the oscillation potential measurement is shown in Fig. 1(b) in the wavenumber range between 2200 and 1200 cm^{-1}. A spectrum recorded at 1.4 V in the presence of formic acid was used as the reference. According to the literature [19,39,41], the assignment of each absorption band is as follows: 2052 cm^{-1}, CO linearly bonded to a Pt atom; 1830 cm^{-1}, CO bridge-bonded to two Pt atoms; 1320 cm^{-1}, formate bonded via both oxygen atoms to two surface Pt atoms, that is, in a bridging configuration. The three bands are, respectively, denoted as CO_L, CO_B, and $HCOO_B$ in this paper. We regard the integrated band intensity of CO_L as proportional to the amount, or coverage, of CO_L [5,19,42–44]. We can see that CO_L, CO_B, and $HCOO_B$ also oscillate in absorbance synchronously with the oscillating potential.

To investigate the relationship between the oscillating potential and the integrated band intensities of CO_L, CO_B, and $HCOO_B$ during oscillation, we have plotted them for one period of oscillation in Fig. 2. In the figure, the changes in the wavenumber of CO_L and CO_B are also included, although that of $HCOO_B$ is not shown because it was very small, only ca. 2 cm^{-1} up at around a higher limit potential.

When the potential slowly increases during oscillation, the integrated band intensities and wavenumbers of the three species change very little. When the potential increases rapidly, however, the band intensities of CO_L and CO_B decrease, while that of $HCOO_B$ increases. Such a change in the band intensities is reasonable if we remember their change in the voltammogram [17,19,37,41,45,46], which is partially shown in Fig. 4(b1-b4). Namely, when the potential increases from 0.6 to 0.8 V, the band intensities of CO_L and CO_B decrease and that of $HCOO_B$ increases, both monotonically. Regarding the wavenumbers of CO_L and CO_B, they increase during a rapid potential increase in the oscillation. This is thought to be due to the Stark tuning effect [47,48] or electron back-donation from the metal to $2\pi^*$ orbital of CO [49], or both, which is also observed