Electrochemical Oscillations

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Current Oscillations during Formic Acid Oxidation on a Pt Electrode: Insight into the Mechanism by Time-Resolved IR Spectroscopy**

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Various types of instabilities occur in chemical systems maintained under nonequilibrium conditions,[1] and this is also the case for several electrochemical systems.[1,2] In the

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electrochemical oxidation of formic acid on Pt and Pt-group metals, instabilities can cause spontaneous potential and current oscillations under galvanostatic (constant current) and potentiostatic (constant potential) conditions, respectively. The electrooxidation of formic acid is one of the most fundamental electrocatalytic systems and has a great relevance to low-temperature fuel cells; therefore, the mechanism of the oscillations has long been the focus of experimental[3] and theoretical[3b,c,4] investigations.

It is generally accepted that the oxidation of formic acid follows the so-called "dual-pathway" mechanism[5]: one path involves a fast reaction via a reactive intermediate (direct path) and the other path includes a step in which an inhibiting intermediate is formed (indirect path). The reactive intermediate is generally assumed to be a carboxylic acid species (COOH) adsorbed on the surface through the C atom, whereas adsorbed CO produced by dehydration of formic acid has definitely been identified as the poisonous species by in situ IR reflection–absorption spectroscopy (IRAS).[6] The electrochemical oscillations in the oxidation of formic acid have been explained basically in terms of the dual-pathway mechanism: the periodic adsorption and oxidative removal of CO inhibits and accelerates, respectively, the direct path. The ohmic drop (iR, where i is the current and R is the resistance of the electrochemical system) also plays an important role, and current oscillations result from the interplay of chemical and electrical variables.[2,3g,4a,4c] Nevertheless, the details of the oscillations are still controversial[2–4] and further investigations are required.

The identification of the reactive intermediate and probing of the reaction dynamics are essential for a full understanding of the oscillations. Infrared spectroscopy is suitable for this purpose. Honda et al.[7] studied current oscillations by time-resolved IRAS and reported that CO coverage does not change during the oscillations. This result is inconsistent with the general consensus, and these authors proposed a model in which the periodic adsorption and desorption of the OH species ($H_2O \rightleftarrows OH_{ads} + H^+ + e^-$) results in current oscillations. However, the observed current is much larger than that expected from the adsorption and desorption of the OH species. We reexamined the current oscillations by an alternative IR spectroscopy method having a sensitivity higher than that of IRAS, namely, surface-enhanced infrared absorption spectroscopy (SEIRAS) in a Kretschmann-type attenuated-total-reflection (ATR) mode,[8] and found that the reactive intermediate is not COOH but formate (HCOO) adsorbed on the electrode surface through two oxygen atoms. Note that formate is different from the COOH species in molecular structure. On the basis of the results reported herein, we propose a new mechanism of current oscillations that is largely different from those suggested earlier.[3,4]

Figure 1a shows a typical current oscillation pattern observed in 0.5 M H_2SO_4 + 1 M formic acid solution after stepping the electrode potential (E) from 0.05 to 1.1 V versus a reversible hydrogen electrode (RHE, to which all potentials hereafter are referred). The electrode used was a thin (≈50 nm) polycrystalline Pt film deposited on the reflecting plane of a Si ATR prism by an electroless deposition technique.[9] A 30-Ω resistor was connected to the electrochemical system in series for observing the oscillations.[2,3g,4a,4c]

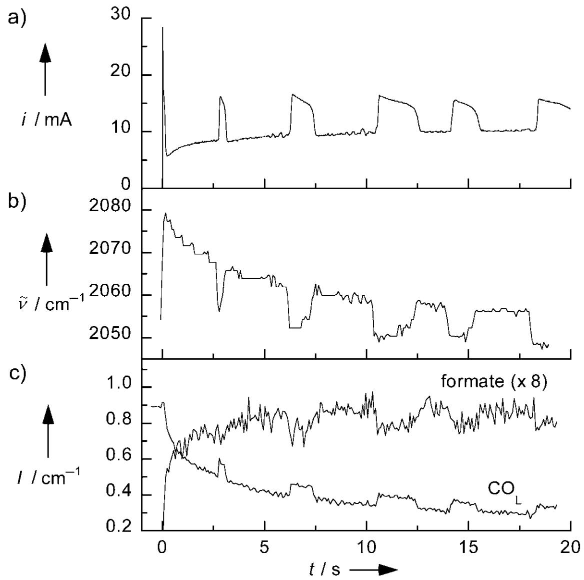

Figure 1. a) Current oscillations observed in the oxidation of formic acid at a constant potential of 1.1 V (RHE) in 0.5 M H_2SO_4 + 1 M HCOOH with a 30-Ω external resistor. b) Peak position of CO adsorbed at an atop site (CO_L). c) Integrated band intensities of CO_L and formate taken from a series of SEIRA spectra acquired simultaneously with the current–time curve.

The high sensitivity of ATR-SEIRAS enabled the time-resolved monitoring of the reaction processes occurring on the Pt electrode during the current oscillations with a time resolution of 80 ms (Figure 2). The spectral data correspond to the 10–15 s region in Figure 1a. A spectrum collected at 0.05 V in the pure electrolyte without formic acid was used as the reference. Other details of the spectral measurements have been described elsewhere.[8–10] Three bands at ≈2060, ≈1850, and 1320 cm^{-1} change their intensities and/or peak positions periodically. These bands have been assigned, from

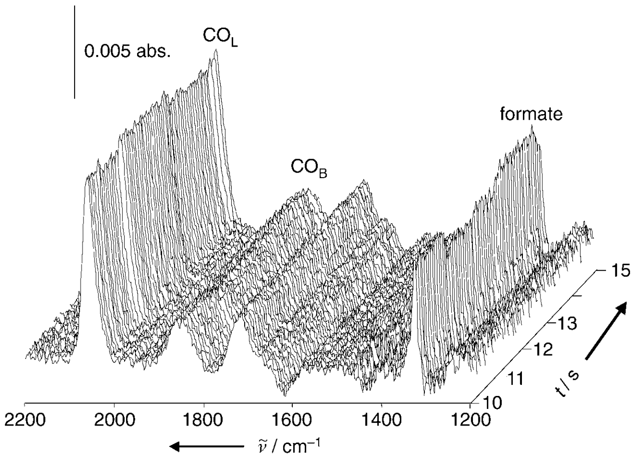

Figure 2. Time-resolved SEIRA spectra of the Pt electrode surface acquired during the current oscillations with a time resolution of 80 ms, which corresponds to the 10–15 s region in Figure 1a. A spectrum of the bare Pt surface collected at 0.05 V in the pure supporting electrolyte without formic acid was used as the reference.

higher to lower, to the stretching modes of CO molecules adsorbed at atop and bridge sites (denoted as CO_L and CO_B, respectively) and to the symmetric OCO stretching mode of formate adsorbed in a bridging configuration (bonded through both oxygen atoms to two Pt surface atoms).[9a] The band at 1720 cm^{-1} corresponds to the C=O stretching mode of formic acid in the bulk solution and thus does not change its intensity. The peak position ($\tilde{\nu}$) of the CO_L band and the integrated intensities (I) of the CO_L and formate bands are plotted in Figure 1 b and c, respectively, as a function of time. The intensity data for CO_B are omitted owing to their negligibly small change. The temporal changes of the spectral features are synchronized with the current oscillations. The CO_L band increases in intensity and decreases in peak position when the current increases (and vice versa), while the change of the formate band intensity is the opposite.

It is well-known that the CO_L band shifts to higher frequencies as the electrode potential increases as a result of the Stark effect and/or electron back-donation from the metal to the $2\pi^*$ orbital of CO.[11] Note that the potential that determines the peak position of the CO vibration is not the externally applied potential E but the potential drop across the double layer, ϕ ($= E - iR$). The peak shift observed during the oscillations can be explained by the change in ϕ; by taking into account the total resistance of the system of 35 Ω (the external resistance of 30 Ω + the measured solution resistance of 5 Ω), ϕ is roughly estimated to be 0.6 and 0.8 V in the high- and low-current states ($i \approx 15$ and ≈ 10 mA), respectively. Consequently, the peak position of the CO_L band is shifted in association with the current oscillations. The global red-shift of the peak position can be ascribed to the gradual decrease of CO_L coverage (nearly proportional to the band intensity, Figure 1 c) through the changes in the dipole–dipole interaction among CO molecules and in the electron back-donation.[11,12]

The temporal changes of the band intensities of CO_L and formate can also be explained by the change of ϕ. The linear-sweep voltammogram shown in Figure 3 a (solid curve) was recorded in the same solution at a sweep rate of 50 $mV\,s^{-1}$ without the external resistor and by correcting for the ohmic drop arising from the solution resistance (that is, $E = \phi$). The oxidation current is found to be higher at 0.6 than at 0.8 V, which is consistent with the current–time curve (Figure 1 a). Associated with the increase of the potential, the band intensity of CO_L decreases by oxidation and that of formate increases, which is also consistent with the spectral changes observed for the transient from the high-current state to the low-current state. A SEIRAS measurement for a potential step from 0.8 to 0.6 V, which corresponds to the reverse transient from the low-current to the high-current state, showed that the formate band intensity decreases quickly and the CO_L band intensity increases slowly.[13] The slow kinetics of CO formation explains the gradual decrease of the global CO band intensity during the oscillations (Figure 1 c).[14]

It is well-established that formic acid is decomposed to CO_2 through adsorbed formate on Pt in ultrahigh vacuum (UHV) and in the gas phase (CO is also produced by a side reaction).[15] Different from the reaction scheme under these conditions, COOH has long been assumed to be the reactive intermediate in the electrooxidation of formic acid without any clear experimental evidence. Despite the very high sensitivity of ATR-SEIRAS and very careful examinations, we could not detect any bands corresponding to this species. Instead we observed that formic acid is chemisorbed on the electrode as formate during the oxidation. Adsorbed formate has not been detected by IRAS, as a consequence of the limited mass transfer arising from the thin-layer geometry required for IRAS as discussed in our previous paper.[9b] As shown in Figure 3, the rapid oxidative removal of CO at $E >$ 0.8 V results in sharp increases of the formate band intensity and the oxidation current, which suggests that adsorbed formate is a reactive intermediate. With reference to the well-established reaction mechanism of formic acid oxidation in UHV and the gas phase, the electrooxidation scheme via adsorbed formate is very likely, and quite reasonable. Support for the oxidation via formate was obtained by a quick solution-exchange experiment (from $H^{13}COOH$ to $H^{12}COOH$, or the reverse) at a fixed potential of 0.6 V,[13] which showed that adsorbed formate species are completely replaced by those supplied from the solution within 1 s. The rate is fast enough to explain the observed current. An additional potential-step experiment from 1.5 V, where no carbonaceous species exist on the electrode surface, to 0.6 V showed that adsorption of formate is very fast and saturates within 80 ms (the time resolution used). Therefore, the decomposition of formate to CO_2 is believed to be the rate-determining step. However, isotopic substitution for adsorbed

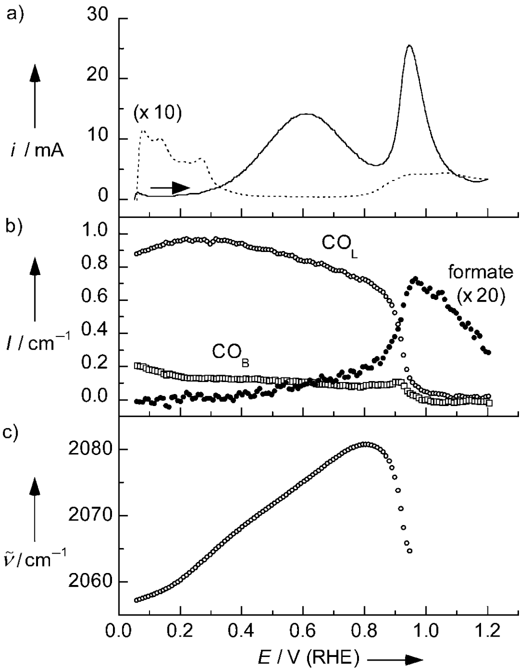

Figure 3. a) Linear-sweep voltammograms for the Pt electrode in 0.5 M H_2SO_4 with (——) and without (-----) 1 M HCOOH recorded at a sweep rate of 50 $mV\,s^{-1}$ by correcting for ohmic drops. b) Integrated band intensities of CO_L, CO_B, and formate and c) peak position of CO_L plotted as a function of potential. The spectral data were taken from a series of SEIRA spectra acquired simultaneously with the solid-line voltammogram.

CO was negligibly slow and thus the indirect path scarcely contributes to formic acid oxidation.

Adsorbed CO can suppress the oxidation of formic acid by blocking vacant sites for formate adsorption. Consequently, the rapid oxidative removal of CO at $E > 0.8$ V leads to an increase of formate coverage and results in a sharp increase of the oxidation current (Figure 3). However, the situation is different in the potential range of 0.6–0.8 V where the current oscillations occur: the oxidation current decreases despite the decrease of CO and the increase of formate. This result indicates that the reaction rate (that is, current) is not a simple function of formate coverage. The suppression of the reaction at $0.6 < E < 0.8$ V, often termed as the negative differential resistance (NDR), plays a decisive role in the oscillation and has been discussed extensively in earlier studies.[2–4] Adsorbed OH species have generally been assumed to cause the NDR. For example, Strasser et al.[3g,4c] proposed that all CO species are oxidized in the NDR region and the adsorption of OH species at vacant sites generated by CO removal block the direct path via COOH formation. This proposal is, however, inconsistent with our data (Figure 3). In addition, the current arising from OH adsorption is not observed at $E < 0.8$ V in the pure supporting electrolyte (Figure 3, dashed curve). Even if the adsorption of OH species could be possible, it would be suppressed by the adsorption of formate.

A hint to help understand the NDR has been given by UHV studies of the decomposition of formate and acetate to CO_2 on transition-metal surfaces.[16] The rate of the decomposition is remarkably slowed down at high formate (or acetate) coverage (θ_f), and once the reaction is initiated the rate is increased *explosively*, which is called surface explosion.[16] The suppression of the reaction before the explosion has been explained by the adsorbed species themselves blocking each other's decomposition by steric hindrance.[16b,c] The necessity for the suppression is high *local* coverage (practically independent of the global coverage).[16b,c] This condition is likely to be fulfilled in the electrooxidation of formic acid, judging by the potential dependence of the CO_L vibrational frequency (Figure 3c). Recalling that the vibrational frequency is a function of both potential and coverage,[11,12] the linear potential dependence up to 0.8 V indicates that CO_L is oxidized without changing the dipole–dipole interactions. This result can be understood by assuming that CO is oxidized to form islands of vacant sites (that is, through a nucleation-and-growth mechanism) and formate is adsorbed at the generated vacant sites (by forming islands of formate).

The rate of decomposition of formate (or acetate) is given by the second-order rate equation (1) by modifying the original rate equation[16] to include CO coverage ($\theta_{CO} = \theta_{CO_L} + 2\theta_{CO_B}$).

$$-\frac{d\theta_f}{dt} = k\,\theta_f(1-2\,\theta_f-\theta_{CO}) \qquad (1)$$

The factor 2 of θ_f and θ_{CO_B} arises from the requirement of two vacant sites for the adsorption of these species. The θ_f dependence of the reaction rate is schematically shown in Figure 4 for low and high CO coverages. These plots show that the rate decreases with an increase of CO coverage and also with an increase of θ_f crossing $(1-\theta_{CO})/4$ (the coverage at which the reaction rate is maximal). Formate coverage increases almost linearly with the potential and CO coverage does not change significantly at $E < 0.8$ V (Figure 3). Therefore, the curves can be regarded as voltammograms by replacing θ_f coverage with potential, although the actual system is more complicated on account of the potential dependence of rate constants and the effect of the diffusion of formic acid.[4] The second-order rate equation (1) can reasonably explain the voltammmetric behavior in the low-potential region (that is, the current peak centered at 0.6 V and the NDR). By using this figure, the current oscillation can be explained as follows. Starting from the active (high-current) state, CO adsorption decreases the reaction rate (a), which results in an increase of ϕ and leads to an increase of formate coverage (b). The increase of formate coverage suppresses formate decomposition and increases ϕ further (that is, autocatalytically) to reach the less-active (low-current) state. Once ϕ reaches a certain high value, both CO oxidation and formate decomposition are accelerated, and the system is shifted to the initial active state (c).

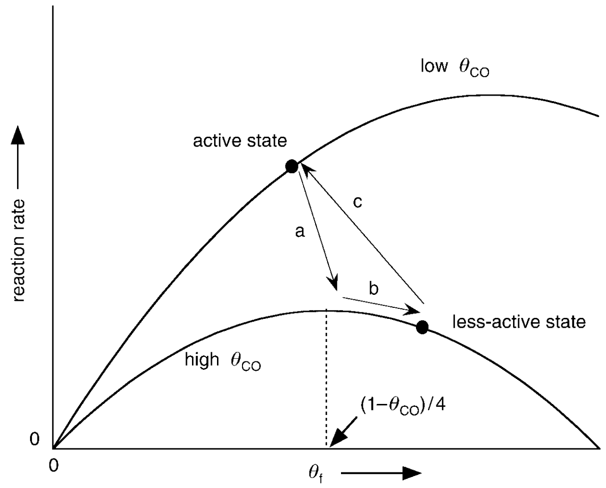

Figure 4. Schematic drawing of the formate coverage (θ_f) dependence of the reaction rate for high and low CO coverages (θ_{CO}) calculated by Equation (1).

Notably, Wojtowicz et al.[3b] proposed a nonlinear rate equation similar to Equation (1) to explain oscillations in the electrooxidation of formic acid, and they showed mathematically that such nonlinear rate equations are indispensable for oscillations, although the reaction mechanism assumed was totally different from that found herein. A mathematical analysis by the same procedure showed that sustained oscillations are possible in the framework of our new mechanism.[13]

In conclusion, we observed that formic acid is oxidized to CO_2 on Pt electrodes via adsorbed formate and that the decomposition of formate is rate-determining. The result forced us to revise earlier models of current oscillations to include adsorbed formate. The central part of the model proposed herein is that formate species suppress each other's decomposition. Adsorbed CO acts not only as a site-blocking species but also suppresses the decomposition of formate. Coupled with the change in ϕ, the oxidation and formation of CO modify the rate of formate decomposition and lead to current oscillations.

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[1] For example, see: U. F. Franck, *Angew. Chem.* **1978**, *90*, 1; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 1.

[2] a) J. L. Hudson, T. T. Tsotsis, *Chem. Eng. Sci.* **1994**, *49*, 1493; b) M. T. M. Koper in *Advances in Chemical Physics*, *Vol. 92* (Eds.: I. Prigogine, S. A. Rice), Wiley, New York, **1996**, p. 161; K. Krischer in *Modern Aspects of Electrochemistry*, *Vol. 32* (Eds.: B. E. Conway, J. O. M. Bockris, R. E. White), Kluwer Academic/Plenum, New York, **1999**, p. 1.

[3] a) E. Müller, S. Tanaka, *Z. Elektrochem.* **1928**, *34*, 256; b) J. Wojtowicz, N. Marincic, B. E. Conway, *J. Chem. Phys.* **1968**, *48*, 4333; c) F. N. Albahadily, M. Schell, *J. Electroanal. Chem.* **1991**, *308*, 151; d) N. Markovic, P. N. Ross, *J. Phys. Chem.* **1993**, *97*, 9771; e) H. Okamoto, *Electrochim. Acta* **1992**, *37*, 37; f) F. Raspel, M. Eiswirth, *J. Phys. Chem.* **1994**, *98*, 7613; g) P. Strasser, M. Lübke, F. Raspel, M. Eiswirth, G. Ertl, *J. Chem. Phys.* **1997**, *107*, 979; h) T. J. Schmidt, B. N. Grgur, N. M. Markovic, P. N. Ross, *J. Electroanal. Chem.* **2001**, *500*, 36.

[4] a) M. T. M. Koper, J. H. Sluyters, *J. Electroanal. Chem.* **1994**, *371*, 149; b) H. Okamoto, *Chem. Phys. Lett.* **1996**, *248*, 289; c) P. Strasser, M. Eiswirth, G. Ertl, *J. Chem. Phys.* **1997**, *107*, 991.

[5] A. Capon, R. Parsons, *J. Electroanal. Chem.* **1973**, *45*, 205.

[6] a) K. Kunimatsu, H. Kita, *J. Electroanal. Chem.* **1987**, *218*, 155; b) D. S. Corrigan, M. J. Weaver, *J. Electroanal. Chem.* **1988**, *241*, 143.

[7] Y. Honda, M.-B. Song, M. Ito, *Chem. Phys. Lett.* **1997**, *273*, 141.

[8] a) M. Osawa, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2861; b) M. Osawa in *Vibrational Spectroscopy*, *Vol. 1* (Eds.: J. Charmers, P. R. Griffiths), Wiley, Chichester, **2002**, p. 785.

[9] a) A. Miki, S. Ye, M. Osawa, *Chem. Commun.* **2002**, 1500; b) A. Miki, S. Ye, T. Senzaki, M. Osawa, *J. Electroanal. Chem.* **2004**, *563*, 23.

[10] a) M. Osawa, K. Ataka, K. Yoshii, T. Yotsuyanagi, *J. Electron Spectrosc. Relat. Phenom.* **1993**, *64*/65, 371; b) K. Ataka, T. Yotsuyanagi, M. Osawa, *J. Phys. Chem.* **1996**, *100*, 10664.

[11] For example, see: R. J. Nichols in *Adsorption of Molecules at Metal Electrodes* (Eds.: J. Lipkowski, P. N. Ross), VCH, New York, **1992**, p. 347.

[12] F. M. Hoffmann, *Surf. Sci. Rep.* **1983**, *3*, 107.

[13] See the Supporting Information.

[14] The rate of CO formation decreases as the potential is increased or the oxidation overwhelms the adsorption at high potentials. Consequently, the slow growth of the CO_L band is not observed clearly in the high-current state where ϕ increases gradually with time. Nevertheless, it can lead to the long-term gradual decrease of the global CO_L band intensity.

[15] a) M. R. Columbia, A. M. Crabtree, P. A. Thiel, *J. Am. Chem. Soc.* **1992**, *114*, 1231; b) M. R. Columbia, P. A. Thiel, *J. Electroanal. Chem.* **1994**, *369*, 1.

[16] a) J. L. Falconer, R. J. Madix, *Surf. Sci.* **1974**, *46*, 473; b) T. J. Cassidy, M. D. Allen, Y. Li, M. Bowker, *Catal. Lett.* **1993**, *21*, 321; c) R. G. Sharpe, M. Bowker, *J. Phys. Condens. Matter* **1995**, *7*, 6379.