

## ARTICLE

# A Revisit to the Role of Bridge-adsorbed Formate in the Electrocatalytic Oxidation of Formic Acid at Pt Electrodes

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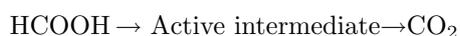
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The mechanism and kinetics of electrocatalytic oxidation of formic acid at Pt electrodes is discussed in detail based on previous electrochemical *in-situ* ATR-FTIRS data [Langmuir **22**, 10399 (2006) and Angew. Chem. Int. Ed. **50**, 1159 (2011)]. A kinetic model with formic acid adsorption (and probably the simultaneous C–H bond activation) as the rate determining step, which contributes to the majority of reaction current for formic acid oxidation, was proposed for the direct pathway. The model simulates well the IR spectroscopic results obtained under conditions where the poisoning effect of carbon monoxide (CO) is negligible and formic acid concentration is below 0.1 mol/L. The kinetic simulation predicts that in the direct pathway formic acid oxidation probably only needs one Pt atom as active site, formate is the site blocking species instead of being the active intermediate. We review in detail the conclusion that formate pathway (with either 1st or 2nd order reaction kinetics) is the direct pathway, possible origins for the discrepancies are pointed out.

**Key words:** Formic acid oxidation, Mechanism, Electrocatalysis, Formate pathway, Direct pathway

## I. INTRODUCTION

Electrocatalytic oxidation of formic acid on Pt group metal electrodes is one of the simplest and most important model reactions for the mechanistic understanding of the electrooxidation of small organic molecules, which are potential fuels for low temperature fuel cells [1–8]. It was proposed that this reaction proceeds via dual path mechanism with a direct and an indirect pathway [1, 2, 9, 10].



It is generally accepted that the indirect pathway proceeds via the initial dehydration of formic acid to adsorbed carbon monoxide (CO<sub>ad</sub>), which is then, oxidized to CO<sub>2</sub>. And formic acid is directly oxidized to CO<sub>2</sub> through some active intermediate (other than CO<sub>ad</sub>) in the direct pathway. Although extensive studies have been carried out by both experimental [11–19] and theoretical [20–23] means, however, the exact mechanism for the direct pathway and the nature of the weakly adsorbed reaction intermediates are still under debate.

From time-resolved measurements of the build-up and oxidative removal of the CO adlayer using electro-

chemical *in-situ* infrared absorption spectroscopy under the attenuated total reflection configuration (EC-ATR-FTIRS) in a flow cell with negligible influence from diffusion, the rates for HCOOH dehydration (CO<sub>ad</sub> formation) and CO<sub>ad</sub> oxidation in the indirect path has been derived [11, 13]. The results demonstrated that the indirect pathway represents a minority pathway at potentials below 0.75 V (*vs.* RHE), which contributes by less than 0.1% to the total faradaic current (*i*<sub>tot</sub>) at room temperature. And even at 0.75 V and temperature up to 80 °C its contribution is less than 5%. It is concluded that CO mainly acts as poisoning species which blocks the direct pathway for formic acid oxidation at Pt electrode, and the majority current for formic acid oxidation comes from the direct pathway. This conclusion is also well supported by studies at single crystalline Pt electrodes using conventional electrochemical techniques [24–26].

In the direct pathway, weakly adsorbed reaction intermediates, COH [3, 4], CHO [4], COOH [27–29], and HCOO [15–19, 30, 31] have all been proposed as possible reaction intermediates, through which formic acid is oxidized to CO<sub>2</sub>. However, by now only bridge-bonded formate (HCOO<sub>ad</sub>) has been well confirmed by EC-ATR-FTIRS [11–19, 32, 33]. Recently, a series of studies on the possible roles of formate in formic acid oxidation have been carried out [11–19, 24–26]. Although the IR spectroscopic behavior obtained from both Oseawa's and Behm's labs are essentially the same, however, opposite conclusions were derived on for- whether

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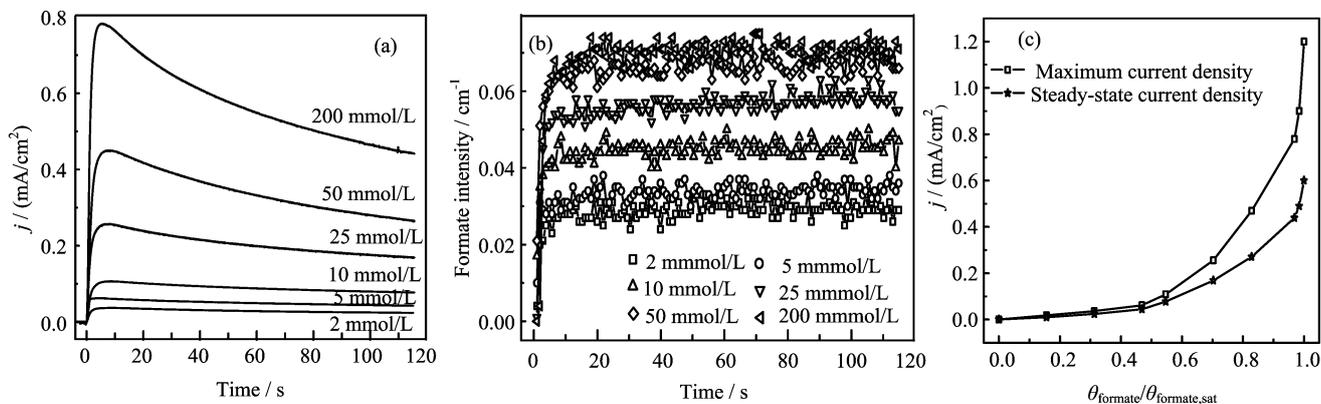
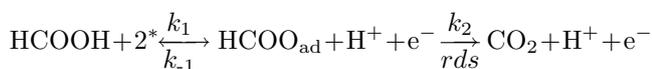


FIG. 1 (a) and (b) Chronoamperometric transients and adsorbed formate band intensity transients upon solution exchange from 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> to 0.5 mol/L H<sub>2</sub>SO<sub>4</sub>+DCOOH with different HCOOH concentrations (2, 5, 10, 25, 50, and 200 mmol/L) at 0.7 V. (c) Variation of the anodic current 3–10 s (initial current maximum) and 120 s (steady-state conditions) got from (a) with normalized DCOO<sub>ad</sub> coverage. Data reproduced from Ref.[12].

mate is the active intermediates or poisoning species for the direct pathway [11–18]. Furthermore, the exact mechanism for the formate pathway is also under debate [12, 19, 24]. The formation of HCOO<sub>ad</sub> and its subsequent desorption and/or oxidation can be represented by the following equation [15, 17, 18]:



Both Osawa's and Feliu's groups proposed that formate pathway was responsible for the major current for formic acid oxidation, in which formate decomposition was the rate determining step (*rds*) [19, 24]. Feliu *et al.* proposed that formate decomposition follows first order reaction kinetics [24]. On the other hand, Osawa *et al.* proposed that the decomposition of HCOO<sub>ad</sub> follows a pseudo 2nd order reaction kinetics: HCOO<sub>ad</sub> needs a neighboring free site for its oxidative decomposition. In contrast, from systematic studies on the concentration, potential, temperature and H/D kinetic isotope effects on formic acid oxidation using ATR-FTIRS [11–14], Chen *et al.* found that neither 1st order nor 2nd order reaction kinetics for the formate pathway can simulate the electrochemical *in-situ* IR spectroscopic data, hence they concluded that formate was not the reaction intermediates for the direct pathway, instead it acted as a site blocking species for the direct pathway.

In this work, we first point out the flaws which lead to the conclusions that formate pathway with 1st or 2nd order reaction kinetics is the direct pathway which contributes to the majority current for formic acid oxidation. Then we present a new kinetic model for the direct (non-formate) pathway, which fits well the concentration dependent spectroscopic data [12]. The mechanistic implications on formic acid oxidation is discussed based on such kinetic analysis, evidences from both experiments as well as DFT calculations which support the direct (non-formate) pathway are also given.

## II. COMMENTS ON PREVIOUS REPORTS CLAIMING FORMATE PATHWAY DELIVERS MAJOR CURRENT FOR HCOOH OXIDATION

### A. First order reaction kinetics for formate pathway

If the oxidation of bridged bonded formate goes through a first order reaction mechanism and this step is the *rds* for formic acid oxidation through this pathway, it is expected that the current for formate pathway is proportional to the rate constant for this step and the surface coverage of formate, *i.e.*  $i_{\text{formate}} \propto k(E) \cdot \theta(E)$ . In order to figure out the role of formate pathway in formic acid oxidation, Chen *et al.* specially designed an experiment by running formic acid oxidation at constant potential (*i.e.*, 0.7 V vs. RHE) and systematically varying formic acid concentrations [12]. The changes of formic acid oxidation current and the IR spectra including the formate band as a function of reaction time are recorded. A reaction potential of 0.7 V is chosen since at this potential the adsorption of CO<sub>ad</sub> and OH<sub>ad</sub> is negligible, hence the poisoning effects from these two species are largely eliminated. From a systematic ATR-FTIRs study, it is found that with the increase in formic acid concentration, formic acid oxidation current increases much faster than that of the increase formate band intensity (Fig.1), *e.g.*, when increasing DCOOH concentration from 2 mmol/L to 0.2 mol/L, current increases ca. 10 times, but formate surface coverage increases only 4 times [12].

Since the adsorption of formate at Pt electrode is weak, it is reasonable to assume that (i) the IR band intensity of formate is just proportional to formate surface coverage and (ii) at constant potential the rate constant for the oxidative decomposition of formate does not change much with formate coverage. Based on this and supposing that formic acid oxidation current just comes from the formate pathway in the case with the lowest HCOOH or DCOOH con-

centration ( $C_{\text{HCOOH}}/C_{\text{DCCOOH}} \leq 2$  mmol/L), from the non-linear relationship between formate coverage and formic acid oxidation current, it was estimated that the contribution of the formate pathway should be less than 25% of the total current in the case with  $C_{\text{HCOOH}}/C_{\text{DCCOOH}} \geq 0.1$  mol/L according to first order reaction kinetics.

On the other hand, Feliu *et al.* found that on Pt(111) and Pt(554) electrodes and in the potential region of  $0.3 \text{ V} < E < 0.6 \text{ V}$ , the potential-dependent faradaic current for formic acid oxidation ( $i(E)$ ) was just proportional to  $\theta_{\text{formate}}(E)$ . Based on this result, they proposed that formate was the right intermediate for the direct pathway for formic acid oxidation, which was responsible for the majority reaction current for formic acid oxidation [24]. However, their conclusion is only valid when the reaction rate constant  $k(E)$  is potential independent, based on the assumption that the formate pathway is with formate decomposition as the *rds* and the elementary step follows a first order reaction kinetics. Recent DFT calculations suggested that the barrier for the formate pathway changed with electrode potential at a rate of ca.  $0.2 \text{ eV/V}$  [20, 21]. For a rough estimation, a change in activation barrier of  $5 \text{ kJ/mol}$  (*e.g.* from  $0.3 \text{ V}$  to  $0.6 \text{ V vs. RHE}$ ) will result in a change in  $k(E)$  of ca. 8 times at room temperature. Obviously, if including the change of both formate band intensity and the rate constant with electrode potential, according to first order reaction kinetics linear correlation between  $i(E)$  and  $\theta_{\text{formate}}$  does not hold at all.

Even if the rate constant may be a function of  $\theta_{\text{formate}}$ , *i.e.*,  $i_{\text{formate}} \propto k(\theta, E) \cdot \theta(E)$ , the above conclusion will only hold when the potential induced change in the rate constant can be exactly canceled by the coverage induced change in rate constant. Since for formic acid oxidation in the potential region of  $0.3 \text{ V} < E < 0.6 \text{ V}$  both formate coverage and the rate constant increase with electrode potential, this means that a negative coverage effect on  $k(\theta, E)$  should exist, this is in contraction with the required positive coverage effect in order to explain the concentration effect on formic acid oxidation (Fig.1) as discussed above. Furthermore, it is found that under otherwise identical condition (Fig.2), formic acid oxidation current in  $0.05 \text{ mol/L HCOOH}$  is nearly twice as that in  $0.01 \text{ mol/L HCOOH}$  [34]. If a negative coverage effect exists, at least a two times increase in  $\theta_{\text{formate}}$  should be expected. From the result of the fast scan voltammetry in  $0.01 \text{ mol/L HCOOH}$ , the charge of formate adsorption at  $0.6 \text{ V}$  is found to be ca.  $0.08 \text{ mC/cm}^2$ , and the maximum theoretical charge of bridge-bonded formate adsorption is only  $0.12 \text{ mC/cm}^2$  [24, 36].

In fact, a rough proportionality of potential-dependent faradaic current for formic acid oxidation  $i(E)$  to  $\theta_{\text{formate}}(E)$  is also observed by Behm and Osawa's group during ATR-FTIRS studies by cyclic voltammetry [11, 12, 16, 18], however, one should pay attention that the slopes of  $i(E)$  vs.  $\theta_{\text{formate}}(E)$  plots

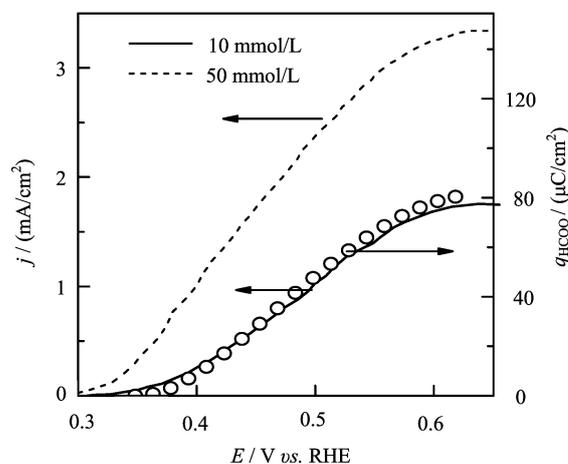


FIG. 2 Voltammogram of a Pt(111) electrode in  $0.1 \text{ mol/L HClO}_4 + 0.01 \text{ mol/L HCOOH}$  (solid line) and  $0.1 \text{ mol/L HClO}_4 + 0.05 \text{ mol/L HCOOH}$  (dashed line) at  $50 \text{ mV/s}$ . Circle symbols show the charge of adsorbed formate on Pt(111) measured from the scan at  $50 \text{ V/s}$  in  $0.1 \text{ mol/L HClO}_4 + 0.01 \text{ mol/L HCOOH}$  [24].

differ a lot in the same potential region but with different potential scan directions. Furthermore, if one mixes formic acid with acetic acid, similar linear relationship between formic acid oxidation current with the band intensity of formate and acetate can also be obtained (Fig.3) [12]. In these measurements, it was found that the potential-dependent change in coverage of formate and acetate just mirrors the coverage change of  $\text{CO}_{\text{ad}}$  due to the competitive adsorption between these species.

In a word, the potential-dependent change in formate or acetate band intensity is just a combined effect from both the change of electrode potential and the  $\text{CO}_{\text{ad}}$  coverage, it does not necessary mean that the observed adsorbate is just the reaction intermediates involved in the pathway which contributes to the majority current for formic acid oxidation. Instead, we would rather think that the exact match of potential-dependent reaction current with potential-dependent formate coverage as observed in the case with Pt(111) and Pt(554) serves as a good evidence that another pathway other than the formate pathway must operate during formic acid oxidation.

## B. The 2nd order reaction kinetics of formate pathway and its correlation with IR spectroscopic data

According to the proposal by Osawa *et al.*, formate oxidation is the *rds* for formate pathway and formate needs one neighboring free site to turn from perpendicular orientation to tilting or flat lying configuration in order that C–H bond can be close enough to the Pt surface and be cut with help of Pt surface atoms [37, 38]. Hence, the reaction current for the formate path-

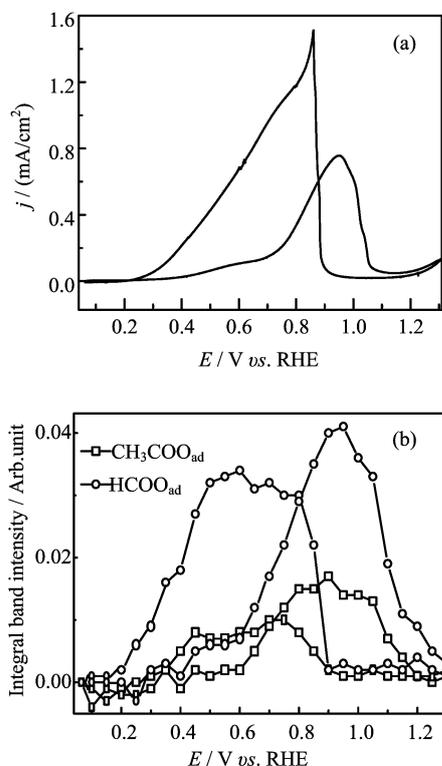


FIG. 3 (a) Cyclic voltammograms of formic acid oxidation at Pt thin film electrode in 0.07 mol/L HCOOH+0.01 mol/L CH<sub>3</sub>COOH+0.5 mol/L H<sub>2</sub>SO<sub>4</sub>. (b) Potential-dependent band intensity of adsorbed formate (square) and acetate (circle), potential scan rate of 10 mV/s. Data reproduced from Ref.[12].

way can be represented by a second-order rate equation [15–17, 19]:

$$i_{\text{formate}} \propto k_2 \theta_{\text{formate}} (1 - \theta_{\text{tot}}) \quad (1)$$

$$\theta_{\text{tot}} = \theta_{\text{CO}_L} + 2\theta_{\text{CO}_M} + 2\theta_{\text{formate}} + q\theta_{\text{anions}} \quad (2)$$

where  $\theta_{\text{formate}}$  is the coverage of bridge adsorbed formate, and  $(1 - \theta_{\text{tot}})$  represents the numbers of free surface sites, and  $\theta_{\text{tot}}$  is the sum of the sites occupied by all possible adsorbates, the stoichiometric factors before  $\theta$  of different adsorbates denote the number of neighboring Pt sites occupied by each adsorbate. In solution with relative high HCOOH (or DCOOH) concentration, formate adsorption/desorption is assumed in a fast pre-equilibrium as similar to the case with the dynamic behavior of typical anions such as sulfate/bisulfate in the supporting electrolyte. Under conditions where the coverage of CO<sub>ad</sub>, OH<sub>ad</sub>, and anions such as sulfate are negligible, the rate for formate adsorption and desorption can be expressed as

$$k_1 (1 - 2\theta_{\text{formate}})^2 c_{\text{HCOOH}}^s = k_{-1} \theta_{\text{formate}} \quad (3)$$

where  $k_1$ ,  $k_{-1}$  are the rate constant for the adsorption and desorption process,  $(1 - 2\theta_{\text{formate}})$  is the number of free sites available for HCOOH adsorption, and  $c_{\text{HCOOH}}^s$

is formic acid concentration at electrode surface. By rearrange Eq.(3) and Eq.(2), one obtains that the faradaic current for formate pathway is as follows [19]:

$$i_{\text{formate}} \propto k_2 \theta_{\text{formate}} (1 - 2\theta_{\text{formate}}) \\ \propto \frac{k_2}{\sqrt{(k_1/k_{-1}) c_{\text{HCOOH}}^s}} \theta_{\text{formate}}^{3/2} \quad (4)$$

In solution with relative high HCOOH (or DCOOH) concentration, where reaction induced concentration gradient at the interface is negligible,  $c_{\text{HCOOH}}^s = c_{\text{HCOOH}}^b$  (superscript s and b indicate the concentration of formic acid at the electrode surface and in bulk solution). From Eq.(4), it is clearly seen that the current from the formate pathway (with 2nd order reaction kinetics) should increase linearly with  $\theta_{\text{formate}}^{3/2} / \sqrt{c_{\text{HCOOH}}^b}$ . If formate pathway is responsible for the majority of reaction current measured for formic acid oxidation ( $i_{\text{tot}}$ ), *i.e.*,  $i_{\text{tot}} = i_{\text{formate}}$ , from Eq.(4) a similar linear-plot of  $i_{\text{tot}} \propto \theta_{\text{formate}}^{3/2} / \sqrt{c_{\text{HCOOH}}^b}$  is also expected.

From the electrochemical *in-situ* infrared spectroscopic data (*i.e.*,  $i_{\text{tot}}$  and  $\theta_{\text{formate}}$  as a function of reaction time measured at 5 and 120 s after switching to formic acid containing solution at constant reaction potential of 0.7 V where the adsorption of CO and OH is negligible (original data was given in Fig.1). Figure 3 shows rough linear-plots of  $i_{\text{tot}} \propto \theta_{\text{formate}}^{3/2} / \sqrt{c_{\text{HCOOH}}^b}$  actually obtained with 5 mmol/L  $< c_{\text{DCOOH}} \leq 500$  mmol/L. However, opposite to that predicted by Eq.(4), the measured  $i_{\text{tot}}$  decreases monotonically with the increase in  $\theta_{\text{formate}}^{3/2} / \sqrt{c_{\text{HCOOH}}^b}$ . In fact, at formic acid concentrations higher than 0.1 mol/L when  $\theta_{\text{formate}}$  is saturated, Eq.(4) predicts that the current for the formate pathway ( $i_{\text{formate}}$ ) decreases with further increase in formic acid concentration. This obviously contrasts to the observed experimental results that  $i_{\text{tot}}$  increase with formic acid concentration. In order to clearly show this discrepancy, the line for  $i_{\text{formate}} \text{ vs. } \theta_{\text{formate}}^{3/2} / \sqrt{c_{\text{HCOOH}}^b}$  is also plotted with  $k_2 / \sqrt{(k_1/k_{-1})} = 0.1$  (the value is arbitrarily chosen after considering that  $k_1$ ,  $k_{-1}$  are orders of magnitude higher than that of  $k_2$ ). From Fig.3, it is clearly seen that if the formate pathway operates, it only contributes to a minor part of the total current observed from formic acid oxidation, and its contribution decreases with increase in the concentration of formic acid in the bulk solution (to the left direction of the axis as shown in Fig.4). This is opposite to the monotonically increase in the total formic acid oxidation current with the concentration of formic acid in bulk solution, which further confirms that formate pathway just has a minor contribution, if it works.

Recently, Cuesta *et al.* also proposed that formate pathway is the direct pathway which was responsible for the majority current for formic acid oxidation, however,

in contrast to mechanism suggested by Osawa *et al.*, he suggested that the formate might probably go through a chemical reaction between two bridged adsorbed formate at neighboring sites [39]. We think this is less likely based on the following facts: (i) since formate is under dynamic adsorption/desorption the chances for formate adsorbate to orient with molecular orbital in proper orientation for the bimolecular reaction is small. (ii) At Pt(111) electrode surface modified with  $\text{CN}^-$ , where well organized hexagonal pattern of  $\text{CN}^-$  adlayer is formed [40], no sites with four neighboring Pt atoms are available for parallel adsorption of two formate anions in bridged adsorbed configuration. However, significant oxidation current for formic acid oxidation is observed. One may suggest that formate may also adsorb on top of neighboring  $\text{CN}^-$  adlayer, however, under such circumstance bimolecular reaction between adsorbed formate should also be hardly possible due to steric reason.

Furthermore, the conclusion that formate pathway cannot be the direct pathway is also well supported by previous experimental results using solutions containing the mixture of  $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$  in which, IR band intensity of adsorbed formate is greatly suppressed by the stronger adsorbed acetate. Even under conditions when formate band is not observed at all, it is found that the formic oxidation current only drops to approximately 1/3 of the case in solutions free of  $\text{CH}_3\text{COOH}$  under otherwise identical condition [12]. Bridge-bonded acetate is well confirmed to be a “dead” species which can be hardly further oxidized [41, 42], the similar bonding configuration of formate to that of acetate at Pt electrode surface further supports that bridge-bonded formate is not the reactive intermediate for formic acid oxidation at Pt electrode. Such conclusion is also supported by recent DFT calculations that a rather high activation barrier ( $>1.1$  eV) is encountered for the oxidation of bridge-bonded formate [20, 21].

In a word, bridge-bonded formate is not the reactive intermediate in the direct pathway for formic acid oxidation, which is responsible for the majority current for formic acid oxidation. Neither 1st nor 2nd order reaction kinetics for formate pathway can fit the experimental data well. Thus, we support the previous conclusion that formate is most probably site blocking species rather than the reactive intermediate for the direct pathway [11–14].

### III. POSSIBLE MECHANISM FOR THE DIRECT PATHWAY

From the above discussion, it is clear that formate pathway does not work. Furthermore, from the ca. 1.9 times of kinetic isotope effect on  $\text{HCOOH}/\text{DCOOH}$  oxidation [14], it is reasonable to assume that the cleavage of C–H and C–D should be the *rds* in the direct pathway. And no other reactive intermediate as well as

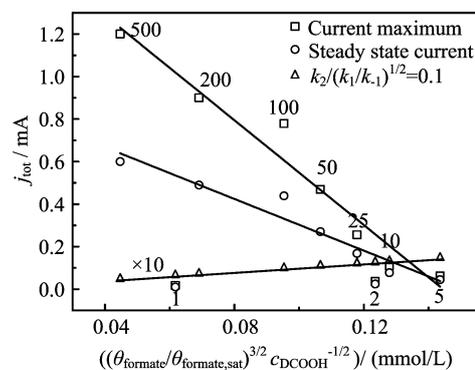
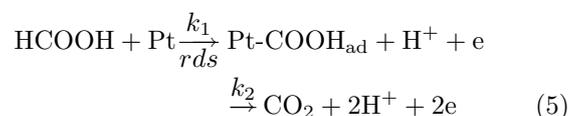


FIG. 4 Plot of total current density for formic acid oxidation  $j_{\text{tot}}$  vs.  $\theta_{\text{formate}}^{3/2}/\sqrt{c_{\text{DCOOH}}^b}$  at Pt film electrode in 0.5 mol/L  $\text{H}_2\text{SO}_4 + x$  mmol/L  $\text{DCOOH}$ .  $\theta_{\text{formate}}/\theta_{\text{formate, sat}}$  is the relative surface coverage of bridge-bonded formate, as derived from the IR band intensity,  $c_{\text{DCOOH}}^b$  is the concentration of  $\text{DCOOH}$  in bulk solution, numbers given in the figures are the  $\text{DCOOH}$  concentration in mmol/L, the original data is given in Fig.1. For comparison, the plot of  $j_{\text{formate}}$  vs.  $\theta_{\text{formate}}^{3/2}/\sqrt{c_{\text{DCOOH}}^b}$  according to Eq.(4) with  $k_2/\sqrt{(k_1/k_{-1})}=0.1$  is also given.

precursors such as  $\text{HCOOH}_{\text{ad}}$  are observed by experimental means. Based on the above facts, we think it is most probable that formic acid molecules to be oxidized firstly collide with CH end facing the Pt electrode surface. There must be certain probability that  $\text{HCOOH}_{\text{ad}}$  with C–H bond facing toward Pt surface is promptly activated, which is followed by fast cleavage of C–H bond and the transfer of one electron. Then after OH bond in Pt-COOH breaks and accompanies with the transfer of 2nd  $\text{H}^+$  and electron, as similar to discharge of  $\text{H}_3\text{O}^+$  and HER process, where the discharge of  $\text{H}^+$  (in the water network probably in the form of  $\text{H}_9\text{O}_4^+$  or  $\text{H}_5\text{O}_2^+$ ) is finished at the OHP and right upon the OH bond is breaking [43]. This mechanism may be simply expressed as the following:



where  $\text{Pt-COOH}_{\text{ad}}$  denoted the activated  $\text{HCOOH}$  complex with C–H bond contacting the Pt surface, as suggested by DFT calculation [21]. If assuming that all surface active sites are uniformly distributed, under conditions that (i) at relative low formic acid concentration where the first step is both kinetic and mass transport limited and (ii) where the coverage of  $\text{CO}_{\text{ad}}$ ,  $\text{OH}_{\text{ad}}$  is negligible and only bridged bonded formate is the main stable adsorbate, the relationship between the faradaic current for this pathway, formic acid concentration and the surface coverage of formate for the proposed direct pathway can be expressed as the following:

$$i_{\text{direct}} \propto k_1 c_{\text{HCOOH}} (1 - 2\theta_{\text{formate}}) \quad (6)$$

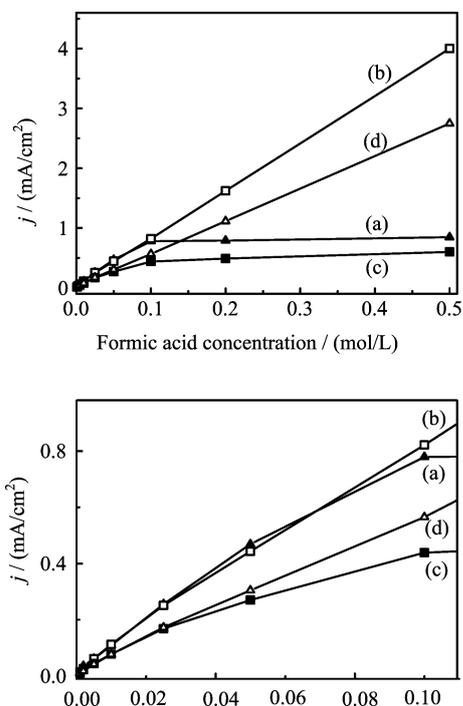


FIG. 5 Values of current density  $j_{tot}$  for (a) DCOOH oxidation at 0.7 V with data points measured at ca. 3–5 s (initial current maximum) and (c) at ca. 120 s (near steady state) as a function of DCOOH concentration, data measured at Pt film electrodes in 0.5 mol/L  $H_2SO_4+x$  mmol/L DCOOH (the original data is given in Fig.1). (b) and (d) are the corresponding fittings of  $j_{direct}$  as a function of  $c_{DCOOH}$  according to Eq.(6).

The simulated  $i_{direct}$  vs.  $c_{DCOOH}$  according to Eq.(6) is given in Fig.5.

From Fig.5 it is seen that under conditions of  $c_{DCOOH} < 0.1$  mol/L, the  $i_{direct} \propto c_{DCOOH}$  curve superimposes well the  $i_{tot}$  vs.  $c_{DCOOH}$  curve obtained from electrochemical *in situ* IR spectroscopic measurement by Chen *et al.* [12] (the data obtained from Osawa's lab can also be well simulated by Eq.(6). Eq.(6) cannot be used to simulate the data with  $c_{HCOOH} > 0.1$  mol/L since at higher concentration formic acid oxidation is mainly kinetic controlled). This indicates that the kinetics for formic acid oxidation can be reasonably explained by a direct (non-formate) pathway with first order reaction kinetics. In this mechanism, most probably only a single free Pt atom sites is needed for helping to cut the C–H bond probably through the formation of activated complex with the form of Pt-COOH<sub>ad</sub>, as in well agreement with recent DFT calculation [20, 21]. If such mechanism operates, one would expect that the surface coverage and life time for HCOOH<sub>ad</sub> is small, hence it will not be detected by IR spectroscopy as in agreement with previous literature reports [11–17, 19]. The reasonably good match between the fitted  $i_{direct}$  and the measured  $i_{tot}$  also supports that the contributions of pathways which go through stable adsorbates such

CO<sub>ad</sub> and HCOO<sub>ad</sub> to the total reaction are negligible.

Unfortunately, so far, we do not have direct experimental evidence to support the direct pathway proposed here. The fast reaction kinetics for the direct pathway, the short life time and small surface coverage may explain why no active intermediate is observed by spectroscopic means so far. Here we just list a number of well known results which may serve as indirect evidences indicating the existence of the direct (“non-formate”) pathway. Earlier DEMS measurements demonstrated that after Pt surface is saturated with <sup>13</sup>CO from H<sup>13</sup>COOH (with  $\theta_{CO_{ad}} \approx 0.5$  ML), <sup>12</sup>CO<sub>2</sub> are produced at relative low potentials ( $E < 0.5$  V) where the oxidation rate of <sup>13</sup>CO<sub>ad</sub> is negligible [44]. From the electrochemical *in-situ* IR spectroscopic studies, it is found that once Pt surface is covered by ca.0.5 ML of CO<sub>ad</sub> (this is roughly the saturated coverage for CO<sub>ad</sub> formed from formic acid decomposition), no formate is observed at  $E \leq 0.5$  V, although formic acid oxidation current is clearly observed under such conditions and which display a clear increase in reaction current with temperature [11]. These facts clearly indicate that formate pathway is not the direct pathway for formic acid oxidation. The lacking of formate adsorption at Pt surface with  $\theta_{CO_{ad}} \approx 0.5$  ML can be easily explained by the lateral repulsion between adsorbed CO<sub>ad</sub> molecules which renders the chances for finding free sites with two neighboring Pt atoms under the circumstance of  $\theta_{CO_{ad}} \approx 0.5$  ML quite low. This indicates that oxidation of formic acid at CO<sub>ad</sub> covered Pt surface with  $\theta_{CO_{ad}} \approx 0.5$  ML most probably goes through the direct pathway which probably only interacts with one free Pt atom at the electrode surface.

Furthermore, recent DFT calculations by various theoretical groups [20, 21, 23, 45] reveal that the direct pathway are the most energetic favorable pathway among all possible pathways for formic acid oxidation. Neurock *et al.* [20] and Liu [21] *et al.* found independently that formate pathway has a large reaction barrier as high as ca. 1.1 eV which is more than two times higher than alternative direct pathway (<0.5 eV). Neurock *et al.* suggested that COOH is most probably the reactive intermediate while HCOO is just a spectator [20], which supports our conclusion well. Liu *et al.* suggested that a weakly adsorbed HCOOH\* with its CH bond in a “down” configuration is the reactive intermediate, and the presence of preadsorbed formate is a catalyst for the direct oxidation of formic acid [21]. In contrast, without the preadsorbed formate, formic acid is only able to adsorb with its carboxyl O linking to Pt, which is however difficult to decompose further [21]. On the other hand, from DFT calculation of formic acid oxidation at water covered Pt(111) surface Jacob *et al.* concluded that electrochemical oxidation of HCOOH on platinum proceeds via a dual-path mechanism involving a formate pathway via the HCOO<sub>B</sub>\* intermediate and a direct pathway from HCOOH\* via a highly transient CO<sub>2</sub>\* intermediate. And it is found that at Pt(111)

surface the activation energy of these two pathways are nearly identical [23]. Possible discrepancies of the calculated results from different groups may probably due to the different model (*e.g.*, double layer structure and different initial stable  $\text{HCOOH}_{\text{ad}}$  configuration due to different solvation model used) used for calculation by different groups. Furthermore, so far, no calculation has taken the effect of co-adsorbed CO into account. We do hope our present analysis will greatly help in constructing more realistic model for future theoretical studies.

#### IV. CONCLUSION

In summary, the mechanism on formic acid oxidation at Pt electrodes is re-investigated based on the kinetic analysis of previous electrochemical ATR-FTIRS data. Our analysis further confirms that formate pathway cannot be the direct pathway which contributes to the majority of reaction current for formic acid oxidation. Possible mistakes involved in previous analysis which lead to the conclusion that formate pathway (with either 1st or 2nd order reaction kinetics) is the direct pathway are pointed out.

We have proposed a kinetic model for the direct pathway with formic acid adsorption (and probably the simultaneous C–H bond activation) is the rate determining step, which simulates the IR spectroscopic data well under conditions where the poisoning effect of  $\text{CO}_{\text{ad}}$  and  $\text{OH}_{\text{ad}}$  is negligible. And for direct pathway, the kinetic simulation predicts that formic acid oxidation probably only needs one Pt atom as active site, formate is the site blocking species instead of being the active intermediate.

We hope discussions made in this communication finally settle the long standing debate on such topics and will be of great help for guiding theoreticians to construct more realistic model for simulating electrocatalytic problems. We also hope that the methodology used in present analysis and the discussion on the mistakes involved in previous analysis will be greatly helpful for the similar spectroscopic techniques.

Finally, It should be pointed out that due to the complexity of electrochemical system, most kinetic analysis are based on the assumption that the all the surface actives are uniformly distributed, and the reactions takes place evenly at the electrode surface. At molecular/atomic scale, the probability for the same reaction at different surface sites may change, mesoscopic theories and statistics which bridge the gaps between molecular level behavior and macroscopic phenomena may be necessary in order to correctly deriving microscopic mechanistic information from macroscopic data. Researches along this line are underway in our group.

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