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From HCOOH to CO at Pd Electrodes: A Surface-Enhanced Infrared Spectroscopy Study

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S *Supporting Information*

ABSTRACT: The decomposition of HCOOH on Pd surfaces over a potential range of practical relevance to hydrogen production and fuel cell anode operation was probed by combining high-sensitivity in situ surface-enhanced IR spectroscopy with attenuated total reflection and thin-layer flow cell configurations. For the first time, concrete spectral evidence of CO_{ad} formation has been obtained, and a new main pathway from HCOOH to CO_{ad} involving the reduction of the dehydrogenation product of HCOOH (i.e., CO_2) is proposed.

The (electro)chemical decomposition of formic acid (FA) on metal surfaces has attracted considerable interest not only because it is a model system in fundamental (electro)catalysis[1−6] but also because it is closely relevant to hydrogen production[7] and clean energy utilization.[7−12] In fact, with suitable catalysts, FA may serve either as an in situ source of hydrogen[7] production or as a direct liquid fuel per se[8−10] for low-temperature polymer electrolyte membrane fuel cells (PEMFCs), playing a very significant role in energy-efficient green power generation in the future, especially in driving portable electronic appliances.

Despite the controversy over adsorbed formate as the reactive intermediate,[5,7,13−16] simple dual pathways[16−18] are widely recognized for the net decomposition of FA, namely, dehydrogenation and dehydration. The former pathway may proceed via either $HCOOH \rightarrow CO_2 + H_2$ or $HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$. The latter pathway leads to CO via $HCOOH \rightarrow CO_{ad} + H_2O$. The adsorbed CO ($CO_{ad}$) on electrode can be oxidized only at higher potentials, contributing largely to the suppressed dehydrogenation.[19] Depending on the nature of the catalyst and/or the electrode potential, dehydrogenation or dehydration may predominate, and the dehydrogenation pathway is highly desired in designing new catalysts for the best utilization of the chemical energy stored in FA.

Pd-based catalysts possess lower cost and higher activity than Pt-based ones for FA (electro)chemical dehydrogenation[7−10,20−22] and will be very promising for practical hydrogen energy utilization if the quick deactivation issue can be reasonably overcome on the basis of a further understanding of the decomposition reactions.[23−26] However, in comparison with that on Pt electrodes, mechanistic studies on Pd electrodes in FA have far less been heeded,[23−26] leaving behind two important and yet unclear issues. First, does any CO_{ad} form on a Pd electrode during FA decomposition with or without potential control? Disputing conclusions have emerged in literature[23−26] because different methods, FA concentrations, and potentials were used in these investigations [see section II in the Supporting Information (SI)]. Second and more intriguingly, if any CO_{ad} forms, does it originate chiefly from the commonly assumed dehydration pathway? Answering these questions would provide insights into the deactivation problem and benefit the theory-guided design of efficient catalysts for FA dehydrogenation.

In the present work, real-time high-sensitivity surface-enhanced IR absorption spectroscopy (SEIRAS)[27−30] was applied to investigate the decomposition of FA on Pd surfaces in order to clarify the above two uncertainties. To that end, instead of a Pd film directly deposited on Si,[24] we used a pinhole-free Pd overfilm on Au-coated Si as the working electrode,[29] taking advantage of its superior rigidity against hydrogen absorption and significantly improved electrical conductivity and SEIRA effect. In combination with other delicate experimental designs, including the thin-layer flow cell (see SI section I), this enabled us to unravel the two puzzles over the practically important potential range from the open-circuit potential (OCP) to 0.4 V vs RHE. Notably, the OCP operation may yield hydrogen to drive a portable $H_2{-}O_2$ PEMFC[7] and also occurs upon refueling of a direct FA fuel cell (DFAFC) without potential control. The FA decomposition at increasingly higher potentials up to 0.4 V vs RHE correlates with regular anode operation in a DFAFC.

As shown in Figure 1A, upon addition of an aliquot of 96 wt % FA to 0.1 M $HClO_4$ with bubbling Ar (to attain a final FA concentration of 0.5 M), the OCP of the Pd electrode dropped quickly from a high potential to ca. 0.02 V vs RHE. The rather low and stable OCP arises from the mixed equilibria shown in eqs 1−4:

$$HCOOH \rightleftharpoons CO_2 + 2H^+ + 2e^- \left(E^0 = -0.17\ \text{V vs SHE}\right) \tag{1}$$

$$2H^+ + 2e^- \rightleftharpoons H_2 \quad \left(E^0 = 0\ \text{V vs SHE}\right) \tag{2}$$

$$Pd + H^+ + e^- \rightleftharpoons PdH_{ad} \tag{3}$$

$$Pd + \frac{x}{2} H_2 \rightleftharpoons PdH_x \tag{4}$$

Figure 1B shows the time-evolved IR spectra after FA addition. The bands at 1720, 1400, and 1214 cm^{-1} respectively represent

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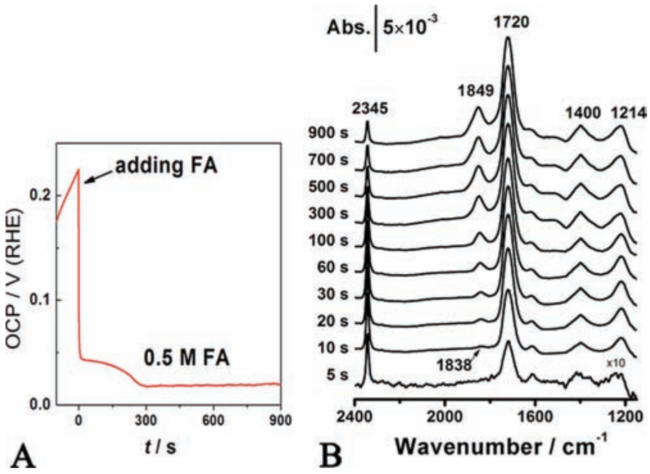


Figure 1. (A) Variation of OCP vs time initiated by introducing FA into the base electrolyte. (B) Real-time IR spectra for a Pd electrode in 0.1 M $HClO_4$ after the injection of an aliquot of highly concentrated FA (at 0 s) to attain a final concentration of 0.5 M under the stirring of Ar bubbles. The reference spectrum was recorded at 0.1 V vs RHE in 0.1 M $HClO_4$ solution.

the $\nu_{C=O}$, $\delta_{COH}/\delta_{HCO}$, and ν_{C-O} vibrations of the FA molecules[25] in the interfacial region (see SI section III). The nearly constant band at ~1612 cm^{-1} could be assigned to H-down H_2O adsorbed on Pd.[23] The band at 2345 cm^{-1} is characteristic of the asymmetric $\nu_{C=O}$ vibration of the decomposition product CO_2 accumulated at the solution side of the interface. The CO_2 band intensity sharply increased and then decreased in a slower fashion as a result of the interplay of the decomposition of FA to CO_2 at the surface and diffusion of the resulting CO_2 into the bulk solution.

Interestingly, 5−10 s after the CO_2 band was detected, a band at 1838 cm^{-1} clearly emerged, characteristic of triply bonded CO (CO_T) on the Pd surface (i.e., CO adsorbed on hollow sites of the Pd surface).[29,31−33] The CO_T band showed up after the CO_2 band with its center frequency blue-shifted and its band intensity increased during the self-decomposition of FA at OCP. Moreover, increasing the FA concentration tended to increase the intensity and frequency of the CO_T band (not shown). This CO_T band is in fact a landmark species to confirm the formation of CO_{ad} without spectral interference from the FA solution (see SI section III). Further investigation revealed that electro-oxidation of FA at a controlled potential of up to ca. 0.4 V vs RHE may also lead to the CO_T band, the intensity of which decreased with increasing potential (see SI section V). It should be pointed out that IR spectroscopic characterization of CO_{ad} formation on Pd electrodes in FA solutions is rather controversial mainly because of its much lower coverage if any (relative to that on Pt electrodes). In fact, Arenz et al.[26] and Pronkin et al.[23] did not detect any CO bands using IRAS and attenuated total reflectance (ATR)-SEIRAS on Pd monolayers deposited on Pt(111) and quasi-Au(111) substrates, respectively, and neither did Brandt et al.[25] on a Pd(111) electrode in 10 M FA solution at the OCP. In contrast, Miyake et al.[24] observed a weak band around 1830 cm^{-1} on a chemically deposited Pd film electrode during its positive scan from 0.22 V vs RHE in 25 mM FA using ATR-SEIRAS, but they were unable to obtain spectral information at more negative potentials because of the instability of the film. In this regard, the present measurements for the first time provide concrete spectral evidence of CO_{ad} formation on a Pd electrode in FA solution from the OCP to 0.4 V. By comparison, no appreciable CO signal was detected with confidence in the subsequent stripping measurement in blank 0.1 M $HClO_4$ on a Pd film electrode after it was operated in 0.5 M FA + 0.1 M $HClO_4$ for 900 s at the OCP (see SI section III), demonstrating the advantage of high-sensitivity SEIRAS in elucidating this issue.

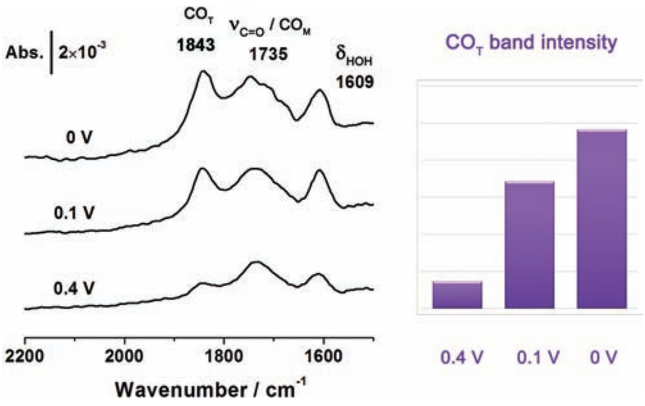


Figure 2. IR spectra of Pd electrodes in CO_2-saturated 0.1 M $HClO_4$ recorded after the given potentials were held for 600 s. Reference spectra were collected in Ar-saturated 0.1 M $HClO_4$ at 0.1 V.

More importantly, as for the origin of CO_{ad} on Pt-group metals in FA solution,[17,18] only the dehydration pathway was mentioned. According to a recent density functional theory calculation,[34] initial FA adsorption via its O atoms is energetically more favorable on Pd surfaces, in contrast to the C-atom adsorption on Pt surfaces. As a result, cleavage of the C−OH bond to form CO via dehydration of FA is not favorable on Pd. On the other hand, the dehydrogenation pathway to yield CO_2 is well-known to be facile for FA on Pd.[9] All of these results prompt us to assume that the slowly accumulated CO_{ad} on Pd in FA solution may be chiefly from the eletroreduction of dehydrogenation-produced CO_2.

The reduction of CO_2 on transition-metal surfaces has been reported, mainly on the basis of electrochemical measurements.[33,35−38] It has been assumed that adsorbed H on the Pd surface is essential for the reduction to proceed,[33] and CO has been suggested as a main product at hydrogen-evolution potentials, in addition to other minor carbonyl-containing byproducts.[35−37] However, no convincing spectral evidence of CO_2 reduction on Pd electrodes at more positive potentials has been provided.

To clarify whether CO_{ad} can result from CO_2 reduction at non-hydrogen evolution potentials of interest, ATR-SEIRA spectra for Pd electrodes in CO_2-saturated 0.1 M $HClO_4$ were acquired after the potential was kept at 0, 0.1, and 0.4 V vs RHE for 600 s. These potentials ensured increasing H adsorption/absorption from 0.4 to 0 V vs RHE. In Figure 2, the 1843 cm^{-1} band corresponds to the CO_T species and the broad 1735 cm^{-1} band to the CO_M species and/or the resulting interfacial FA, respectively. Notably, such a band for low-coverage CO_{ad} could hardly be ascertained by using conventional electrochemical measurements. It can be seen that the CO_{ad} coverage increases with decreasing potential. At a potential higher than 0.4 V, the CO_T band could hardly be detected (not shown). To date, we have confirmed that a small amount of CO_{ad} can be formed at a Pd electrode from CO_2 reduction at hydrogen-adsorption

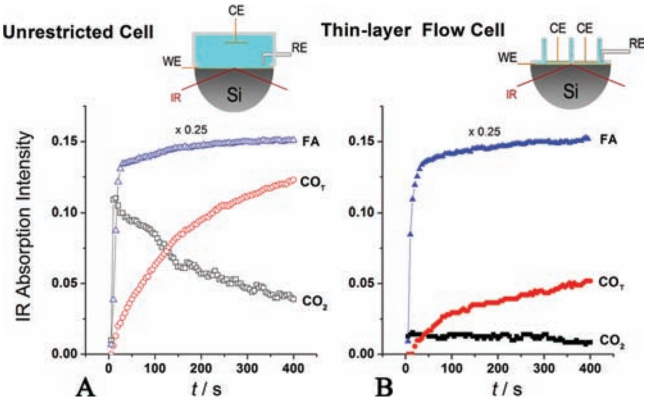


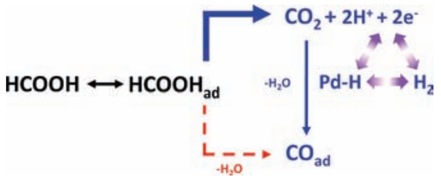
Figure 3. Evolution of the IR peak intensities related to the near-surface CO_2 product (□, ■) and interfacial FA molecules (△, ▲) in the solution phase as well as the adsorbed CO_T species (○, ●) on the Pd surface, recorded at the OCP in 0.1 M $HClO_4$ + 0.5 M FA. In (A), FA was added to the regular unrestricted ATR cell containing blank 0.1 M $HClO_4$ at t = 0 s. In (B), however, FA-containing solution was pumped into the flow cell to replace the supporting base electrolyte.

potentials, laying the basis for further clarification of the main pathway for CO_{ad} formation on Pd in FA solution.

In order to determine whether direct dehydration of FA or reduction of the dehydrogenation product CO_2 is the primary pathway for CO_{ad} formation, we designed parallel experiments in a regular-volume ATR cell (Figure 3A) and a thin-layer ATR flow cell (Figure 3B) with 0.1 M $HClO_4$ + 0.5 M FA solution as the electrolyte. The latter configuration facilitates mass transport, that is, quicker replenishment of the reactant FA from the bulk solution to the surface and quicker removal of the product CO_2 from the surface to the bulk solution. The integrated intensities of the IR peaks related to the interfacial FA molecules increased dramatically, eventually reaching identical values for the two cases. Interestingly, the CO_2 peak intensity (at 2345 cm^{-1}) obtained with the thin-layer flow cell was lower than that with the regular cell. Correspondingly, the detection of CO_T in the flow cell was delayed and only observed ca. 20 s after FA injection. The CO_T band intensity was weaker throughout the measurement. The much smaller CO_T coverage on Pd with an expected higher surface FA concentration (Figure 3B) cannot be explained by the direct dehydration pathway. On the other hand, the increased CO_2 diffusion off the surface does not favor its subsequent reduction to CO. In other words, the detected CO_T band is positively related to the interfacial CO_2 concentration, suggesting that the CO_{ad} formation on Pd in FA solution arises mainly from the reduction of the hydrogenation product CO_2.

The proposed mechanism was further supported by the dependence of the CO_{ad} coverage on the H^+ concentration ($[H^+]$) and the applied potential. IR spectra for Pd electrodes in 0.1 and 0.5 M $HClO_4$ solutions containing 0.5 M FA at 0.1 V vs RHE were recorded 300 s after the addition of FA (see SI section IV). They revealed that as $[H^+]$ increased from 0.1 to 0.5 M, the CO_T band intensity decreased from 0.016 to 0.004. A parallel experiment was also conducted under the same conditions except that 0.1 M $HClO_4$ + 0.4 M $NaClO_4$ + 0.5 M FA was used (not shown), resulting in a CO_T band intensity that was approximately the same as that detected in 0.1 M $HClO_4$ + 0.5 M FA, suggesting a negligible ClO_4^- ionic strength effect. Since ClO_4^- anions are weakly adsorbed species at 0.1 V,[24,26] the decrease in CO_{ad} formation could be reasonably explained by assuming the CO_2 reduction pathway, recalling that less CO_2 is generated with increasing $[H^+]$ for the dehydrogenation reaction. In fact, a much weaker CO_2 band was observed in 0.5 M $HClO_4$ than in 0.1 M $HClO_4$ at the same FA concentration (see SI section IV). In contrast, it is difficult for the direct dehydration pathway to account for such a $[H^+]$ effect, as no H^+ is involved in that pathway.

Scheme 1. Proposed Reaction Scheme from HCOOH to CO_{ad} on a Pd Surface with Reduction of the Dehydrogenation Product CO_2 as the Main Pathway



The effect of potential on the formation of CO_{ad} during FA oxidation is shown in Figure S9 (see SI section V), which displays time-evolved IR spectra recorded for two freshly prepared Pd electrodes at 0.1 and 0.4 V vs RHE in 0.1 M $HClO_4$ + 0.1 M FA. From 0.1 to 0.4 V, the CO_2 band intensity increased dramatically, consistent with the substantially increased oxidation current density. The higher consumption rate of FA at 0.4 V also led to reduced bands of interfacial FA. The CO_T band at 0.4 V was visible 20−30 s later than that at 0.1 V with a much smaller intensity throughout the reduction process. At 300 s after FA injection, the integrated CO_T band intensity at 0.4 V was only ~37% of that obtained at 0.1 V.

The potential-dependent CO_{ad} coverage is in qualitative agreement with that in Figure 2 for the CO_2 reduction test. Notably, it has been reported[38] that the dissociation of CO_2 at the solid−gas interface involves electron transfer from the metal to the adsorbed CO_2 to form a possible intermediate with a weakened C═O bond, $CO_2^{\delta-}$, that is then converted to CO and O at a transition-metal surface. For the reverse water-gas shift reaction on Pd supported on oxides, the reaction kinetics was consistent with reaction between two dissociatively adsorbed H and CO_2 species.[39] Extending the above main idea to the Pd−electrolyte interface, a lower potential favors electron transfer from the metal to surface CO_2 and increased coverage of adsorbed H, facilitating the formation of CO_{ad}.[33,37] On the other hand, the potential-dependent CO_{ad} formation on the Pd electrode appears not to conform to the direct dehydration pathway, as it involves no net electron transfer. Actually, for a Pt electrode in FA solution (see SI section V), where dehydration of FA is regarded as responsible for CO_{ad} formation, far less difference in the CO coverage can be found at 0.1 and 0.4 V vs RHE. Notably, in early mechanistic studies,[5,16] a bidentate formate species was proposed as the intermediate leading to CO on catalyst surfaces. Nevertheless, in our case, the 1333 cm^{-1} band of bidentate formate was not detected on the Pd electrode in 0.1 M $HClO_4$ + 0.5 M FA (see SI section VI) at potentials negative of 0.2 V vs RHE where CO formation was more significant, suggesting that this species is either not involved or out of detection in the CO_{ad} formation.

On the basis of all the above arguments, a new pathway from FA to CO_{ad} may be proposed, as depicted in Scheme 1: rather than direct dehydration, reduction of the FA dehydrogenation product CO_2 should be mainly responsible for low-coverage

CO_{ad} formation on Pd surfaces in an FA solution at potentials where adsorbed H species exist. Disclosure of the CO_{ad} formation mechanism is beneficial for the development of new Pd-based catalysts for hydrogen energy utilization. In fact, anti-CO-poisoning Pd-based catalysts, including B-doped Pd[20] (see SI section VII) and Ag@Pd[7] are efficient and durable for FA dehydrogenation. Furthermore, the present study also suggests that special attention should be paid to the management of CO_2 in practical hydrogen production and DFAFC operation when Pd-based catalysts are used.

In summary, the formation of CO_{ad} on a Pd electrode in FA solutions at the OCP and practical working potentials has been confirmed using in situ high-sensitivity ATR-SEIRAS. On the basis of our investigation of the effects of mass transport, the concentrations of FA and the supporting electrolyte, and the potential, we propose that the reduction of the FA dehydrogenation product CO_2 should be mainly responsible for the above CO_{ad} formation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details; brief overview of previous relevant investigations; further consideration of the CO_T band; effect of $[H^+]$ on CO_{ad} formation and CO_2 production; spectra for FA oxidation on Pd and Pt electrodes; detection of bidentate formate; and an application of the mechanistic study. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Equation 4 was corrected and reposted ASAP on September 8, 2011.