



Supporting Information

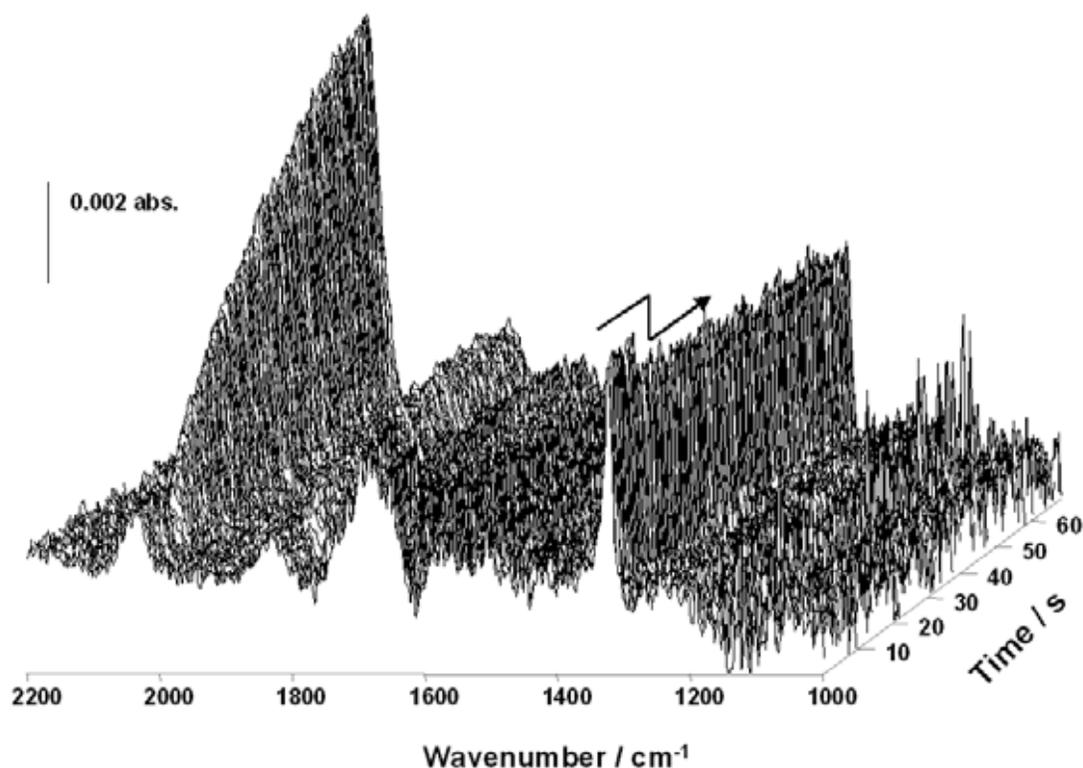
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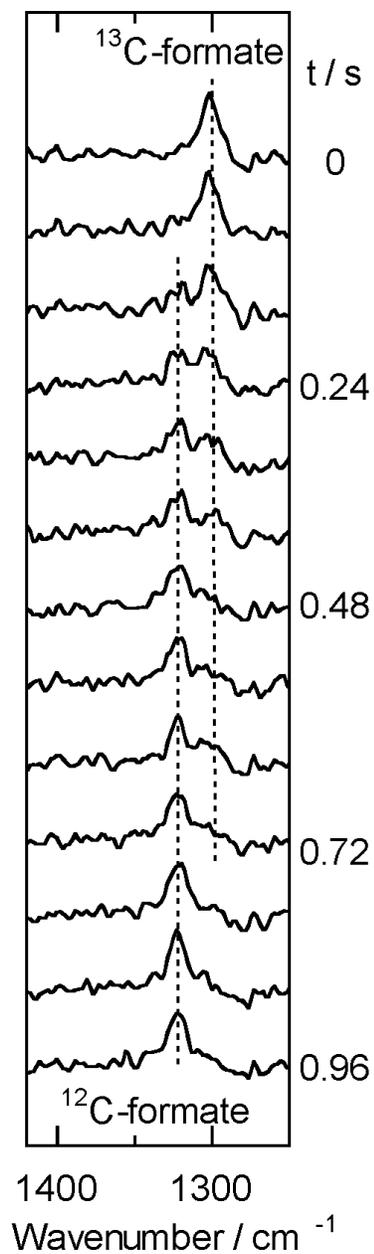
# Current Oscillations during Formic Acid Oxidation on a Pt Electrode: A New Insight into the Involved Mechanism by Time-Resolved IR Spectroscopy

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**Figure S1.** Change in SEIRA spectra of a Pt electrode surface in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M HCOOH for a potential step from 0.80 to 0.6 V (RHE). The time-resolution used was 0.38 s. The formate band decreases its intensity quickly (arrow), while the growth of the CO<sub>L</sub> band at ~2060 cm<sup>-1</sup> is slow. The spectra were recorded using a Bio-Rad FTS60A/896 FT-IR spectrometer equipped with a liquid N<sub>2</sub>-cooled MCT detector and a homemade single-reflection accessory (incident angle of 70°).

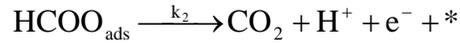
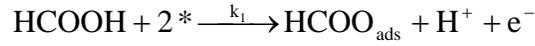


**Figure S2.** Isotopic substitution of adsorbed formate associated with an exchange of solution from 0.5 M  $\text{H}_2\text{SO}_4 + 0.1 \text{ M H}^{13}\text{COOH}$  to 0.5 M  $\text{H}_2\text{SO}_4 + 0.1 \text{ M H}^{12}\text{COOH}$  at 0.6 V (RHE) observed with a time-resolution of 80 ms. The symmetric OCO stretching mode of  $^{13}\text{C}$ -formate at  $1305 \text{ cm}^{-1}$  is replaced by that of  $^{12}\text{C}$ -formate at  $1320 \text{ cm}^{-1}$  within 1 s.

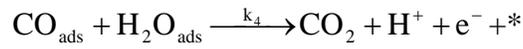
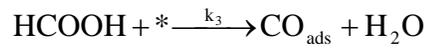
## Theoretical prediction of sustained oscillations for the proposed model

The proposed model is analyzed mathematically by using the procedure by Wojtowicz et al.<sup>[3b]</sup> to check whether it can give sustained oscillations. Following the experimental results, formic acid oxidation can be represented as

(Direct path)



(Indirect path)



where *ads* and \* stand for adsorbed species and a surface site, respectively.  $\theta_{\text{CO}_B}$  is nearly constant in the oscillation (*Figure 2*) and treated as a constant. It is assumed that water molecules occupy vacant sites (that is,  $\theta_{\text{vacant}} = \theta_{\text{H}_2\text{O}} = 1 - 2\theta_f - \theta_{\text{CO}_L} - 2\theta_{\text{CO}_B}$ ) and do not inhibit the adsorption of formate and CO.

The fluxes of the direct and indirect paths (reaction velocities) are as follow under Langmuir conditions, writing *f* for formate,  $\text{CO}_L$  for linearly bonded CO, and  $\text{CO}_B$  for bridge-bonded CO:

$$v_f = k_1\theta_{\text{vacant}}^2 - k_2\theta_f\theta_{\text{vacant}} \quad (\text{S1})$$

$$v_{\text{CO}_L} = k_3\theta_{\text{vacant}} - k_4\theta_{\text{CO}_L}\theta_{\text{H}_2\text{O}} \quad (\text{S2})$$

The second term in Eq. (S1) is identical to Eq. (1) in the text.

The conditions required for sustained oscillations are

$$\left(\frac{\partial v_f}{\partial \theta_{\text{CO}_L}}\right) \times \left(\frac{\partial v_{\text{CO}_L}}{\partial \theta_f}\right) < 0$$

and

$$\left(\frac{\partial v_f}{\partial \theta_f}\right) \times \left(\frac{\partial v_{\text{CO}_L}}{\partial \theta_{\text{CO}_L}}\right) < 0.$$

The partial derivatives for Eqs. (S1) and (S2) are given as

$$\frac{\partial v_f}{\partial \theta_f} = -(4k_1 + k_2)(1 - 2\theta_f - \theta_{\text{CO}_L} - 2\theta_{\text{CO}_B}) + 2k_2\theta_f$$

$$\frac{\partial v_f}{\partial \theta_{\text{CO}_L}} = -2k_1(1 - 2\theta_f - \theta_{\text{CO}_L} - 2\theta_{\text{CO}_B}) + k_2\theta_f$$

$$\frac{\partial v_{\text{CO}_L}}{\partial \theta_{\text{CO}_L}} = -(k_3 + k_4) + 2k_4(\theta_f + \theta_{\text{CO}_L} + \theta_{\text{CO}_B})$$

$$\frac{\partial v_{\text{CO}_L}}{\partial \theta_f} = 2(k_4\theta_{\text{CO}_L} - k_3)$$

Since the adsorption of formate reaches a saturation within 80 ms (the time-resolution used) and about 1 s is required for the desorption as shown in *Figure 2S*,  $k_1 \gg k_2$  and thus both  $\partial v_f / \partial \theta_f$  and  $\partial v_f / \partial \theta_{CO\_L}$  are negative except for at very high adsorbate coverage ( $1 - 2\theta_f - \theta_{CO\_L} - 2\theta_{CO\_B} \approx 0$ ). On the other hand,  $\partial v_{CO\_L} / \partial \theta_{CO\_L}$  and  $\partial v_{CO\_L} / \partial \theta_f$  can be positive if  $(\theta_f + \theta_{CO\_L} + \theta_{CO\_B}) > (k_3 + k_4) / 2k_4$  and  $\theta_{CO\_L} > k_3 / k_4$ , respectively. These conditions are realizable since  $\theta_{CO\_L}$  decreases as potential increases at potentials more positive of  $\sim 0.4$  V as shown in *Figure 3* (that is,  $k_3 < k_4$ ). Consequently, oscillations are possible at medium coverage of adsorbates.