Supplementary Information

Adsorbed formate: the key intermediate in the oxidation of formic acid on platinum electrodes

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Supplementary Figures.

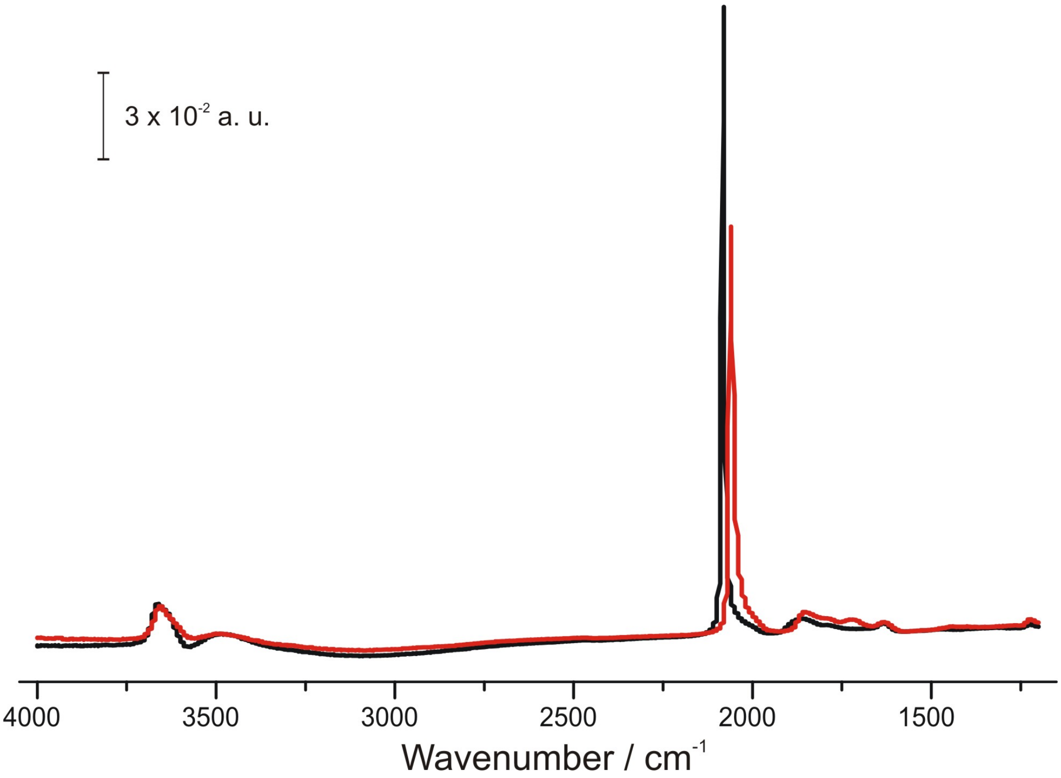

Fig. S1. ATR-SEIRA spectra at the open circuit potential of a CO adlayer formed on a thin-film Pt electrode by bubbling CO through an HCOOH-free solution (black) and by dehydration of HCOOH in a HCOOH-containing solution (red). Both the lower intensity of the CO_L band around 2050 cm^{-1} and the lower peak frequency when the CO adlayer is formed by dehydration of HCOOH are clear indications of a lower coverage. Taking into account that at least three contiguous Pt atoms are necessary for HCOOH dehydration, and that both CO_L and CO_B (band around 1880 cm^{-1}) coexist in the CO adlayer, the latter occupying more than one Pt atom per CO molecule, the maximum CO coverage achieved by dehydration of HCOOH must be below 0.5 ML.

Discussion of the possible mechanisms compatible with the results reported in Figure 2 of the main text

1. Chemical dehydration of formic acid followed by displacement of $HCOO_{ad}$ by CO_{ad}

The experimental result that $HCOO_{ad}$ is observed transitorily during dehydration of formic acid to CO_{ad} has been interpreted in the main text as being an evidence that $HCOO_{ad}$ is the reaction intermediate. However, an alternative mechanism can be suggested, in which CO_{ad} forms directly from formic acid through a purely chemical dehydration. In this case $HCOO_{ad}$ would appear on the surface due to its reversible electroadsorption from formic acid, but only transitorily, since it would be displaced by CO_{ad}. In this case, the rate of CO formation at low CO coverage would be:

$$\frac{\mathrm{d}\theta_{\mathrm{CO}}}{\mathrm{d}t} = k_{\mathrm{chem}} c_{\mathrm{HCOOH}} ,$$

where k_{chem} is the rate constant of the hypothetical chemical dehydration reaction. Since the dehydration mechanism would be purely chemical, the rate of formation of adsorbed CO should be potential-independent, this being in complete contradiction with the results of Capon and Parsons,[1] Wieckowski and co-workers[2, 3] and Chen et al.[4] However, it must be noted that the adsorption of a neutral species is expected to depend on the availability of surface sites, which is expected to be maximum at the pzc. Then, the rate of formation of CO_{ad} should be expected to have a maximum at the pzc, in agreement with the results reported by Grozovski et al.[5]

Assuming that the electroadsorption of formate can be described by a Langmuir isotherm, the formate coverage at low total surface coverage would be given by:

$$\theta_{\mathrm{HCOO}} = \frac{k_{\mathrm{ad}}}{k_{\mathrm{des}}} \exp\left(\frac{\Delta\phi F}{RT}\right) c_{\mathrm{HCOOH}} ,$$

where k_{ad} is the rate constant of formate electroadsorption and k_{des} is the rate constant of formate electrodesorption. Hence:

$$\frac{\mathrm{d}\theta_{\mathrm{CO}}}{\mathrm{d}t} = k_{\mathrm{chem}} \frac{k_{\mathrm{des}}}{k_{\mathrm{ad}}} \exp\left(\frac{-\Delta\phi F}{RT}\right) \theta_{\mathrm{HCOO}}$$

According to this equation, at constant potential a plot of $\mathrm{d}I_{\mathrm{CO}}/\mathrm{d}t$ vs. I_{HCOO} would also be linear at low total surface coverage, as in the model proposed by us. However, the slope of a dI_{CO}/dt vs. I_{HCOO} plot would be $k_{\mathrm{chem}}\dfrac{k_{\mathrm{des}}}{k_{\mathrm{ad}}}\exp\left(\dfrac{-\Delta\phi F}{RT}\right)$, and, accordingly, the plot in Fig. 3 of the main text should have a slope of -60 mV, in contradiction with the value of -120 mV found experimentally.

2. Rate-determining reduction of formic acid followed by rapid oxidation of the resulting species and by displacement of $HCOO_{ad}$ by CO_{ad}

An alternative electrochemical mechanism was proposed by Lu et al.[2] in order to explain the decrease of the rate of poisoning by adsorbed CO with increasing potential. According to this mechanism, the first, rate-determining step, would correspond to the reduction of formic acid to adsorbed $HC(OH)_2$. Consequently, the rate of CO_{ad} formation at low total surface coverage would be:

$$\frac{\mathrm{d}\theta_{\mathrm{CO}}}{\mathrm{d}t} = k_{\mathrm{Lu}}\exp\left(\frac{-(1-\beta)\eta F}{RT}\right)c_{\mathrm{HCOOH}},$$

where k_{Lu} is the rate constant for the rate-determining step of the mechanism proposed by Lu et al., β is the symmetry factor (usually assumed to be 0.5) and $\eta = E - E_{\mathrm{eq}}$ is the overpotential. This equation predicts (for $\beta = 0.5$) a decrease of the reaction rate with increasing potential with a Tafel slope of 120 mV, in good agreement with their experimental results.[2]

As before, assuming that the electroadsorption of formate can be described by a Langmuir isotherm, the formate coverage at low total surface coverage would be given by:

$$\theta_{\mathrm{HCOO}} = \frac{k_{\mathrm{ad}}}{k_{\mathrm{des}}}\exp\left(\frac{\Delta\phi F}{RT}\right)c_{\mathrm{HCOOH}}$$

And, hence:

$$\frac{\mathrm{d}\theta_{\mathrm{CO}}}{\mathrm{d}t} = k_{\mathrm{Lu}}\frac{k_{\mathrm{des}}}{k_{\mathrm{ad}}}\exp\left(\frac{(-(1-\beta)\eta - \Delta\phi)F}{RT}\right)\theta_{\mathrm{HCOO}}$$

Again, this equation predicts a linear dependence of dI_{CO}/dt on I_{HCOO}. Assuming $\beta = 0.5$, the equation above predicts a slope of -40 mV for the plot in Fig. 3 of the main text, in complete contradiction with the experimentally observed value of -120 mV.

3. Oxidative electroadsorption of $HCOO_{ad}$ followed by its rate-determining reduction to CO_{ad}

In the two-step electrochemical dehydration of HCOOH proposed by us in the main text, the first step is the reversible electroadsorption of HCOOH, for which:

$$\theta_{\mathrm{HCOO}} = \frac{\frac{k_{\mathrm{ad}}}{k_{\mathrm{des}}}\exp\left(\frac{\Delta\phi F}{RT}\right)c_{\mathrm{HCOOH}}}{1+\frac{k_{\mathrm{ad}}}{k_{\mathrm{des}}}\exp\left(\frac{\Delta\phi F}{RT}\right)c_{\mathrm{HCOOH}}}$$

The rate-determining step is the subsequent electroreduction of $HCOO_{ad}$ CO_{ad}. At low CO coverage:

$$\frac{\mathrm{d}\theta_{\mathrm{CO}}}{\mathrm{d}t} = k\exp\left(\frac{-(1-\beta)\eta F}{RT}\right)\theta_{\mathrm{HCOO}}$$

Substitution yields:

$$\frac{\mathrm{d}\theta_{\mathrm{CO}}}{\mathrm{d}t} = k\exp\left(\frac{-(1-\beta)\eta F}{RT}\right)\frac{\frac{k_{\mathrm{ad}}}{k_{\mathrm{des}}}\exp\left(\frac{\Delta\phi F}{RT}\right)c_{\mathrm{HCOOH}}}{1+\frac{k_{\mathrm{ad}}}{k_{\mathrm{des}}}\exp\left(\frac{\Delta\phi F}{RT}\right)c_{\mathrm{HCOOH}}}$$

Where η is the overpotential with respect to the equilibrium potential, E_{eq}, of this second step. In Figure S2, $k\exp\left(\frac{-(1-\beta)\eta F}{RT}\right)$, θ_{HCOO}, and their product, namely $\frac{d\theta_{\mathrm{CO}}}{\mathrm{d}t}$, have been plotted as a function of potential. Three possible cases, namely those in which $\Delta\phi = 0$ (i.e., when the potential coincides with the pzc) at η = -0.1, 0 and 0.1 V, have been considered. As can be seen, the global rate of dehydration of HCOOH has a symmetric bell shape with a maximum around the pzc. The exact position of the maximum depends on the ratio between $k_{\mathrm{ad}}/k_{\mathrm{des}}$ and k and on c_{HCOOH}. This in agreement with the results of Chen et al.[4] (who observed an increase of the rate of formation of CO_{ad} with increasing potentials for $E < 0.2$ V, but a decrease of the rate of formation of CO_{ad} at $E > 0.2$ V) and, particularly, of Grozovski et al.,[5] who found that a plot of the rate of formation of CO_{ad} vs. potential has a symmetric bell shape, with a maximum at the pzc. It can also be observed that the maximum is more pronounced the more negative is the pzc, this explaining the observation by Grozovski et al.[5] that the activity for the dehydration of HCOOH of Pt(111) is negligible, since its pztc is very positive (0.37 V vs. RHE in 0.1 M $HClO_4$[6]). Furthermore, this also explains that, for the same density of steps, Pt single-crystal electrodes with (111) terraces and (100) steps are less active than those with (111) terraces and (110) steps, because the pzc of (100)-oriented steps is more positive than that of (110)-oriented steps.

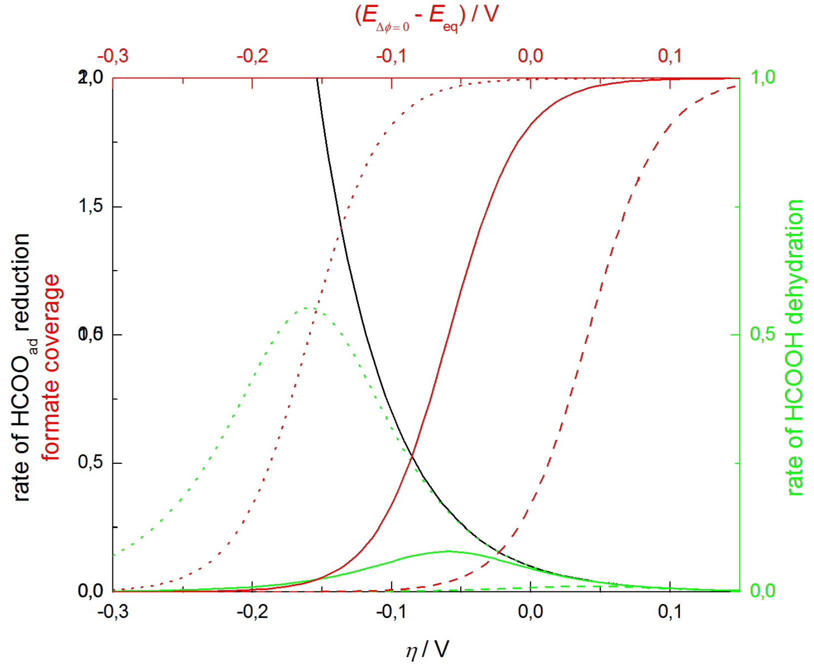

Figure S2. Plot of the rate constant of the second step, $k\exp\left(\frac{-(1-\beta)\eta F}{RT}\right)$, corresponding to the reduction of $HCOO_{ad}$ to CO_{ad} (black line), of the formate coverage, θ_{HCOO} (red lines), and of their product, which is the global rate of dehydration of HCOOH to CO_{ad} (green lines), as a function of potential. The curves have been calculated for k = 0.1 s^{-1}, k_{ad}/k_{des} = 100 and c_{HCOOH} = 0.1 M. Three cases have been considered: $\Delta\phi = 0$ at η = -0.1 V (dotted lines), $\Delta\phi = 0$ at $\eta = 0$ V (solid lines) and $\Delta\phi = 0$ at $\eta = 0.1$ V (dashed line).

Finally, we would like to note that, in this case, the plot in Fig. 3 of the main text must always have a slope of -120 mV, because our spectroscopic experiments detect only the reactant and the product of the second step, namely $HCOO_{ad}$ to CO_{ad}, and the rate constant for this reaction must always decrease with potential with a slope of $\frac{-(1-\beta)\eta F}{RT}$ (-120 mV if $\beta = 0.5$).

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