Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information:
Formic Acid oxidation on platinum-
a simple mechanistic study

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1 Passivation of Pt(111) by H

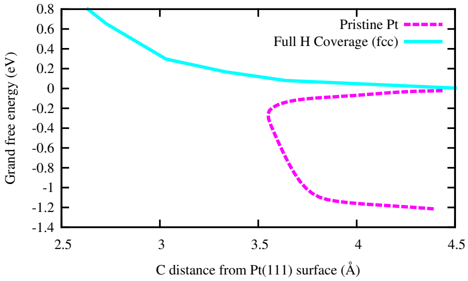

Figure 1: Formate approaching pristine Pt(111), and Pt(111) covered with H, both at 0 V

Figure 1 illustrates the repulsive interaction between formate and a Pt(111) surface fully covered with hydrogen at the fcc sites.

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2 Rate Dependence

We will evaluate the rate dependence on pH, where the rate equations are written as:

$$\mathrm{HA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^- + \mathrm{H}^+ \tag{1}$$

$$\mathrm{Pt} + \mathrm{A}^- \xrightarrow{k_2} \mathrm{CO}_2 + \mathrm{H}_{ads} + \mathrm{e}^- \tag{2}$$

$$\mathrm{H}_{ads} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{H}^+ + \mathrm{e}^- + \mathrm{Pt}. \tag{3}$$

We will first evaluate the pH dependence of these reactions in the regime where equation 2 is the limiting step, when Equations 1 and 3 are at equilibrium.

The equilibrium constant of the formic acid is written as:

$$K_1 = K_a = \frac{[A^-][H^+]}{[HA]}. \tag{4}$$

Given an initial formic acid concentration of HA_{tot}, we must separate out the H^+ dependence in this equation, so

$$[HA] = [HA_{tot}] - [A^-]. \tag{5}$$

Solving for A^-, this gives

$$[A^-] = \frac{K_a[HA_{tot}]}{[H^+] + K_a} \tag{6}$$

We assume that we are in a voltage and concentration regime where the adsorbates that block the platinum sites are only the adsorbed hydrogen atoms:

$$[\mathrm{Pt}_{tot}] - [\mathrm{H}_{ads}] = [\mathrm{Pt}] \tag{7}$$

(Alternatively, if the adsorbates do not bind with a pH dependence, Pt_{tot} represents sum of available sites and sites with adsorbed hydrogen, at a given voltage.)

Using the steady-state assumption for Equation 3, we get:

$$K_3 = \frac{[H^+]f(E)([Pt_{tot}] - [H_{ads}])}{[H_{ads}]} \tag{8}$$

where f(E) is the standard exponential dependence on voltage assuming Butler-Volmer kinetics. Solving for $[H_{ads}]$:

$$[H_{ads}] = \frac{[H^+]f_3(E)[Pt_{tot}]}{K_3 + [H^+]f_{-3}(E)} \tag{9}$$

Now, the rate-limiting step is the middle reaction, which can be written as:

$$\text{rate} = k_2([Pt_{tot}] - [H_{ads}])[A-]f_2(E) \tag{10}$$

and now using the expression for H_{ads} above, we can write this as:

$$\text{rate} = k_2([Pt_{tot}] - \frac{[H^+]f_3(E)[Pt_{tot}]}{K_3 + [H^+]f_{-3}(E)})[A-]f_2(E) \tag{11}$$

When K_3 is relatively very large (i.e. not much H_{ads}), the rate is just dependent on A^-. As the pH increases, we expect the current to follow the concentration of A^-, which increases sharply at the pK_a, and then plateaus.

On the other hand, if K_3 is smaller, than the hydrogen adsorption term can contribute to the rate dependence. However, this term will lead to increases in current with pH, so will not lead to a peak as seen by Joo et al. If, instead of the hydrogen of Equation 3 being the dominant poison species of the platinum sites, species that poison that require a proton to desorb are more important, then we have:

$$\mathrm{H^+ + PO_{4\,ads} \rightleftharpoons HPO^{2-}_{4solv} + Pt} \tag{12}$$

where we use adsorbed phosphate as an example of a possible poisoning species.

This leads to

$$K_{13} = \frac{[HPO^{2-}_{4solv}][Pt]}{[H^+][PO_{4ads}]} \tag{13}$$

Solving for PO_{4ads}, we have:

$$PO_{4ads} = \frac{[Pt_{tot}]}{1 + \frac{K_{13}[H^+]}{[HPO^{2-}_{4solv}]}} \tag{14}$$

The pH dependence of this term leads to the overall rate having a maximum near the pK_a of formic acid.