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:

\[ \text{HA} \xrightleftharpoons[k_1]{k_{-1}} A^- + H^+ \]  

\[ \text{Pt} + A^- \xrightarrow{k_2} \text{CO}_2 + H_{ads} + e^- \]  

\[ H_{ads} \xrightleftharpoons[k_3]{k_{-3}} H^+ + e^- + \text{Pt} \]  

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:

\[ K_1 = K_a = \frac{[A^-][H^+]}{[HA]} \]  

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

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

Solving for A^-, this gives

\[ [A^-] = \frac{K_a[H_{A_{tot}}]}{[H^+] + K_a} \]  

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:

\[ [Pt_{tot}] - [H_{ads}] = [Pt] \]  

(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:

\[ K_3 = \frac{[H^+] f(E)([Pt_{tot}] - [H_{ads}])}{[H_{ads}]} \]
where \( f(E) \) is the standard exponential dependence on voltage assuming Butler-Volmer kinetics. Solving for \([H_{ads}]\):

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

(9)

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

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

(10)

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

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

(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:

\[
H^+ + PO_{ads} \rightleftharpoons HPO_2^{2-}_{4solv} + Pt
\]  

(12)

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

This leads to

\[
K_{13} = \frac{[HPO_2^{2-}_{4solv}][Pt]}{[H^+][PO_{ads}]}
\]  

(13)

Solving for \( PO_{4ads} \), we have:

\[
PO_{4ads} = \frac{[Pt_{tot}]}{1 + \frac{K_{13}[H^+]}{[HPO_2^{2-}_{4solv}]}}
\]  

(14)

The pH dependence of this term leads to the overall rate having a maximum near the pK\(_a\) of formic acid.