

Effect of pH on the electrocatalytic oxidation of HCOOH/HCOO⁻ on platinum: A mechanistic study

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Electro-oxidation of formic acid on Pt in acid is one of the most fundamental model reactions in electrocatalysis. It is generally believed that HCOOH is oxidized to CO₂ via a dual-pathway mechanism: main reaction pathway via a reactive intermediate and a reaction involving adsorbed CO (poison). Despite the intensive studies over four decades, however, the main reaction pathway is still a matter of strong debate. Two different mechanisms, bridge-bonded adsorbed formate mechanism and direct HCOOH oxidation mechanism, have been proposed by assuming *a priori* that HCOOH is the major reactant. Through systematic examination of the reaction over a wide pH range (0–12) by cyclic voltammetry and surface-enhanced infrared spectroscopy (SEIRAS), we will show that the formate ion, HCOO⁻, is the major reactant over the whole pH range examined, even in strong acid (Figure 1). The performance of the reaction is maximal at a pH close to the pK_a of HCOOH. The pH dependence is explained by simple kinetic modeling. The reaction serves as a generic example illustrating the importance of pH variation in catalytic proton-coupled electron transfer reactions.

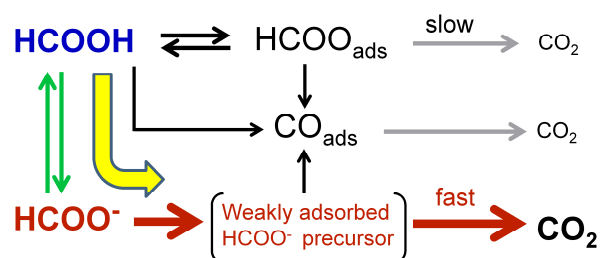


Figure 1. Electrooxidation of HCOOH via HCOO⁻ provided through the acid-base equilibrium.