

Formic Acid Electro-oxidation on Pt Group Metals: Revisiting an Old Problem

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Formic acid electro-oxidation reaction (FAOR) is of both fundamental and practical importance. On the one hand, FAOR is the anodic half reaction of a direct formic acid fuel cell (DFAFC) that is currently under development for its potential use to power portable electronics. On the other hand, chiefly due to its perceived simplicity, FAOR has long been used as a model reaction to illustrate two-electron oxidation reactions of small (C_1) organic molecules in electrocatalysis in general. However, notwithstanding decades' studies, its detailed reaction mechanism is still under intense debates in terms of reaction intermediates and pH dependence, exemplifying a fundamental challenge of current interest. In this presentation, we report the identification of a key reaction step in FAOR on Pt, PtRu and Pd that has been missed in previous mechanistic studies but appears to be the key link for a unifying mechanistic picture for the reaction. Specifically, by combining *in situ* electrochemical attenuated-total-reflection surface-enhanced IR reflection adsorption spectroscopy (ATR-SEIRAS), isotope labeling and flow-cell operation, we were able to unravel that the reaction between the surface-bound formate from FA and OH group from activated water is the key reaction step to reconcile the contradictory observations reported in the literature and by which to achieve a much better understanding of the FAOR mechanism.