

# **Deciphering the roles of surface mono- vs bi-dentate formate in formic acid oxidation reaction on Pd and Pt electrocatalysts by in situ IR spectroscopy**

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The formic acid oxidation reaction (FAOR) has applications as both a standard electrochemical reaction for testing potential electrocatalysts and as an anode reaction in a direct formic acid fuel cell (DFAFC). While it has long been generally accepted that the FAOR proceeds via a dual pathway mechanism (direct and indirect reaction pathways), there has been continued debate into the identity of the reactive intermediate and proposals of a triple (direct, indirect, or formation) reaction pathway. In this presentation, we will discuss our recent mechanistic studies of the FAOR on both Pd and Pt electrocatalysts using deuterated formic acid (DCOOD) and attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS). We have observed not only the previously documented bidentate formate ( $\text{HCOO}_B$ ) vibrational band at  $\sim 1303\text{ cm}^{-1}$  but also a new vibrational band at  $\sim 2150\text{ cm}^{-1}$ . By careful analysis of the peak integral ratio between those two IR bands,  $I_{2150}/I_{1303}$ , under different experimental conditions, we will present convincing evidence to discern a substantial contribution to the C–D band by a species other than the bidentate formate in the FAOR active potential range. We will argue that this new species is more likely than not a monodentate formate that is also the true active FAOR intermediate. Further more, we will present the results of DFT calculations that support the D-out instead of D-in molecular configuration of the monodentate formate. Finally, we will discuss the surface molecular processes that underpin the potential oscillatory behavior of FAOR under constant oxidative galvanostat current.