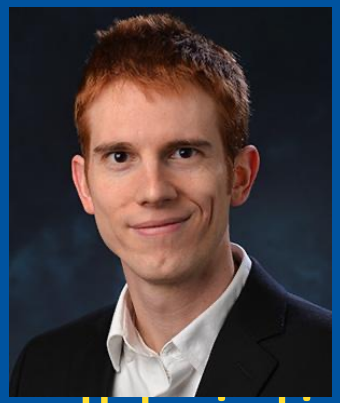
INORGANIC CHEMISTRY SEMINAR

Kinetic Fingerprints of Electro-Oxidations on Bimetallics: Understanding the Interplay of Bifunctional and Electronic Effects



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219 BRL

Electro-oxidations of small organic molecules are some of the most widely studied processes in electrocatalysis for both fundamental and technological reasons. Many reactions relevant to wastewater treatment, sensing, distributed-scale chemical synthesis, and a variety of direct-organic fuel cells all converge in a network of interconnected C_1 oxidation steps. Bottlenecks are often identified from pathways that culminate in formation of CO strongly bound to electrode surfaces. Thus, there is particular interest in developing CO-tolerant materials to improve the efficiency of organic-converting fuel cells, electrolyzers, and other related devices.

Multi-component electrocatalysts provide wide possibilities to tune reactivity, though the fundamental origins of modification are often ambiguous. For example, a number of bimetallics, (e.g., Pt_xRu_{1-x}, Ag_xPd_{1-x}) show enhanced oxidation activity relative to their constituent components, and the effects are often interpreted in terms of “bifunctional” mechanisms, in which one element activates carbon-containing species and the other serves to introduce oxygen (from water) to the surface to facilitate C-O coupling. Conversely, each component can perturb the electronic structure of the other and modulate the intrinsic activity at each site. Here we demonstrate methods to elucidate operant mechanisms on such materials with microkinetic analysis based on generalized degrees of rate control and second-order kinetic observables. Reaction orders, activation barriers, and transfer coefficients (all sensitivities of rate) can vary strongly across operating conditions, providing a rich dataset with complex interdependencies. Our analysis leads to support for several counterintuitive reaction mechanisms and more broadly illustrates the need for more rigorous kinetic characterization in electrocatalysis.

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