



# CHE SEMINAR SERIES

## Elucidating the Origins of Electrocatalytic Phenomena with Electrochemical Steady State Isotopic Transient Kinetic Analysis

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Electrocatalysis enables chemical transformation to be directly driven by electricity. The viability of electrocatalytic technologies is currently limited by a lack of highly active and earth abundant electrocatalytic materials. The intrinsic activity of an electrocatalyst is the ratio between the steady state coverage of reaction intermediates and their surface lifetimes. Unfortunately, no technique currently exists for measuring either of these critical activity parameters for electrocatalytic systems. However, both have been measured for thermal heterogeneous catalysts using steady state isotopic transient kinetic analysis (SSITKA). During SSITKA, the transient isotopic composition of the reaction product is monitored in response to a rapid change in the isotopic composition of the reactant. The resulting product isotopic transients are directly related to the coverage and lifetime of the corresponding reaction intermediates. SSITKA measurements require continuous real-time product analysis and the ability to rapidly change the isotopic composition of the reacting species. These requirements are difficult to satisfy for electrocatalytic systems due to the mass transfer resistance associated with the condensed phase electrolyte. This presentation will outline the first quantitative method for performing electrochemical SSITKA (eSSITKA). The approach is based on differential electrochemical mass spectrometry, an analytical technique that interfaces an electrochemical reactor to a mass spectrometer using a pervaporation membrane. This configuration enables volatile electrochemical reaction products to be continuously sampled, identified, and quantified in real time. The insights made possible by eSSITKA are demonstrated using methanol (MeOH) oxidation to CO<sub>2</sub> over platinumized Pt as a test reaction. This reaction exhibits an odd volcano-like potential dependent activity. eSSITKA measurements suggest that the surface is populated by two distinct pools of reaction intermediates, in agreement with the contemporary understanding of the reaction mechanism. A direct correlation between the intrinsic activity calculated using the parameters measured via the isotopic transients and the CO<sub>2</sub> partial current density was observed, which validates the accuracy of the approach. The data suggests that at low overpotential the rate of reaction is limited by long intermediates surface lifetimes, while at high overpotential the rate of reaction is limited by a low intermediate surface coverage. The eSSITKA technique is compatible with any reaction or electrocatalyst that produces a volatile product and will thus accelerate our understanding of a variety of different electrocatalytic phenomena.

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Ezra L. Clark is the Thomas K. Hepler Early Career Professor of Chemical Engineering at the Pennsylvania State University. His research group focuses on the development of electrocatalytic technologies for sustainable fuel and chemical production. Currently, his group is focused on the development of electrochemical isotopic transient measurements, the design of intermetallic electrocatalysts, and the exploration of thermo-electrocatalytic synergy. Ezra earned his undergraduate degree in Chemical Engineering from the University of Louisville and his doctoral degree in Chemical Engineering from the University of California at Berkeley. Before arriving at Penn State, he performed postdoctoral research at the Danish Technical University outside of Copenhagen, Denmark. He has received numerous recognitions at every stage of his career, including a Goldwater Scholarship, a National Science Foundation Graduate Research Fellowship, a Marie Skłodowska-Curie Postdoctoral Research Fellowship, and the Hepler endowed professorship. He is also the president-elect of the Pittsburgh-Cleveland Catalysis Society (PCCS).

