

Electrochemical Steady State Isotopic Transient Kinetic Analysis (e-SSITKA): A New Technique for the Investigation of Electrocatalytic Materials

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Electrolyte cations significantly influence the activity and selectivity of many electrochemical reactions¹. However, the mechanism of cation promotion remains unclear. The intrinsic activity of an electrocatalyst is a function of both the steady state coverage of reaction intermediates and their surface lifetimes. Unfortunately, no technique currently exists for measuring either of these critical parameters for electrocatalytic systems. Herein, we aim to develop the first analytical instrument capable of directly measuring these critical parameters, with the goal of leveraging this advancement to elucidate the origins of cation promotion in electrocatalytic processes. The approach is based on differential electrochemical mass spectrometry (DEMS), an analytical technique that interfaces an electrochemical reactor to a mass spectrometer using a pervaporation membrane². This configuration enables volatile electrochemical reaction products to be continuously sampled, identified, and quantified in real time. The sensitivity and time response of the technique are dependent on the proximity of the pervaporation membrane to the electrocatalyst surface. Coating the electrocatalyst directly onto the pervaporation membrane enables product sampling to be performed directly from the electrode-electrolyte interface, maximizing both the sensitivity and time response of the technique. We have coupled this reactor to a custom flow setup that enables the isotopic composition of the reacting species to be rapidly changed in under one second, collectively enabling steady state isotopic transient kinetic analysis (SSITKA) to be applied to electrocatalytic materials for the first time. SSITKA enables the steady state coverage and surface lifetimes of reaction intermediates to be directly measured³. We demonstrate this capability using methanol (MeOH) oxidation over Pt as a test reaction. In the future, we will implement this technique to elucidate the origins of several process parameters, such as applied potential, cation identity, and electrocatalyst composition, on electrocatalytic activity.

References:

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