

Reducing ensemble averaging for mechanistic insight in electrocatalysis

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Abstract: Mechanistic insight in electrocatalysis is generally inferred from ensemble-averaged empirical data from product and catalyst characterizations as well as theoretical analyses of reaction intermediate adsorption energies. Ensemble measurements average over large populations of single entities, such as transient chemical intermediates, providing general trends but lost is a vast amount of information on how molecules interact and evolve on an electrocatalyst surface which could reveal over- or underperforming subpopulations within an ensemble. To meet the challenge of lowering spatial and temporal averaging to observe discrete steps in electrocatalysis, I will discuss our development of time-resolved (μs) electrocatalytic measurements using Raman scattering microscopy as a readout. Operando Raman microscopy is aptly suited to reduce spatial averaging of electrochemical events because vibrational signatures from unique chemical species can be spatially isolated with diffraction-limited resolution. To reduce temporal averaging of Raman spectra, a modulated excitation strategy is used: pulsed-potential spectroelectrochemistry. As a model system, we study the electrocatalytic reduction of CO_2 on Ag electrodes in acetonitrile. By tracking key reaction intermediates, we find that local environments markedly affect electrochemical performance. Time-resolved Raman spectra also reveal that the evolution of intermediate concentrations on the electrocatalyst surface depend on the applied potential. The observed dynamics of reaction intermediates, hidden by spatially and temporally averaged ensemble measurements, provide critical information on the reaction mechanism and illustrate the importance of studying chemical reactions on catalysts beyond the ensemble.