

Mechanism Of Dioxygen and Peroxide Reduction On Metal Monolayer Modified Electrode Surfaces

Andrew Gewirth,¹ Xiao Li¹ and Ilwhan Oh¹

¹University of Illinois
Department of Chemistry
600 S. Mathews Avenue
Urbana, IL 61801
USA

Metal monolayers formed by the underpotential deposition (upd) process have long been known to function as catalysts for the electroreduction of a variety of small molecules, especially dioxygen and peroxide. By using a combination of spectroscopic, imaging, and x-ray scattering techniques combined with detailed calculations, we have elucidated the mechanism of this activity for several upd systems. These measurements show that the upd adatom induces charge transfer between the substrate and the adatom, leaving a net positive charge on the substrate near the upd adatom. This electropositive area is the locus of small molecule attachment to the surface. Detailed spectroscopic and calculational efforts reveal that the initial stage of reactivity involves cleavage of the O-O bond to form a mixed metal-hydroxide complex. This hydroxide complex is reduced during the electron transfer event, leading to the product water. This analysis provides new directions for synthesis of novel cathode materials.