MECHANISM OF DIOXYEN REDUCTION ON METAL MONOLAYER MODIFIED ELECTRODE SURFACES

Andrew A. Gewirth, Ilwhan Oh, Xiao Li, and Show-jon Hsieh
Department of Chemistry, University of Illinois,
600 S. Mathews Avenue, Urbana, IL 61801

Metal monolayers formed by the underpotential deposition process have long been known to function as catalysts for the electroreduction of a variety of small molecules, especially dioxygen. By using a combination of spectroscopic, imaging, and x-ray scattering techniques combined with detailed calculations, we have elucidated the mechansim 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 postive charge on the substrate near the upd adatom. This electropositive area is the locus of small molecule attachment to the surface and is the initial site of electron transfer to the adsorbate.