Poisoning the Active Site of Electrochemical Reduction of Dioxygen on Metal Monolayer Modified Electrode Surfaces

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One of the most important reactions in the electrochemical environment is the electroreduction of dioxygen to water. [1, 2] This importance stems not only from the utility of this reaction in fuel cells and fuel cell devices, but also because of its relevance to corrosion and other processes. Despite intensive effort extending over several decades, there is no real understanding of the mechanisms associated with cleavage of the O-O bond, the sites of absorption of dioxygen or peroxide on the electrode surface, nor the origin of the overpotential for dioxygen reduction.

One set of systems exhibiting catalytic activity for dioxygen and peroxide electroreduction are those formed by the underpotential deposition (upd) process. [3, 4] In the acid electrochemical environment, underpotentially deposited submonolayers of Pb, Tl, and Bi on Au(111) all enhance the rate of peroxide reduction relative to the bare Au surface. While probably of limited practical utility, these upd systems provide ideal assemblages to test ideas concerning the interplay between surface structure and electrocatalytic activity particularly because the surface structures associated with this activity have been examined using scanning probe microscopy [5, 6, 7] and x-ray scattering techniques.

In this work [8] we report the results of measurements designed to help elucidate the role of the particular configuration maintained in the Bi upd system that acts as a dioxygen reduction catalyst. In particular, we use anions that appear to replace the hydroxide whose presence in the Bi upd structure we inferred from electrochemical measurements. This anion replacement scheme has consequences with regard to both the structure and reactivity of the (2X2) Bi monolayer.
References


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Current Interest:
1) Dioxygen reduction chemistry on underpotentially deposited (upd) metal surfaces;
2) Electrochemical noble metal deposition on semiconductor substrate.