Surface Coverage and Structure of Catalytic Metal Monolayers on Au(111) Electrodes

Brian Niece   Final Seminar   July 17, 1997

Small molecule oxidation and reduction in fuel cells is one possible source of electrical energy which may make widespread use of electric vehicles practical. In addition, catalytic electroreduction of common wastes such as nitrogen oxides to ammonia and N_2 has great potential as a method for conversion of pollutants to useful products. Effective catalysis of reactions used in these and other electrosynthetic systems is dependent on fast electron transfer between electrodes and reacting molecules at the electrode/electrolyte interface.

One reaction of particular interest is the two electron reduction of hydrogen peroxide to water according to equation 1. This reaction is important because it is often the limiting step in

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \qquad (1)$$
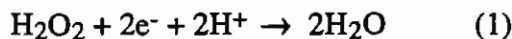
the reduction of molecular oxygen, which occurs as the cathode reaction in many potential fuel cell schemes. Incomplete two electrode reduction of O_2 results in a buildup of H_2O_2 as a waste product and less efficient energy conversion of the reactants. On electrodes where peroxide reduction is facile, however, reduction of O_2 proceeds as a four electron process with water as the only by-product.

Underpotentially deposited[1] monolayers and submonolayers of foreign metals on electrode surfaces have been found to catalyze a variety of small molecule redox reactions.[2] The peroxide reduction reaction is catalyzed by the presence of underpotentially deposited Bi,[3,4] Tl,[5] and Pb[5] on gold electrodes. Cd upd adlayers have been found to exhibit catalytic activity for the electroreduction of nitrate to nitrite and other lower oxides of nitrogen on both gold and silver electrodes.[6,7] There has been much interest in elucidating the structure of these modified electrodes in order to determine the nature of the catalytic activity.

We are particularly interested in understanding the formation of adlayers in three upd systems on Au(111) which are known to catalyze small molecule redox reactions. The Bi and Tl systems catalyze the peroxide reduction discussed above. The peroxide reduction in these systems is characterized by three potential regions in which the catalytic activity is alternately off, on, and off again.[8] Structural investigations have indicated that the surface exhibits three distinct structures in the Bi underpotential deposition region.[9,10] At the positive and negative extremes of the region, the surface is composed of close-packed Au and Bi respectively. In the catalytically active region, the structure is an open (2 x 2)-Bi adlayer. The Tl upd system, similarly, forms a close-packed Tl monolayer at negative potentials in acid solution where peroxide reduction catalysis ceases.[11] There is no direct structural information available about the catalytically active structure in this system, however. Upd Cd on Au(111) has been found to catalyze the reduction of nitrate ions.[6,7] The surface is catalytically active throughout the upd potential region in this system. Knowledge of the exact structure and nature of the species present at the electrode surface in these catalytically active systems is necessary in order to understand the mechanism of catalysis. In addition, information about the forces which control the open adlayer in the Bi system is desirable.

Chronocoulometric and quartz crystal microbalance (QCM) measurements have confirmed the low coverage of Bi and Tl present in the catalytically active regions. The coverage of hydroxide anions in the presence of upd Bi is shown in Figure 1. The surface concentration of hydroxide rises in the region where Bi forms an open adlayer, and decreases
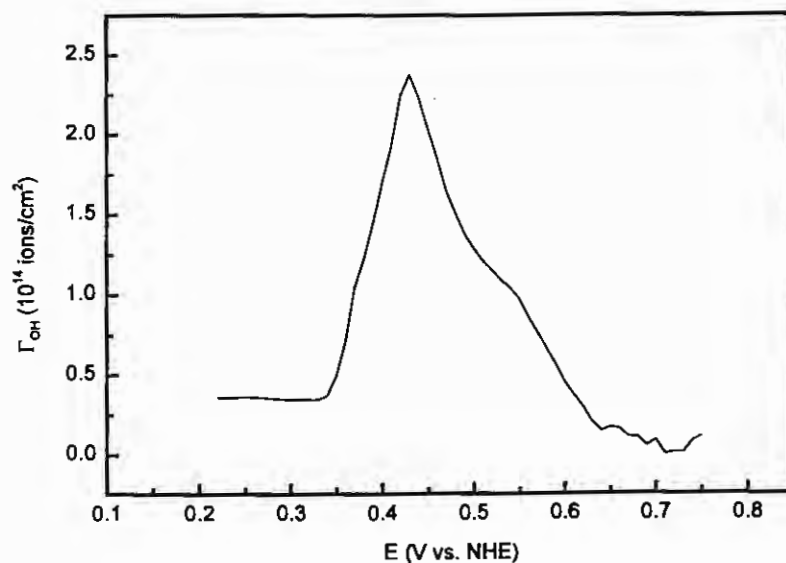
Figure 1. Surface Concentration of OH⁻ on Au(111) in the presence of 1.0 mM Bi^{3+} + 0.1 M ClO$_4^-$.

again at more negative potentials. The presence of coadsorbed hydroxide in the intermediate potential region is believed to be responsible for the open adlayer observed at these potentials. The Bi adatoms on Au(111) are found to be fully discharged in the low coverage phase.

The electrosorption valency of Cd upd on Au(111) is shown in Figure 2. The Cd adatoms retain a significant portion of their initial 2+ charge throughout the upd potential region.
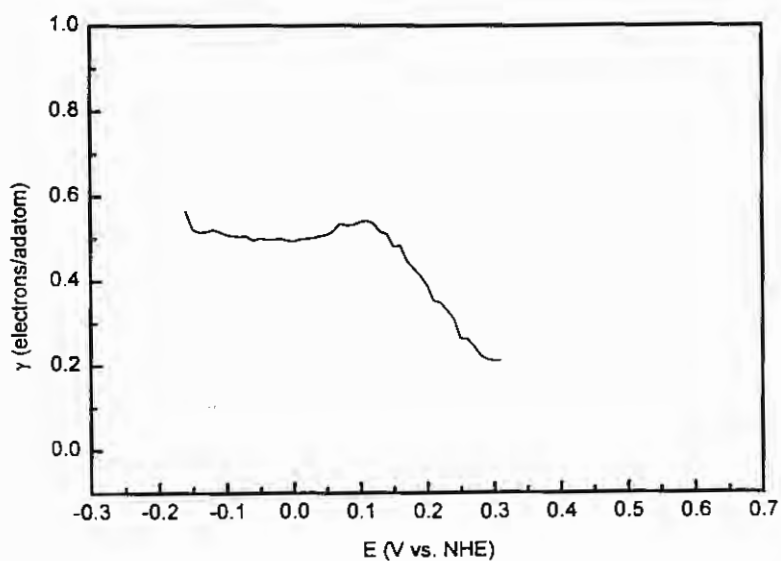

Figure 2. Electrosorption valency of Cd on Au(111) calculated from potential step data.

Sulfate anions are found to be coadsorbed with the upd Cd. In the absence of sulfate in the electrolyte, no ordered upd structures are observed. In the presence of sulfate, Cd forms linear upd structures.[12] These structures are believed to arise from the positively charged adsorbate which causes a reconstruction of the surface similar to that observed on the bare gold electrode under appropriate conditions. This residual positive charge may also have important consequences for the catalytic activity of the upd surface.

The Tl on Au(111) upd system exhibits characteristics of both of these other systems. The Tl adatoms are partially charged during the early stages of upd, where there is a partial monolayer of Tl on the surface. At more negative potentials, the Tl layer condenses to one which is close packed and not charged. Hydroxide anions are involved in stabilizing the charged low coverage adlayer found in the catalytically active region.

References

1. Kolb, D. M.; In *Advances in Electrochemistry and Electrochemical Engineering*; Gerischer, H.; Tobias, C. W., Eds.; Wiley: New York, 1978; Vol. 11, pp. 125-271.

2. Adzic, R. R.; In *Advances in Electrochemistry and Electrochemical Engineering*; Gerischer, H., Tobias, C. W., Eds.; Wiley-Interscience: New York, 1984; Vol. 13, pp. 159-260.

3. Adzic, R. R.; Despic, A. R. *Z. Phys. Chem. (Munich)* **1975**, *98*, 95-110.

4. Jüttner, K. *Electrochim. Acta*, **1986**, *31*, 917-927.

5. Kokkinidis, G.; Sazou, D. *J. Electroanal. Chem.* **1986**, *199*, 165-176.

6. Huang, H.; Zhao, M.; Xing, X.; Bae, I. T.; Sherson, D. A. *J. Electroanal. Chem.* **1990**, *293*, 279-284.

7. Xing, X.; Scherson, D. A.; Mak, C. *J. Electrochem. Soc.* **1990**, *137*, 2166-2175.

8. Sayed, S. M.; Jüttner, K. *Electrochim. Acta* **1983**, *28*, 1635-1641.

9. Chen, C-h. C.; Gewirth, A. A. *J. Am. Chem. Soc.* **1992**, *114*, 5439-5440.

10. Chen, C-h. C.; Kepler, K. D.; Gewirth, A. A.; Ocko, B. M.; Wang, J. *J. Phys. Chem.* **1993**, *97*, 7290-7294.

11. Adzic, R. R.; Wang, J. Ocko, B. M. *Electrochim. Acta* **1995**, *40*, 83-89.

12. Bondos, J. C.; Gewirth, A. A.; Nuzzo, R. G. *J. Phys. Chem.* **1996**, *100*, 8617-8620.