

The Oxidative Deposition of Thiulates and Dithiolates on Gold - D. Qu, S. Rifai, and M. Morin (Department of Chemistry, University of Ottawa)

Electrochemistry provides a simple reliable method of forming monolayers of a variety of compounds containing sulfur on metallic surfaces. We will present the results of studies of the mechanisms of oxidative deposition of thiulates and dithiolates on gold. These results show that electrodeposition of these compounds allows a control of the deposition rate, which is not possible under open-circuit conditions.

The kinetics of oxidative deposition of alkylthiolates on a gold surface has been studied with the Electrochemical Quartz Crystal Microbalance (EQCM) method. The surface concentrations obtained from the oxidative charge and the surface concentrations calculated from the Sauerbrey equation are in excellent agreement in various alkaline aqueous solutions. Differential capacitance measurements suggest that the validity of the Sauerbrey equation (i.e. the frequency is proportional to the mass) is related to the fact that double layer changes occur prior to the oxidative deposition and after the reductive desorption of alkylthiolates. The EQCM results obtained in a 1mM butanethiolates or octanethiolates in 0.1M KOH aqueous solution show that the oxidative deposition of alkylthiolates occurs in two-step: A fast, potential dependent step and a slow potential independent step. The EQCM data is compatible with the initial oxidative deposition following a potential dependent instantaneous nucleation-growth process. For slow deposition rates, once the coverage is at least 80%, the deposition occurs via a slower potential independent Langmuir process. At faster deposition rates, the deposition occurs only by the nucleation and growth mechanism. We will also discuss the dissociative electrodeposition of thiols and the effect of the breaking of the S-H bond on the deposition mechanism.

The electrodeposition of dithiolates yields bilayers. EQCM, FTIR and chronoamperometric measurements show that dithiolates are oxidatively deposited in a vertical orientation. The unreacted sulfur group of the adsorbed dithiols can be made to react with thiulates in the solution and form a bilayer by applying a sufficiently positive potential. This process that was not (clearly) observed in solution or gas phase depositions shows that electrodeposition of organic adsorbates can yield new organic interfaces. The ortho-, meta-, para-dimethylthiolbenzene series reveals changes of the oxidative deposition mechanism. These changes are found to be related to the structure of these rigid molecules. AFM/STM measurements of the structures of monolayers and bilayers of these aromatic dithiolates are underway and will be presented.