

## Electrochemical Surface Oxidation of Ru(0001)

J. Wang, N. Marinkovic, H. Zajonz, B. Ocko, and R. Adzic (BNL)

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It is now generally believed that detailed structural phase behavior of a thin layer ruthenium oxide plays a key role in determining its unusual electroadsorption and catalytic properties. In the gas phase, initial oxidation of Ru(0001) involves oxygen adsorption of up to one full monolayer and the spacing between the top two Ru layers increases with increasing oxygen coverage. In this study, *in situ* x-ray specular reflectivity technique has been used to characterize the surface oxidation of a Ru(0001) electrode in 1 M H<sub>2</sub>SO<sub>4</sub> solution. The Ru(0001) crystal was sputtered and annealed in UHV followed by five cycles of oxygen adsorption/desorption, and then transferred in Ar to the solution and the cell. The experimental data and the best fits are shown in the figure (upper panel). The results are illustrated in the bottom panel. The spacing between the top two Ru layers is 2.13 Å at 0.1 V and 2.20 Å at 1.0 V, similar to those found in gas phase for bare Ru (2.10 Å) and for a full monolayer of oxygen on Ru (2.22 Å), respectively. A larger spacing at low potentials has been observed in solutions with nonadsorbing anions due to the strong Ru-water interaction. In 1 M H<sub>2</sub>SO<sub>4</sub> solution, the bisulfate adsorption, which has constant and saturation coverage between 0 and 0.5 V, protects Ru(0001) from water-induced oxidation at low potentials. In contrast to Pt(111) and Au(111) surfaces, no place exchange is involved in the Ru(0001) surface oxidation. On the oxidized surface, the oxygen species stays on top of a smooth ruthenium surface causing a partial desorption of the bisulfate ions. The lack of subsurface oxygen on a Ru(0001) electrode is postulated to be the origin of its inactivity for CO oxidation found in a separate study.

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