

X-Ray Studies of RuO₂(110) Surface Structures

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Despite the great importance of metal oxide surfaces for chemical processes such as catalysis, electrolysis and supercapacitance phenomena, relatively little is known in detail about atomic-scale mechanisms governing the surface properties of these materials. Of particular importance for phenomena occurring in aqueous solution is the presence of interfacial water layers.

Here, we will discuss experiments in which (110) surfaces of high-quality RuO₂ single crystals were prepared electrochemically and subsequently transferred to a UHV surface scattering chamber. Measurement of specular and off-specular crystal truncation rods (CTR's) allows determination of the surface structure, both in-plane and along the surface normal. Our previous in-situ x-ray/electrochemical studies under potential control in 0.1 M NaOH have established the existence of distinct commensurate H₂O layers that are produced electrochemically by site-specific redox processes. Observation of these weakly scattering commensurate layers is made possible by the unique symmetry of the rutile structure, giving rise to a set of CTR's for which the bulk Ru contribution cancels.

It was found that two commensurate water structures (with different densities) are possible depending on the applied potential. Since one of the structures exists at the open-circuit potential (OCP), the possibility exists that this structure may be stable when removed from solution. By performing the cyclic voltammetry in a conventional cell and subsequently transferring the sample to the vacuum chamber, its structure may be measured in the vacuum environment and compared directly with the in-situ electrochemical measurement. By heating the sample in vacuum, we observed a structural transition which we attribute to desorption of the commensurate water layer. Desorption of the water layer results in a highly modified surface structure which may be oxygen-deficient. In addition, complimentary experiments were performed in which the surface was prepared by conventional surface techniques (ion bombardment followed by annealing in an oxygen environment) to produce the stoichiometric (1x1) surface. Comparison of the two preparation methods highlights certain advantages of the electrochemical preparation, and demonstrates the ability of synchrotron X-ray diffraction to resolve the positions of oxygen atoms at the surface.