

Oxidation of the ruthenium dioxide (110) surface: observation of commensurate water

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Introduction

Ruthenium dioxide is the most investigated and well-known candidate oxide material for ultracapacitors, and it exhibits the most ideal ultracapacitor behavior. Additionally, the pseudocapacitance was generally found to dominate over the simple double-layer capacitance. The essential surface reaction of the RuO_2 electrode is expected to cover the full range of Ru^{2+} , Ru^{3+} , and Ru^{4+} oxidation states. We studied the transition from Ru^{3+} to Ru^{4+} and the reverse transition.

Methods and Materials

Single crystals of RuO_2 were grown in a multizone furnace using a vapor transport method under oxygen flow. A selected crystal embedded in a Teflon perk was mounted in an *in situ* electrochem./x-ray cell. The experiment was performed in 0.5 M sulfuric acid.

Results

The (110) surface is composed of a layer of a rectangular lattice ($a = \sqrt{2}a_0 = 6.36$ and $b_0 = c_0 = 3.11$ Å) of Ru atoms in a two-dimensional body-centered position. Because of that, there are rods of x-ray scattering produced only by the oxygen atoms, henceforth referred as oxygen truncation rods (OTR), due to the precise cancellation of the scattering from the two body-centered Ru atom positions.

We acquired and analyzed complete data sets at three potentials, marked I, II, and III in the cyclic voltammogram (CV, Figure 1A). We show in Figure 2 one OTR measured at the three potentials. The scans are shown for potentials I, II, and III (-200, 330, and 500 mV) starting with the top scan. Note that the rod intensity at -200 and 500 mV are qualitatively similar but they are very different from the rod at 330 mV. In particular, the intensity near $L = 4$ radically changes from "peak-like" to "valley-like" and back to "peak-like." This position is extremely sensitive to the position of the surface oxygen atoms commensurate to the surface lattice. (Incommensurate atoms such as floating water molecules do not contribute to the intensity of OTR.) The peak at the anti-Bragg position indicates that there is an additional commensurate layer above the surface at approximately twice the regular bulk oxygen spacing. The scattering factor of this layer matches to that of a layer of oxygen atoms. At this distance, these oxygen atoms are not likely chemically bonded to the surface ruthenium atoms. Therefore, we come to a conclusion that this additional layer is a layer of water molecules commensurate to the surface lattice.

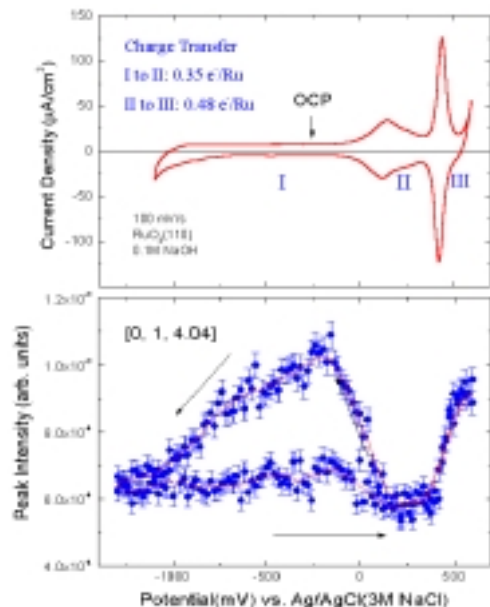


Figure 1: (top) CV of $\text{RuO}_2(110)$ surface reaction. (bottom) X-ray intensity as a function of potential. The arrows indicate the directions of the potential changes.

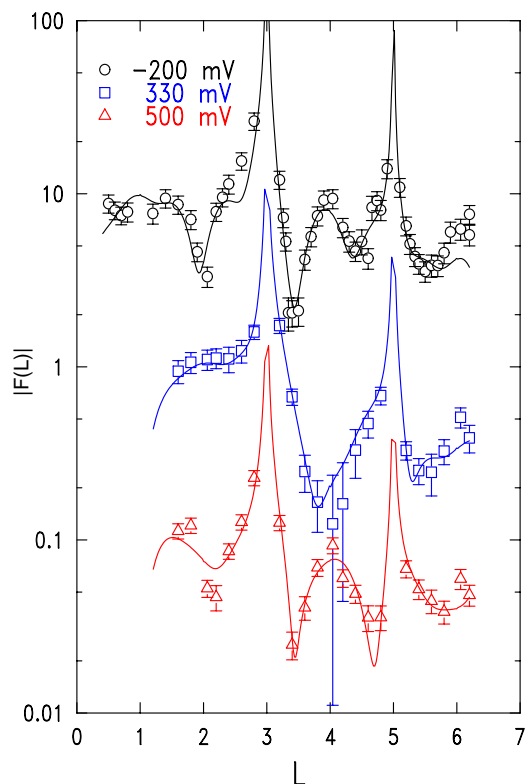


Figure 2: An oxygen truncation rod at three potentials.

Discussion

The intensity at $L = 4$ measured as a function of potential is shown in Figure 1B. There are several distinct regions in the scan. (i) Starting in the cathodic direction (upper arrow) at 500 mV, the x-ray intensity rapidly decreases corresponding to the peak position in the CV that is due to the desorption of the bridging water molecules by reducing the atop oxygen atoms to OH. (ii) The intensity is flat in the potential region between the two peaks in the CV. (iii) The intensity starts rising as the bridging OHs are further reduced to water molecules corresponding to the peak at 150 mV in the CV. (iv) The x-ray intensity continues to rise even after the charge transfer ceases at around 0 mV indicating that the position of the water molecule layer continues to rise during this potential sweep. (v) Eventually, the water molecules become discommensurate with the underlying lattice and the intensity falls, as the potential becomes increasingly negative.

During the reverse scan (following the lower arrow), the potential increases but the water molecules do not recover the commensurate positions and the intensity does not recover until the surface is fully oxidized at 400 mV. It means that the layer of water comes back to the surface at 0 mV but does not form a commensurate network. Also, the full oxidation to 400 mV is required for the commensurate water layer observed at OCP. This scenario is reinforced by the fact that the change in x-ray intensity at the anti-Bragg position occurs without observable charge transfer during the discommensuration of water molecules. Our analysis of the full data set reveals that the water monolayer at OCP bridges the atop OH molecules by forming a frozen network of ice molecules on the water.

Acknowledgments

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