In Situ Scanning Tunneling Microscopy of (Bi)sulfate, Oxygen, and Iodine Adlayers Chemisorbed on Well-Defined Ru(001) Electrode Prepared in a Non-Ultrahigh Vacuum Environment

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This work shows that it is possible to prepare a well-defined Ru(001) surface by annealing in an airtight quartz cell purged continuously with hydrogen gas. Running cyclic voltammetry on the as-prepared Ru(001) electrode in 0.1 M hydrofluoric and perchloric acid solutions resulted in well-defined redox characteristics. **Figure 1** shows the cyclic voltammograms at 50 mV/s in 0.1 M $HClO_4$ of Ru(001) electrodes prepared by annealing in a hydrogen environment (solid line) and mechanically polishing (dotted line). Evidently, different pretreatment of the Ru(001) electrodes results in unlike morphology of the CV profiles. In particular, the solid trace contains the well-defined hydrogen characteristics at the neighborhood of –0.1 V and the adsorption of oxygen near 0.3 V. These two features appear to be weak or totally missing in the dotted trace. The strong resemblance of the solid curve to those obtained in ultrahigh vacuum (UHV) suggests that the Ru(001) electrode is electrochemically well-defined.[1,2]

The cyclic voltammograms of Ru(001) obtained in 0.1 M H_2SO_4 contrast markedly with that obtained in 0.1 M $HClO_4$. It appears that the well-resolved hydrogen features near –0.1 V are eliminated, replaced by irreversible broad wave centered at 0 V. on the other hand, the CV features associated with the adsorption of oxygen persist. We will present high-quality STM results to show that the presence of an ordered structure of $(\sqrt{3} \times \sqrt{7})$oblique, attributable to the adsorption of (bi)sulfate anions. The formation of an oxygen adlayer however prevailed at potentials higher than 0.3 V.

Irreversible adsorption of the (bi)sulfate anions from 0.1 M sulfuric acid at –0.1 V (vs. Ag/AgCl) renders a highly ordered structure, identified as $(\sqrt{3} \times \sqrt{7})$*oblique* by in situ STM (**Figure 3**). This arrangement of (bi)sulfate anions is the same as those found at the (111) surfaces of Au, Pt, Rh, Pd, Ir, and Cu electrodes.[3-9] Potential excursion to 0.4 V results in a well-ordered (2×2) – oxygen adlayer at the expense of the $(\sqrt{3} \times \sqrt{7})$*oblique* – (bi)sulfate structure. Iodine atoms are adsorbed stronger than the (bi)sulfate and oxygen adlayer species, irrespective of the potential.

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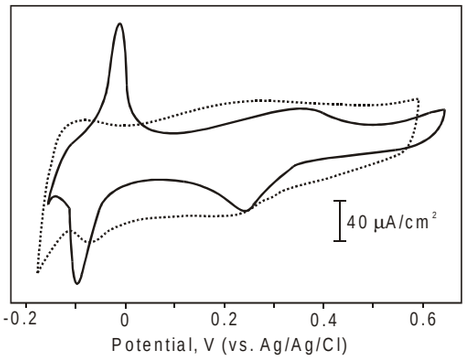

Figure 1. Cyclic voltammograms of Ru(001) at 50 mV/s in 0.1 M $HClO_4$. The solid and dotted lines were obtained for Ru(001) prepared by annealing in hydrogen and mechanically polishing, respectively.

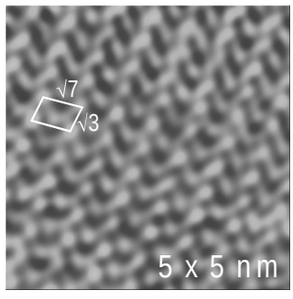

Figure 3. In situ STM atomic resolution of Ru(001) - $(\sqrt{3} \times \sqrt{7})$oblique - (bi)sulfate structure.