

Structure of Oxygen and CO Adsorption on Ru(0001) Electrode

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Abstract: Electrosorption of oxygen and CO on Ru(0001) surface were investigated by *ex-situ* electron diffraction (LEED/RHEED), AES and electrochemical data. The Ru(0001) surface exhibited a strongly affinity for oxygen which gave preference to form a (2×2)-O phase. However, anodization of Ru(0001) electrode produced a (1×1)-O phase. A coadsorption structure (2CO+O)(2×2) / Ru(0001) was performed from electrosorption of CO on Ru(0001) surface in electrolyte solution.

Keywords: Ru(0001), electrosorption, oxygen, carbon monoxide.

It is important to understand the chemisorption of oxygen and CO on Ru(0001) surface. CO oxidation at oxygen precovered Ru(0001) surface at low oxygen coverages gave an extremely low CO oxidation rate, and it was also observed that, with a nominal oxygen coverage exceeding *ca.* 3 mL, rather high CO/CO₂ conversion probabilities were achieved¹. In the case of coadsorption of CO and oxygen on Ru(0001) surface under UHV conditions, a model comprising two CO molecules in an (2×2)-O unit cell has been proposed². In this letter, we take a closer look at the electrosorption of oxygen and CO on Ru(0001) surface from electrolyte solution.

The experiments were performed in a UHV system which consists of a main chamber incorporating low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED) and Auger spectroscopy (AES), and an electrochemical chamber. After or before the electrochemical measurements, the electrode was characterized in the main UHV chamber. As has been described previously³. CO electrosorption was achieved by immersion of the Ru(0001) electrode in a CO-saturated 0.1 mol/L HClO₄ solution at a potential of -0.1 V for 2 min. CO stripping voltammetry was carried out in a N₂-saturated 0.1 mol/L HClO₄ base electrolyte. All experiments were performed at room temperature and all potentials are given *vs* the Ag/AgCl electrode in saturated KCl solution.

Experiments were performed with Ru(0001) surfaces brought to an atomically clean ordered state by Ar⁺ ion bombardment and annealing in UHV. **Figure 1** shows a reversible hydrogen adsorption/desorption and surface oxidation/reduction peaks.

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Figure 1 Voltammetry curves for Ru(0001) in 0.1 mol/L HClO₄ electrolyte solution with scan rate of 50 mVs⁻¹

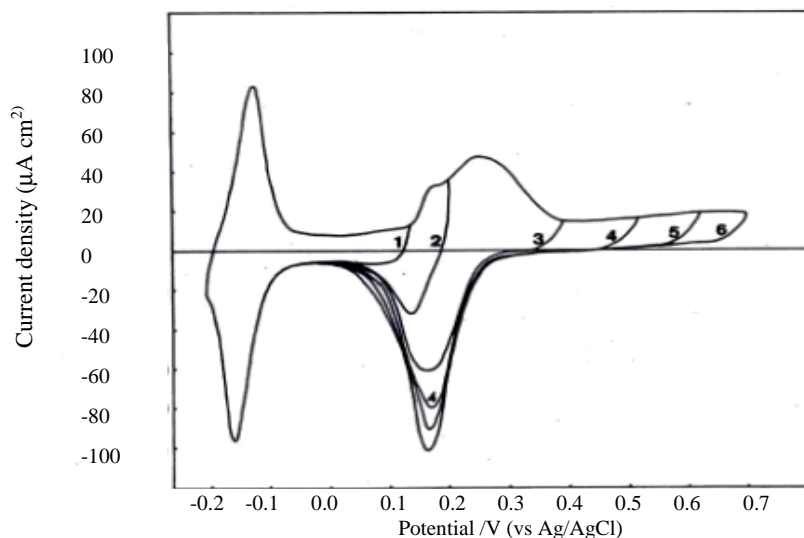
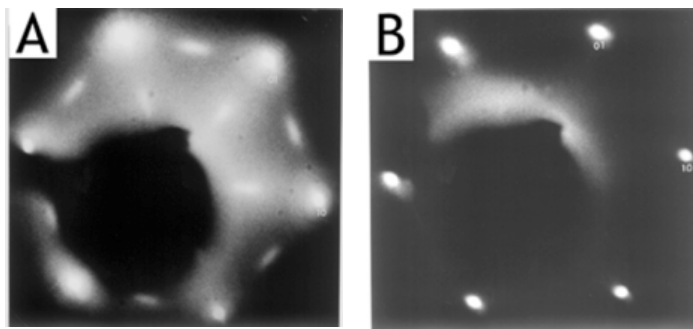
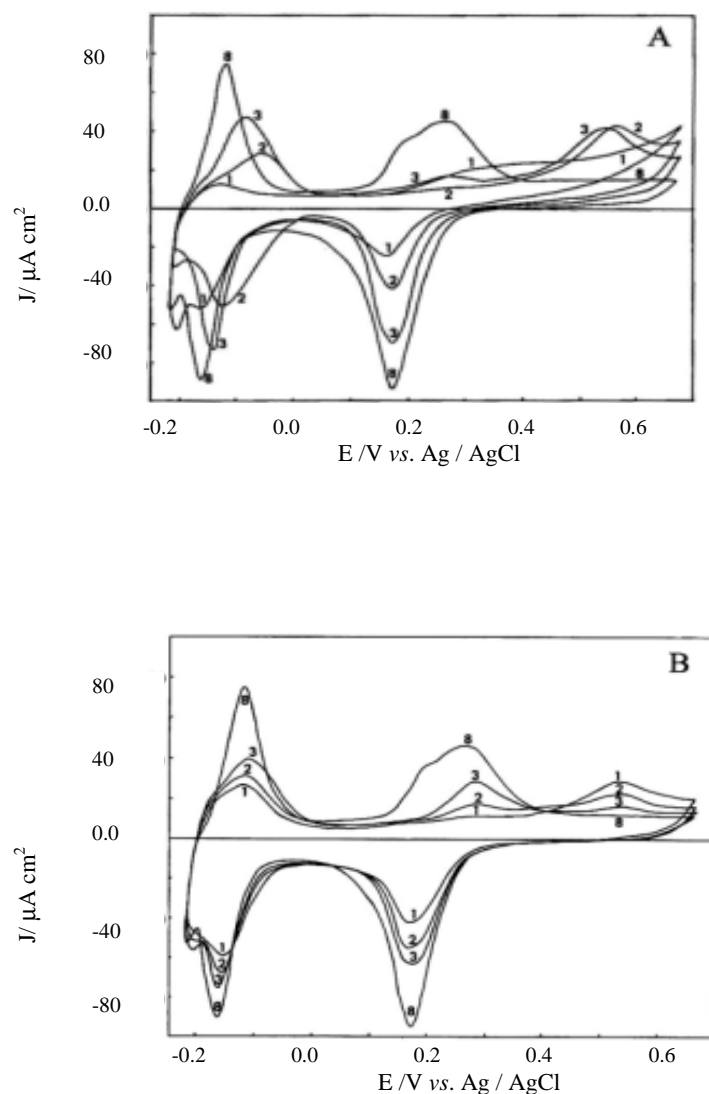


Figure 2 A, B LEED (62 eV) patterns



Combination with the structural analysis (LEED/RHEED) and oxygen coverages calculation (AES) showing that a strongly affinity for oxygen at the Ru(0001) structure which gave preference to form a (2×2)-O phase. The adsorbed (2×2)-O phase can not be removed at electrochemical negative-going scan, even passing over the hydrogen adsorption peak (-0.2 V). This result implies that the (2×2)-O structure can firstly be formed when the Ru(0001) electrode contact with electrolyte solution. However, electrochemical anodization of Ru(0001) electrode produces a (1×1)-O phase. **Figure 2A, B** shows the typical (2×2)-O and (1×1)-O surface structures were recorded after each electrochemical scan.

Figure 3 Voltammetry curves showing the oxidation of the preadsorbed CO adlayer in 0.1 mol/L HClO₄ electrolyte solution



(A) Directly after CO electrosorption. (B) After a brief exposure to the UHV and characterization.

Figure 3A shows the cyclic voltammograms for CO electrooxidation on the Ru(0001) electrode in 0.1 mol/L HClO₄ base electrolyte. CO had been adsorbed on the Ru(0001), then the solution was changed with the N₂-saturated base electrolyte. It was found that the CO oxidation peaks at potential around 0.55 V disappears after several

cycles of oxidative stripping. A maximum oxidation charge density of $260 \mu\text{C}/\text{cm}^2$ was obtained by the coulombic charge under the stripping peaks, which corresponds to a saturated coverage of 0.52 ML. The CO saturated electrode as characterized by **Figure 3A** was emersed from the solution and transferred into the UHV chamber for structural investigation. A clearly (2×2) structure was observed. Subsequently, it was transferred back into the electrochemical cell at -0.1 V and the cyclic voltammograms reproduced in **Figure 3B**. A maximum oxidation charge density of $110 \mu\text{C}/\text{cm}^2$ was obtained, obviously this transfer procedure decreased the amount of adsorbed CO molecular. Its coverage as derived from the charge of CO stripping is only about 0.22 ML, the CO sticking coefficient shows an abrupt decrease at the CO coverage of ~0.25 ML. This result is considered to be due to the CO molecules on Ru(0001) surface are in a different binding state. In contrast with UHV conditions, the above (2×2) phase cannot be produced by exposure of Ru(0001) to gaseous CO, but a sharp (2×2) structure was formed by the coadsorption of oxygen (0.25 ML) and CO (0.5 ML) on Ru(0001) surface. Now we are able to determine the present electrosorption of CO on Ru(0001) surface model: (2CO+O)(2×2)/Ru(0001). This saturated (2CO+O)(2×2)/Ru(0001) structure can be change into (CO+O)(2×2)/Ru(0001) structure after partial CO desorption under UHV condition.

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