

X-ray Surface Scattering Study of Pt(111)/CO/Acidic Solution Interface

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Introduction

In addition to having direct relevance to the mechanism of poisoning in modern low-temperature fuel cells, adlayers of CO on the Pt(111) surface are fascinating model systems of the electrochemical interface. For these reasons, they have been extensively studied in the decades since Kitamura, Takahashi, and Ito [1] discovered the existence of two new types of CO adlayers on the Pt(111) surface in CO-saturated solutions, which have never been seen in an ultrahigh-vacuum (UHV) environment. Their infrared (IR) data suggested adsorption of CO (1) on atop (i.e., at the top) and threefold hollow sites in the potential region close to zero volts (0 V) versus reversible hydrogen electrode (RHE) and (2) on atop and bridging sites at more positive potentials. Subsequently, Villegas and Weaver [2] reported *in situ* scanning tunneling microscopy (STM) images of these ordered high-density CO adlayers on Pt(111). By combining the STM results with IR measurements [2], they concluded that the molecular structure of the CO layer is an hcp (2×2) -3CO lattice with a coverage of $3/4$ per surface Pt atom at potentials close to 0 V (RHE), and that it transforms to another hcp $(\sqrt{19} \times \sqrt{19})$ R23.4°-13CO lattice with a coverage of $13/19$ at more positive potentials.

Methods and Materials

The Pt(111) crystals used in our experiments were 10-mm-diameter disks polished with a miscut of less than 0.2° . The crystal selected for measurements was annealed in a hydrogen-air flame. Then it was transferred to and cooled down in a glass tube under a flow of Ar mixed with 2% H₂. The electrolyte used in our experiment was 0.1 M HClO₄ + 0.01 M NaBr in ultrapure water. The solution was saturated with CO in a bubbler before being introduced into the surface x-ray scattering (SXS) cell. A flow of CO was maintained over the Kapton[®] film during the experiment. Ag/AgCl + 3 M NaCl was used as the reference electrode. However, all potentials in this work were converted to RHE scale by adding 300 mV.

Results and Discussion

We studied the ordered structures that formed on the Pt (111) surface in 50 mM H₂SO₄ and 0.1 M HClO₄ + 10 mM NaBr in the presence of solution phase CO.

Both (2×2) -3CO and $(\sqrt{19} \times \sqrt{19})$ R23.4°-13CO commensurate superlattices found previously in STM studies [2] were confirmed by SXS measurements. The (2×2) reflections are observed at negative electrode potentials [3] and are replaced by the $(\sqrt{19} \times \sqrt{19})$ R23.4° reflections positive to the CO oxidation pre-wave (Fig. 1). Integrated SXS intensities as a function of potential in a CO-saturated solution are shown in Fig. 1 (bottom). The current peak at around 780 mV (RHE) in the anodic scan (solid line in top of Fig. 1) is due to the oxidation of about 9% of the preadsorbed CO, which accompanies the transition from (2×2) to $(\sqrt{19} \times \sqrt{19})$. This transition occurs at a less positive potential (650 mV) in the x-ray measurements because of the differences in the CO pressures and time scales of the two experiments. Whereas the cyclic voltammetry (CV) data were acquired at 50 mV/s, the x-ray data were acquired stepwise with a time delay of about 4 minutes. Upon a further increase in potential, adsorbed CO was completely oxidized, as manifested by the anodic CV peak at 1020 mV (Fig. 1, top) and by the disappearance of the $(\sqrt{19} \times \sqrt{19})$ reflection at 930 mV (Fig. 1, bottom). Again, the discrepancy between the values of the CO stripping potential can be attributed to the different experimental conditions.

Upon reversal of the potential scan direction, restoration of the $(\sqrt{19} \times \sqrt{19})$ structure is delayed to 720 mV, showing about 200 mV hysteresis between CO stripping and reordering. Since CV in the presence of solution-phase CO shows a similar hysteresis between CO oxidation and adsorption peaks, we conclude that CO does not adsorb on Pt(111) in the potential range between CO stripping and $(\sqrt{19} \times \sqrt{19})$ formation. This hysteresis appears to be an intrinsic phenomenon related to competition between CO and anions for Pt sites and not related to the slow ordering of the $(\sqrt{19} \times \sqrt{19})$ phase.

We found that the superlattice reflection of the $(\sqrt{19} \times \sqrt{19})$ phase obtained by CO readsorption in the cathodic scan shows no significant broadening, but its integrated intensity is only 40% of that of the $(\sqrt{19} \times \sqrt{19})$ phase obtained by partial oxidation of the (2×2) structure in the anodic scan. There are three possibilities for the remaining 60% of the surface: (1) a disordered CO layer, (2) no CO at all, or (3) an ordered CO layer other than the $(\sqrt{19} \times \sqrt{19})$ structure. The last

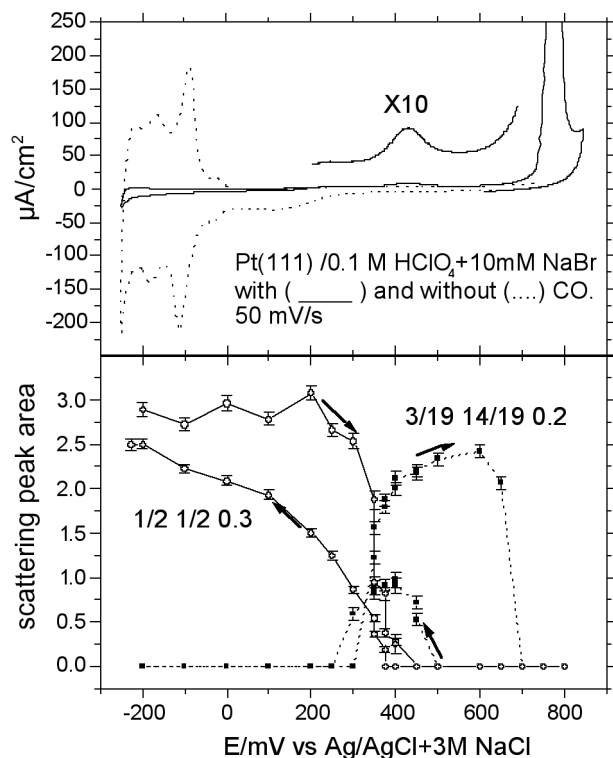


FIG. 1. Cyclic voltammogram (upper panel) and x-ray cyclic voltammograms (XCV) for (2×2) and $(\sqrt{19} \times \sqrt{19})$ $R23.4^\circ$ superlattice peaks (lower panel) of Pt (111) facet.

case is unlikely, since our extensive search for other ordered structures was unsuccessful. We found that the steady-state hydrogen oxidation is totally blocked at 700 mV (RHE) regardless of whether the electrode potential is stepped from 50 or 1100 mV (RHE) in the same solution saturated with a $H_2 + 2\%$ CO gas mixture (data not shown). Since it is known that Br^- does not inhibit hydrogen oxidation under these conditions, a

full monolayer of CO must have formed in the cathodic scan. Therefore, we can conclude that there should be about 60% disordered CO domains coexisting with the $\sim 40\%$ ordered $(\sqrt{19} \times \sqrt{19})$ CO domains as long as a sufficient amount of CO is present in the solution.

The transition from (2×2) to $(\sqrt{19} \times \sqrt{19})$ in the anodic scan is rather sharp, while the transition from $(\sqrt{19} \times \sqrt{19})$ to (2×2) in the cathodic scan is more gradual (Fig. 1, bottom). The reasons for such different phase transition rates in anodic and cathodic scans can be understood if one considers the mechanism of CO coverage change. The CO removal in the transition from (2×2) to $(\sqrt{19} \times \sqrt{19})$ occurs via the reaction with OH, or direct desorption at the domain boundaries, which creates empty sites available for lattice expansion. This leads to cooperative expansion and rotation of the CO adlayer. CO adsorption in the reverse transition requires individually adsorbed CO, which leads to the nucleation of locally compressed (2×2) structure. In this case, the randomly nucleated (2×2) structure must ripen by annealing the domain walls, leading to a sluggish ordering.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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