

CO Adsorption and its Effect on Hydrogen Oxidation at the Pt(111) Electrode Surface: Formation of the (2x2)-3CO Phase in CO/H₂ Mixture Saturated Solutions

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Introduction: Intensive research activity has been devoted to CO adsorption on Pt because it often greatly reduces the catalytic activity of Pt for many important reactions. In particular, the CO induced loss of electrocatalytic activity for hydrogen electro-oxidation in fuel cells is a major obstacle to the utilization of the reformat H₂, which inevitably contains small amounts of CO, as the fuel of choice for electric vehicles. On the Pt(111) electrode surface, the ordered (2x2)-3CO phase was found to exist over a wide potential region in CO saturated solution by in situ x-ray scattering technique [1]. Here, we examine the relationship between the structural phase behavior of adsorbed CO and hydrogen oxidation activity.

Methods and Materials: A single crystal Pt(111) electrode was prepared by flame annealing and cooling in Ar/ H₂ mixed gas flow. The electrochemical cell was sealed by a Prolene x-ray film (Chemplex Industries, Inc.), which acts as the x-ray window and allows gas to diffuse through into the solution. A constant gas flow to the outer chamber, either pure H₂ or CO/H₂ mixture, was kept during the x-ray measurements.

Results and Discussion:

Fig. 1 shows the time-dependent x-ray diffraction intensity at the (1/2,1/2,0.12) position, whose presence is indicative of the (2x2)-3CO phase, and the hydrogen oxidation current on the Pt(111) electrode in 0.5 M H₂SO₄. At t=0 min the flow of a 2% CO/ H₂ mixture was initiated and at t=20min it was switched back to pure H₂. The Pt(111) electrode potential was held at 0.2 V versus reversible hydrogen electrode (RHE). The x-ray intensity starts to rise after the CO has diffused through the x-ray film, signaling the formation of the (2x2)-3CO phase. The hydrogen oxidation current decreased correspondingly. When the current dropped to zero, the (1/2,1/2,0.12) intensity stabilized at the maximum value. Switching back to pure hydrogen caused an immediate decrease of the diffraction intensity by about 80%. This shows that the ordering of CO at saturated coverage requires a thermodynamic equilibrium with the CO concentration in the solution. Some irreversibly adsorbed CO molecules, albeit at a lower coverage, appeared to inhibit a recovery of the activity for hydrogen oxidation since no current recovered after the (1/2,1/2) diffraction intensity was stabilized at a low value. Similar behavior can be observed by using 0.1% CO/H₂ with a significantly longer time and weaker diffraction intensity at the (1/2,1/2,0.12) position.

As shown in Fig. 2, during a positive potential sweep, the diffraction intensity from the (2x2)-3CO phase weakened as oxidative removal of CO occurred with increasing potential. Although there is a small increase in the current above 0.4 V, the major recovery of the current happened at more positive potentials than that where the (2x2)-3CO phase had disappeared. The second drop in intensity at the (1,0,3.6) position, which is also sensitive to the OH adsorption, suggests that the removal of more strongly adsorbed CO requires stronger OH adsorption at high potentials. In the reversed potential sweep, the current vanished at about 0.2 V before a full recovery of the (2x2)-3CO phase.

In conclusion, the saturation coverage for CO on the Pt(111) electrode surface is 0.75 monolayer and the commensurate (2x2)-3CO phase exists at low potentials in the presence of rather low CO concentration in a acid solution. The hydrogen oxidation activity on Pt(111) is completely blocked by the formation of this ordered adlayer.

References: [1] C.A. Lucas, N.M. Markovic, and P.N. Ross, *Surf. Sci.*, 425 (1999) L381.

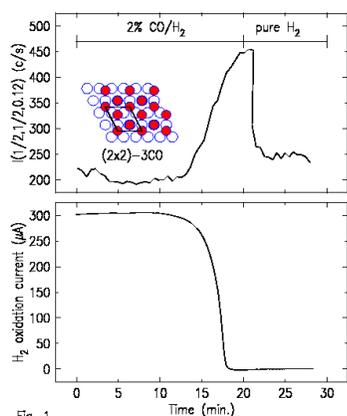


Fig. 1

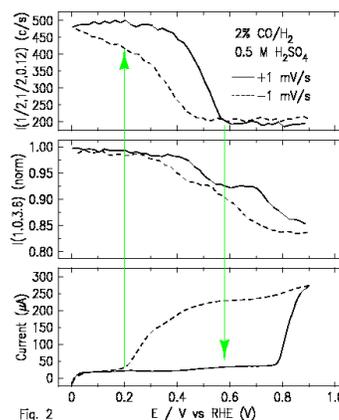


Fig. 2