

**CO Adsorption on the Pt(111) Electrode Surface in the Presence of Halide Ions: an in situ Surface X-Ray Diffraction Study**

K. Tamura, J. Wang, B. Ocko, and R. Adzic (BNL)

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**Introduction:** Platinum is the most active catalyst for many reactions and particularly important as a fuel cell catalyst for  $H_2$  and methanol oxidations. The reformat  $H_2$ , the fuel of choice for fuel cells that may be used in electric vehicles, inevitably contains small amounts of CO that causes poisoning of Pt catalysts. To reduce poisoning, CO tolerant Pt-based materials have been investigated intensively. The  $(2 \times 2)$ -3CO structure of CO adsorbed on a Pt(111) electrode surface has been found by in situ x-ray scattering technique [1], while in situ scanning tunneling microscopy technique indicates that some other commensurate structures also appear [2]. Halides are known to adsorb strongly on Pt and form ordered adlayers. A possible reduction of CO adsorption on Pt by a competitive adsorption of these anions may be an interesting strategy to learn about Pt-CO interactions and obtain new insights for designing CO tolerant catalysts. In this study, the behavior of the CO adsorption in the presence of halide ions has been investigated by x-ray scattering techniques.

**Methods and Materials:** A single crystal Pt(111) electrode was prepared by flame annealing in a propane flame, followed by cooling in a  $H_2/Ar$  gas mixture. A 0.1 M  $HClO_4$  solution containing halide anions was used as the electrolyte and all potentials are referenced with respect to a  $Ag/AgCl, Cl^-$  electrode. A standard x-ray diffraction-electrochemical cell was used. CO gas was introduced into the cell through the outer chamber.

**Results and Discussion:**

Fig. 1 shows the time-dependent x-ray intensities at two in-plane diffraction positions when CO gas was induced to the cell at 0 min, while the potential was held at 0.1 V. The intensity at  $(-1/7, 5/7)$  drops to zero within 2 min, which indicates that the  $(\sqrt{7} \times \sqrt{7})$ -4I phase was removed by the adsorption of CO. The formation of the ordered  $(2 \times 2)$ -3CO phase occurs soon afterward, as indicated by the sharp increase of the  $(1/2, 1/2)$  intensity around 3 min. The slower intensity increase after 4 min continued for more than 30 min. Further increase of the peak intensity was found after several potential cycles up to 0.9 V. The average domain size grew to about 350 Å.

After replacing CO by nitrogen gas, the diffraction intensity at the  $(1/2, 1/2)$  position vanished in 40 min. Although the  $(2 \times 2)$ -3CO phase disappeared, the  $(\sqrt{7} \times \sqrt{7})$ -4I structure did not reappear. It is likely low coverage, disordered CO still exist on the Pt(111) electrode surface.

$Br^-$  and  $Cl^-$  are less strongly adsorbed on Pt than I.

The  $(2 \times 2)$ -3CO structure was observed in the presence of Br or Cl ions and it exists for longer time in both cases than in the presence of iodide after stopping the flow of CO.

These results suggest that all three halide ions compete with CO, but are weaker adsorbates than CO on Pt(111) in CO saturated solution. They can, however, cause disordering of the  $(2 \times 2)$ -3CO structure when its concentration falls below a critical value.

**References:** [1] C.A. Lucas, N.M. Markovic, and P.N. Ross, *Surf. Sci.*, 425 (1999) L381.  
[2] I. Villegas and M.J. Weaver, *J. Phys. Chem.*, 101 (1994) 1648.

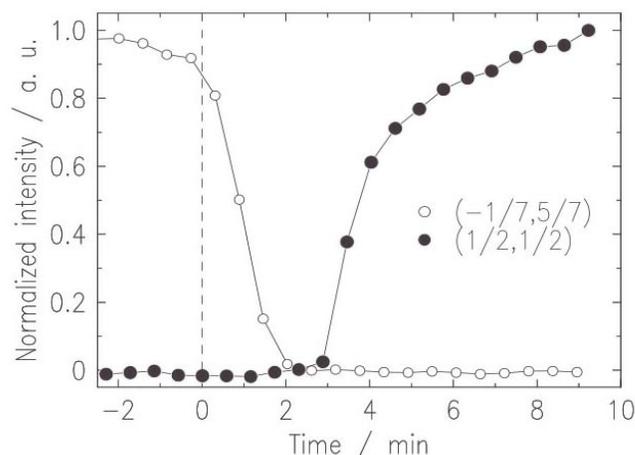


Fig. 1 Time dependent x-ray intensities at two in-plane diffraction positions for Pt(111) in 0.1 M  $HClO_4$ . CO was introduced at 0 min.