Long-Range Ordered ("19×"19)R23.4º-13CO Structure on Pt(111) in Aqueous Electrolytes

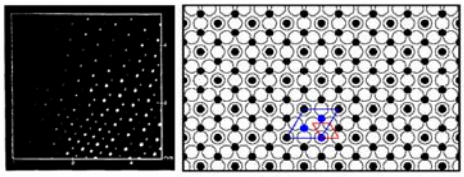
Yuriy V. Tolmachev,[1] Andreas Menzel,[1] Andrei V. Tkachuk,[2] Yong S. Chu,[2] and Hoydoo You[1]
[1]Materials Science and [2]Experimental Facilities Divisions, Argonne National Laboratory

ABSTRACT

Carbon monoxide poisoning of platinum or platinum-alloy catalysts is one of the most serious problems in modern low-temperature fuel cells where hydrogen or other fuels are converted to electricity. For this reason, CO monolayers on Pt(111) has been studied extensively in the past decade by electrochemical methods, as well as scanning tunneling microscopy (STM), infra-red (IR) spectroscopy, sum frequency generation (SFG), and surface x-ray scattering (SXS). Despite intense research on this subject, there has been controversy to whether there is a direct link between the long-range structures and poisoning. In this poster, we show a new long-ranged structure, namely ("19×"19)*R*23.4º-13CO, closing the missing link in the intermediate potential range between the low potential for the previously known (2×2) ordered structure and high potential for CO oxidation. Thereby, we show that CO remains long-ranged until oxidized as the cell potential increased. Based on this observation, we further propose that the CO poisoning is the result of the CO long-range ordering.

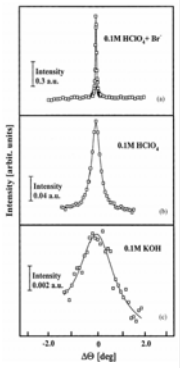
(2×2)-3CO

STM: I.Villegas and M.J. Weaver, JCP **101** (1994) 1648
SXS: C.A.Lucas, *et al*., SS **425** (1999) L381



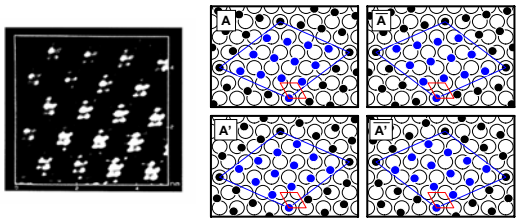
In-situ STM image and the proposed ball model of CO

(½, ½, 0.2) superlattice SXS peaks in different solutions confirm long-range order of (2×2) phase.

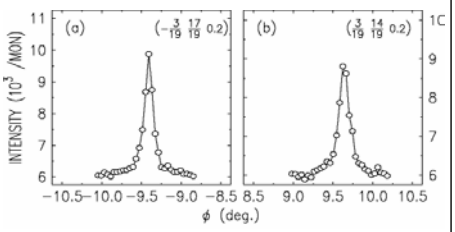


("19×"19)-13CO

STM & IR: I. Villegas, M.J. Weaver, JCP **101** (1994) 1648

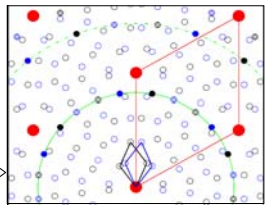


In-situ STM image (no x-ray scattering signal of this phase had been found previous to our study) and four-possible proposed ball models.



[Above] Rocking curves through the reciprocal space positions corresponding to A and Ā domains of the ("19×"19) phase. The width of the SXS peaks suggests long-range order over ca. 150 Pt unit cells, i.e., ~400Å. No evidence for A' and Ā' was found.

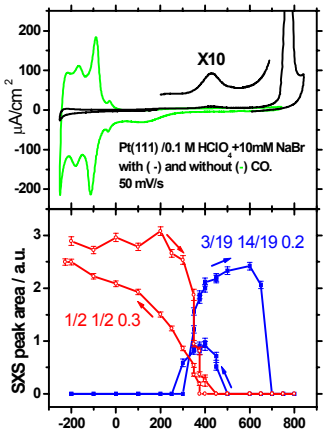
Red circles indicate Pt peaks and black/blue symbols mark the unprimed/primed "19×"19-13CO phases. Two domains with on top and bridging CO, A and Ā, shown as solid circles, produced well-defined SXS signals. Other stereochemically possible domains, Ā and Ā', marked as crosses, could not be found. The absence of the x-ray signals in the open-circle positions indicate the close-packed nature of the layer.

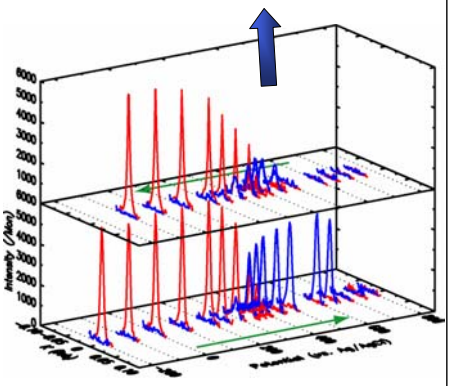


Electrochemical and Solid-State Letters (2003), in press

The "19 ×"19 structure clarifies detailed features of the cyclic voltammetry

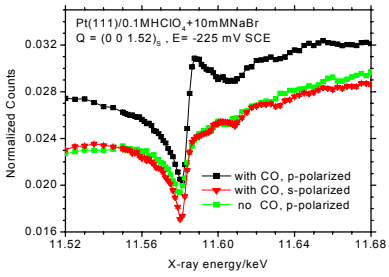
The transition from (2×2) with 75% coverage and ("19×"19) with 68% coverage occurs by oxidative stripping peak, shown as an (x10) inset in the cyclic voltammogram around 450 mV vs. SCE.





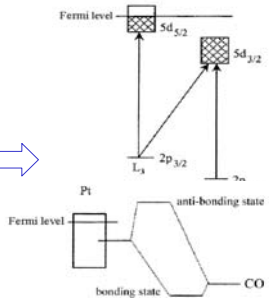
SXS data show that (2x2) structure [red] is replaced by ("19×"19) [blue] at potentials positive to 450 mV with a coexistence region.

Future: Polarization Dependence Surface Resonance X-ray Scattering: Way to see the chemical nature of CO layers under electrolyte



We found that Resonant SXS spectra near the Pt L_3-edge with *s*-polarized x-rays are not sensitive to the presence of adsorbed CO [green and red], in contrast to the *p*-polarized spectrum [black]. The latter clearly shows an additional peak, ca. 8eV above the Pt Fermi level, which corresponds to unoccupied CO orbitals.

Spin-orbit coupling effects in the x-ray absorption, as well as molecular orbit picture of bonding and anti-bonding orbitals.
Hammer and Norskov, Nature, **376** (1995) 238.
D. E. Ramaker *et al*., PCCP, 1 (1999) 2293



BES - DOE

This work and the use of Advanced Photon Source were supported by the U. S. Department of Energy, Basic Energy Sciences, under contract W-31-109-ENG-38.

MSD - ANL