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FUEL CELL ELECTROCATALYSIS:
ANNUAL REPORT, FY 1985

P.N. Ross, Jr.

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ANNUAL REPORT

FY 1985

"Fuel Cell Electrocatalysis"

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Prepared for:
The Assistant Secretary for Fossil Energy, Office of Coal Utilization, Advanced Energy Conversion Systems Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, through the Fuel Cell Project Office, NASA Lewis Research Center, Cleveland, Ohio.

INTRODUCTION

Commercialization of phosphoric acid fuel-cell technology requires a capital cost reduction and an extension of power section life compared to currently available technology. Significant capital cost reduction can be achieved if an oxygen-reduction catalyst which is catalytically more active than Pt supported on graphitized carbon black can be developed. Surface studies of gas-phase oxygen adsorption by x-ray photoemission spectroscopy (XPS) suggest that modification of the adsorptive properties of Pt by the substitution of ligands to the Pt coordination sphere could result in enhanced Pt catalysis. Of particular interest are the insertion of strong-bonding base metals like Ti, Zr and Ta into the Pt surface coordination, e.g. ordered alloys like Pt_3Ti. The objective of the present research is to develop the physical and chemical understanding of oxygen-platinum-ligand interaction necessary for the rational selection of alloying components. Fundamental studies of the Pt alloy-electrolyte interface using modern surface science techniques should provide the means to optimize the alloy ligand or to redirect the search for more active materials along the most rational paths. Alloying may have significant beneficial effects on electrode performance above and beyond effects on the oxygen-reduction kinetics, e.g., reduced Pt dissolution and surface-area loss. These additional alloying effects will also be studied at the atomic level, e.g., surface reconstruction and surface self-diffusion.

1. Structure and Chemisorptive Properties of the Pt_3Ti Surface (Publication 3)

U. Bardi, D. Dahlgren and P.N. Ross

Low energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy were used to determine the structure and composition of the surfaces of [111] and [100] oriented crystals of an ordered alloy of bulk stoichiometry Pt_3Ti. Thermal desorption spectroscopy (TDS) was used to study the adsorption of carbon monoxide and hydrogen on these surfaces. The clean annealed surface of [111] orientation has the ordered structure expected from truncation of the bulk crystal, consisting of alternating atomic rows of (50% Pt + 50% Ti) and 100% Pt. The surface of [100] orientation also has a regular truncation structure with the outermost layer being 50% Ti in a c(2x2) lattice and the second layer the 100% Pt layer. At near-ambient temperature, the adsorption of CO at the Ti sites is dissociative and at the Pt sites is molecular. The orderly substitution of Ti for Pt atoms in the surface changes the Pt-Pt pair site distribution such as to eliminate most of the sites for bridge bonding of the CO molecule. As shown in Figure 1-1, only a single symmetric TDS peak was observed for CO desorbing from the alloy surface, as opposed to the asymmetric peak shape observed from pure Pt surfaces, which we suggest is a consequence of bridge-site elimination. At low temperature (230 K), a second molecular state of CO was observed which we assigned to a pre-dissociative state on Ti sites with CO lying parallel to the surface. No hydrogen could be observed to desorb from

clean annealed Pt_3Ti surfaces dosed with hydrogen at room temperature. Unfortunately, we were not able to distinguish between the possibilities: (1) that hydrogen does not adsorb on the surface at room temperature; or (2) that hydrogen adsorbed at room temperature is not desorbed by flashing the surface temperature to ca. 900 K.

Present address: Department of Chemistry, University of Florence, Italy.

2. CO Adsorption on (111) and (100) Surfaces of the Pt_3Ti Alloy: Evidence for Parallel Binding and Strong Activation of CO (Publication 4)

S. Mehendru,† A. Anderson,† and P.N. Ross

The atom superposition and electron delocalization molecular orbital technique has been applied to elucidate bonding interactions of CO adsorption on a 40 atom cluster model of the (111) surface and a 36 atom cluster model of the (100) surface of the Pt_3Ti alloy. Parallel binding to high coordinate sites associated with Ti and low CO bond scission barriers are predicted for Ti sites on both alloy surfaces. (Figure 2-1). The binding of CO to Pt sites occurs in an upright orientation. These distinct orientations are a consequence of the nature of the CO π donation interactions with the respective metal atoms. On the Ti sites the π orbitals donate to the nearly empty Ti 3d band and the antibonding counterpart orbitals are empty. On the Pt sites, however, they are in the filled Pt 5d region of the alloy band,

which causes CO to bond in a vertical orientation by 5 σ donation from the carbon end.

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†Department of Chemistry, Case Western Reserve University, Cleveland, OH 44601.

3. Pt-Ti Alloy Formation from High Temperature Reduction of a Titania Impregnated Pt Catalyst: Implications for SMSI (Publication 6)

B. Beard and P.N. Ross

Highly dispersed Pt supported on carbon black was impregnated with titania and heated in an inert atmosphere. The amount of titania used was twice the stoichiometric amount required for the formation of the ordered alloy phase Pt_3Ti. The chemical state of the Ti at various stages of heating was determined by x-ray photoelectron spectroscopy and by extended x-ray adsorption fine structure (EXAFS) analysis. The results from EXAFS analysis are summarized in Figure 3-1. The formation of alloy phases were also determined by conventional x-ray diffraction methods. These characterizations showed unambiguously the conversion of separate Pt and TiO_2 dispersed phases into Pt-Ti alloy phases at progressively higher heat treatment temperatures, eventually resulting in the formation of crystallites of the ordered (intermetallic) phase Pt_3Ti. Based on this observation and other related work in the literature, we present a model for the chemistry occurring during the formation of the SMSI state of Pt/TiO_2 catalysts.

4. Surface Structure of Pt Crystallites Supported on Carbon Black (Publication 7)

M. Sattler† and P.N. Ross

Small crystallites were deposited onto a carbon black support by adsorption from a solution containing a Pt^{+4} sulfite colloid. The colloidal particles were reduced in H_2 to form metallic clusters with a very narrow size distribution of 2-4 nm. Larger clusters (crystallites) were formed by heating in a high purity He atmosphere at progressively higher temperatures. The microstructure of the crystallites was analyzed using a combination of direct lattice imaging and weak-beam thickness fringe imaging. <111> lattice planes were observed for all crystallites independent of size, indicating there were no "amorphous" microstructures. For the largest crystallites analyzed (35-50 nm), comparison of direct lattice images with projected images from a model 55-atom subo-octahedron indicated these crystallites were complete cubo-octahedra. Investigation of these fairly large (35-50 nm) crystallites using weak beam dark field TEM techniques corroborated these findings. The extinction contours over the dark field particles were compared (Figure 4-1) to contour lines from models of cubo-octahedron at various orientations. In the intermediate size range of 10-35 nm, the surface structures could be considered as "nearly-complete" cubo-octahedra, with an increasing tendency for surface curvature with decreasing size. For the smallest crystallites, 2-5 nm, the apparent structure is the "nearest-sphere" formed by incomplete cubo-octahedra. It is shown that incomplete

cubo-octahedral surface structures are predominantly (110) - 1x1 type structures. These characteristic changes in surface structure with size appear to correlate with the effect of crystallite size on catalytic activity of Pt for the reduction of oxygen in acid electrolyte.

This work was performed at the National Center for Electron Microscopy (NCEM) at LBL. Funding for the operation of NCEM is provided by the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy.

5. Work in Progress

These previous studies have clearly shown two important properties of Pt Group IVb intermetallic surfaces: (1) there is a strong ligand effect from the intermetallic bonding in the chemisorption of reducing gases like hydrogen and carbon monoxide; (2) the intermetallic surface is unstable with respect to oxidizing conditions like that of a fuel-cell cathode. Further studies are in progress to determine the composition and structure of the surface formed by electrochemical oxidation using the gas-phase oxidation-formed surfaces as a guide. Also, studies directed at relating the behavior of bulk surfaces to supported bimetallic clusters (the practical catalyst) are under way. These studies will utilize XPS and EXAFS (extended x-ray absorption find structure) in characterizing changes to the state of the base metal and the coordination about the Pt surface atoms during use as a fuel-cell cathode catalyst.

1985 PUBLICATIONS AND REPORTS

Refereed Journals

1. U. Bardi and P.N. Ross, "Initial Stages of Oxidation of the Pt_3Ti (111) and (100) Single Crystal Surfaces," J. Vac. Sci. Technol. A, 2 (1984) 1461.
2. G. Derry and P.N. Ross, "A Work Function Change Study of Oxygen Adsorption on Pt (111) and Pt (100)," J. Chem. Phys. 82 (1985) 2772.

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3. U. Bardi, D. Dahlgren, and P.N. Ross, "Structure and Chemisorptive Properties of the Pt_3Ti Surface," J. Catal. (in press); LBL-200054.
4. S. Mehendru, A. Anderson, and P.N. Ross, "CO Adsorption on (111) and (100) Surfaces of the Pt_3Ti Alloy: Evidence for Parallel Binding and STrong Activation of CO," J. Catal. (in press); LBL-20034.
5. B. Beard and P.N. Ross, "Characterization of a Titanium Promoted Supported Pt Electrocatalyst," J. Electrochem. Soc. (in press); LBL-19970.
6. B. Beard and P.N. Ross, "Pt-Ti Alloy Formation from High Temperature Reduction of a Titania Impregnated Pt Catalyst: Implications for SMSI," submitted to J. Phys. Chem.; LBL-20367.
7. M. Sattler and P.N. Ross, "Surface Structure of Small Crystallites of Pt on Carbon Black", presented at Workshop on Atomic Structure and Properties of Small Particles, Arizona State University, Tempe, AX, Jan. 7-11, 1986; LBL-20873.

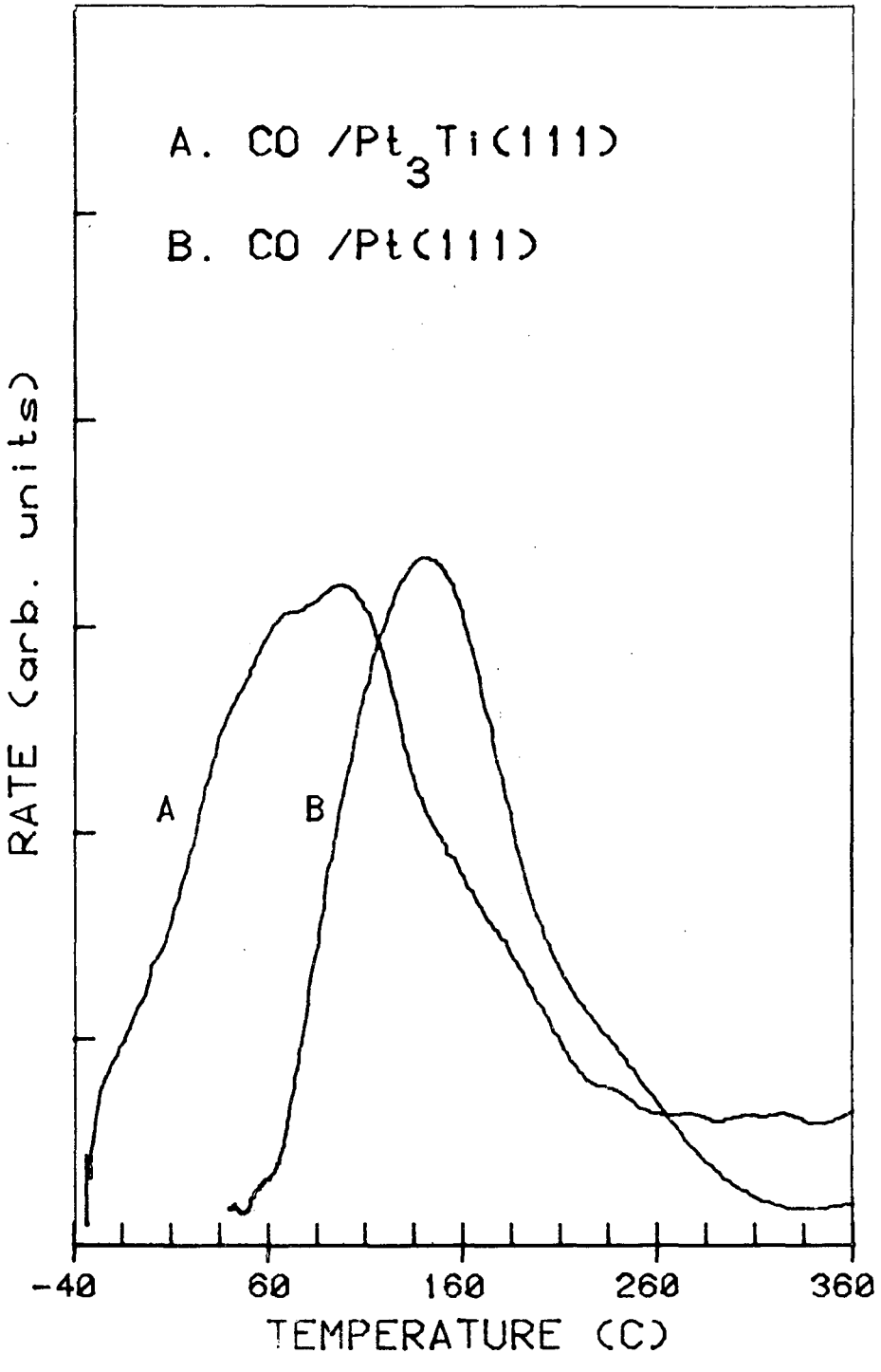
Figure Captions

Figure 1-1. Comparison of the TDS Spectrum after saturation with CO of the Pt_3Ti (111) and of the Pt (100). (XBL 858-3295)

Figure 2-1. The "lying down" parallel orientations of CO on the Ti-Pt pair sites in the ordered alloy surface. (XBL 858-3628)

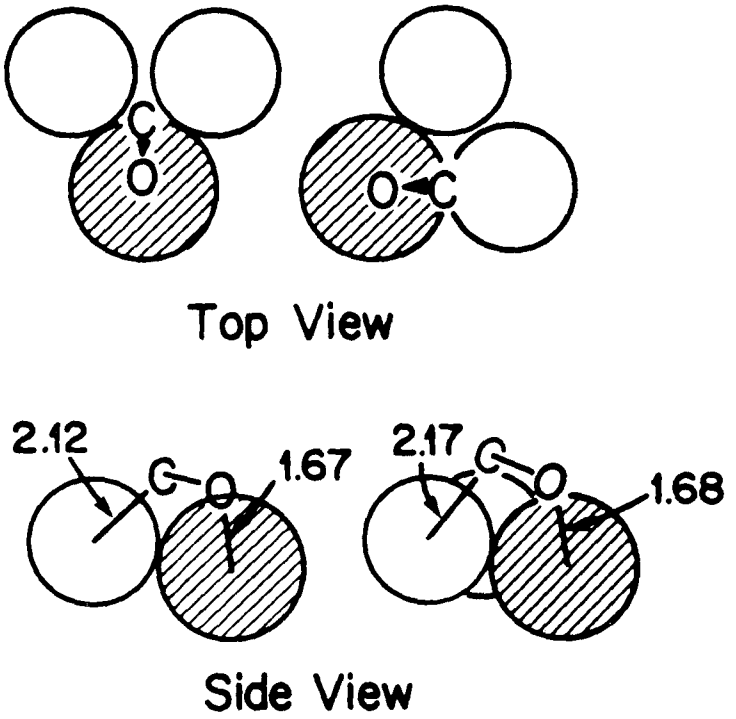
Figure 3-1. Radial distribution function for Ti atoms in Pt-Ti bimetallic catalyst. Peak at ca. 1.7 Å is characteristic of O ligands in TiO_2. Peaks at ca. 2.5 Å and 4.7 Å are characteristic of Pt ligands in Pt_3Ti. (XBL 857-3117)

Figure 4-1. (Left) Weak-beam extinction contours of Pt crystallites of ca. 20 nm characteristics particle size; (Right) Real space projection profile for cubo-octahedral fcc crystallites matching the thickness fringe image. (XBB 858-6699A)



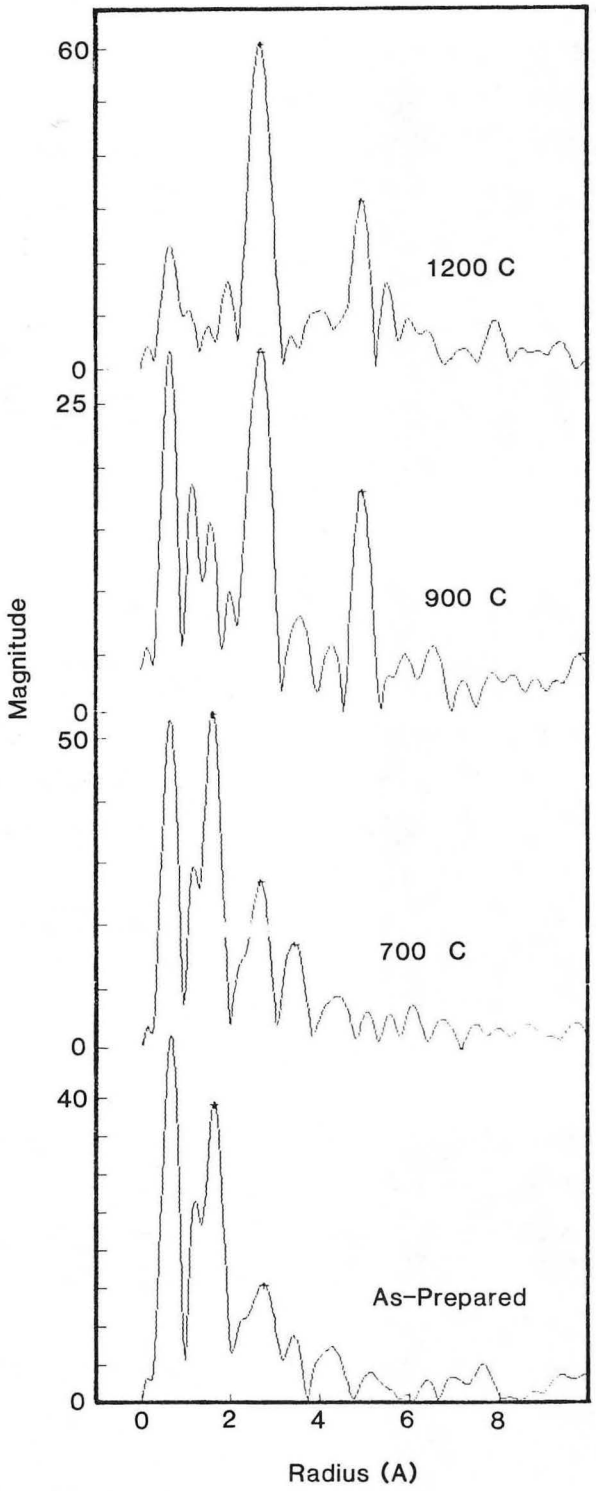
XBL 858-3295

Fig. 1-1



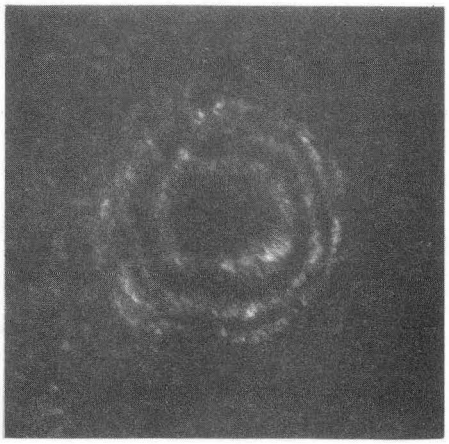
XBL 858-3628

Fig. 2-1



XBL 857-3117

Fig. 3-1



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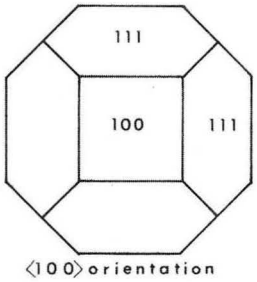
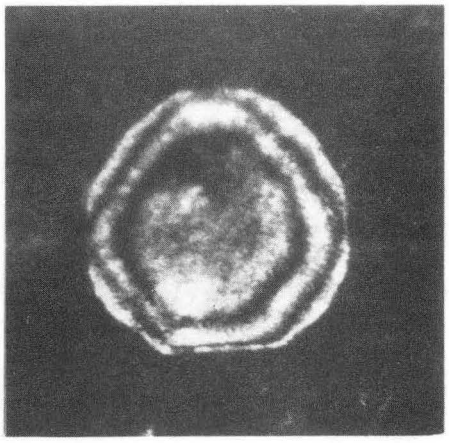
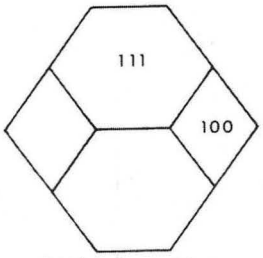
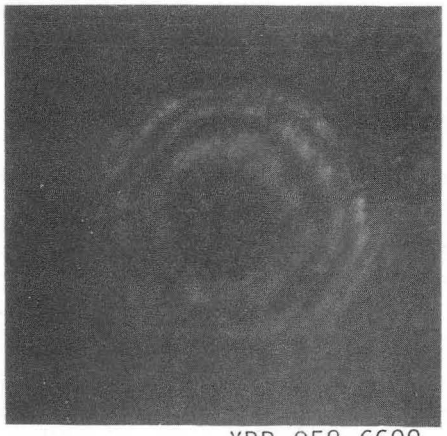


⟨100⟩ orientation

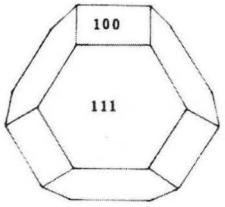




⟨110⟩ orientation



XBB 858-6699



⟨111⟩ orientation

Fig. 4-1

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