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BIMETALLIC FUEL CELL CATALYSTS

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### **Publication Date**

1985-12-01



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BIMETALLIC FUEL CELL CATALYSTS

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B.C. Beard and P.N. Ross

December 1985

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December 1985

To be published in the Stanford Synchrotron Radiation Laboratory Activity  
Report, 1986.

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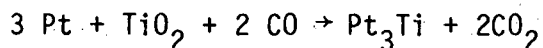
## Introduction

Platinum electrocatalysts alloyed with various transition metals have been found to give improved acid fuel cell performance over pure Pt catalyst electrodes (1). In this study we have investigated the chemical and structural environment of the transition metal in the alloy catalyst. EXAFS analysis is an ideal structural probe of the lattice of these low concentration (10 wt% Pt with ca. 1 wt% transition metal) supported catalysts. EXAFS analysis of such materials has been run with the intention of establishing a better picture of the local chemical environment of the Pt and transition metal in these bimetallic catalysts.

## System of Study

EXAFS data were collected for Pt-Ti and Pt-Co systems. A Ti foil, a Co crystal and a Pt catalyst supported on carbon black (Prototech 10 wt% Pt on Cabot Vulcan XC-72R, heat treated to 1200°C) were analyzed as metallic standards. The Ti compounds  $TiO_2$ , and TiC were analyzed as Ti edge reference compounds, while CoO and  $Co_3O_4$  were analyzed as Co edge reference compounds. The catalysts were prepared by precipitation from solution onto the Pt catalyst. In the Pt-Ti

case the pH of the solution was acidic due to the  $\text{TiCl}_4$  used to introduce the titanium ions. For the Pt-Co catalyst the pH of the solution was slightly alkaline. The solution was then filtered and the catalyst was air dried. Heat treatment of the catalyst followed. Several heat treatment temperatures were used ( $700^\circ\text{C}$ ,  $900^\circ\text{C}$  and  $1200^\circ\text{C}$ ) to observe the temperature dependence of alloy formation. The formation of the titanium-platinum intermetallic may be depicted as:



Data from the Ti K-edge and Co K-edge were collected in both fluorescence and transmission modes. The specimen holder and fluorescence detector were obtained from The EXAFS Co., Seattle, WA. The catalysts studied were in a highly dispersed form with particle sizes of ca. 100 Å. Metal loadings were 10 wt% Pt for both alloys with 0.5 wt% Ti in the one system and 0.3 wt% Co in the other. The catalysts were mixed with PTFE to form a paste which was applied to a graphite fiber mat. The specimen was then taped inside the cell for data collection. Data was collected in January and June on beamline VI.

## Results

The results of the Pt-Ti catalyst Ti K-edge work are summarized in Figures 1 and 2. In Figure 1, three standard EXAFS spectra are compared at various stages of heat treatment of the Pt-Ti catalysts. The as-prepared specimen can be seen to be virtually identical to the  $\text{TiO}_2$  standard. As heat treatment temperatures increase the EXAFS oscillations change dramatically until at  $1200^\circ\text{C}$  the spectrum is different from all of the standards. Comparison to a bulk  $\text{Pt}_3\text{Ti}$  specimen indicated the  $1200^\circ\text{C}$  catalyst to have Ti present as the alloy. Figure 2 illustrates the Fourier transform of the four catalyst samples. The as-prepared sample has a nearest neighbor distance of  $1.61 \text{ \AA}$ , which when corrected for phase shift yields the Ti-O distance in  $\text{TiO}_2$ . At  $900^\circ\text{C}$ , another peak appears at  $2.649 \text{ \AA}$ , which when corrected for phase shift is the proper spacing for Ti-Pt in  $\text{Pt}_3\text{Ti}$ . At  $1200^\circ\text{C}$  this Ti-Pt peak dominates, suggesting complete conversion to the alloy. These data along with XPS and XRD have made a complete picture of the conversion of  $\text{TiO}_2$  co-dispersed with Pt on carbon (2,3).

The results of the Co K-edge experiments on the Pt-Co catalyst have compared very closely to those given above for the Pt-Ti materials. EXAFS analysis of the as-prepared catalyst demonstrated Co to be present as a highly dispersed oxide, most likely  $\text{Co}_3\text{O}_4$ . At  $900^\circ\text{C}$  the EXAFS results illustrated increased cobalt oxide particle size, with only

weak interactions due to Pt-Co. Finally, at 1200°C, strong Pt-Co interactions were observed indicating alloying of the cobalt.

#### References

1. "Oxygen Reduction on Supported Pt Alloys and Intermetallic Compounds in Phosphoric Acid," P.N. Ross, Jr., EPRI Report #EM-1553, Sept. 1980.
2. "Characterization of a Titanium Promoted Supported Platinum Electrocatalyst," Bruce C. Beard and Philip N. Ross, Jr. Submitted to The Journal of the Electrochemical Society.
3. "Pt-Ti Alloy Formation from High Temperature Reduction of a Titania Impregnated Pt Catalyst: Implications for SMSI," Bruce C. Beard and Philip N. Ross. Submitted to The Journal of Physical Chemistry.

#### Acknowledgments

This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Utilization, Advanced Conversion and Gasification, Advanced Energy Conversion Systems Division of the US Department of Energy under Contract No. DE-AC03-76SF00098.



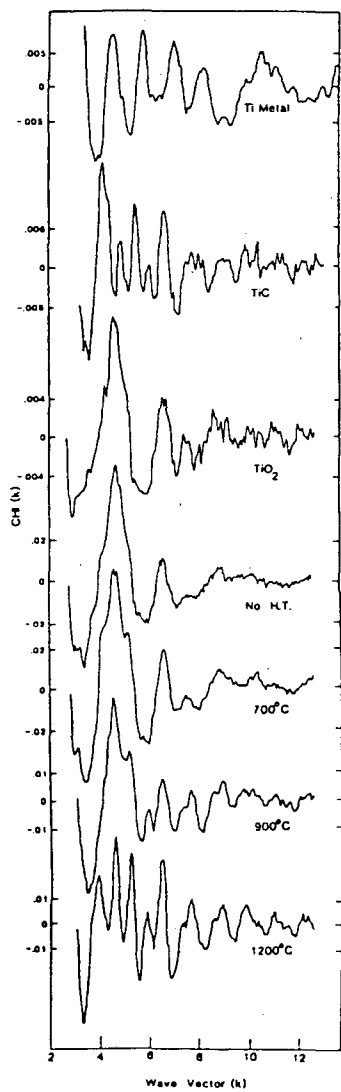


Fig. 1. Normalized EXAFS spectra for the standard compounds Ti (foil), TiC, TiO<sub>2</sub> and the Pt-Ti catalysts. Dashed lines denote features unique to the standard spectrum for Pt<sub>3</sub>Ti.

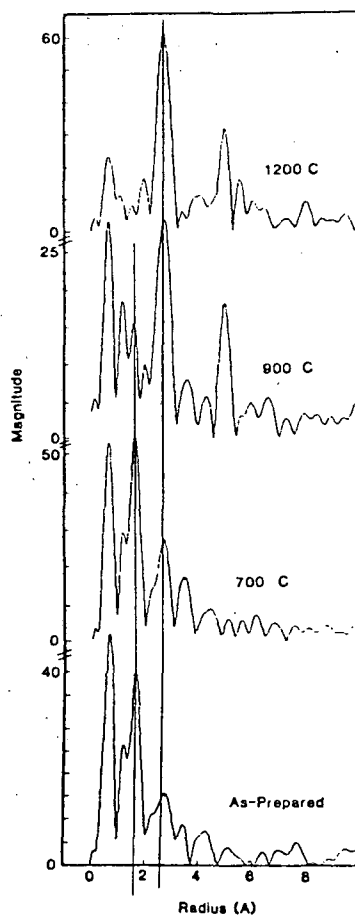


Fig. 2. EXAFS Fourier transform radial distribution spectra of the Pt-Ti catalysts.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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