

# V.P.24 Development and Mechanistic Characterization of Alloy Fuel Cell Catalysts

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## Technical Barriers

This project addresses the following technical barriers by understanding the mechanistic pathway of the ORR reaction and by establishing fundamental guidelines to design new low Pt containing catalyst by optimizing the geometric and electronic structure of catalyst along the mechanistic pathway.

- Electrode performance
- Low cost
- Durability

## Abstract

We have discovered a new family of Pt-Cu nanoparticle/nanopore catalyst that exhibits the highest ever reported ORR activities of up to 5-6x compared to pure Pt electrocatalysts. The composition of the surface, lattice arrangement and electronic structure of these catalysts has been characterized by synchrotron based x-ray diffraction and photoelectron spectroscopy methods. We discovered an order of magnitude reduction of Cu in near surface region of these catalysts, due to electrochemical leaching and a lattice contraction in the nanoparticle/nanopore structures. This affects the overall reactivity by weakening the bonding of intermediate oxygenated species.

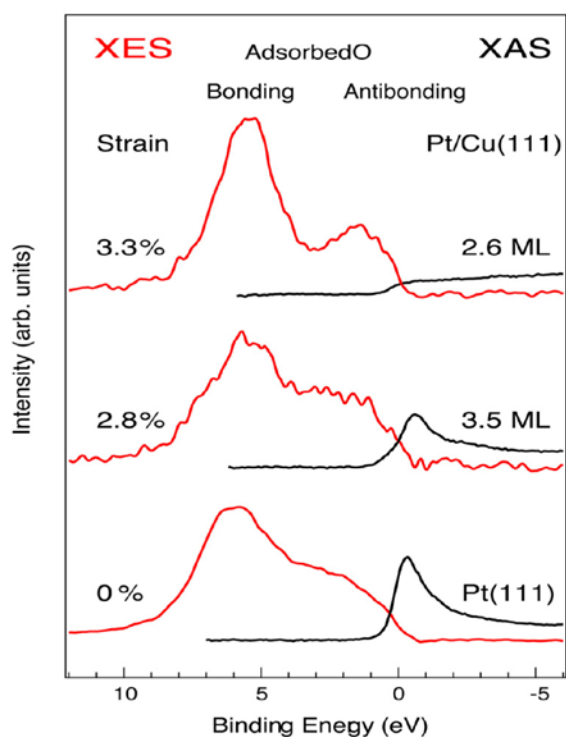
We have undertaken a major effort to obtain in-situ information during electrochemical conditions of the nature of intermediate oxygenated species that controls the rate of the ORR. With high resolution Pt L edge spectroscopy of a single Pt monolayer we have observe the evolution of a surface Pt oxide layer.

## Objectives

- Develop new synchrotron radiation based x-ray diffraction and spectroscopy methods that allow in-situ probing of the intermediates in the oxygen reduction reaction (ORR) on the cathode in fuel cells where both species identification, geometric and electronic structure properties can be fully characterized.
- Gain insight into how various catalytic properties on Pt surfaces can be modified due to alloying.
- Perform combinatorial synthesis and high throughput electrochemical screening methodologies of alloy catalyst with different chemical compositions and structures to obtain optimum performance.

## Progress Report

While the oxidation of pure hydrogen is not considered a technical hurdle in fuel cells, the power loss at the cathode during the electroreduction of oxygen is found to be significant. Therefore the identification of a catalyst for the electroreduction of oxygen with improved performance is a major scientific priority. Pt has been the only metal which offers a good compromise in terms of performance and durability, and catalyst costs dominate at high Pt loading. Our goal is to understand the mechanistic pathway of the ORR reaction and to design new low Pt containing catalyst by optimizing the geometric and electronic structure of catalyst along the mechanistic pathway.



**FIGURE 1.** Electronic interactions between p-level of oxygen and the d-band in the metal results in the formation of bonding and antibonding states. Thin layer of Pt on Cu(111) results in strained films and x-ray spectroscopy of adsorbed oxygen shows that this results in a weakening of the oxygen-metal bond through increased population of the antibonding states. This allows for oxygen to become more active for reactions with hydrogen at the cathode of the fuel cell.

### Novel alloy catalyst for fuel cell cathode reaction

Dealloying is the preferential dissolution of the electrochemically more reactive component from a bimetallic alloy (precursor) consisting of a less reactive (here Pt) and more reactive metal (here Cu). We have shown that dealloyed Pt-Cu nanoparticles show uniquely high catalytic reactivity for the oxygen reduction reaction (ORR) in fuel cell electrodes (1-4). Dealloyed Pt catalysts, however, meet and exceed the technological activity targets in realistic fuel. Owing to their reactivity, dealloyed Pt catalysts can reduce the required amount of Pt by more than 80%. Despite this importance, the mechanistic origin of their enhanced reactivity remains poorly understood.

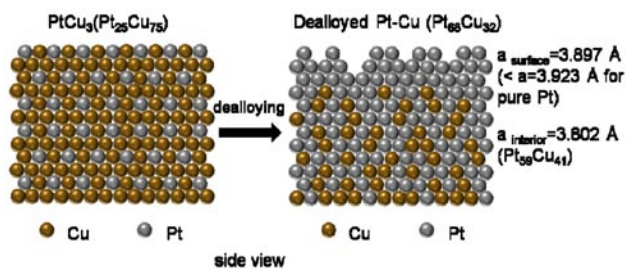
We have shown based on a combination of electron microscopy, x-ray photoelectron spectroscopy and anomalous x-ray diffraction studies of dealloyed Pt-Cu catalysts (6) that a core-shell structure is formed during dealloying, which involves removal of Cu from the surface and subsurface of the precursor nanoparticles. X-ray diffraction shows that the resulting Pt-rich surface shell exhibits compressive strain that depends on the composition of the precursor alloy. Based on model

electron and x-ray spectroscopy experiments of strained Pt films on Cu(111) the existence of a downward shift of Pt d-band resulting in a weakening of the bond strength of intermediate oxygenated species due to strain (see fig.1). Theoretical simulations of the fuel cell catalytic process also shows that strain enhance the overall reactivity via a weakening of the oxygen adsorption bond strength. The stoichiometry of the precursor, together with the dealloying conditions, provides experimental control over the resulting surface strain and thereby allows continuous tuning of the surface electrocatalytic reactivity – a concept that can be generalized to other catalytic reactions.

To build on the above results and to better understand the structure-activity relationships in dealloyed Pt-alloy electrocatalysts, we have used uniform, single phase, polycrystalline  $\text{Cu}_3\text{Pt}$  thin films and single crystal  $\text{Cu}_3\text{Pt}(111)$  as model catalysts for accurate characterization of structure and the resulting ORR activity enhancement. Anomalous x-ray diffraction (AXRD) is used to study the structure of the dealloyed Pt-Cu thin film (lattice constant and composition) (7). We have obtained a detailed understanding of the structure and composition relationships in these Pt-skeleton structures prepared by dealloying base metal rich alloy. Compositional inhomogeneity of the dealloyed films is observed with a Pt enriched surface region and Cu depleted interior. The composition of Cu depleted interior is different from that of as-deposited  $\text{Cu}_3\text{Pt}$  showing that dealloying of Cu occurs at the surface and proceeds into the interior, leaving a compressively strained Pt-enriched surface region as shown in Fig. 2. Work on single crystal  $\text{Cu}_3\text{Pt}(111)$  is ongoing, but qualitatively consistent with the film studies.

### Mechanistic understanding of fuel cell cathode reaction

In order to develop more efficient fuel cell catalysts it is essential that we can gain information regarding the nature of intermediate species during oxygen reduction reaction (ORR) that contribute to the sluggish kinetics. Hard x-rays penetrate several millimeters

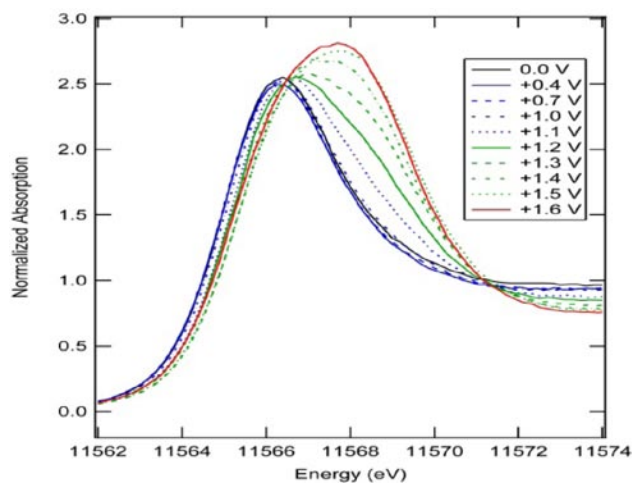


**FIGURE 2.** Schematic of the dealloying of  $\text{PtCu}_3$  film.

through electrolyte solutions, thus providing a unique capability for *in situ* x-ray absorption spectroscopy (XAS) studies of active fuel cell catalysts under electrocatalytic conditions. Of particular interest is determining the nature of Pt–O interactions at high potentials since this is essential for understanding the origin of the overpotential of the electrochemical oxygen reduction reaction (ORR). We have chosen to study a well-defined, simple model system, consisting of one monolayer Pt on a Rh(111) single-crystal surface. By tuning the energy to the Pt  $L_3$  absorption edge this allows for the – intrinsically bulk sensitive – hard x-ray spectroscopy to probe only surface Pt atoms and their interaction with oxygen. Fig. 3 shows the L-edge x-ray absorption spectra (XAS) of a Pt monolayer on Rh(111) detected using High Energy Resolution Fluorescence Detection (HERFD), where the life time broadening of the Pt L-edge has been experimentally removed, resulting in much higher resolved spectral features (8). By using the  $L_3$ -edge, the unoccupied Pt 5d-states are probed. The intensity increase, broadening, and shift of the spectra with increasing potential have been identified, through theoretical spectral simulations, to result from the development of a Pt surface oxide. Complementary extended x-ray absorption fine structure (EXAFS) measurements have been carried out under identical conditions. Pt–Pt and Pt–O bond lengths and coordination numbers have been derived, confirming the interpretation of the growth of a surface Pt oxide (8). Weaker changes in the spectral features at lower potentials can be related to adsorbed hydrogen and to the presence of other oxygenated species.

### Future Directions

We will continue the *in-situ* spectroscopy studies of the ORR of a single Pt monolayer to other substrates



**FIGURE 3.** Pt  $L_3$  edge high resolution fluorescence detection XAS spectra of 1ML Pt/Rh(111) in 0.01M  $\text{HClO}_4$  as a function of increasing potentials.

which are expected to bind oxygen stronger where we expect that the onset of Pt surface oxide formation will occur at lower potentials. We will also extend these studies to nanoparticles of Pt with different sizes since there is a hypothesis that small nanoparticles could induce oxide formation at lower potentials. We will also continue our effort to develop *in-situ* spectroscopic techniques to the soft x-ray regime. We will extend the studies of the dealloying process to Pt–Cu single crystals. We are currently exploring dealloyed bimetallic Pt systems other than Pt–Cu. Current studies focus on dealloyed PtCo<sub>3</sub> and PtNi<sub>3</sub>. Dealloying behavior of these bimetallic compounds is unknown to date. Preliminary results suggest a similar core shell behavior for PtCo<sub>3</sub> as found in PtCu<sub>3</sub>. PtNi<sub>3</sub> showed less susceptibility to leaching. Future experiments will include morphological studies of dealloyed PtCo<sub>3</sub> and PtNi<sub>3</sub>, monitoring of the compositional changes upon extended cycling protocols.

### Publications

1. Srivastava, R., Mani, P., Hahn, N. & Strasser, P. Efficient Oxygen Reduction Fuel Cell Electrocatalysis on Voltammetrically De-alloyed Pt–Cu–Co Nanoparticles. *Angew. Chem. Int. Ed* **46**, 8988–8991 (2007).
2. Koh, S. & Strasser, P. Electrocatalysis on bimetallic surfaces: Modifying catalytic reactivity for oxygen reduction by voltammetric surface de-alloying. *J. Am. Chem. Soc.* **129**, 12624–12625 (2007).
3. Strasser, P. in *Handbook of Fuel Cells: Advances in Electrocatalysis, Materials, Diagnostics and Durability*, Vol. Volumes 5 & 6. (eds. W. Vielstich, H.A. Gasteiger & H. Yokokawa) 30–47 (John Wiley & Sons Ltd, Chichester, West Sussex, UK; 2009).
4. Strasser, P., Koh, S. & Greeley, J. Voltammetric Surface Dealloying of Pt bimetallic nanoparticles: An experimental and DFT computational analysis. *Phys. Chem. Chem. Phys.* **10**, 3670–3683 (2008).
5. Koh, S., Hahn, N., Yu, C. & Strasser, P. Effects of Compositions and Annealing Conditions on the Catalytic Activities of Pt–Cu Nanoparticle Electrocatalysts for PEMFC. *J. Electrochem. Soc.* **155**, B1281–1288 (2008).
6. Strasser, P.; Shirlaine, K.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z.; Kaya, S.; Nordlund, D.; Ogasawara, H.; Toney, M.F.; and Nilsson, A. Lattice-strain control of exceptional activity in dealloyed core-shell fuel cell catalysts *Nature Chem.* (2010) in press.
7. Yang, R.; Leisch, J.; Strasser, P.; Toney M. F. Origin of Enhanced Oxygen Reduction Activity on Dealloyed PtCu, Thin Films, submitted.
8. Friebe, D.; Miller, D.J.; O’Grady, C.P.; Anniyev, T.C.; Bargar, J.; Bergmann, U.; Ogasawara, H., Wikfeldt, K.T.; Petterson, L.G.M.; Nilsson, A. *In-situ* probing reveals the importance of surface platinum oxide formation, submitted.

- 9.** T. Schiros, L.Å. Näslund, K. Andersson, J. Gyllenpalm, G.S. Karlberg, M. Odelius, H. Ogasawara, L.G.M. Pettersson and A. Nilsson, Structure and bonding of the water-hydroxyl mixed phase on Pt(111) *J. Phys. Chem. C* **111**, 15003 (2007).
- 10.** H. Ogasawara L.Å. Näslund, J. McNaughton . Anniyev, and A. Nilsson, Double Role of Water in the Fuel Cell Oxygen Reduction Reaction, *ECS Transactions* **16**, 1385 (2008).
- 11.** Yu, C., Koh, S., Leisch, J., Toney, M., Strasser, P. Size and composition distribution dynamics of alloy nanoparticle electrocatalysts probed by anomalous Small Angle X-ray Scattering (ASAXS). *Faraday Discussions*, *FD* **140**, 283-296 (2008) (selected as hot article !).
- 12.** Mani, P.; Srivastava, R.; Strasser, P. Dealloyed Pt-Cu Core-Shell Nanoparticle Electrocatalysts for use in PEM Fuel Cell Cathodes. *J. Phys. Chem. C*, **112**, 2770-2778 (2008).
- 13.** Srivasta, R.; Mani, P.; Strasser, P. In-situ Voltammetric Dealloying of Fuel Cell Catalyst Electrode Layer: A combined SEM/EPMA study *Journal of Power Sources* **190**, 40-47 (2008).
- 14.** Koh, S.; Leisch, J.; Toney, M.F.; Strasser, P. Structure-activity-stability relationships of Pt-Co alloy electrocatalysts in gas-diffusion electrode layers. *J. Phys. Chem. C*, **111**, 3744-3752 (2007)
- 15.** S. Yamamoto, H. Bluhm, K. Andersson, G. Kettler, H. Ogasawara, M. Salmeron and A. Nilsson In-situ X-ray Photoelectron Spectroscopy Studies of Water on Metals and Oxides at Ambient Conditions *J. Phys: Condensed Matter* **20**, 184025 (2008).
- 16.** MacNaughton, J.; Näslund, L.Å; Anniyev, T.C; Ogasawara, H.; Nilsson, A.; Peroxide-like intermediate observed at hydrogen rich condition on Pt(111) after interaction with oxygen, *Phys. Chem. Chem. Phys.* In press.