

---

## V.C.1 New Electrocatalysts for Fuel Cells

Philip N. Ross

Materials Sciences Division  
Lawrence Berkeley National Laboratory  
University of California  
Berkeley, CA 94720  
Phone: (510) 486-6226; Fax: (510) 486-5530  
E-mail: pnross@lbl.gov

DOE Technology Development Manager:  
Nancy Garland

Phone: (202) 586-5673; Fax: (202) 586-9811  
E-mail: Nancy.Garland@ee.doe.gov

Project End Date: September 30, 2006

### Objectives

- Conduct research on the kinetics and mechanism of electrode reactions in low temperature fuel cells.
- Develop new electrocatalysts using a materials-by-design approach.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost

### Approach

- Study the kinetics of fuel cell electrode reactions on well-characterized model electrodes and high surface area fuel cell electrocatalysts using modern electroanalytical methods.
- Study the mechanisms of the reactions using state-of-the-art *in situ* spectroscopes.
- Use ultra-high vacuum (UHV) methods of surface preparation and surface analyses to form tailored surfaces.
- Synthesize nanoclusters to have a tailored surface.
- Characterize the microstructure of the nanoclusters by high-resolution electron microscopy.
- Transfer new technology to developers and/or component suppliers.

### Accomplishments

- Steady progress made towards reduction in Pt loading from current levels, e.g., near 1 g per kW, to 0.25 g/kW.
- Demonstrated promise of even further gains through control of particle shape.

### Future Directions

- Project in its present form will conclude at the end of FY 2006.

---

### Introduction

The last decade has witnessed a tremendous growth in our understanding of chemical and electronic properties of thin metal films supported on foreign metal substrates. Using modern molecular (atomic) surface characterization techniques combined with *ab initio* quantum chemical theory, we have shown that variations in interfacial bonding and energetic constraints produced between monolayer metal films and their substrates provide a means for modifying the kinetics of the oxygen reduction reaction [1]. While many different metals have been studied as monolayer films in UHV, in electrochemical studies only thin metal films of Pd have received significant attention. Another way to create monoatomic thin metal film on the host metal is to use thermodynamic driving force, which would lead to preferential surface enrichment (segregation) in one element over a core of the other, i.e., the outermost layer is a “skin” of one element. In principle, one could use this thermodynamic property to replace the “buried” atoms in Pt nanoparticles with a non-precious metal, resulting in 100% Pt dispersion (all Pt atoms are surface atoms) without the need to create extremely small particles, e.g., <2 nm. For example, if a standard pure Pt catalyst consists of particles having on average a dispersion of 20%, replacement of the buried atoms in those particles with a base metal would enable the Pt loading to be reduced by a factor of five, all other factors being the same. Development and optimization of either thin metal films or nanoparticles having a “skin” microstructure is the basic strategy we are currently pursuing to reduce precious metal loading in proton exchange membrane (PEM) fuel cell (air) cathodes.

### Approach

New electrocatalysts are developed using a materials-by-design approach. Selection of new

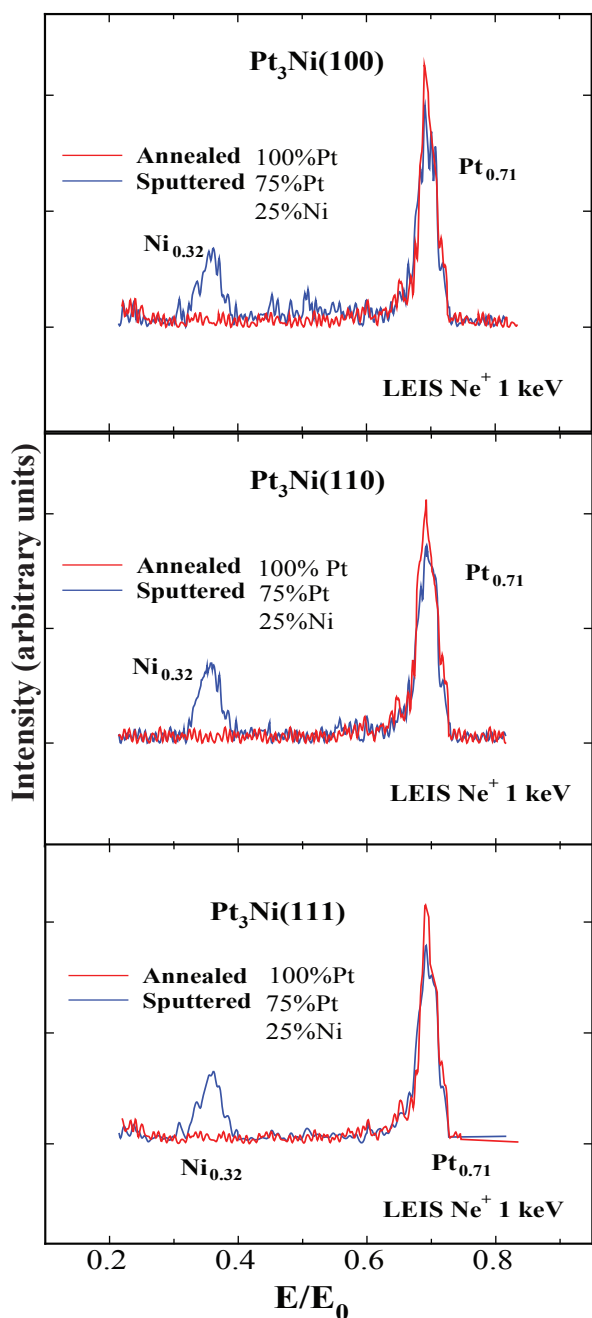
catalytic materials is based on research conducted on the kinetics and mechanisms of the electrode reactions using model systems, e.g., metallic single crystals, bimetallic bulk alloys and bimetallic thin films. All model system samples are prepared and characterized in a UHV chamber and transferred to electrochemical cells. Surface composition and structure are determined using a combination of surface analytical techniques, e.g., low energy electron diffraction (LEED), low energy ion scattering (LEIS), and Auger electron spectroscopy (AES). Multimetallic catalysts are synthesized under carefully controlled conditions producing tailor-made surfaces. Once a promising new catalytic material is identified in these model studies, prototype fuel cell electrodes are synthesized and tested against established benchmarks.

## Results

*Understanding the role of nanoparticle shape on the specific activity of Pt-TM alloy catalysts.*

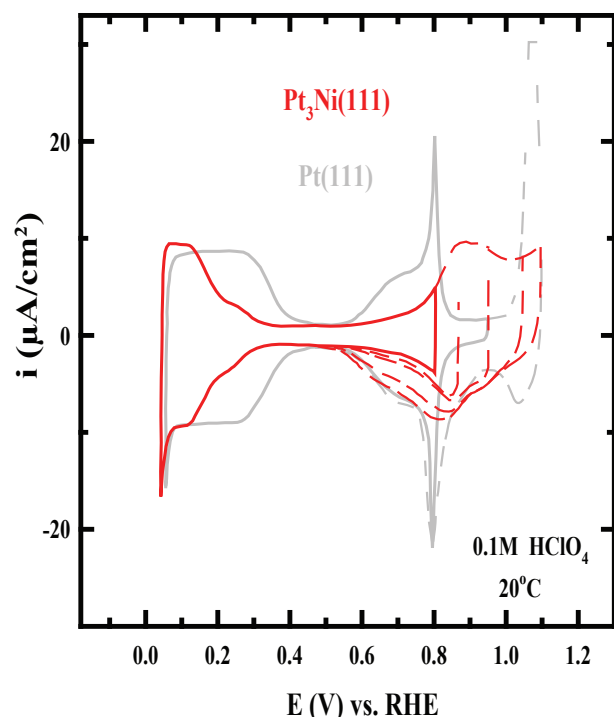
In principle, platinum-transition metal (Pt-TM) nanoparticles could be synthesized in a variety of particle shapes, each shape exposing different distributions of low index faces, e.g., (111), (110) and (100). Whether certain particle shapes would have superior catalytic activity would depend on the *structure sensitivity* of the oxygen reduction reaction (ORR), e.g., whether the kinetics on single-crystal surfaces varies strongly between different orientations. We have studied the structure sensitivity of the ORR (and other reactions) on pure Pt surfaces and found relatively weak crystal face dependence [1]. During FY 2005 and 2006 we studied the kinetics of the ORR on the three low index single crystals of Pt<sub>3</sub>Ni. The results showed unexpected remarkable structure sensitivity.

Low energy ion scattering spectra clearly show, in Figure 1, that the annealed surfaces of all three low index faces are pure Pt. Yet cyclic voltammetry, shown in Figure 2 for the (111) orientation, clearly shows dramatic shifts in both H<sub>ad</sub> and OH<sub>ad</sub> underpotentials for the Pt<sub>3</sub>Ni versus the pure Pt surface even though the surface of the Pt<sub>3</sub>Ni is pure Pt. This is due to the electronic effect of the Ni-enriched second layer, as we have previously observed [3]. Because the surface of Pt<sub>3</sub>Ni is pure Pt and the irreversible OH<sub>ad</sub> potential (the one at > 1 V) is shifted positively to about 1.2 V, the surface of Pt<sub>3</sub>Ni is at least as stable as Pt to potential cycling in the 0–1 V range. Because the irreversible OH<sub>ad</sub> potential is shifted positively, it is possible that Pt<sub>3</sub>Ni is even more stable than pure Pt in the problematic 1.0–1.2 V region, since the irreversible OH<sub>ad</sub> corresponds to the Pt place-exchange which causes some Pt dissolution during potential cycling [4]. Figure 3 shows the current-potential curves for the ORR on a Pt<sub>3</sub>Ni(111) electrode vs. a Pt(111) electrode. Even though both surfaces are

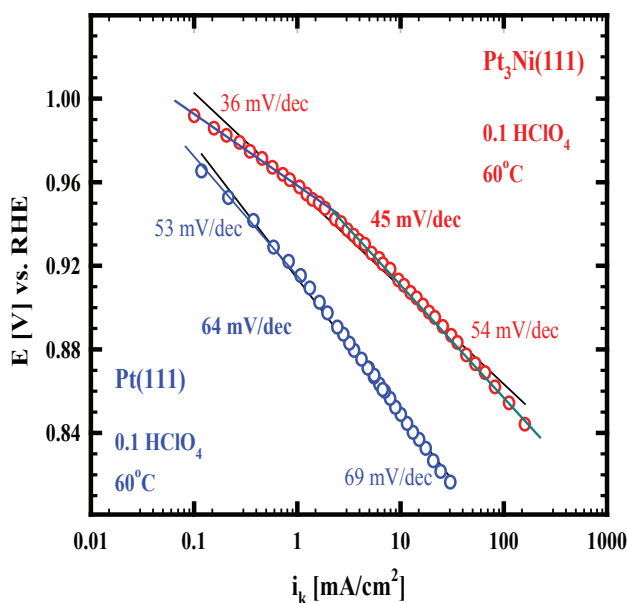


**FIGURE 1.** Low Energy Ion Scattering Spectra of Low Index Surfaces of Pt<sub>3</sub>Ni Showing Strong Surface Segregation of Pt Following Thermal Annealing

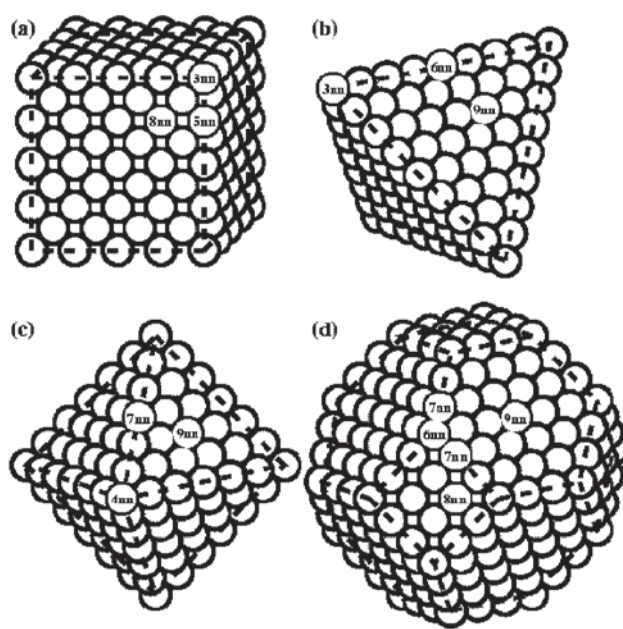
pure Pt, the Pt<sub>3</sub>Ni surface has a dramatically enhanced activity (10-fold), again due to the presence of Ni in the second layer. Another interesting detail seen in Figure 3 is the difference in so-called Tafel slopes, the slope of the E vs. log i<sub>k</sub> curves, where the slopes are significantly lower for the alloy surface than for the pure Pt. It is not a simple matter to explain differences in Tafel slopes that are not multiples of RT/F (ca. 60 mV/dec). These results



**FIGURE 2.** Cyclic voltammety (50 mV/s) comparing  $\text{Pt}_3\text{Ni}(111)$  to  $\text{Pt}(111)$ . Both  $\text{H}_{\text{ad}}$  and  $\text{OH}_{\text{ad}}$  underpotentials are shifted by about 0.2 V due to the electronic effect of the Ni-enriched second layer. Qualitatively similar but smaller shifts are observed for the (100) and (110) orientations.



**FIGURE 3.** Rotating disk electrode current-potential curves for ORR, corrected for  $\text{O}_2$  diffusion resistance, for (111) single crystal surface of pure Pt and  $\text{Pt}_3\text{Ni}$ . The kinetic current ( $i_k$ ) on the  $\text{Pt}_3\text{Ni}$  surface is more than an order of magnitude higher than on the pure Pt surface even though both surfaces are composed solely of Pt atoms.



**FIGURE 4.** Highly faceted nanoparticle geometries of atoms in fcc packing: (a) simple cube; (b) tetrahedron; (c) octahedron; (d) cubo-octahedron. For the tetrahedron/octahedron, all the surface atoms are in facets of (111) orientation, while in the cubo-octahedron, 2/3 of the surface atoms are in (111) facets, and in the cube, none of the surface atoms are in (111) facets.

will require a re-examination of the kinetic theory of the ORR to understand.

In conclusion, ORR kinetic measurements with  $\text{Pt}_3\text{Ni}(hkl)$  single-crystal model catalysts show a strong variation in activity with crystal face. This conclusion suggests it may be possible to further enhance or tune the activity of  $\text{Pt}_3\text{TM}$  nanoparticle catalysts by controlling nanoparticle shape. Particle shape could present a new avenue for further enhancement of the activity of Pt-TM catalysts. Figure 4 shows examples of highly faceted shapes taken by atoms with face-centered cubic (fcc) packing. Shapes like the tetrahedron and the octahedron are composed entirely of (111) oriented crystal planes and thus would maximize the activity of this crystal face in a  $\text{Pt}_3\text{Ni}$  nanoparticle. Other shapes like cubes or spheres would have no (111) planes exposed and thus would have only the lower level of enhancement in activity seen with polycrystalline electrodes, e.g., factor of two to three. Therefore, control of particle shape as well as size is the challenge to the synthetic chemist seeking to maximize the catalytic activity of Pt-TM alloys.

## Conclusions

- Further enhancement in activity (relative to pure Pt) by use of Pt-TM nanoparticle catalysts beyond the present factor of two to three may be possible by controlling the particle shape. Enhancements of a factor of 10 appear possible by optimizing nanoparticle shape and size.

## References

1. Stamenkovic, V., B.S. Mun, K.J. Mayrhofer, P.N. Ross, N.M. Markovic, J. Rossmeisl, J. Greeley, and J.K. Nørskov, "Changing the activity of electrocatalysts for oxygen reduction by tuning the electronic structure", *Angew. Chemie Int. Ed.* 45, 1 (2006).
2. Mayrhofer, K., B. Blizanac, M. Arenz, V. Stamenkovic, P. Ross, N. Markovic, "The impact of geometric and surface electronic properties of Pt-nanocatalysts on the particle size effect in electrocatalysis", *J. Phys. Chem. B* 109, 14433 (2005).
3. Mun, B.S., M. Watanabe, M. Rossi, V. Stamenkovic, P. Ross, N. Markovic, "A study of electronic structure of Pt<sub>3</sub>M polycrystalline alloys using valence band photoelectron spectroscopy", *J. Chem. Phys.* 123, 204717 (2005).
4. F.T. Wagner and P.N. Ross, "LEED spot profile analysis of the structure of electrochemically treated Pt(111) and (100) surfaces", *Surf. Sci.* 160, 305 (1985).

## FY 2006 Publications/Presentations

1. Mayrhofer, K., B. Blizanac, M. Arenz, V. Stamenkovic, P. Ross, N. Markovic, "The impact of geometric and surface electronic properties of Pt-nanocatalysts on the particle size effect in electrocatalysis", *J. Phys. Chem. B* 109, 14433 (2005).
2. Mayrhofer, K., B. Blizanac, M. Arenz, V. Stamenkovic, P. Ross, N. Markovic, "CO surface electrochemistry on Pt-nanoparticles: A selective review", *Electrochimica Acta* 50, 5144 (2005).
3. Arenz, M., V. Stamenkovic, B.B. Blizanac, N.M. Markovic, P.N. Ross, "Carbon-supported Pt-Sn electrocatalysts for the anodic oxidation of H<sub>2</sub>, CO, and H<sub>2</sub>/CO mixtures. Part II: The structure-activity relationship", *J. Catal.* 232 (2): 402-410 (2005).
4. Radmilovic, V., T.J. Richardson, S.J. Chen, N.M. Markovic, P.N. Ross, "Carbon-supported Pt-Sn electrocatalysts for the anodic oxidation of H<sub>2</sub>, CO, and H<sub>2</sub>/CO mixtures. Part I. Microstructural characterization", *J. Catal.* 232 (1): 199-209 (2005).
5. Arenz, M., K.J. Mayrhofer, V. Stamenkovic, N.M. Markovic, P.N. Ross, "The effect of the particle size on the kinetics of CO electrooxidation on high surface area Pt catalysts", *J. Amer. Chem. Soc.*, 127, 6819-6829 (2005).