

V.D.8 Studies of Model Electrocatalysts for Fuel-Cell Cathodes

H. You (Primary Contact), N.M. Markovic,
G. Karapetrov, P. Zapol, D. Myers

Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439
Phone: (630)252-3429; Fax: (630) 252-7777
E-mail: hyou@anl.gov

DOE Program Officer: Richard Kelley

Phone: (301) 903-6051
E-mail: Richard.Kelley@science.doe.gov

Subcontractors:

- Professor J. Woods Halley, U. Minnesota
- Professor Y. V. Tolmachev, Kent State University

Objectives

- Fundamental molecular-level understanding of reactions occurring on fuel-cell cathode materials such as oxygen-reduction, oxidation, dissolution reactions.
- Study of low-dimensional model systems to study chemical states and structures *in situ* during those reactions using electrochemical techniques, advanced x-ray techniques, microscopy techniques, and first-principle and tight-binding theories.
- Understanding the rate limiting steps of the oxygen reduction reaction and the origin of its overpotentials.
- Extend the basic knowledge obtained from the model systems to realistic electrocatalysts to elucidate the mechanism governing their catalytic activities and stabilities in realistic membrane-electrode assembly.

Technical Barriers

- Understanding catalyst particle structure will help optimize catalysts for the oxygen reduction reaction. New model nano-catalysts allow us to better understand the behavior of the support-catalyst system in oxygen reduction reaction.
- Help overcome the durability and performance technical barriers for cathode electrocatalysts in polymer electrolyte fuel cells.
- Basic knowledge gained in our study can help to gain the 10-fold reduction of noble-metal loading necessary to making the low-temperature fuel-cell technology economically competitive and sustainable.

Abstract

Model electrocatalysts, one-dimensional (1d) and two-dimensional (2d) nanoparticle arrays, and single crystal surfaces were studied for their oxygen reduction reaction (ORR) and dissolution reaction. 1) The ORR activities of 1d model catalysts are found to be considerably higher than expected from their geometry where oxy-species of reaction intermediates cross over between adjacent facets in nanometer proximities. ORR studies of 2d arrays are in progress. Density-functional theory and tight-binding methods are used to theoretically model the equilibrium shapes and electrocatalytic activities. 2) The dissolution reactions were found sensitive to the crystallographic orientations and nanostructures although the overall dissolution rates increase with electrochemical potential as expected. 3) Studies of some nanoparticle electrocatalysts and comparison to the model electrocatalysts will also be presented.

Progress Report

1d and 2d array model electrocatalysts and oxygen reduction reactions

We prepared 1d and 2d array structures of platinum crystal of nanoscale sizes to model electrocatalysts. The 1d arrays were prepared by annealing and faceting high-index crystal planes of platinum single crystals.¹ The oxygen reduction reaction (ORR) was studied on (111)-(100) nanofaceted platinum surfaces in sulfuric and perchloric acids using the rotating disk electrode technique. Activities of nanofaceted surfaces are found to be considerably higher than a simple geometric average of the activities of (111) and (100) surfaces. We find that the high activity in sulfuric acid is consistent with the higher activity of (111) facets due the weaker sulfate adsorption on finite-size (111) surfaces than on (111) single crystal surfaces where the ORR activity is suppressed by strong sulfate adsorption. However, the high activity found in the weakly absorbing perchloric acid cannot be explained by the finite-size effect since the activities are reportedly insensitive to terrace sizes.² Based on our results, we proposed a cooperative activity, unique to nanoscale objects, which results from oxy-species crossing over between adjacent facets in nanometer proximities.³ Figure 1 schematically shows this model.

2d arrays were prepared with thermal annealing combined with electron-beam lithography technique. Initially platinum films were prepared with vapor deposition on Nb-doped SrTiO₃ (STO) substrates.

Annealing a submonolayer Pt film at 850°C in UHV chamber produced randomly distributed clusters with a rather uniform size but mostly on step edges (Figure 2a). Annealing several layers of Pt film resulted in epitaxial films. The epitaxial films were then subjected to electron-beam lithography to create precisely registered 2d arrays of Pt particles (Figure 2b). Preliminary measurements of oxygen reduction, hydrogen evolution, and hydrogen oxidation are in progress.

We have theoretically studied morphology of Pt particles on the STO substrates. Partial wetting of Pt particles during annealing led to equilibrium shapes. The equilibrium shapes were then simulated through a combination of DFT calculations and Wulff-Kaischew theorem. The predicted shapes, degree of wetting, and reconstructions agree with the experimental observation as illustrated in Figure 3. We also completed a nonrelativistic parameterization of platinum metal. The parameterization for self-consistent tight-binding is a significant step towards to realistic simulation of the oxygen reduction reaction (see Future directions).

Platinum dissolution of low-index single crystal surfaces and nanoparticles

Stability and dissolution of platinum single crystal surfaces were investigated with atomic force microscopy and inductively coupled plasma mass spectrometry. Both low-index surfaces and nanofaceted surfaces¹ were investigated. A clear difference was observed between the large low-index surfaces and the nanofaceted surfaces.⁴ The left panel of Figure 4 summarizes the results. At 0.65 V vs. RHE, all three basal Pt single crystals dissolve considerably. Dissolution of Pt(111) occurs at the step edge, and proceeds by a layer-by-layer fashion. At 0.95 V, platinum content in solution is *smaller* than at 0.65 V due to passivation. Atomic

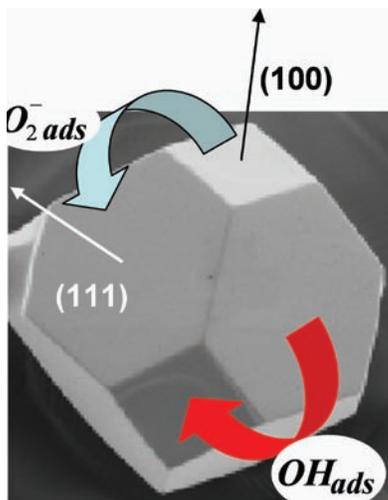


FIGURE 1. Model for reactants crossing over between different facets of a nanoparticle.

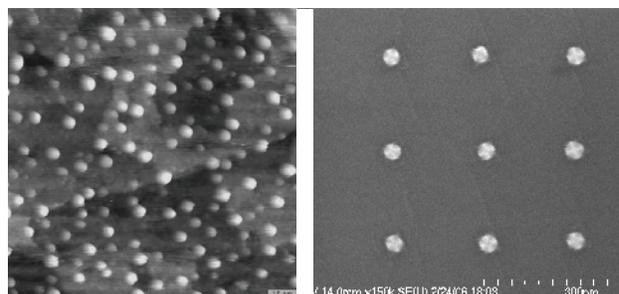


FIGURE 2. Left: A STM image of 100x100 nm². Right: A SEM image showing a perfect 2d array of Pt cubo-octahedra of ~30 nm on STO(100).

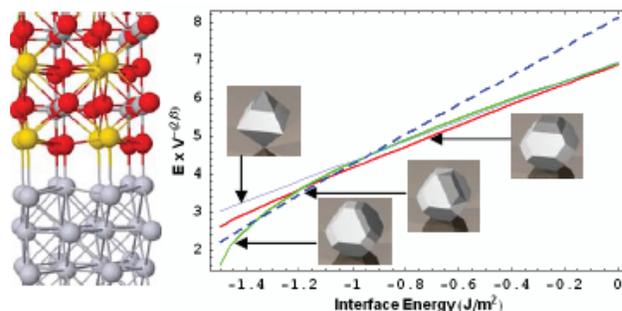


FIGURE 3. Top left: DFT-Optimized structure of Pt/STO interface. Top right: Stability of Pt particles of different shapes as a function of interface energy. Bottom left: SEM image of the Pt particle. Bottom right: Particle shape as obtained from Wulff-Kaischew theorem based on DFT-calculated energies.

pits and deep (~3.5 nm, ~1 μm wide) holes form in case of Pt(111), but step corrugation occurs in Pt(100). At 1.15 V, Pt(111) dissolves in “uncontrolled way” forming many 0.6 nm deep rough etch holes while other two surfaces passivate. On the other hand, the nanofaceted surface dissolves faster at a higher potential indicating the edges and corners are the main sources of dissolution. This is qualitatively similar to nanoparticle dissolution determined by measuring equilibrium Pt concentrations for nanoparticle Pt catalysts supported on high-surface-area carbon, Pt₃Co/C and Pt/C (see Figure 4). However, these data show in more detail that the equilibrium concentration increases with increasing potential from 0.65 to 1.0 V but decreases at >1.0 V. The decrease of dissolved Pt concentration at >1.0 V is

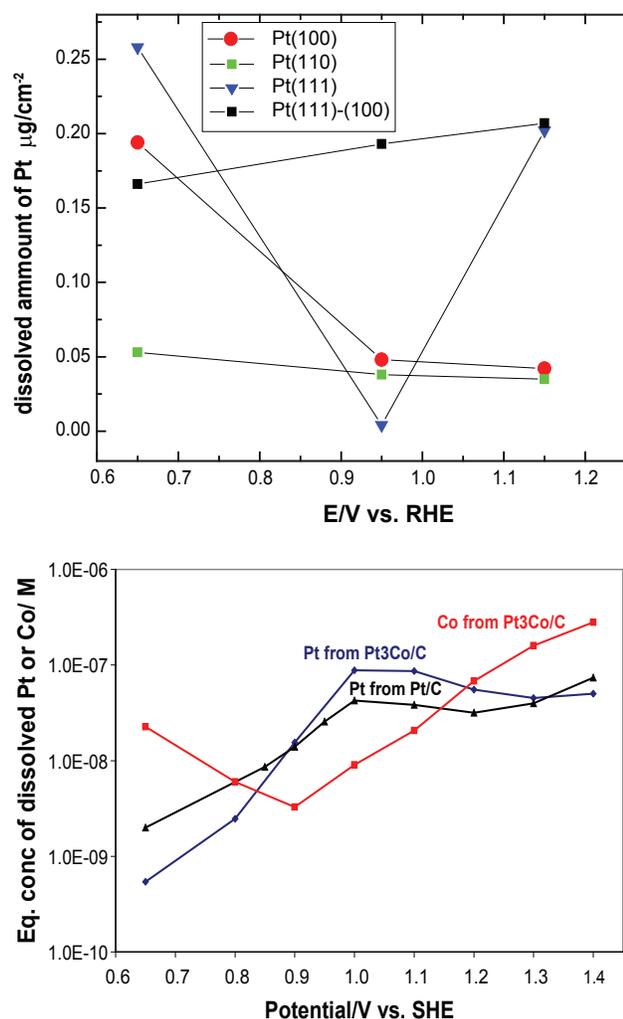


FIGURE 4. Dissolution rates of single-crystal surfaces over 24 hrs (top) and equilibrium concentration of Pt and Pt₃Co nanoparticles (bottom) in aqueous perchloric acid electrolyte as a function of potential for supported on high-surface-area carbon.

consistent with the proposed idea of ‘passivation’ with the place-exchange of surface Pt and adsorbed oxygen atoms.⁵

X-ray studies of nanoparticle catalysts:

Se-modified Ru nanoparticles are known to be highly active in ORR while tolerant to CO and methanol. We used the *in situ* Se K edge x-ray spectroscopy to characterize Se-skin Ru nanoparticles. X-ray powder diffraction verified that the Se/Ru catalyst had largely pure Ru cores. The analysis of the extended x-ray absorption fine structure shows an enhancement of the Se-Ru bonds and disappearance of Se-O bonds during the oxygen reduction reaction. This supports the view that the role of Se in the Se/Ru ORR catalysis is to inhibit the formation of RuO₂. Based on our study, we can conclude that the major factor governing the activity

of the Se/Ru catalysts is the incomplete coverage and non-uniform distribution of Se atoms on the Ru surface that expose 2-fold Ru sites to oxygen molecules.

Future Directions

We will electrochemically characterize the 2d array nanostructures shown above for ORR activities. These arrays will also be studied *in situ* using x-ray scattering techniques to examine the morphological and chemical evolution during ORR.

The dissolution measurements will continue to determine the soluble platinum species formed as a result of potentiostatic and potential cycling of Pt/C and Pt₃Co/C using X-ray absorption spectroscopy. In addition, the effect of temperature on the dissolution kinetics and equilibrium concentration of dissolved platinum will be determined for the Pt/C and Pt₃Co/C electrocatalysts.

We will continue to study the surface-modified electrocatalysts. We demonstrated in Figure 5 using the atomic layer deposition technique⁶ that we can make pin-hole free Pt-skin Ni nanowires. We will implement electrodeposition of Ni into nanoporous alumina. This method will enable us to produce significant quantity of Pt-skin Ni nanowires for testing ORR performance.

In theoretical fronts, we will study the role of adsorbate in determining morphology of Pt particles and evolution of the particles under reaction conditions. Of particular interest are oxygen and water molecules, which are present at the surface during oxygen reduction. In Figure 6, we compare the model band structure and the DFT band structure as well as the total energies as a function of the amplitudes of distortions of the lattice corresponding to frozen longitudinal and transverse phonons. We will begin work on a simulation of the reaction steps using the existing water model

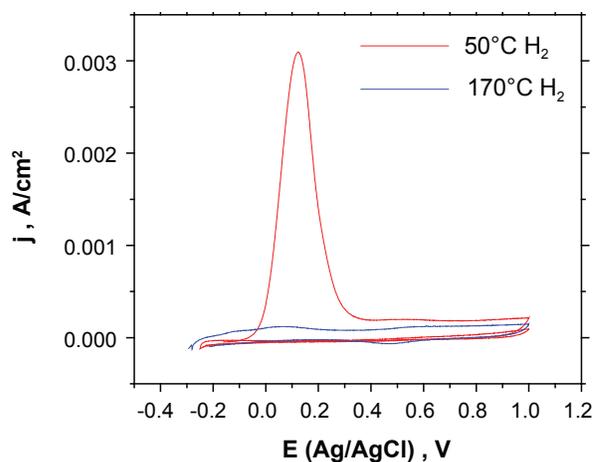


FIGURE 5. Cyclic voltammograms (50 mV/s) of incomplete Pt skin prepared at 50°C (red) and pinhole-free Pt skin prepared at 170°C (blue).

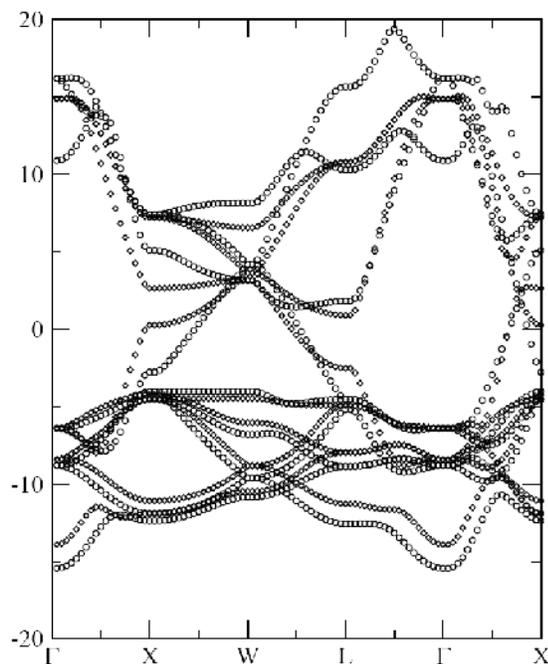


FIGURE 6. DFT (circles) and SCTB (diamonds) band structures for Pt at the equilibrium density. Fermi energy on this scale is -3.8 eV.

and model titanium surface which has already been characterized.⁷

References

1. V. Komanicky, A. Menzel, K. C. Chang, H. You, *J. Phys. Chem. B*, 109, 23543 (2005).
2. M. D. Macia, J. M. Campina, E. Herrero, J. M. Feliu, *J. Electroanal. Chem.*, 564, 141(2004).
3. V. Komanicky, A. Menzel, K. C. Chang, H. You, *J. Chem. Phys.*, 109, 23550 (2005).
4. V. Komanicky, K. C. Chang, A. Menzel, N. M. Markovic, H. You, X. Wang, and D. Myers, *J. Electrochem. Soc.*, 153 B446 (2006).
5. M. Teliska, W.E. O'Grady, and D.E. Ramaker, *J. Phys. Chem. B*, 2005, 109, 8076.
6. T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen, M. Leskela, *Chem. Mat.* 15 (2003) 1924-1928.
7. S. Erdin, Y. Lin, and J. Woods Halley, *Phys. Rev B* 72, 035405 (2005).

Publications Acknowledging the Grant or Contract

1. V. Komanicky, A. Menzel, K. C. Chang, H. You, *Investigation of Oxygen Reduction Reaction Kinetics at (111)-(100) Nanofaceted Platinum Surfaces in Acidic Media*, *J. Chem. Phys.*, 109, 23550 (2005).
2. V. Komanicky, K. C. Chang, A. Menzel, N. M. Markovic, H. You, X. Wang, and D. Myers, *Stability and Dissolution of Platinum Surfaces in Perchloric Acid*, *J. Electrochem. Soc.*, 153, B446 (2006).
3. K.-C. Chang, A. Menzel, V. Komanicky, H. You, J. Inukai, A. Wieckowski, E. V. Timofeeva, Y. V. Tolmachev, *Resonance elastic and inelastic X-ray Scattering Processes for in-situ Investigation of Electrochemical Interfaces*, A chapter to Elsevier book entitled "In-situ Spectroscopic Studies of Adsorption at the Electrode and Electrocatalysis", ed, S.-G. Sun, P. A. Christensen, A. Wieckowski, 2006.
4. H. You, J. Inukai, A. Wieckowski, K.-C. Chang, and V. Komanicky, *In-situ Synchrotron X-ray Spectroscopy of Ruthenium Nanoparticles Modified with Selenium for Oxygen Reduction Reaction*, *ECS Trans.* 3, 161 (2006).
5. V. Komanicky, K.-C. Chang, A. Menzel, D. Hennessy, G. Karapetrov, and H. You, *Fabrication of platinum nano-array model catalysts*, *Proc. SPIE Vol. 6340, 634010* (Sep. 8, 2006).
6. J. Inukai, D. Cao, A. Wieckowski, K.-C. Chang, A. Menzel, V. Komanicky, and H. You, *In-situ Synchrotron X-ray Spectroscopy of Ruthenium Nanoparticles Modified with Selenium for an Oxygen Reduction Reaction*, Submitted to *J. Phys. Chem.* (2007).
7. H. Iddir, V. Komanicky, P. Zapol and H. You, Pt nanoparticles supported on SrTiO₃: A combined SEM and DFT investigation, (in preparation).