

VII.C Catalysts

VII.C.1 New Electrocatalysts for Fuel Cells

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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 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- High Cost of Fuel Cell Stacks
- Durability of Fuel Cell Components

Technical Targets

Table 1. Progress Toward Meeting DOE Technical Targets for Electrocatalysts

Characteristic	Units	2004 Status	2010 Target
PGM Total Content	g/kW rated	1.3	0.5

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 the 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.

- Improved understanding of peroxide formation chemistry in polymer electrolyte membrane (PEM) fuel cells.

Future Directions

- Complete development of the last of the bimetallic Pt catalysts that has the potential to reduce Pt loading to 0.25 g per kW.
- This 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. Modern molecular (atomic) surface characterization techniques operating under UHV conditions have revealed that variations in interfacial bonding and energetic constraints produced between monolayer metal films and their substrates provide a means for modifying the chemical properties of surfaces [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 5, 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 PEM fuel cell (air) cathodes.

Approach

New electrocatalysts are being 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 mechanism of peroxide generation in PEM cells

Peroxide by itself does not attack the polymer electrolyte membrane. However, in the presence in the membrane of dissolved Fe^{2+} , which can be present as an impurity from a variety of sources, the peroxide is reduced by the Fe^{2+} , generating hydroxyl radicals ($\bullet\text{OH}$) which are extremely strong oxidizers, and these radicals attack the membrane. Therefore, the generation of peroxide in the cell, by whatever chemistry, is to be avoided, and the chemistry/conditions leading to its formation need to be understood.

One condition of cell operation of concern is low temperature, i.e., does operation at low temperature cause an increase in peroxide formation. The reduction of oxygen on pure polycrystalline Pt, and on a few Pt-TM (transition metal) alloys, was studied using the ring-disk electrode technique in aqueous

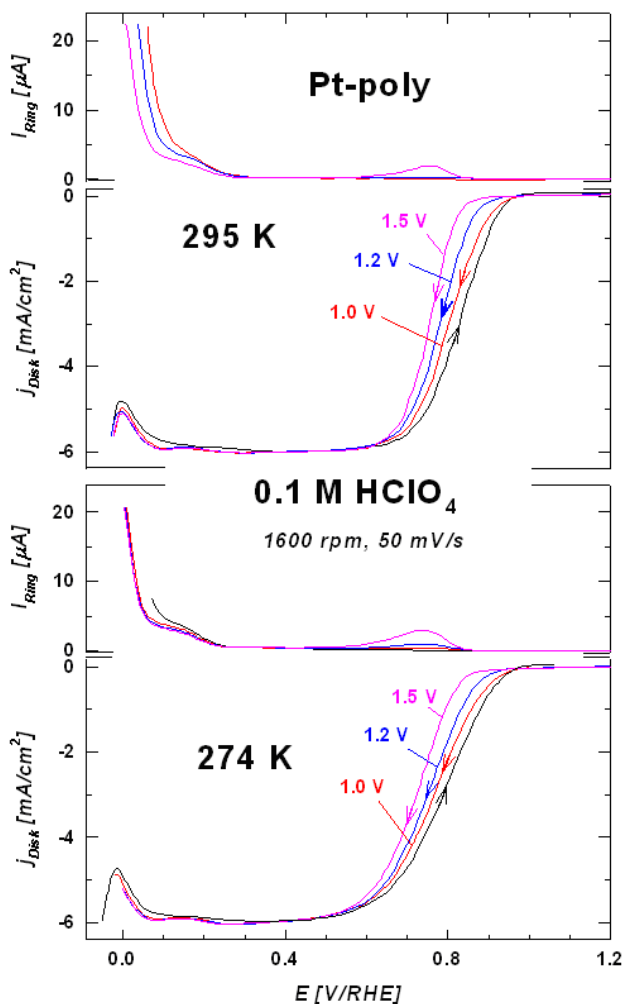


Figure 1. Current (j) – Potential Curves at a Pt Rotating Ring Disk Electrode in O_2 -Saturated Solution as a Function of Temperature and Positive Potential Limit. Ring potential held at 1.2 V to oxidize peroxide produced at the disk. Collection efficiency is 0.18.

electrolyte ($HClO_4$ solutions) as a function of temperature (274 – 333 K) and pH (1 – 3). A characteristic result for pure polycrystalline Pt is shown in Figure 1. The conclusions regarding peroxide formation were as follows: i.) operation at 274 K does not produce any more peroxide from the reduction of oxygen at either electrode than operation at higher temperatures; ii.) there was no change in peroxide yield with pH in the range examined; iii.) the primary source of peroxide is at the hydrogen electrode from reduction of oxygen permeating through the membrane; iv.) supported Pt catalyst does not produce more peroxide than unsupported Pt

except at potentials below 0.4 V, and differences are still small and probably not of practical importance; v.) some Pt-TM alloys do produce substantially more peroxide than pure Pt, and thus alloy catalysts in general need to be evaluated on a case-by-case basis. It should be noted that permeation of oxygen through the membrane has an autocatalytic effect on membrane degradation leading to sudden failure, consistent with experience.

Understanding the enhanced specific activity of Pt-TM alloy catalysts

Hammer and Norskov [1] have shown that the interactions between adsorbates and transition metal surfaces involve the entire d-band of the valence electrons. They suggested that a convenient metric which captures the interaction with the entire d-band is the “d-band center”, the first moment of the density of states (DOS) from the Fermi level. Later, Norskov and co-workers [2] calculated from density functional theory (DFT) the shift in d-band center for model bimetallic systems consisting of a monolayer of Pt (a Pt skin) on various transition metal (TM) substrates and found a direct correlation with position in the Periodic Table. We recently examined this correlation experimentally with valence electron energy distribution curves (EDCs) obtained by photoelectron spectroscopy. This metric from our EDCs, as noted in Figure 2, shows a clear correlation with the TM substrate in remarkably good agreement with that predicted by DFT. Furthermore, there was a clear correlation between the shift of the d-band center and the electrocatalytic activity of model Pt_3TM bimetallic systems for the oxygen reduction reaction (ORR), as shown in Figure 3. The annealed Pt_3TM surfaces have a pure Pt outermost layer with a second layer enriched in the TM (relative to the bulk), produced essentially by an exchange of TM atoms in the surface for Pt atoms in the second layer (there is also a similar exchange between the second and third layers, raising the second layer concentration of TM to about 75%). The Pt atoms on this TM-enriched second layer experience a lateral in-plane compression that, as shown by the experimental photoelectron energy distribution curves, shifts the valence electron (d-band) DOS. A fundamental prediction from the Norskov theory is that this shift in d-band center weakens the interaction of the surface Pt atoms with adsorbates

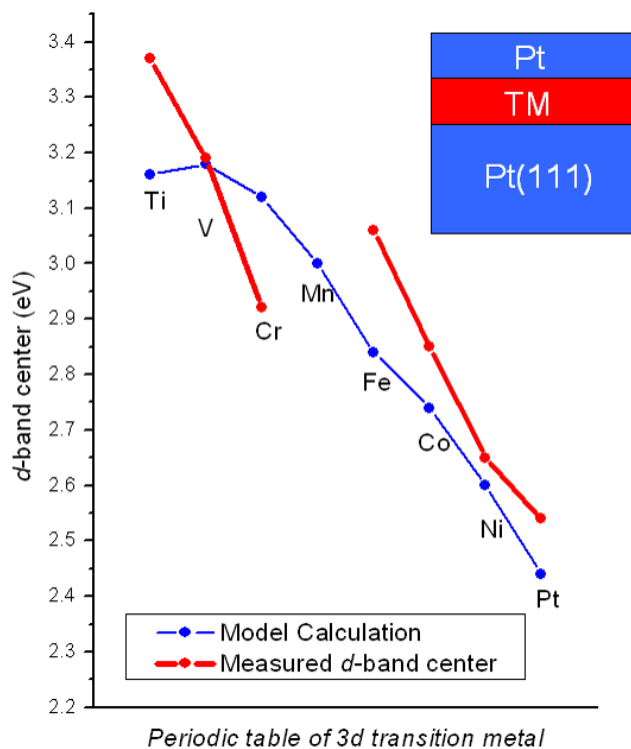


Figure 2. Comparison of Experimental d-Band Center Obtained from EDCs Versus DFT Calculation for Model Pt-TM Sandwich Structures

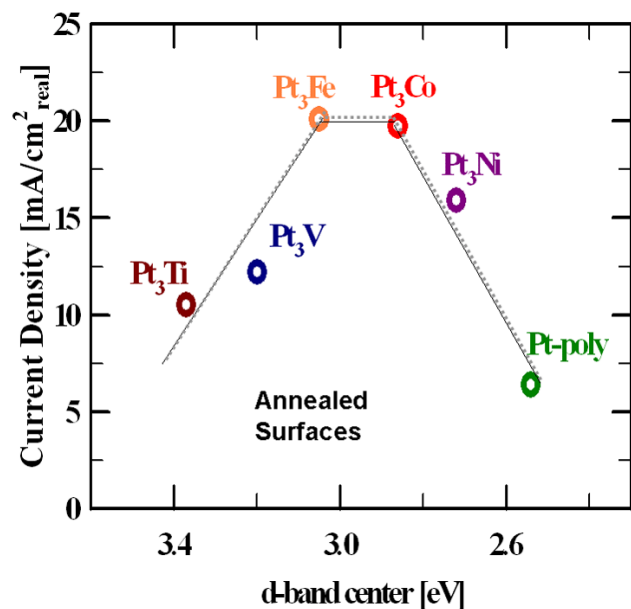


Figure 3. Correlation of ORR Activity with Measured d-Band Centers for Thermally Annealed Pt₃TM Alloy Model Catalysts Having the Sandwich Surface Structure Like That Shown in Figure 2

like O and H [1]. We propose here that the weaker interaction with OH_{ad} reduces the steady-state

coverage by this species, which is a site-blocking species in the ORR, and increases the reaction rate as long as the weakening is not too large. If the shift in d-band center is too large, then the interaction with O₂ is weakened, leading to a decrease in rate, producing a classic “volcano” relation between reaction rate and shift in d-band center.

As shown in Figure 3, the annealed surface of the Pt₃Co alloy has the highest stable activity for the ORR (under PEM conditions) of any catalyst, about 4 times that for polycrystalline Pt. We have confirmed in emersion experiments (removing the sample from electrolyte and examining the surface in UHV) that the Pt-skin structure of the annealed surface of Pt₃Co is stable to potentiodynamic cycling from 0 – 1.0 V at PEM conditions. Pt₃Fe, on the other hand shows extensive “leaching” of Fe and unstable catalytic activity. Monte-Carlo simulations also indicate that the Pt-skin structure is the thermodynamically preferred microstructure in Pt₃Co nanoparticles, i.e., as in the practical fuel cell catalyst. In practical nanoparticle catalysts, Pt₃Co nanoparticle catalysts demonstrate factors of 2 – 3 enhancement in activity versus pure Pt nanoparticle catalysts in the same size range.

Preliminary studies of Pt₃Ni(hkl) single crystal model catalysts, i.e., strong variation in activity with crystal face, suggest it may be possible to further enhance or tune the activity of Pt₃TM nanoparticle catalysts by control of nanoparticle shape. Particle shape could present a new avenue for further enhancement of the activity of Pt-TM catalysts.

Conclusions

- Operation at 274 K does not produce any more peroxide at either electrode than operation at higher temperatures.
- The primary source of peroxide is at the hydrogen electrode from reduction of oxygen permeating through the membrane.
- Supported Pt catalyst does not produce more peroxide than unsupported Pt except at potentials below 0.4 V. Differences are still small and probably not of practical importance.
- A correlation has been found between electronic modification of surface Pt atoms by underlying transition metal atoms and the activity for the ORR.

- Further enhancement of Pt-TM nanoparticle catalysts beyond the present factor of 2 – 3 may be possible by controlling the particle shape.

References

1. B. Hammer and J. Norskov, *Adv. Catal.* 45, 71 (2000)
2. J. Kitchen, J. Norskov, M. Barteau, and J. Chen, *J. Chem. Phys.* **120**, 10240 (2004)

FY 2005 Presentations

1. N.M. Markovic, Keynote Address, “Electrocatalysis at the Atomic and Molecular Levels”, International Society of Electrochemistry (ISE), Thessaloniki, Greece, September 2004

2. P.N. Ross, “Effect of Temperature on Reduction of Oxygen to Peroxide on Pt Electrodes”, Workshop on Freezing of PEM Fuel Cells, Phoenix, AZ, February 2005

FY 2005 Publications

1. Stamenkovic V, Grgur BN, Ross PN, et al. “Oxygen reduction reaction on Pt and bimetallic Pt electrodes covered by adsorbed CO- Mechanism of air bleed effect with reformat”, *Journal of the Electrochemical Society* 152 (2): A277-A282 (2005)
2. Arenz M, Stamenkovic V, Ross PN, et al. “Surface electrochemistry on Pt(111) modified by a pseudomorphic Pd monolayer”, *Surface Science* 573 (1): 57-66 (2004)