

V.P.6 Activity and Stability of Nanoscale Pt-based Catalysts

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Objectives

In this project, Shao-Horn examines whether fundamental knowledge of electrocatalytic activity established on single-crystal surfaces can be applicable to understanding of nanoparticle activity by studying the influence of surface steps and near-surface composition of Pt-based nanoparticles on electrocatalytic activity. In addition, the stability and the mechanism by which Pt alloy nanoparticles lose activity for oxygen reduction in PEMFCs are studied. Marzari at MIT investigates the effects of applied electrochemical potentials on the adsorption energies and reactions rates of fundamental electrochemical processes, respectively. The overall goal of the modeling work of Morgan at UW is to model oxidative processes on Pt in order to understand and control their influence on Pt-based-nanoparticle stability and electrocatalytic activity.

Technical Barriers

The estimated cost of PEM fuel cell systems for automotive applications is significantly higher than existing, internal combustion technologies (~\$35/kW for advanced technologies). In addition, the lifetime of PEM fuel cell systems is limited to 2000 hours, significantly shorter than the required 5500 hours of

operation in a vehicle. This work help identify near-surface chemical compositions of Pt-based catalysts that can provide 1) high activity to reduce catalyst and PEM fuel cell cost, and 2) stability to overcome long-term catalyst degradation problems in aggressively corrosive and oxidizing environments (e.g. PEM fuel cell cathode).

Abstract, Progress Report and Future Directions

Abstract. Our recent experimental work has shown that near-surface compositions but not surface steps, can greatly influence ORR activity. We have obtained direct evidence of near-surface compositions of Pt-Co alloy nanoparticles, which exhibit specific ORR activity 2-4 times relative to Pt. The stability of these Pt and Pt alloy nanoparticles will also be discussed. On the other hand, surface steps do not appear to influence activity for oxygen reduction unlike for methanol oxidation, from which the origin responsible for this difference will be discussed. Our recent theory work has revealed some stable hybrid Pt-O surface structures, which can play an important role in the stability and activity of Pt-based catalysts.

The influence of near-surface compositions of “Pt₃Co” on oxygen reduction activity. Acid-treated “Pt₃Co” supported on carbon (46 wt% Pt) with an average atomic Pt/Co ratio of 3.6 (having a number-averaged particle size of ~4 nm), was prepared from leaching of a “PtCo” sample in acid. Acid-treated nanoparticles were subsequently heat-treated at 1000 K for 3 hours in vacuum (~10⁻² Torr). Annealed “Pt₃Co” was found to have a number-averaged particle size of ~5 nm. ORR activity of “Pt₃Co” and Pt nanoparticles was measured by sweep voltammetry in O₂ saturated HClO₄ electrolyte using a rotating disk electrode at room temperature. Cyclic voltammetry of “Pt₃Co” nanoparticles was performed in O₂ free electrolyte, from which the electrochemical active area was obtained from integrating the charge associated with hydrogen desorption. Specific ORR activity of acid-treated (with Pt-enriched surface in Figure 1) and annealed “Pt₃Co” nanoparticles normalized to the Pt surface area was compared with that of Pt nanoparticles as a function of potential in. At 0.9 V vs. RHE, the activity of acid-treated “Pt₃Co” nanoparticles is ~0.74 mA/cm²_{Pt} (~2 times of Pt), which is comparable to acid-leached Pt alloy nanoparticles reported previously. On the other hand, the specific activity of annealed “Pt₃Co” at 0.9 V vs. RHE (with surface-sandwich-segregation of Pt-enriched and Co-enriched, not shown here, Shuo et al., JPCC 2009) was increased to ~1.39 mA/cm²_{Pt} (~4 times of Pt) after annealing, which could be attributed to surface Pt sandwich-segregation structures (not shown here).

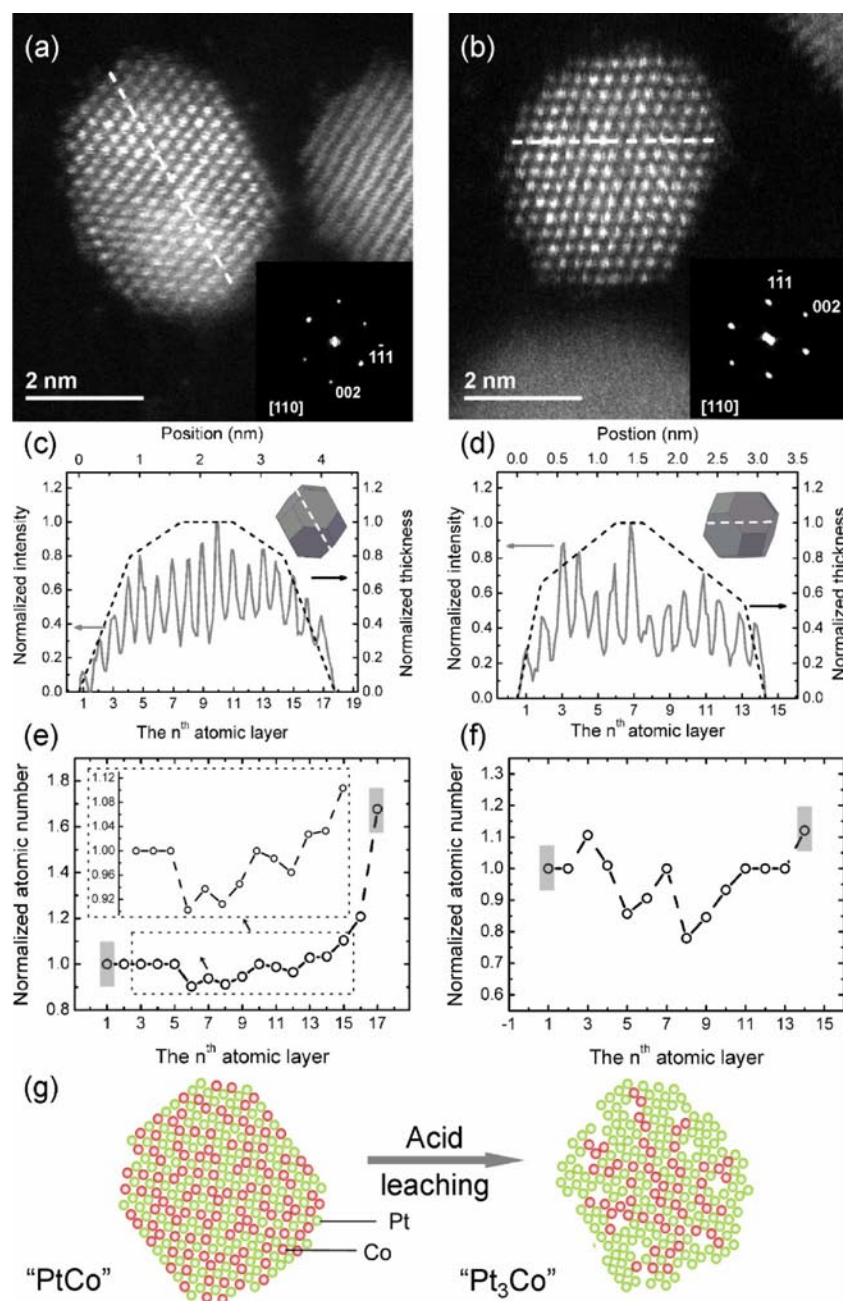


FIGURE 1. Atomically resolved structures and compositions of Pt alloy nanoparticles (acid-treated), which was correlated to specific ORR activity based on electrochemically active Pt surface area. The enhanced specific ORR activity (~ 2 times relative to Pt) of acid-treated “Pt₃Co” nanoparticles can be related to composition variation at the atomic scale and the formation of a Pt enriched skeleton structure within individual particles (Shuo et al. JPCC 2009).

The influence of surface steps of Pt nanoparticles on oxygen reduction activity. ORR activity of Pt/MWNT samples was measured using a rotating disk electrode (RDE) and linear sweep voltammetry in O₂-saturated HClO₄ electrolyte. The electrochemical surface area (ESA) of Pt nanoparticles was obtained from integrating the charge associated with hydrogen

desorption in the O₂-free electrolyte. Specific ORR activity normalized to the Pt ESA is independent of heat-treatment temperature, which indicates that surface steps on Pt nanoparticles do not greatly influence intrinsic ORR activity. Specific ORR activity of Pt nanoparticles at 0.9 V vs. RHE is ~ 200 mA/cm²_{Pt}, which is in good accordance with reported specific activity

for Pt nanoparticles of comparable sizes in HClO_4 . In addition, projecting the reported activity of stepped single-crystal surfaces onto nanoparticle surfaces of Pt/MWNT samples, no ORR activity difference was noted for Pt/MWNT samples. It is interesting to compare the role of surface steps on Pt nanoparticles on the intrinsic activity of ORR with that of MOR. Specific ORR activity at 0.85 V and specific MOR activity at 0.5 V (current density in the positive-going cyclic voltammetry) is plotted as a function of area fraction of surface steps normalized to that of 548 K (Figure 2). Specific ORR activity at 0.85 V is independent of normalized area fraction of stepped surfaces while MOR activity linearly increases with the amount of stepped surfaces on Pt nanoparticles.

Future work in Shao-Horn's group will focus on varying near-surface chemical compositions of Pt-based alloy nanoparticles (e.g. PtAu) and studying its role in the activity and stability for oxygen reduction.

Oxidation of Pt on Pt Nanoparticle stability.

Pt oxidation plays an essential role in the long-term stability and catalytic properties of Pt based nanoparticle catalysis used in PEMFC cathodes. However, at present the structure, thermodynamics and kinetics of oxide phases on Pt are not known. As a first step in understanding Pt oxidation it is necessary to establish the stable Pt-O surface phases as a function of oxygen coverage. Due to the challenges of experimental determination of these complex and near monolayer surface structures we are pursuing an approach based on *ab initio* energy calculations. We have integrated previous *ab initio* studies that treat specific oxygen structures and their energetics, adjusting results to a consistent reference (see Figure 3). These results consider three major classes of oxygen surface phases,

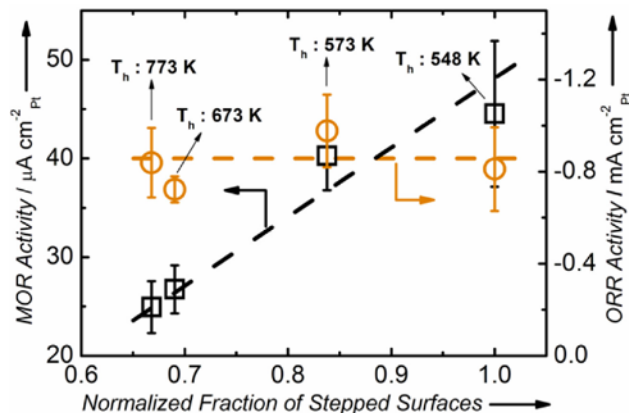


FIGURE 2. Specific MOR (left axis) and ORR activity (right axis) as a function of area fraction of stepped surfaces normalized to the 548 K sample. Specific MOR activity was measured at 0.5 V vs. RHE after subtraction of the double layer current. Specific ORR activity was measured at 0.85 V vs. RHE at 1600 rpm (Lee et al., JPC Letters, ASAP 2010).

Formation Energy of Phases

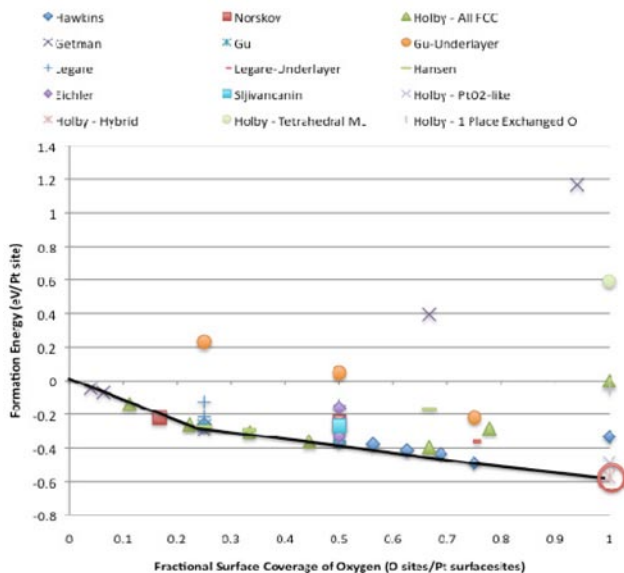


FIGURE 3. Summary of previous calculations of oxide surface structure energetics and results from our recent calculations, plotted as a function of oxide coverage. The dark solid line represents the convex hull. The points on the convex hull are the predicted stable structures and compositions between the points are two-phase regions. The circled point represents a new buckled/place exchanged hybrid structure that we found to be more stable than previously reported structures. References to previous work are given below.

including surface, place-exchanged, and buckled oxygen structures. We have now explored a wide range of new oxygen surface structures with an intent to understand the key mechanisms (e.g., electrostatic interaction, oxygen subsurface vs. surface energetics, etc.) governing stability of oxide phases. In particular, we have developed a set of hybrid place-exchanged and buckled phases with some of the key stabilizing features of each phase. Certain hybrid structures we identified are in fact more stable than previous structures at near one monolayer composition, as can be seen by their residing on the convex hull of all the calculated energies (dark line in Figure 3). These hybrid structures are therefore likely to be the stable form of oxide on Pt near one monolayer. Our future work will further investigate additional new Pt-O structures to establish the correct stable phases that are expected during Pt oxidation.

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Publications (including patents) acknowledging the grant or contract

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