

V.P.23 Metal- and Metal Oxide-Supported Platinum Monolayer Electrocatalysts for Oxygen Reduction

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Objectives

This program involves studies of platinum monolayer electrocatalysts for the O_2 reduction reaction (ORR) aiming at producing ultimately low Pt content electrocatalysts with high activity and high stability, supported by metal-, alloy-nanoparticles, nanorods, nanowires, as well as oxide-, carbide-, nitride- and hollow metal-nanoparticles, and carbon nanotubes. Theoretical calculations are carried out for a deeper insight into the kinetics of the ORR. Studies using well-defined surfaces are carried out to gain understanding of the atomic-scale phenomena involved in the interactions of Pt monolayers with supporting surfaces, as well as developing new efficient catalysts for ethanol oxidation.

Technical Barriers

The project is focused at developing several Pt monolayer catalysts that are likely to have the highest Pt mass activity, and excellent potential to overcome the obstacles hindering the broad application of fuel cells. The results will enhance our understanding of the metal monolayer-support interactions for a viable approach for controlling chemical reactivity in the top atomic layer. In addition, we explore the catalyst capable of C – C bond splitting at low overpotentials in the oxidation of small organic molecules.

Progress Report

Improved understanding of factors affecting the ORR activity of Pt monolayer

We examined the effects the thickness of the Pt shell, lattice mismatch, and particle size on specific and

mass activities from the changes in effective surface area and activity for oxygen reduction induced by stepwise Pt monolayer (Pt ML) depositions on Pd and Pd_3Co nanoparticles. The core-shell structure was characterized at the atomic level using Z-contrast scanning transmission electron microscopy coupled with element-sensitive electron energy loss spectroscopy.

The enhancements in specific activity are largely attributed to the compressive strain effect based on the density functional theory calculations using a nanoparticle model, revealing the effect of nanosize-induced surface contraction on facet-dependent oxygen binding energy. The results suggest that moderately compressed (111) facets are most conducive to the ORR on small nanoparticles and indicate the importance of concerted structure and component optimization for enhancing core-shell nanocatalysts' activity and durability.

In the nanometer range, a particle's size and shape profoundly affect the ORR specific activity because both the surface fraction of active facets and the facet-dependent binding energy for oxygen vary with size. These results point the way to tailoring a Pt shell's structure and properties by controlling core particle's components, size, and shape, for high activity and durability of the ORR electrocatalysts.^{1,2}

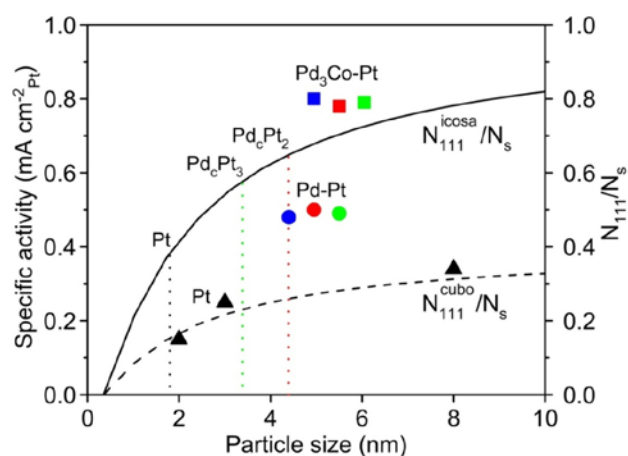


FIGURE 1. ORR specific activities at 0.9 V measured at 10 mV s^{-1} (symbols, left axis) and surface fraction of atoms on the (111) facets (solid and dashed lines, right axis) as a function of particle size. The vertical dotted lines mark the sizes of three nanoparticle models that have the BE-O close to the optimal value of 3.89 eV. The blue, red, and green colors are used, respectively, for particles with 1-, 2-, and 3-Pt layers.

Improving activity and stability of Pt monolayer electrocatalysts for the ORR

Several methods for improving Pt ML catalysts have been developed based on understanding of the factors affecting the ORR. The new strategies include:

1. Surface and sub-surface modification of cores to tune the interaction with a Pt ML.
2. Reducing number of low-coordination surface atoms by Br- adsorption/desorption.
3. Using smooth surfaces of Pd nanorods and nanowires to support a Pt ML.
4. Contracting Pt-Pt separation with hollow particles
5. Using intermetallic compounds as supports

Sub-surface modification of cores to tune the interaction with a Pt ML

This strategy is based on the expectation that a monolayer of a metal can be driven in sub-surface of support. The subsurface layer of Ir in Pd support, obtained by galvanic displacement of a Cu monolayer by Ir and annealing at 350°C to induce segregation of Pd to the surface and Ir into the particle, enhances the ORR kinetics at Pt monolayer on PdIr nanoparticles (Fig. 2). The subsurface Ir causes a Pd skin to contract, so Pt monolayer on PdIr/C is compressed more than on Pd/C. The Pt-O bond will weaken and ORR activity increased. This was verified by the data in Fig.2.

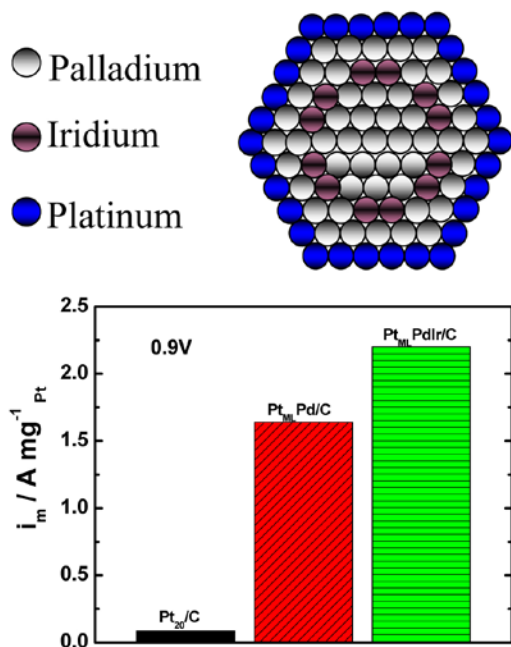


FIGURE 2. Model of a Pd nanoparticle with a Pt ML on its surface and a sub-surface Ir ML (top). Pt mass activity of a commercial Pt/C, Pt/Pd/C and Pt/Pd/Ir/C (bottom)

Modifying surface properties by alloying the core.

Au submonolayer, deposited on a Pd_3Co surface by displacing Co atoms in the surface, or AuPd alloy, as a support for Pt monolayer cause a significant increase in the activity of and stability of such catalysts compared with original $\text{Pt}_{\text{ML}}/\text{Pd}_3\text{Co}/\text{C}$ catalyst.³ The $\text{Pt}/\text{Au}_1\text{Pd}_9/\text{C}$ catalyst has a high activity and durability, i.e., $E_{1/2} = 0.901\text{V}$ before and 0.895V after 30,000 potential cycles from 0.75-0.95V, dwell time 30 sec, of an accelerated stability test. The increased catalytic activity and durability originate from the reduced Pt oxidation (PtOH formation), which inhibits the ORR and is a precursor of Pt dissolution, as inferred from *in situ* XANES spectra of Pt L3 edge.

Ordered intermetallic compound cores

A new class of core-shell electrocatalysts for the ORR consists of a Pt monolayer shell and ordered intermetallic compound cores. We coupled highly stable, inexpensive intermetallics with a Pt monolayer producing electrocatalysts with high activity, low metal content, and very high stability. Our data indicate strategies suitable for selecting the types of intermetallic compounds as the support for a Pt monolayer.²

Smooth support surfaces

Smooth surfaces, having a small number of low-coordination atoms, are suitable support for a Pt monolayer for the ORR due to a reduced Pt oxidation that takes place on such surfaces. This assertion has been verified with the Pd surfaces, obtained by removing low-coordination atoms using Br⁻ adsorption/desorption, Pd nanowires (Fig. 3a) and Pd nanorods used as a support for a Pt monolayer. Unprecedentedly high Pt mass activity of 3.4 A/mg has been obtained (Fig. 3b).

Electrocatalysts for ethanol oxidation

Further studies of the ternary Pt-Rh-SnO₂/C electrocatalysts capable of splitting the C-C bonds at room temperature involved varying the atomic ratio Pt:Rh:Sn = 3:1:x, where x varies from 2 to 6. The catalysts composed of homogeneous PtRh alloy and SnO₂, having all three constituents coexisting in single nanoparticles with the average particle size around 1.4nm and a narrow size distribution.⁴ While all the electrocatalysts investigated exhibited high catalytic activity for ethanol oxidation, the most active one had the composition with the Pt:Rh:Sn = 3:1:4 atomic ratio.

Future Directions

We plan to continue with exploring the interaction of Pt monolayers with smooth surfaces of Pd nanorods, nanowires, and nanotubes. This will help in developing of Pt ML catalysts with predominantly high-

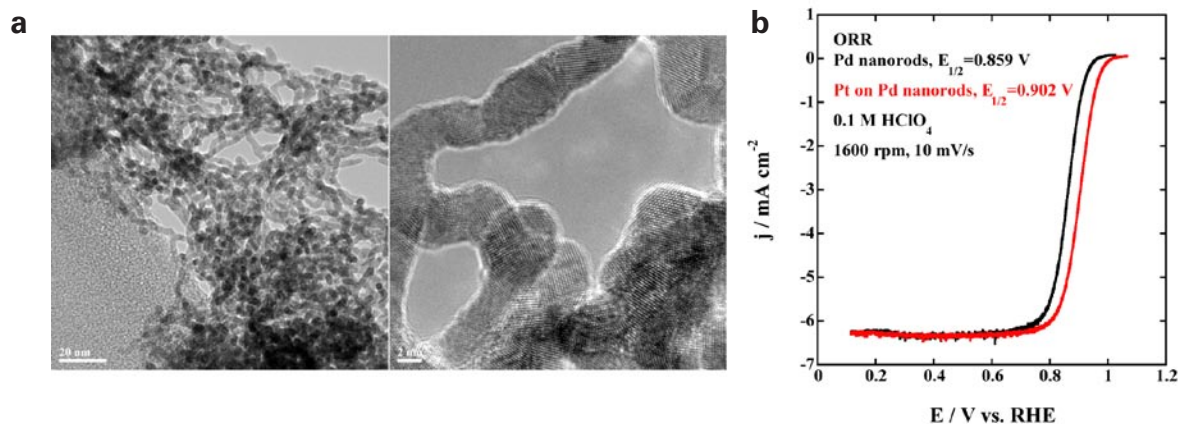


FIGURE 3. (a) Carbon-supported Pd nanowires (b) ORR on a Pt monolayer on Pd nanorods obtained by electrodeposition. Pt mass activity=3.4 A/mg; Specific activity=1.4 mA/cm²

coordination atoms deposited on smooth cores of: i) Pd or its alloy nanorods, nanowires or nanotubes cores; ii) Pd or Ir alloy nanoparticles with refractory metals that preclude core dissolution in acid environment. We will study the ternary catalysts for ethanol oxidation using CeO₂ instead SnO₂. Magnelli phases will be selected as support because they are conductive and stable in acids. Our new method of depositing metal on oxide surfaces will be employed for designing active catalysts.

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Patents

1. Two patents issued; three patent applications submitted in 2009.