

# Metal and Metal Oxide-Supported Platinum Monolayer Electrocatalysts for Oxygen Reduction

Principal Investigator: Radoslav Adzic

Brookhaven National Laboratory

Upton, NY 11973-5000

Phone: 631-344-4522

Email: adzic@bnl.gov),

Team members

Additional PIs: Jia Wang, Miomir Vukmirovic,  
Kotaro Sasaki, Ping Liu

Post-docs: Stoyan Bliznakov, Meng Li, Kurian Kuttiyiel

Graduate Students: Yu Zhang (Stony Brook U),  
Guangyu Chen (Beijing U. China)

DOE Program Manager: Paul Maupin

Phone: 301 903-4355

Email: Paul.Maupin@science.doe.gov

## Objectives

This program involves studies of basic problems of electrocatalysis of fuel cell reactions while focusing on platinum monolayer electrocatalysts for the O<sub>2</sub> reduction reaction (ORR) and the electrocatalysts for ethanol and methanol oxidation to CO<sub>2</sub>. The goals include developing the fundamental understanding of these catalytic systems to allow syntheses of electrocatalysts with ultimately low Pt content. These catalysts have high activity and high stability facilitated by fine-tuning of the activity of Pt monolayer (Pt ML) in the interaction with cores. The nanoparticle, nanorod and nanowire cores will have tailored compositions and shapes, and modified surfaces and sub-surfaces. Kinetic modeling and theoretical calculations are carried out for a deeper insight into the kinetics of the ORR and ethanol oxidation. Studies using well-defined surfaces are carried out to gain understanding of the atomic-scale phenomena involved in the interactions of Pt monolayers with supports as well as developing new catalysts for ethanol and methanol oxidation.

## Technical Barriers

The project is focused on developing several Pt ML 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. They will also provide

insights into catalytic behavior of core-shell nanoparticles and possibilities for designing their properties. In addition, we explore the catalyst capable of C – C bond splitting at low overpotentials in the oxidation of small organic molecules.

## Progress Report

Strategies for improving Pt ML electrocatalysts for the ORR and designing catalysts for the oxidation of methanol and ethanol

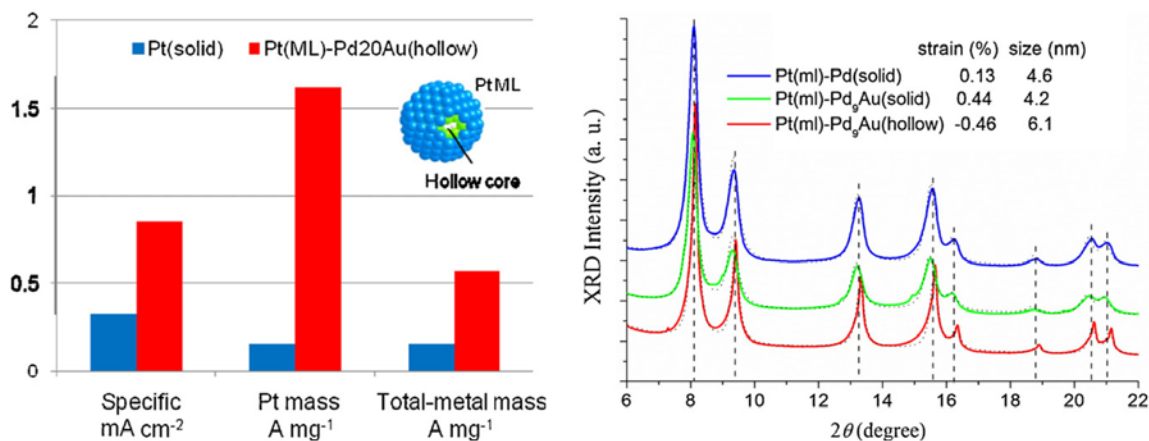
Several methods for improving Pt ML catalysts have been developed based on earlier results and the current understanding of this topic. These include fine-tuning of the Pt ML-support interaction to enhance activity and stability using: i) noble metal-, and noble metal-non noble metal-alloy cores, ii) hollow metal or alloy cores, iii) ultra-thin nanowires, iv) electrodeposited nanowires on carbon nanoparticles, v) nitride-stabilization of Pt alloys, vi) tensile strain for increasing activity of Pt for methanol and ethanol oxidation. The methods ii)-vi) have been demonstrated in this project.

Pt ML on hollow Pd nanoparticles electrocatalysts for the ORR

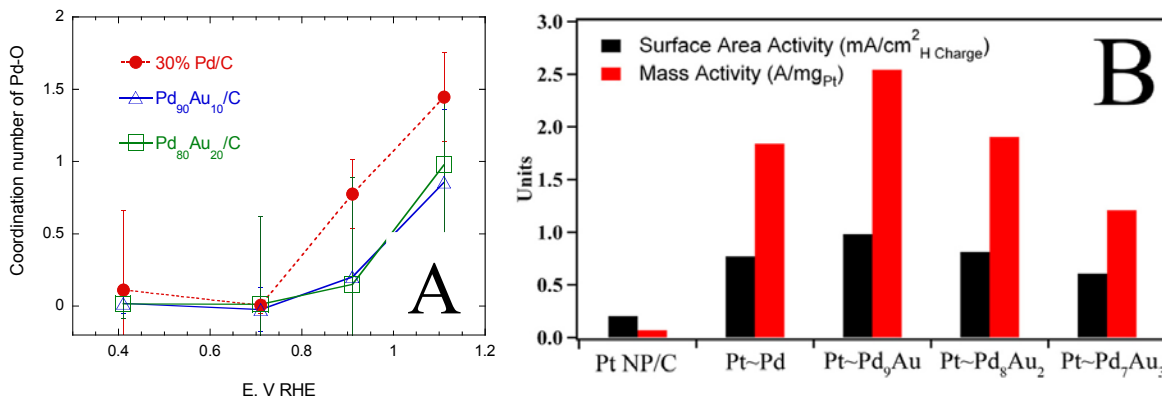
We synthesized high-activity electrocatalysts for the ORR comprising a Pt monolayer shell on compact hollow Pd and Pd-Au nanoparticles. Pulse electrodeposited Ni nanoparticles were replaced galvanically by Pd and Pd-Au ions to obtain corresponding hollow nanoparticles. The hollow architecture of the Pd-Au particles was achieved by the delicate balance between galvanic displacement and Kirkendall effect in controlling reaction kinetics. Pt ML catalysts supported on such hollow cores exhibited total-metal mass activities ranging from 0.41 to 0.57 A mg<sup>-1</sup>. We attribute this enhanced activity to the smooth surface morphology and hollow-induced lattice contraction, in addition to the mass-saving geometry of hollow particles.

Tuning the Pt ML activity by core alloy composition

Alloying Pd with Au increases the stability of such cores, which plays a role under condition of potential excursions to high anodic values. EXAFS spectra show retardation of Pd oxidation with increasing potentials for Pd<sub>90</sub>Au<sub>10</sub>/C and Pd<sub>80</sub>Au<sub>20</sub>/C compared with Pd/C nanoparticles. The changes in coordination number of Pd-O demonstrate this tendency more clearly (left figure). This is not observed with Pd<sub>70</sub>Au<sub>30</sub>/C, presumably due to agglomeration of Au (as also suggested by XRD data). Importantly, Pd<sub>5</sub>Au NPs, as well as



**FIGURE 1.** The ORR specific and mass activities derived from the kinetic currents at 0.9 V (vs. RHE) for hollow Pt<sub>ML</sub>/Pd<sub>20</sub>Au(h)/C nanocatalysts (red) and solid Pt/C nanoparticles (blue) (left panel). Profiles of X-ray powder diffraction intensity for three Pt ML catalysts cores. The dotted lines are the fits, yielding the average particle diameters and lattice constants. The lattice strains listed are calculated with respect to the lattice constant of bulk Pt, 3.923Å.



**FIGURE 2.** Coordination Pd-O number for Pd oxidation with increasing potentials of Pd/C and Pd<sub>x</sub>Au<sub>1-x</sub>/C (A); Kinetic currents at 0.9 V normalized to the measured ESA and the Pt mass for the Pt~Pd<sub>1-x</sub>Au<sub>x</sub> NW/C and commercial Pt NP/C, respectively (B)

NWs show significantly enhanced ORR after the deposition of a Pt monolayer. It has a volcano-type composition dependence, which likely results from the competition between the structural and electronic effects, as gold content increases.

**Nitride stabilized PtNi core-shell nanocatalysts for high ORR activity**

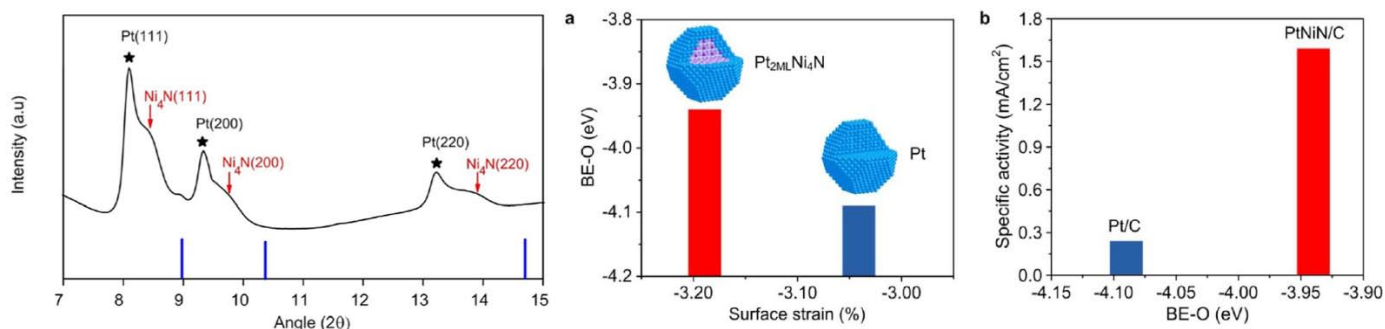
The PtNiN synthesis involves nitriding Ni nanoparticles and simultaneously encapsulating them by 2–4 monolayer-thick Pt shell. The experimental data and the DFT calculations indicate nitride has the bifunctional effect that facilitates formation of the core-shell structures and improves the performance of the Pt shell by inducing both geometric and electronic effects. Synchrotron XRD indicates the Ni<sub>4</sub>N stoichiometry, while *in situ* XAS shows the Ni<sub>4</sub>N cores protected by Pt shell causing the delayed oxidation of Pt and high stability of the catalyst. Little change in ECSA

and a small decrease in half-wave potential after 35,000 potential cycles indicate a high stability of Ni<sub>4</sub>N@Pt core-shell NPs. The nitride core lowers the *d*-band center of Pt and promotes Pt diffusion to defect sites on the surface. High ORR activity for Ni, Fe, Co follows the sequence: PtNiN > PtFeN > PtCoN.

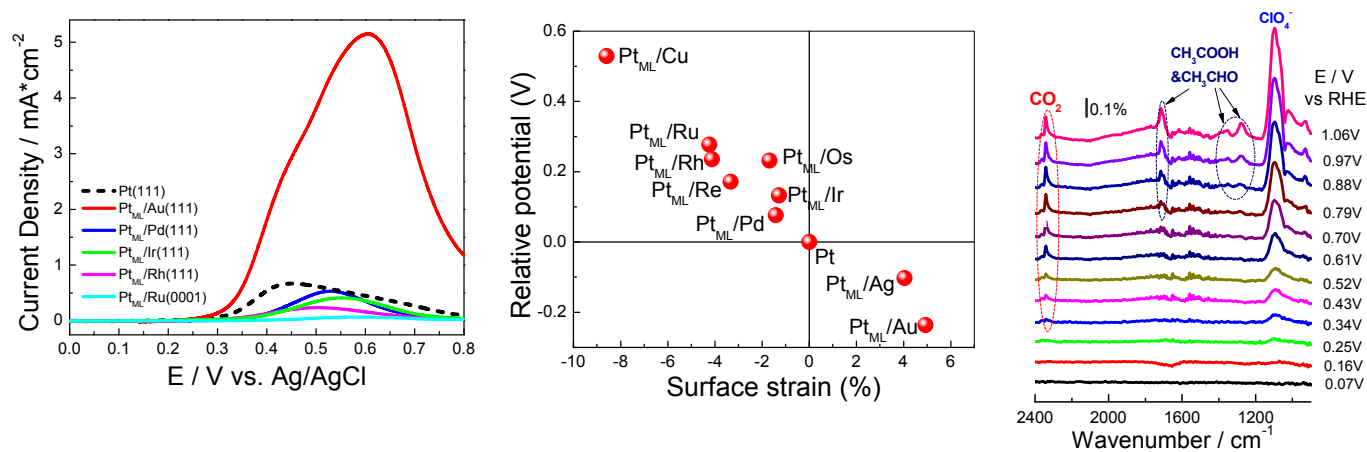
**Electrocatalysts for ethanol and methanol oxidation**

Further studies of the electrocatalysts capable of splitting the C-C bonds at room temperature found that Ir can be made activated in Pt-Ir-SnO<sub>2</sub>/C catalyst.

Model catalyst study, supported by DFT calculation, showed that expansive strain caused by underlying Au substrate can dramatically improve the activity of Pt<sub>ML</sub> for methanol and ethanol oxidation. Co-catalysts such as Ru, SnO<sub>2</sub>, RhSnO<sub>2</sub> further improve Pt<sub>ML</sub> due to the bi-functional mechanism, and shift the reaction onset to more negative values with practical interest. IR shows a high catalyst



**FIGURE 3.** Synchrotron XRD pattern for PtNiN catalyst showing Pt and Ni<sub>3</sub>N phases. (blue line denotes Ni<sub>3</sub>N phase). (a) Surface strain versus predicted BE-O on the Pt 2MLNi<sub>4</sub>N and Pt nanoparticle models with ~1.7 nm. (b) Pt specific activity against BE-O on PtNiN/C and Pt/C.



**FIGURE 4.** Model catalysts: Pt-monolayer supported on different single-crystal for MOR (left) DFT-calculated variation of the lowest potential for MOR to occur (middle), *In situ* FTIR of MOR on Pt/Au/C in 0.1M HClO<sub>4</sub>, 0.5 M CH<sub>3</sub>OH (right).

selectivity to CO<sub>2</sub> production. At the potential range of 0.3~0.7V, CO<sub>2</sub> is the only product observed; CH<sub>3</sub>COOH and CH<sub>3</sub>CHO start to show when the potential is higher than 0.7V.

## Future studies

The proposed future work is aimed to improve the most promising results obtained so far, to address the open basic questions of the interaction of Pt monolayer with supports and their effects on the kinetics of the ORR, to explore the possible solution to the barrier imposed by the low open circuit potential of the ORR, to increase our understanding of the mechanism of cores protecting the shells in core-shell catalysts, and to design and synthesize the second generation of core-shell catalysts with tuning the effect of core on a Pt monolayer shell by hetero-layered core structure. The supports will also involve refractory metals, and selected oxides, such as CeO<sub>2</sub>, NbO<sub>2</sub> and Magneli phase oxides. Graphene oxide as support appears promising in our preliminary studies. We will start studies of supported pyrolyzed transition metal macrocycles. Preliminary results

are very promising. How are the ORR activities of metal in the extended surface and in the form of supported-nanoparticles related?

Electrodeposition of selected alloys as stable, inexpensive cores and optimization of the cores shapes. Using non-aqueous solvents for electrodeposition of reactive metal cores, UPD of various MLs for Pt ML deposition on reactive metals and alloys.

Considerable effort will be focused on the electrocatalysts for ethanol oxidation. We will continue with theoretical studies to determine what are the geometries and energetics of reactants, possible intermediates and transition states? On which sites does the reaction take place? The critical size of ensemble of atoms for ethanol adsorption will be determined. To address these questions of ORR and EOR, theoretical calculations will be coordinated with our experiments on well-defined model catalysts. DFT calculations will be combined with micro-kinetic modeling, kinetic Monte Carlo (KMC) and molecular dynamic (MD) simulations.

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