

# Theory-Guided Design of Nanoscale Multimetallic Nanocatalysts for Fuel Cells

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## Objectives

The aims of this project are: (a) characterizing the metal activity and dissolution process in alloy nanocatalysts used for the oxygen reduction reaction in acid medium and their effects on surface structure and composition during electrochemical surface oxidation and surface reduction, as a function of catalyst shape and size; (b) evaluating our hypothesis that electronic and geometric confinement are the reasons for the experimentally observed activity enhancement after the dissolution process takes place; (c) using the insights obtained from these studies to continue our efforts in the design of improved catalysts for this and other technologically relevant reactions.

## Technical Barriers

The complexity of a catalytic surface constantly changing under harsh oxidative conditions poses a significant challenge for modeling and experiments.

## Abstract

First-principles analyses of oxygen reduction catalysts are carried out to answer these questions: 1) How do the catalytic surface and its environment change as the reaction takes place, and how do these changes affect the activity and stability of the catalyst; 2) What are the effects of the dynamics of the catalyst and that of the surrounding medium on the catalytic activity and stability; and 3) What is the effect of important side reactions on the catalytic process?. We use a concerted multiscaled theoretical analysis of nanoscale multi-metallic catalysts including their environment. Our computational approach is directly applicable to other catalytic reactions taking place on nanoscale particles.

## Progress Report

### Surface segregation effects in alloy nanoparticles

A systematic study as a function of core composition starting with monometallic cores of the 3d, 4d, and 5d groups revealed that all the 4d and 5d pure cores may serve as stable cores, and their beneficial effect on the Pt monolayer may be further tuned by alloying the core to another element, here chosen from 3d or 5d groups. The Pd<sub>3</sub>X cores enhance the stability of the surface Pt atoms both in vacuum and under adsorbed oxygen; however the high oxygen-philicity of some of the X elements induces their surface segregation causing surface poisoning with oxygenated species and dissolution of the X metals in acid medium.

### Evolution of nanocatalyst surface under oxidation and reduction conditions.

Buckling of surface Pt atoms is known to occur at high oxygen coverage on pure Pt and alloy surfaces. We developed a novel multi-scale modeling approach where we mimic the oxidation process of extended surfaces of pure Pt and Pt-alloys as a function of increasing oxygen coverage, yielding the time evolution of the surface at a given extent of oxidation. Such oxidation is given by various oxygenated species such as atomic oxygen and water dissociation products. The pH effect is also incorporated. We used the DFT results in force fields for classical MD simulations able to follow the evolution of the catalyst structure and dynamics in slabs and nanoparticles. In our most recent work, we developed a new approach integrating DFT and MD simulations to evaluate the degradation of alloy catalysts at harsh oxidation conditions. Our approach is able to reveal

migration of O atoms into the subsurface and that of non-noble atoms towards the surface, detachment and interactions with solvent and ionic species at the interface of the metal catalyst and the electrolyte. We characterized such catalytic degradation in extended surfaces and nanoparticles in acid medium.

### Effects of geometric and electronic confinement on catalytic reactions.

We investigated the origins of the enhanced catalytic activity found in nanoporous structures after dealloying. The proximity of two transition-metal surfaces separated by a subnanometer gap gives rise to new chemistry that could be potentially useful for enhanced reactivity in catalysis, separations, and sensing processes. Depending on the nature of the interacting surfaces, confined adsorbates may be strongly adsorbed, dissociated, or reacted with other species. Separation of mixed gases or liquids could be obtained by appropriately tuning the composition of the alloy surfaces and the gap geometry. Furthermore, the importance of local atomic disorder on reactivity has been pointed out based on X-Ray absorption spectroscopy experiments.

Recently we have studied the activity improvement on the dissociation of molecular oxygen confined between Pt surfaces separated by subnanometer distances. We found that at certain Pt surface-surface separation, the dissociation of molecular oxygen is spontaneous. We also studied interactions of X/Pt skin surfaces where X is a monolayer of a 3d, 4d, or 5d metal. In this case, the effect of the separation distance between X/Pt surfaces was analyzed in relation to the dissociation of molecular oxygen and water. It was found that the electronic structure of skin surfaces under confinement changes with respect to that of a single surface, becoming more active for catalysis. Changes in the electronic structure of the confined skin surfaces can be detected through other physical properties such as magnetic moments. The influence of the overlayer metal nature on these phenomena offers the possibility of designing specific materials for targeted catalytic applications by manipulation of control variables, such as the surface-surface separation between the skin surfaces but also the composition of the composite system. For example, the interaction between Ti/Pt surfaces separated by a small gap in the order of 0.4 to 0.8 nm facilitates the creation of an enhanced electron density in the gap between surfaces inducing the formation of an ethylene radical that readily reacts with another ethylene radical and starts polymerization without the need of an initiator. These examples illustrate the potential effect of confinement on the ORR. Many other intermediate steps such as coupled proton and electron transfers to the oxygenated species could be equally affected by geometric and electronic confinement. We investigate such effects in porous metallic structures. We found that the experimentally

measured activity enhancement may result from the geometric and electronic confinement resulting from the nanoporous structure originated after the dealloying process. We carried out a systematic plan to verify our hypothesis and investigated additional details that can be applied to a more general class of catalytic processes. Results include density functional theory analysis of reactions occurring in metallic porous structures; Kinetic Monte Carlo simulations of the dealloying process; and formation of porous structures emulating synthesis processes and also emulating dealloying occurring during fuel cell operation, i.e., under oxygenated environments.

### Future Directions

The results of these investigations indicate that the main lines of research that would be most promising for fuel cell electrocatalysis remain centered in the design of **active** and especially **durable** catalysts. Our experience with theoretical analyses of these systems points to the main topics that we suggest as future research directions: 1) design of the optimum alloy composition that could be used as a core under a Pt thin layer acting as a catalyst; 2) design of the best nanoarchitectures that could make such alloy compositions resistant to the acid (or alkaline) medium where the ORR takes place; 3) incorporate the effect of the substrate which, in nanosystems, can make a huge difference for supported catalysts.

### Publication list (including patents) acknowledging the DOE grant or contract:

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