

V.D.3 Development and Mechanistic Characterization of Alloy Fuel Cell Catalysts

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- Electrode performance
- Low cost
- Durability

Abstract

We have discovered a new family of Pt-Cu nanoparticle/nanopore catalyst that exhibits the highest ever reported ORR activities of up to 5-6x compared to pure Pt electrocatalysts. The composition of the surface, lattice arrangement and electronic structure of these catalysts has been characterized by synchrotron based x-ray diffraction and photoelectron spectroscopy methods. We discovered an order of magnitude reduction of Cu in near surface region of these catalysts, due to electrochemical leaching and a lattice contraction in the nanoparticle/nanopore structures. We found a narrowing of the Pt d-band upon lattice contraction.

A management of appropriate humidity level is necessary for the fuel reaction to take place. The fuel cell reaction occurs on the surface of catalyst in confined spatial regions called the triple phase boundary, in which both humid and dry region are present on the surface of the catalyst. We have demonstrated that the role of water on the catalytic properties of the surface is either inhibitor or promoter of the ORR: water inhibits the dissociation of molecular oxygen to produce atomic oxygen but promotes the reduction of adsorbed atomic oxygen to form hydroxyl.

Progress Report

While the oxidation of pure hydrogen is not considered a technical hurdle in fuel cells, the power loss at the cathode during the electroreduction of oxygen is found to be significant. Therefore the identification of a catalyst for the electroreduction of oxygen with improved performance is a major scientific priority. Pt has been the only metal which offers a good compromise in terms of performance and durability, and catalyst costs dominate at high Pt loading. Our goal is to understand the mechanistic pathway of the ORR reaction and to design new low Pt containing catalyst by optimizing the geometric and electronic structure of catalyst along the mechanistic pathway.

Development of novel alloy catalyst for fuel cell cathode reaction

In this program, about 150 different Pt alloy electrocatalysts for fuel cell cathode reaction have been synthesized and characterized electrochemically.

Objectives

- Develop new synchrotron radiation based x-ray diffraction and spectroscopy methods that allow *in situ* probing of the intermediates in the oxygen reduction reaction (ORR) on the cathode in fuel cells where both species identification, geometric and electronic structure properties can be fully characterized.
- Gain insight into how various catalytic properties on Pt surfaces can be modified due to alloying.
- Perform combinatorial synthesis and high throughput electrochemical screening methodologies of alloy catalyst with different chemical compositions and structures to obtain optimum performance.

Technical Barriers

This project addresses the following technical barriers by understanding the mechanistic pathway of the ORR reaction and by establishing fundamental guidelines to design new low Pt containing catalyst by optimizing the geometric and electronic structure of catalyst along the mechanistic pathway.

A new family of Pt-Cu nanoparticle alloy electrocatalyst were identified that exhibit the highest ever reported ORR activities of up to 5-6x compared to pure Pt electrocatalysts (Figure 1). The Pt mass based activity of these catalysts was found to be up to 0.7 A/mg Pt. This value meets and exceeds the current DOE target of 0.44 A/mg Pt. Ex-situ and *in situ* x-ray diffraction studies, as well as compositional studies of the new family of Pt-Cu nanoparticle catalysts suggest that the electrocatalysts lose their Cu atoms partially near the surface, i.e. leached, during the initial electrochemical pretreatment.

In order to study the selective dealloying process, we have investigated Cu_3Pt foils as a model system. Structural and compositional changes after the dealloying process of these binary metal alloy materials have been examined via ex-situ small angle x-ray scattering x-ray diffraction and synchrotron radiation based x-ray photoemission spectroscopy, both before and after dealloying. Nanoparticle/nanopore formation due to the removal of Cu from the alloy surface is observed. Cu 2p core level photoelectron spectroscopy studies indicate a factor 10 reduction of Cu upon dealloying. The sample shows unique lattice constants indicating the presence of induced compressive strain in these materials. This strain is thought to give rise to enhanced catalytic properties, as observed in the leached nanoparticulate systems. A key role in activity and selectivity of metal catalysis is the Pt d-bands interactions with the OH and O reactants on the surface. We have investigated the d-band structure of the dealloyed sample using high resolution photoemission at high photon energy using synchrotron radiation. As shown in Figure 2, a narrowing of the d-band and

low density of states near the Fermi level is found for dealloyed sample with lattice contraction which could explain the enhanced catalytic activity based on the d-band model.

We have also searched the optimum Pt/Co ratio and the degree of structure ordering in Pt-Co fuel cell cathode catalysts. We found disordered face-centered cubic Co-rich (Co >50 at%) alloy phases were shown to cause activity improvements of a factor of 3x compared to Pt catalysts, yet suffered from Co leaching over the course of the fuel cell cathode reaction. An ordered face-centered tetragonal $\text{Pt}_{50}\text{Co}_{50}$ phase was identified to be structurally much more stable against Co leaching compared to the disordered phase, yet exhibited a lower catalytic activity compared to the disordered Pt-Co phases.

Mechanistic understanding of fuel cell cathode reaction

A management of appropriate humidity level is necessary for the fuel cell to operate. The ORR reaction occurs at the triple phase boundary where gas, electrolyte containing water and catalytic metal particle contact forms humid and dry region on the surface of the catalyst. We have demonstrated active site poisoning by water, where the activation of oxygen to the adsorbed atomic phase occurs rapidly in the dry region, but not in the humid region: (1) in Figure 2. On the contrary, there is a promoter effect of water on the reduction of adsorbed atomic oxygen in the formation of a water-hydroxyl surface complex: (2) in Figure 2. We have also demonstrated that on Pt and Cu surfaces the water

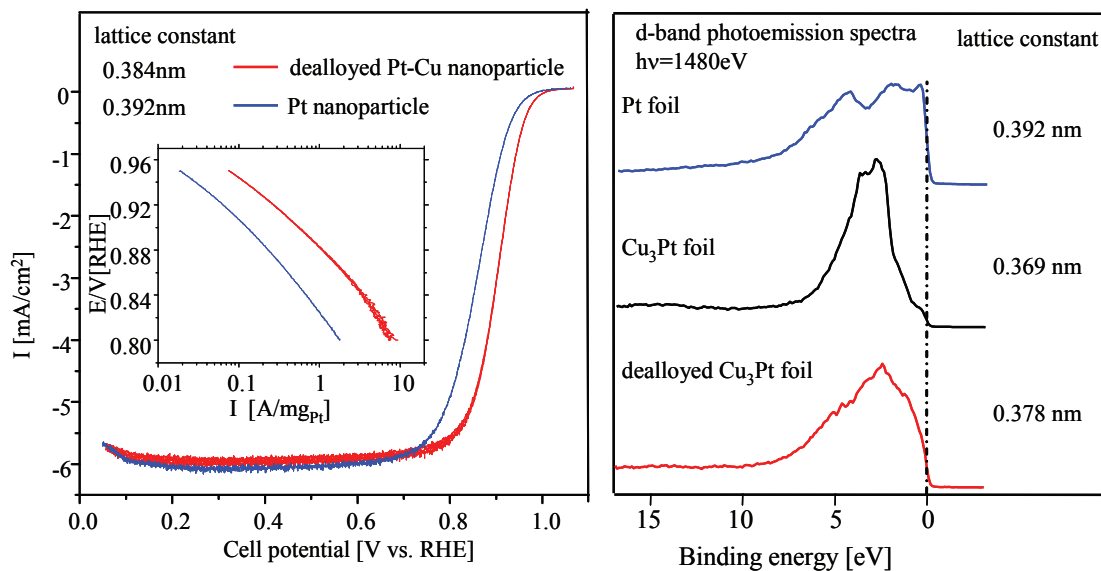


FIGURE 1. (left) Linear sweep voltammogram of Pt and dealloyed Pt-Cu nanoparticle electrocatalyst in oxygen saturated perchloric acid electrolyte (room temperature). (right) Valence d-band photoemission spectra of Pt, Cu_3Pt and dealloyed Cu_3Pt . Lattice constants obtained by x-ray diffraction is indicated.

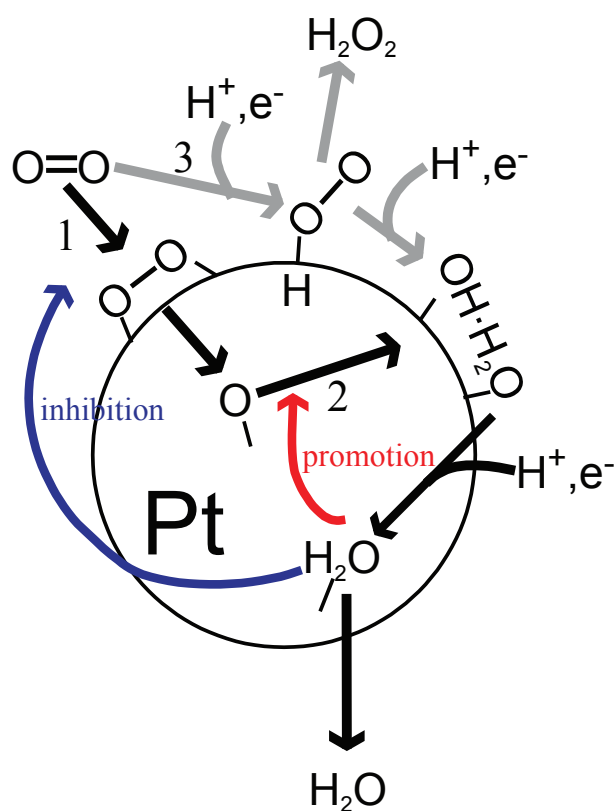


FIGURE 2. Schematic of reaction pathways of the oxygen reduction reaction.

affinity is related to the difference in substrate electronic structure.

Hydrogen peroxide is formed as a by-product during the fuel cell operation and initiates the degradation of the ion exchange membrane: process (3) in Figure 2. The hydrogen peroxide formation becomes prominent by hydrogen underpotential deposition on the catalyst. We have searched for a potential pathway of peroxide formation on the catalyst surface using surface science experiments and found that adsorbed hydrogen plays an important role. The presence of hydrogen stimulates an orientation transition of molecular oxygen from flat-lying to tilted-up with respect to the surface plane. We propose that the peroxide formation reaction channel is stimulated by this orientation transition of oxygen on the surface. Our preliminary studies further indicate that the tilted-up geometry sterically hinders the activation of oxygen for dissociation.

Future Directions

Future work on alloy particles will further substantiate the hypothesis of lattice strain as the origin of the high oxygen reduction reaction activity of the de-alloyed Pt alloys. For this purpose, de-alloyed Pt

shell-core nanoparticle catalysts will be prepared and investigated using structure-sensitive synchrotron based x-ray methods, such as XRD, EXAFS and XPS. The electrochemical stability of the de-alloyed Pt-Cu catalyst in the Rotating Disk Electrode format will be evaluated. Preliminary tests of Pt-Cu catalysts in single membrane electrode assembly's under real fuel cell conditions will be performed. Pt-Cu-X ternary electrocatalyst will be prepared and tested with respect to activity and durability. We will also continue to further characterize the alloy foils and also Pt-Cu single crystals with Pt L-edge x-ray absorption and emission spectroscopies and EXAFS. This will provide information about the unoccupied and occupied parts of the Pt d-band around the Pt atoms and the local coordination structure in the dealloyed films to elucidate the details of the electronic properties that are correlated with the enhanced activity. Further work will also include *in situ* thermal relaxation of these materials, as well as long term stability studies of their morphology. Work is currently underway to effectively determine the activity of such a model system, and to unambiguously correlate strain and activity in a well-controlled manner. We will prepare Pt nanopore-nanoparticle systems by co-evaporation of Pt and rare gas onto the membrane surface covered with a rare gas matrix layer in vacuum at low temperature. The matrix layer limits the sintering of evaporated Pt atoms resulting in the porous structure. Heating to room temperature selectively removes the rare gas matrix layer to yield the Pt nanopore-nanoparticle systems.

We are currently setting up an end station for *in situ* spectroscopic investigations of the ORR reaction. This system will be equipped with an electrochemical cell for soft x-ray spectroscopy studies using an x-ray emission spectrometer. The working electrode is prepared on a soft x-ray transparent Si_3N_4 thin window and is immersed in an electrolyte solution saturated with oxygen. We intend to characterize the electronic structure of catalyst under potentiostatic condition.

Publications (Including Patents)

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