
Nanostructured Catalysts for Fuel Cells

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Objectives

The objective of this interdisciplinary research is to develop new and improved materials for fuel cell electrocatalysis and polymer electrolyte membrane (PEM) fuel cells. To that end we have established research thrusts in the areas of bipolar/end plates materials and design, new synthesis and modification of perfluorinated PEMs, and synthesis of novel nanoparticle catalysts and catalyst supports. In conjunction with all of these efforts we carry out extensive experimental characterization and computational modeling and simulations.

Technical Barriers

The purpose of the research is to resolve fundamental issues related to the performance of PEM fuel cells and related technologies. For example, new materials used in bipolar/end plates improve strength and corrosion resistance without increasing weight. The PEMs themselves have been modified to reduce fuel (e.g., methanol) crossover without sacrificing conductivity. New nanoparticle electrocatalysts and their supports are studied to improve the stability (lifetime) and overall efficiency of the cells.

Abstract, Progress Report and Future Directions

The fuel cell research cluster began with the DOE EPSCoR implementation grant "Fuel Cells: A Mobile Energy Source for the 21st Century" in July of 2001. The focus of this research was developing new and improved materials for hydrogen production and

PEM fuel cells. Building on the major successes of this project, we proposed and were granted a renewed implementation grant "Nanostructured Catalysts for Fuel Cells" that started in August, 2004. Work continues on novel bipolar plate and proton exchange membrane materials. However, recognizing the ubiquitous presence of catalysis in systems to make and use hydrogen in fuel cells, a major new effort to study nanostructured catalytic materials was begun. In response to level funding and the guidance of the site review committee, the catalysis effort has focused on the fuel cell electrocatalysis rather than hydrogen production.

Significant Findings/Events/Accomplishments

1. Bipolar/End Plates

Novel flow field designs were developed based on a serpentine design. A prototype consisted of a single channel running throughout the plate with a defined path and tortuosity. The fuel gases are forced to change direction at every wall resulting in forced convection towards the electrodes. The design was modeled by computational fluid dynamics to describe the velocity, pressure distribution and permeability. The pressure drop was high and the velocity distribution was more uniform compared to conventional designs. Long term stability was tested for 100 hours at a load of 1 A and a constant average potential of 0.8 V was observed. The maximum current drawn at 0.2 V was 3 A (conventional parallel flow field) and 7 A (novel flow field).

Copper-Beryllium and 316 stainless steel bipolar plate surfaces were treated by exposure to a laser. This hardens the near surface only, increasing strength, hardness, and fatigue life and reducing wear. The grain size, boundaries and definition increased with laser power and time of exposure. The increase in grain size is expected to improve the wetting properties of the surface. There was no significant difference in resistivity or the influence of contact pressure.

2. Polymer Electrolyte Membranes

New fluorinated bifunctional co-monomers were synthesized that can modify Nafion[®] to give polymer with specific characteristics. These include

- improved durability and performance for PEM fuel cells and
- increased thermal stability and mechanical strength.

We are also preparing phosphonium salts from fluororous triarylphosphines that are expected to be excellent doping materials for Nafion[®]. These will

inhibit methanol crossover in DMFCs and increase conductivity as well as thermal stability of Nafion[®] in PEMFCs.

Amine-terminated polyamidoamine (PAMAM) G0 dendrimers were found to penetrate into the acidic Nafion[®] membrane because of their small size. The formation of ammonium-sulfonate pairs may change the morphological structure of the Nafion[®] membrane, thus causing changes in some properties of the Nafion[®] membrane. Nafion[®]-117 membranes treated with PAMAM G0 solutions of different concentrations were characterized by X-ray photoelectron spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy, atomic force microscopy phase imaging, alternating current impedance spectroscopy, and gas chromatography/mass spectrometry. The results show ammonium-sulfonate pairs are stable, and methanol permeability decreases after PAMAM G0 treatment.

3. Nanoparticle Catalysts

a. Synthesis

A new reactor system was built to make carbon supports by pyrolysis of benzene and other dopant compounds at 1,000°C. We are currently characterizing these supports and impregnating them with the metal nanoparticles (described below) for use as electrode catalysts.

Our group has developed new chemistry to prepare binary (CoPt, FePt or FePd) and ternary (FeCoPt, FeCuPt, FeAgPt, FeAuPt or FePdPt) nanoparticles. The particles have diameters in the range of 2 to 5 nm and a very narrow distribution of sizes. The particles have a coating of oleic acid and can be dispersed in hexane for deposition onto carbon supports for electrode catalysis experiments. The ability to systematically vary the alloy composition while maintaining a narrow size distribution, allows us to study the effect of electronic structure on the catalytic activity of the particles. Key to catalytic activity is removing the surfactant coating without sintering the particles. Early results are encouraging.

b. Characterization

This year we completed installation of a new Jobin-Yvon LabRam-IR microscope. This instrument is capable of optical, IR, and Raman microscopy and spectroscopy of samples. IR and Raman are complimentary vibrational spectroscopies which we will use to follow chemical reactions over fuel cell catalyst surfaces *in situ*. An environmental stage was very recently added. It allows heating/cooling and analysis of samples under reaction conditions. This powerful new tool will allow us to follow catalytic chemistry over real

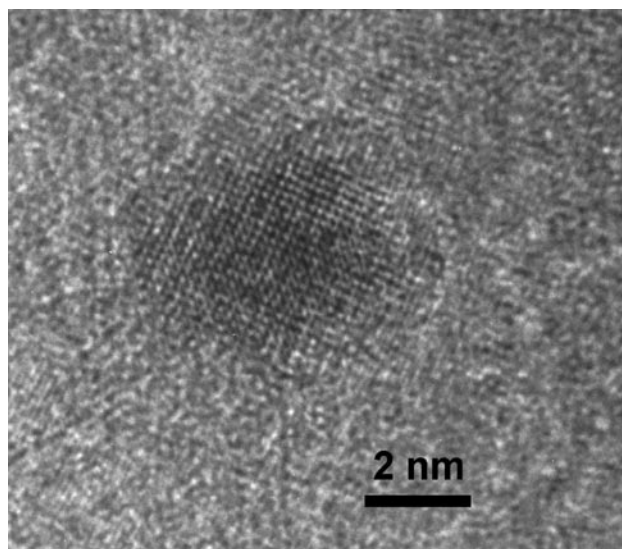
and model fuel cell systems on the molecular-level. We are currently looking at the catalyst surfaces with and without various reacting gases.

c. Model Systems

We developed nanoscale structures using edge decoration lithography, but along with many in the scientific community, we concluded lithographic techniques are incapable of reliably achieving true nanometer-sized structures. Instead, we have embarked on a different approach to creating nanoparticles. Recent developments in sputtering sources have established that ion optics can be applied to filter and direct the flow of metal clusters from magnetron guns. We are partnering with AJA International, a Massachusetts-based sputter tool manufacturer, to develop a new type of nanocluster source for research applications. The design offers the capability of dispersing clusters according to size, laterally across a substrate. When utilized together with a local probe, size effects of nanoparticles can be investigated on a single substrate, thus allowing for a greatly enhanced throughput in optimizing nanoparticle sizes for specific tasks, such as catalytic activity. The cluster source has been designed and we expect delivery sometime in March 2006. We will then characterize the energy of the ions as a function of operating conditions and proceed to construct a magnetic sector ion filter which has the desired dispersal properties.

d. Imaging

We installed new high resolution transmission and scanning electron microscopes. Also, a focused ion beam was acquired for (among other uses) making the sample tips to perform atom probe field-ion microscopy. These are all in use now and several team members have been trained and are making images. We have used



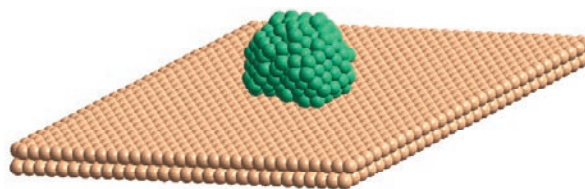
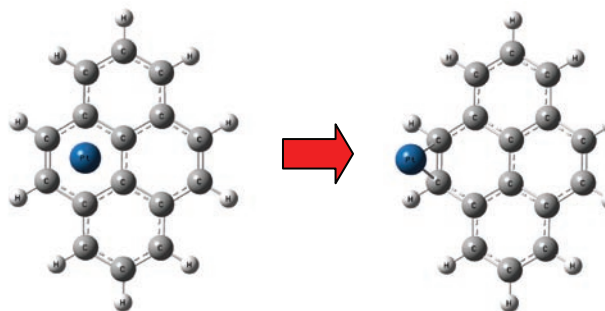
these images to confirm the unusual size and stability of Pt/Al₂O₃ particles prepared with our novel “water-pretreatment” process.

e. Simulations

The goal of our modeling activities is to provide guidance to our materials synthesis efforts by elucidating the mechanism by which the catalyst and its support perform their function. We are using a combination of quantum simulations, classical molecular dynamics (MD) simulations, and novel Monte Carlo (MC) simulations to examine idealized catalytic systems consisting of metal nanoparticles on model surfaces. Interaction potentials are obtained from quantum simulations, and the MD simulations describe the atomic structure of the catalyst/support. Ultimately, reactive MC simulations will describe the reactivity of the catalyst system using nanoparticle/support geometries provided by the MD simulations.

Density functional theory (DFT) calculations have been used to identify the atomic configurations of small Pt nanoparticles, as well as the bond strength of the individual atoms within the particles. In addition, the configurations of the Pt nanoparticles on HOPG supports have been identified. We have calculated the strength of the Pt-carbon support interaction, and we have suggested routes (doping the carbon support) to strengthen this interaction by 10-20 kcal/mol. We expect that this doping procedure would stabilize the catalyst particles during fuel cell operation, and experimental efforts are underway to verify this prediction. In related work, we are currently using the DFT calculations to predict the elementary reaction kinetics of CO oxidation in these systems (pure Pt, Pt on pristine graphite, and Pt on doped graphite).

The primary goal of our molecular dynamics studies is to provide surface geometries as input for our reactive MC studies. The crux of this strategy for obtaining cluster nanostructure is the interaction potentials between the nanocluster atoms and the support atoms. For these we rely heavily on quantum simulations; these quantum simulations are ongoing – examining the energetics of both isolated platinum atoms and small clusters of atoms above a graphite



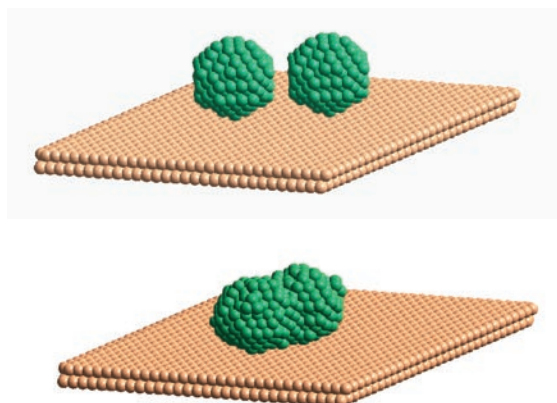
surface. The results below use very simple Lennard-Jones potentials for carbon-platinum interactions. We are now revising the simulations to use a much more realistic, bond order potential that is capable of incorporating results from the quantum simulations describe above.

We have simulated isolated platinum nanoparticles on highly ordered pyrolytic graphite surfaces, and a sample configuration is shown above. Perhaps surprisingly, the simulations predict a substantial amount of mobility for the nanoparticle on the surface. We are currently calculating diffusion coefficients to quantify this mobility.

A major problem facing nanoparticle catalysts is the sintering of small catalyst particles to create larger clusters of particles – effectively reducing the surface area and activity of the catalyst. Molecular Dynamics simulations allow us to study the effects of catalyst-support interactions under various conditions giving insight into sintering. The figure on the right shows before- and after-sintering conformations of two 2 nm platinum particles on a highly ordered graphite support.

Discussion of Plans/Timetable for Next Year

The main goal of the catalysis group is to learn how true nanoparticle alloys behave chemically in the anode and cathode reactions, particularly under the influence of metal support interactions. We have focused our work initially on Pt nanoparticles supported by graphitic carbon and their interaction with probe molecules (CO, H₂, H₂O, O₂, CO₂) present at the anode. Results emerging from these initial studies will guide our future work.



Publications (including patents) acknowledging the grant or contract

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