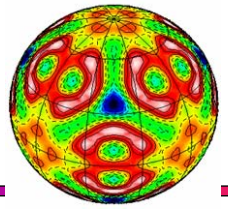
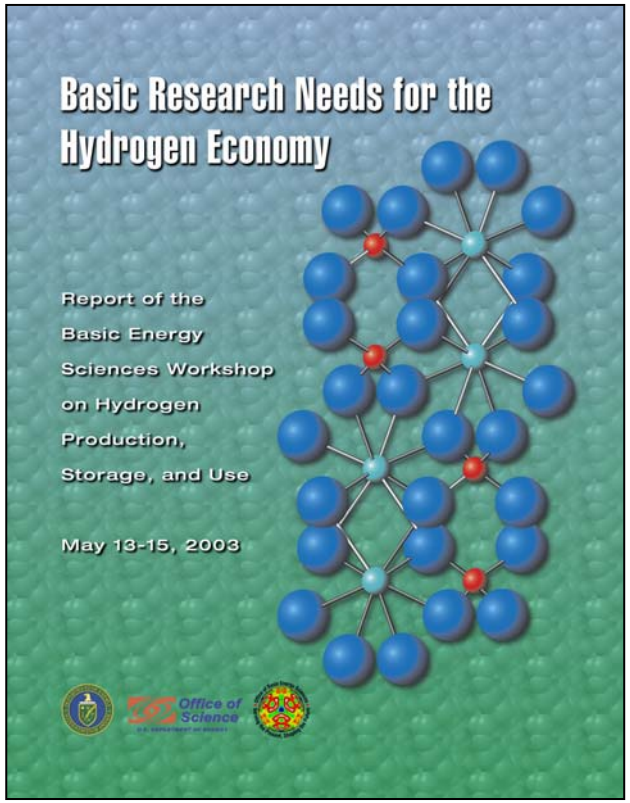


Update on DOE Basic Hydrogen Research

2007 DOE Hydrogen Program
Merit Review and Peer Evaluation Meeting

Dr. Harriet Kung
Director, Materials Sciences and Engineering Division
Office of Basic Energy Sciences (BES)
Office of Science, Department of Energy (DOE)

FY05 Basic Research for Hydrogen Fuel Initiative Solicitation

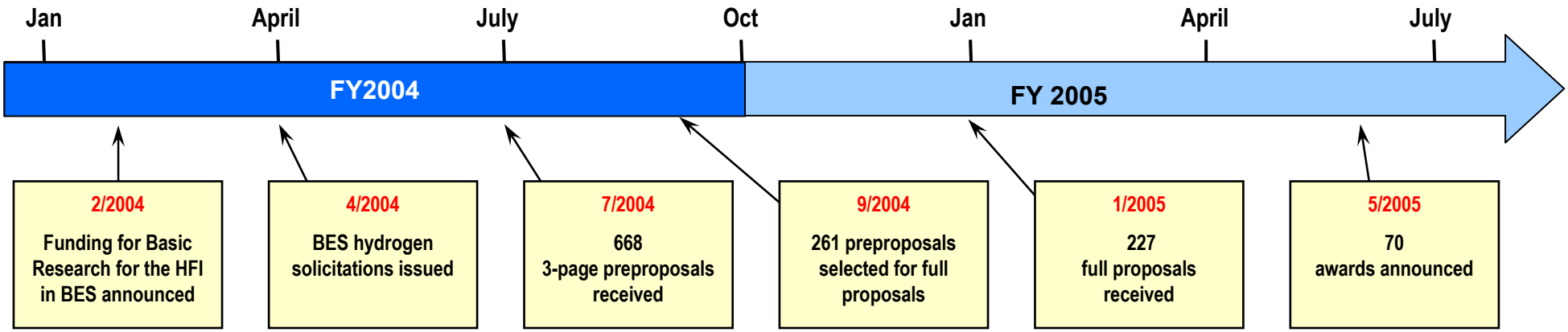


Basic Research for Hydrogen Production, Storage and Use Workshop, May 13-15, 2003

"Bridging the gaps that separate the hydrogen- and fossil-fuel based economies in cost, performance, and reliability goes far beyond incremental advances in the present state of the art. Rather, fundamental breakthroughs are needed in the understanding and control of chemical and physical processes involved in the production, storage, and use of hydrogen. Of particular importance is the need to understand the atomic and molecular processes that occur at the interface of hydrogen with materials in order to develop new materials suitable for use in a hydrogen economy. New materials are needed for membranes, catalysts, and fuel cell assemblies that perform at much higher levels, at much lower cost, and with much longer lifetimes. Such breakthroughs will require revolutionary, not evolutionary, advances. Discovery of new materials, new chemical processes, and new synthesis techniques that leapfrog technical barriers is required. This kind of progress can be achieved only with highly innovative, basic research."

FY05 solicitation based on the five priority research areas identified by the workshop report:

- Novel materials for hydrogen storage
- Membranes for separation, purification, and ion transport
- Design of catalysts at the nanoscale
- Solar hydrogen production
- Bio-inspired materials and processes



2005: BES-HFI Initiative Awards ($64.5M total; $21.5M annual)

Novel Materials for Hydrogen Storage
(17 projects, $19.8M*)

Universities:
- MIT[1]
- Washington
- Pennsylvania
- Colorado School of Mines
- Georgia Tech
- Louisiana Tech
- Missouri-Rolla
- Georgia
- Tulane
- Southern Illinois

DOE Labs:
- Ames
- Brookhaven
- Lawrence Berkeley
- Oak Ridge
- Pacific Northwest
- Savannah River

Membranes for Separation, Purification, & Ion Transport
(16 projects, $12.3M*)

Universities:
- Utah
- Clemson
- Carnegie Mellon
- Rensselaer
- Lehigh
- Pennsylvania
- Case Western Reserve
- Tennessee
- Vanderbilt
- CalTech
- Rochester
- North Carolina
- Cornell

DOE Labs:
- Lawrence Berkeley
- Los Alamos
- Pacific Northwest

Design of Catalysts at the Nanoscale
(18 projects, $15.8M*)

Universities:
- Pittsburgh
- Tufts
- MIT
- Wisconsin
- California-Santa Barbara
- Wyoming
- Yale
- Texas A&M
- Johns Hopkins
- Illinois[1]
- Texas Tech
- Arizona State

DOE Labs:
- Argonne
- Stanford Linear Accelerator Ctr
- Brookhaven
- Sandia
- Oak Ridge

Solar Hydrogen Production
(13 projects, $10M*

Universities:
- Colorado State
- Cal Tech
- Arizona
- California-Santa Cruz
- Penn State[1]
- Purdue
- Washington
- Virginia Tech

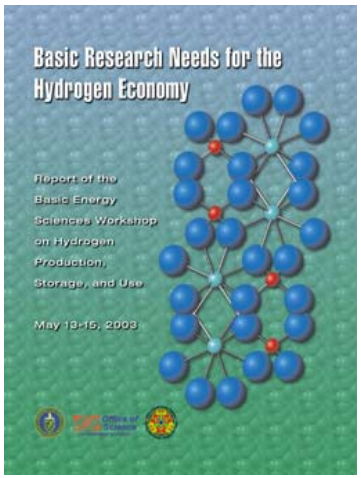
Industry:
- Nanoptek Corp.

DOE Labs:
- Brookhaven
- Pacific Northwest
- National Renewable Energy

Bio-Inspired Materials and Processes
(6 projects, $7M*)

Universities:
- Penn State
- Washington
- North Carolina State
- Georgia
- Pennsylvania

DOE Labs:
- National Renewable Energy

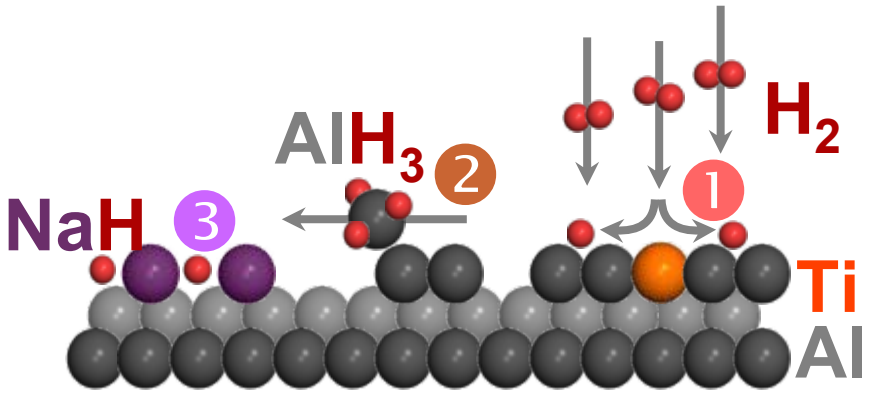


* Over three years

[1] Selected for 2 awards

Detailed information at http://www.sc.doe.gov/bes/BES_Hydrogen_FY05_Awards_25MAY05.pdf

Atomistic Transport Mechanisms in Reversible Complex Metal Hydrides



Objective: Understand the *atomic-scale mechanisms* of hydrogen storage in titanium-doped sodium alanate, a complex hydride that reversibly stores hydrogen.

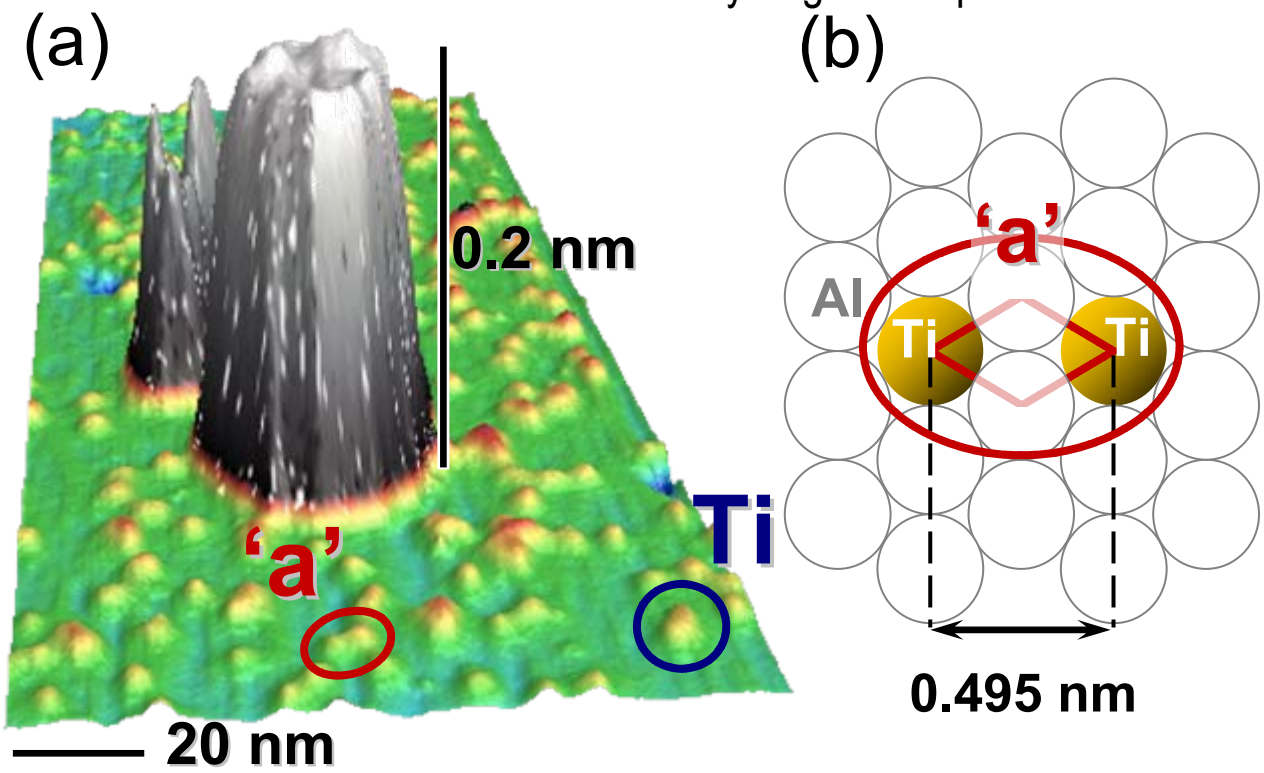
Key: Hydrogenation ('fueling') reaction

1. Di-hydrogen (H_2) adsorption & dissociation.
2. Formation & diffusion of mobile surface species.
3. Solid-state reaction to form hydrogen-rich phases.

H_2 dissociation catalysts - Key enablers of the hydrogenation reaction identified

(a) Identification, using microscopy sensitive to single surface Ti atoms, of Ti atom complexes ('**a**') predicted to efficiently catalyze H_2 dissociation.

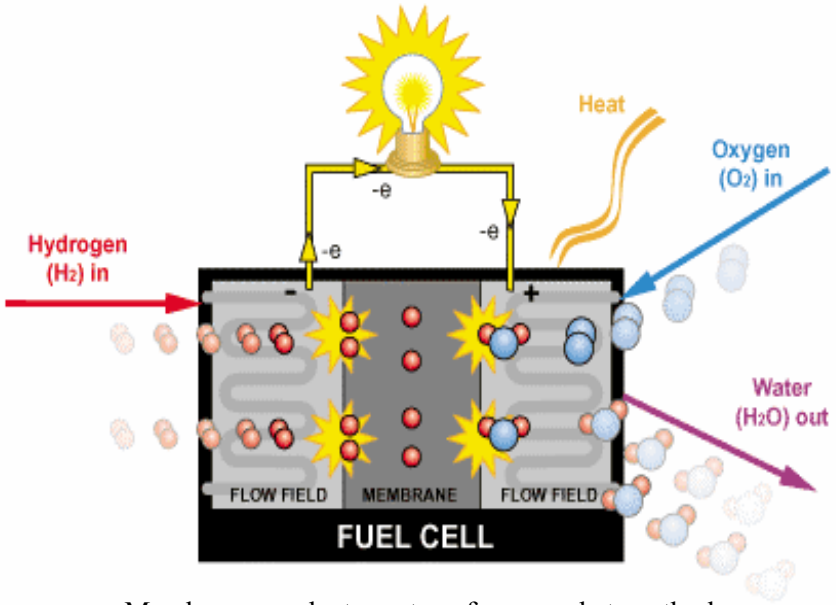
(b) Atomic structure of the prevalent Ti complex on the Al(111) surface.



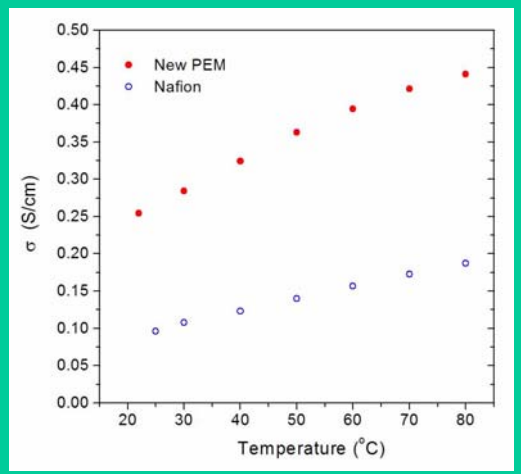
P. Sutter (PI), J. Muckerman, E. Sutter, J. Graetz (Brookhaven National Laboratory)
Y. Chabal (Rutgers University)

Micro- and Nano-Patterning Boost Power Output and Miniaturization of Fuel Cells

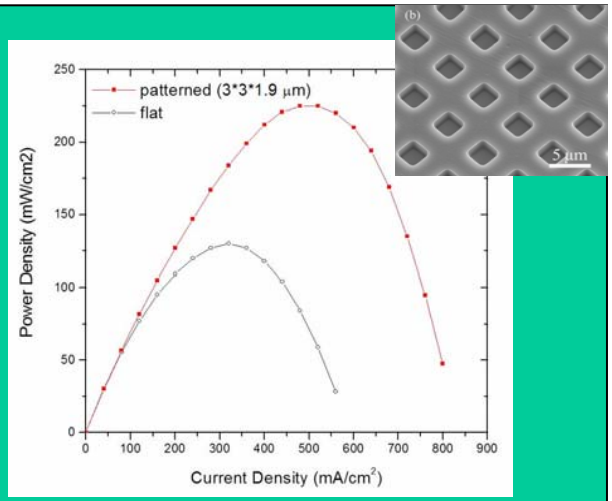
Fuel Cells: $2H_2 + O_2 \rightarrow 2H_2O$ + electrical power + heat



Membrane conducts protons from anode to cathode



New "liquid PEMs" have higher acid content and therefore higher conductivity than Nafion™



Lithographically patterned "liquid PEMs" lead to higher surface area of the membrane and the catalyst, and therefore, to higher power density of fuel cell

Traditional fuel cell proton exchange membranes (PEMs) such as Nafion™ , the current gold standard, have limitations:

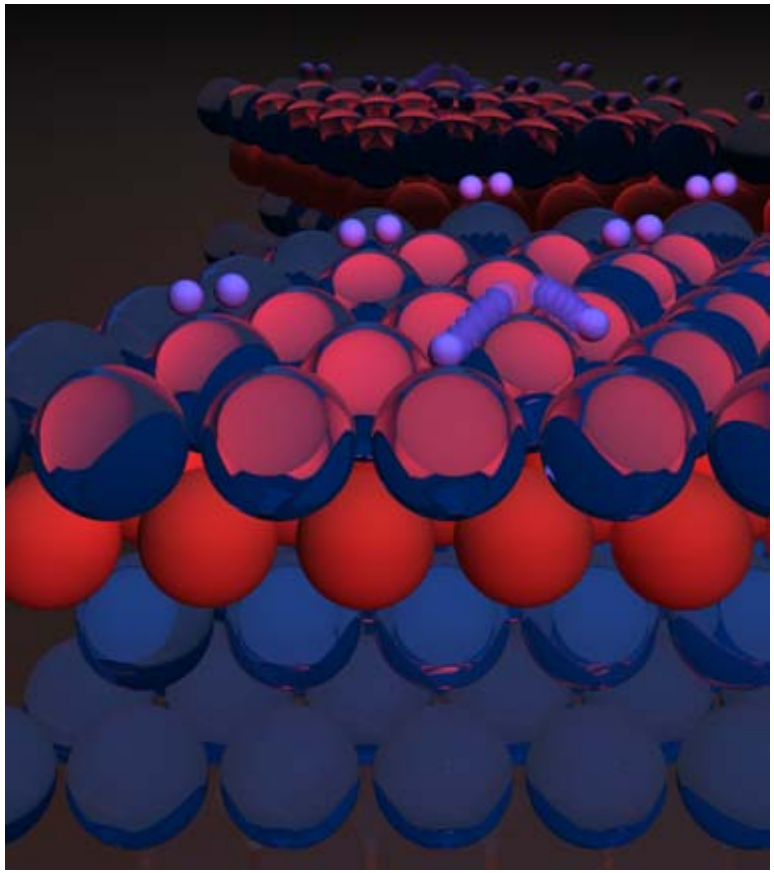
- Have lower-than-desirable conductivity
- Require high humidity for optimal operation, which reduces durability
- Difficult to process, requiring high temperature melt extrusion, followed by exhaustive hydrolysis
- Has smooth surfaces and thus low active surface areas

New Photochemically cured "liquid PEMs" was recently developed:

- Liquid precursors converted directly into membranes
- Can be cured into any desired shape including very thin films
- Can be chemically cross-linked
  Enables higher acid content
  ~ 250% increase in conductivity demonstrated
  Result in higher durability and better performance at lower humidity
- Can be patterned into high-surface area PEMs by soft lithography and micro-molding techniques
  ~ 200% increase in power density
  Could lead to significant size/weight reduction

Z. Zhou, R. N. Dominey, J. P. Rolland, B. W. Maynor, A. A. Pandya, and J. M. DeSimone, "Molded, High Surface Area Polymer Electrolyte Membranes from Cured Liquid Precursors," *Journal of the American Chemical Society*, **128, 12963**-12972, (2006)

Predicting Catalysts for Hydrogen Production, Storage or Fuel-Cell Utilization



Theoretical calculation of molecular hydrogen undergoing dissociation over near-surface alloys.

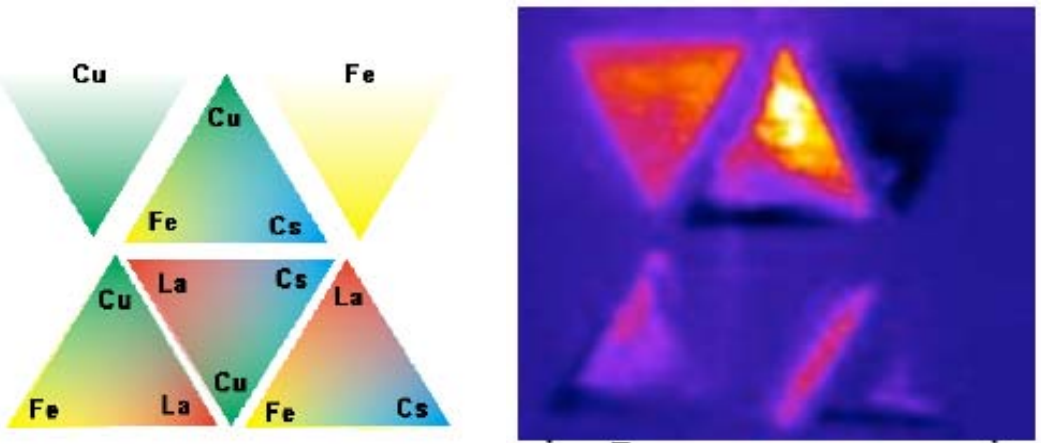
- Small purple spheres: **hydrogen**
- Blue spheres: **platinum** atoms
- Red spheres: **nickel** atoms
- **Bicolor** blue and red spheres: platinum atoms whose electronic properties have been dramatically altered by the underlying nickel.

- Production of hydrogen from biomass or fossil fuels at the large scales commensurate with future demands of a hydrogen-fuel economy calls for low-temperature, highly efficient and durable catalysts, non-existent today.
- New structures and compositions are now being predicted *a priori*, rather than searched empirically, thanks to recent advances in computational quantum chemistry and molecular dynamics.
- Near-surface alloys of two transition metals are unnatural structures that have recently been discovered through calculations. Single metallic layers of one metal embedded within a matrix of another metal have the requisite properties for low-energy hydrogen scission and recombination. No natural materials or homogeneous alloys display BOTH of these properties simultaneously.
- Nickel within platinum, as an example, can attach atomic hydrogen as weakly as inert metals like copper and gold, while simultaneously it can dissociate molecular hydrogen as rapidly as noble metals like platinum and rhodium. Experimental validation has demonstrated the feasibility of this new concept.
- Several families of new alloys with novel architectures and compositions have been identified as potentially suitable for hydrogen reactions, and await experimental validation. This is a rare instance in which theoretical catalysis precedes experiments.
- This study may lead to breakthroughs in the challenging technologies of rapid hydrogen storage and release at room temperature, or selective extraction of hydrogen from natural gas at low temperature, or high-activity hydrogen electrodes for fuel cells.

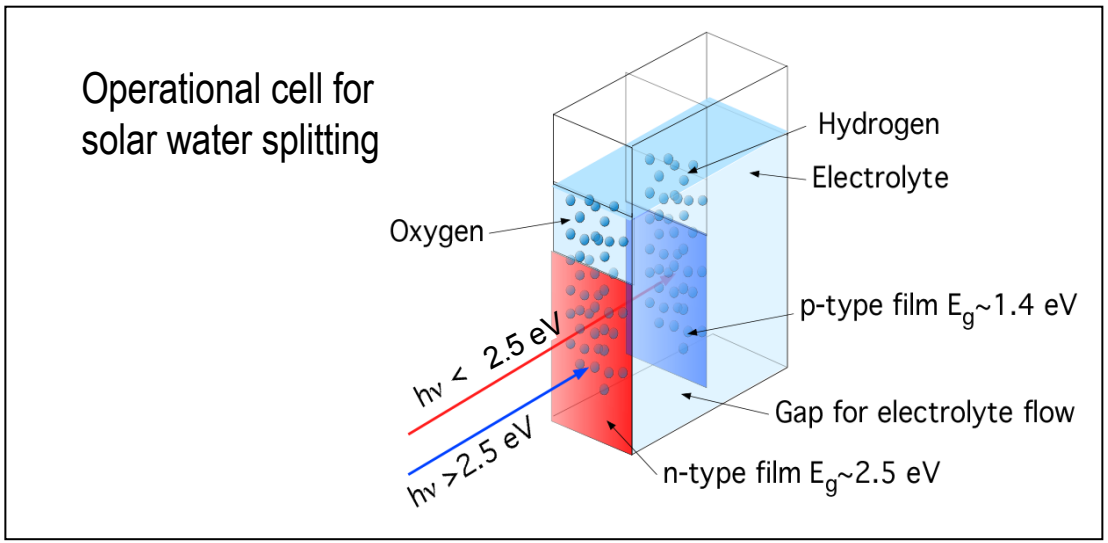
Junliang Zhang, Miomir B. Vukmirovic, Ye Xu, Manos Mavrikakis, and Radoslav R. Adzic, "Controlling the Catalytic Activity of Platinum-Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates," Angew. Chem. Int. Ed. 44, 2132 –2135 (2005)

Jeff Greeley and Manos Mavrikakis, "Alloy Catalysts Designed from First Principles," Nature Materials 3, 810–815 (2004)

Solar Hydrogen Production: The Search for the Ideal Mixed-Metal Oxide Photoelectrode



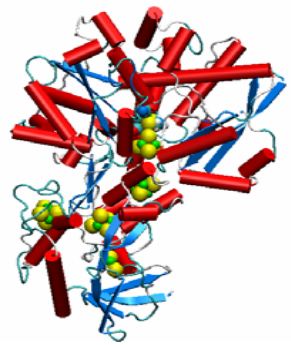
Ink jet patterning of metal oxides



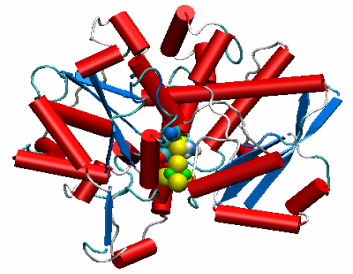
- Solar water splitting by semiconductor electrodes is the ideal method for production of hydrogen fuel.
- A novel high-throughput search seeks to move beyond known single-oxide semiconductors which are inefficient at water splitting in order to find a semiconductor with the band gap of 1.6eV to 2.0 eV needed for simultaneous hydrogen and oxygen evolution.
- This search follows the lead of high temperature superconductors, such as tetrametallic $HgBa_2CaCu_2O_{6+\alpha}$, by seeking compound metal oxides for water splitting that contain up to four different metals. Some metals are found to provide structure and stability, some the color of light absorption, while others are added for charge compensation and recombination suppression.
- The high throughput search is made possible with the use of a three-cartridge ink jet printer where the cartridges are filled with different metal nitrate precursor solutions. Many thousands of candidate compositions of metal oxide semiconductors can be screened.
- A triangular pattern with all possible variations of the three metal inks is printed on a conductive glass where each position contains a different combination of metals. The triangle is scanned point by point with a laser to assess the potential of each combination for water splitting.

Michael Woodhouse, G.S. Herman and B.A. Parkinson, "A Combinatorial Approach to Identification of Catalysts for the Photoelectrolysis of Water," Chemistry of Materials, 17, 4318-4324 (2005)

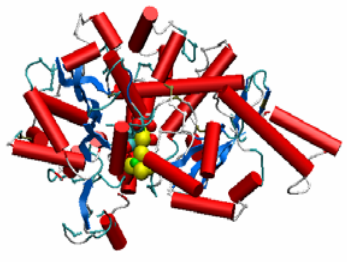
Effects of structure truncation on Oxygen Tolerance of Hydrogenase



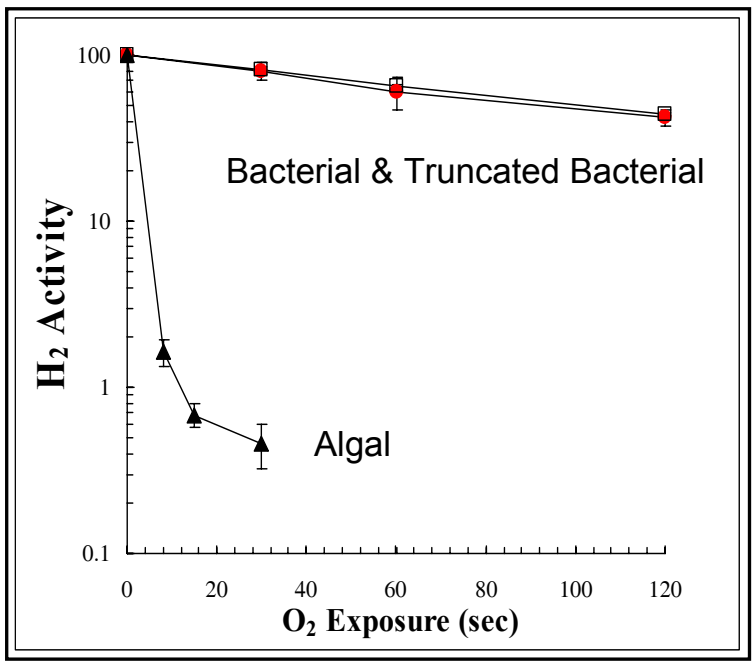
Bacterial



Truncated Bacterial (Genetically Modified)



Algal



- Large scale production of hydrogen by mimicking the processes used by Nature, either in algae or in bacteria, is an attractive strategy.
- While the hydrogenases in algae and bacteria have similar hydrogen production activities, [FeFe]-hydrogenase from bacterium is >100 times more tolerant of oxygen than algal enzyme.
- Natural hydrogenases (e.g., bacterial enzyme) typically have large protein residues surrounding the Fe-S active site, and thus are not robust enough to operate under non-biological conditions.
- A truncated bacterial enzyme with a simpler structure has been developed and exhibited oxygen tolerance similar to natural systems.
- Subtle structural differences between truncated bacterial and algal enzymes provide important insights into the origins of oxygen-tolerance and could guide the design of other bio-mimetic hydrogen production systems.
- Simplified and robust synthetic mimics of bacterial hydrogenase are essential for the development of a commercial hydrogen-producing system that is cost effective, scalable to large production, non-polluting, and self-sustaining.

Paul W. King, Drazenka Svedruzic, Jordi Cohen, Klaus Schulten, Michael Seibert, and Maria L. Ghirardi, "Structural and functional investigations of biological catalysts for optimization of solar-driven H2 production systems," Proc. SPIE Vol. 6340, 63400Y (2006)

FY2007 – FY2008 Funding for BES HFI Program

FY 2007 Additional HFI Budget Request: $17.5M/yr

BES Issued New Solicitation – Notice 06-17

The FY07 solicitation aims to expand the research activities that cross-cut the hydrogen storage, generation, and fuel-cell areas:

- Novel Materials for Hydrogen Storage

Enormous improvements in hydrogen storage capacity and in hydrogen uptake and release kinetics and cycling durability are needed to meet the storage demands for a future hydrogen economy. These breakthroughs may result from research at the nanoscale facilitated by new understanding derived from both theory and experiment. Research will specifically target the development of new materials and the examination of physical and chemical processes involved in hydrogen storage and release. Thus, projects are encouraged in these subareas: new materials; complex hydrides; nanostructured materials; theory, modeling, and simulation; and novel analytical and characterization tools.

- Functional Membranes

Novel membranes optimized with respect to ionic conductivity, thermal stability, cost, and durability are needed to significantly improve the performance of fuel cell systems for hydrogen energy conversion. The molecular design and synthesis of new membranes to selectively transport hydrogen, oxygen and other species is vital to the purification of fuel streams, transport of species between electrodes, and separation of hydrogen in electrochemical, photochemical, or thermochemical production routes. Research is encouraged in these subareas: integrated nanoscale architectures; fuel cell membranes; theory, modeling, and simulation of membranes and fuel cells; and characterization of electrochemical and buried interfaces.

- Nanoscale Catalysts and Electrocatalysts

Catalysis affects areas such as the production of hydrogen from traditional sources –oil, gas and coal – and newer ones –biomass and water. It also impacts the low-activation-energy storage or removal of hydrogen, and the production of electricity from hydrogen fuel cells. Breakthroughs in new low-temperature, high-efficiency catalysts are needed to make a hydrogen fuel economy feasible. Research is thus encouraged in these subareas: synthesis-structure-function relationships of nanoscale catalysts; structural dynamics of catalysts and dynamic behavior of catalytic reactions; innovative synthesis techniques; bio-inspired catalysts; techniques for in-situ characterization under reaction; and theory, modeling, and simulation of catalytic pathways.

Summary of FY2007 BES HFI Solicitation

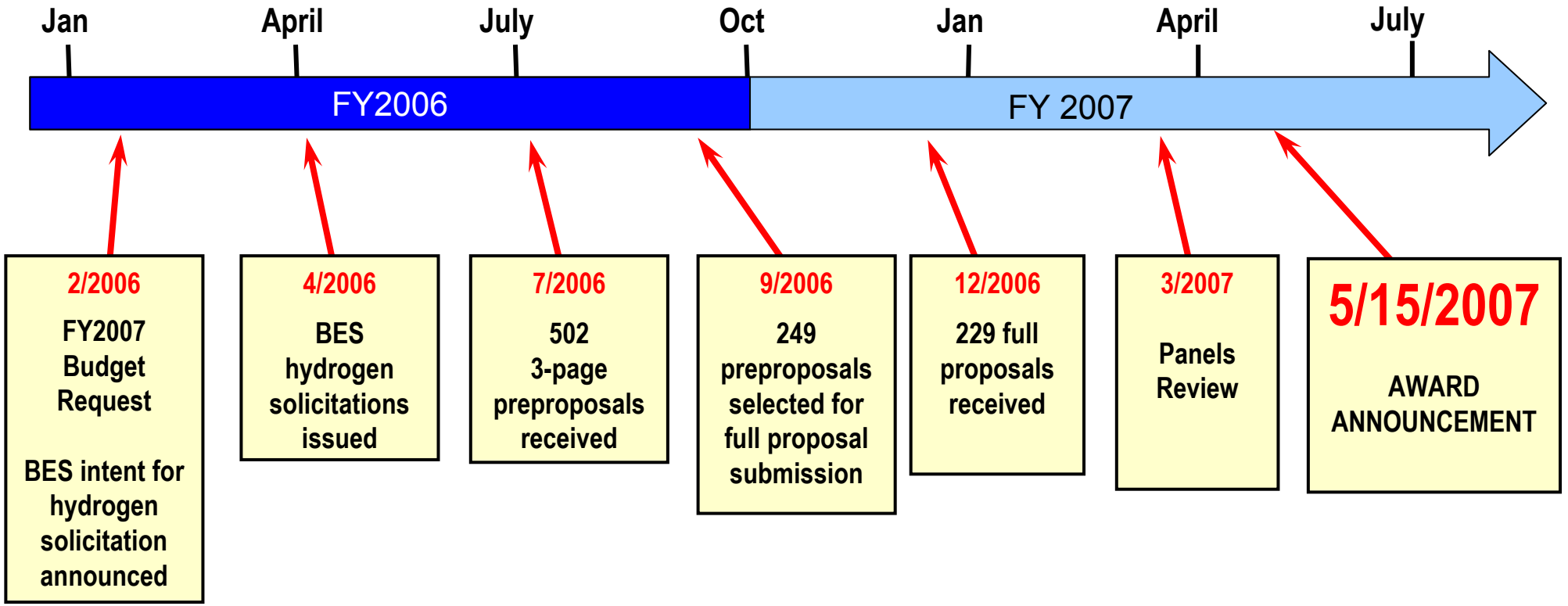
	Pre-proposals Received		Pre-proposals Encouraged		Full proposals received	
	Grant	Lab*	Grant	Lab	Grant	Lab
Novel materials for hydrogen storage	150	14	74	12	68	12
Functional membranes	130	16	62	13	54	13
Nanoscale catalysts	175	17	77	11	71	11
Total	455	47	213	36	193	36
	502		249		229	

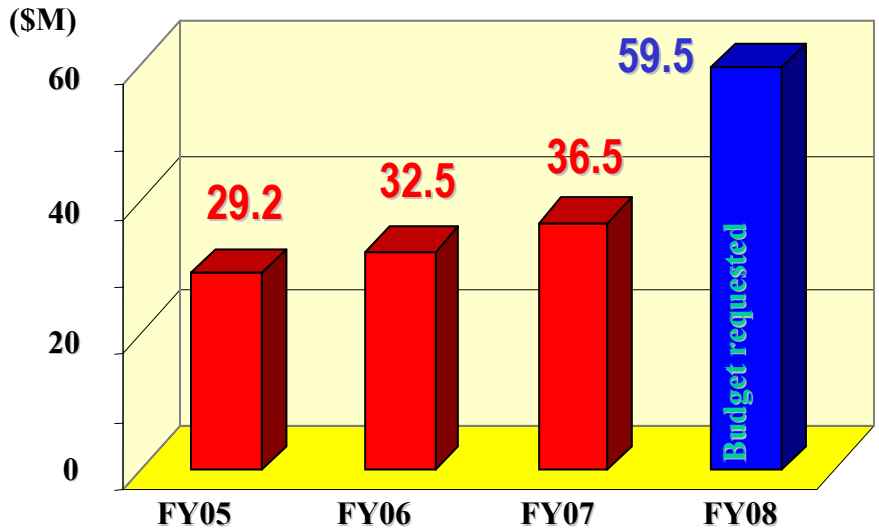
*Each lab was restricted to 4 pre-proposals

Total (annualized) budget request ~$88M/yr

Average proposal budget request ~$270K/yr (Grant), ~$854K/yr (Lab)

Timeline of FY07 BES Solicitation for Basic Research for Hydrogen Fuel Initiative





BES HFI Funding

- FY07 Appropriation: $4M/yr
- The proposed FY2008 budget contains full funding for the original HFI initiative ($17.5M) plus additional $9.5M funding for a total of $27.0M.
- All full applications submitted in response to Notice 06-17 that are not funded in FY2007 will be held in consideration for funding in FY2008, pending Congressional appropriation of budget request.

BES FY07 HFI Awards - Novel Hydrogen Storage Materials

Principal Investigator			Project Title
Last Name	First Name	Institution	
Weitering	Hanno	Oak Ridge National Laboratory	Quantum Tuning of Chemical Reactivity for Storage and Generation of Hydrogen Fuels
Chabal	Yves	Rutgers University	Novel Theoretical and Experimental Approaches for Understanding and Optimizing Hydrogen-Sorbent Interactions in Metal Organic Framework Materials
Chen	Jiuhua	Stony Brook University	Influence of Pressure on Physical Property of Ammonia Borane and its Re-hydrogenation
Power	Philip	University of California, Davis	Activation of Hydrogen Under Ambient Conditions by Main Group Molecules
Van de Walle	Chris	University of California, Santa Barbara	Computational Studies of Hydrogen Interactions with Storage Materials
Pfeifer	Peter	University of Missouri-Columbia	Networks of Boron-Doped Carbon Nanopores for Low-Pressure Reversible Hydrogen Storage
Eddaoudi	Mohamed	University of South Florida	Novel Porous Metal-Organic Frameworks for Hydrogen Storage

Total 7 projects with $5.6 million over three years

BES FY07 HFI Awards - Nanoscale Catalysts

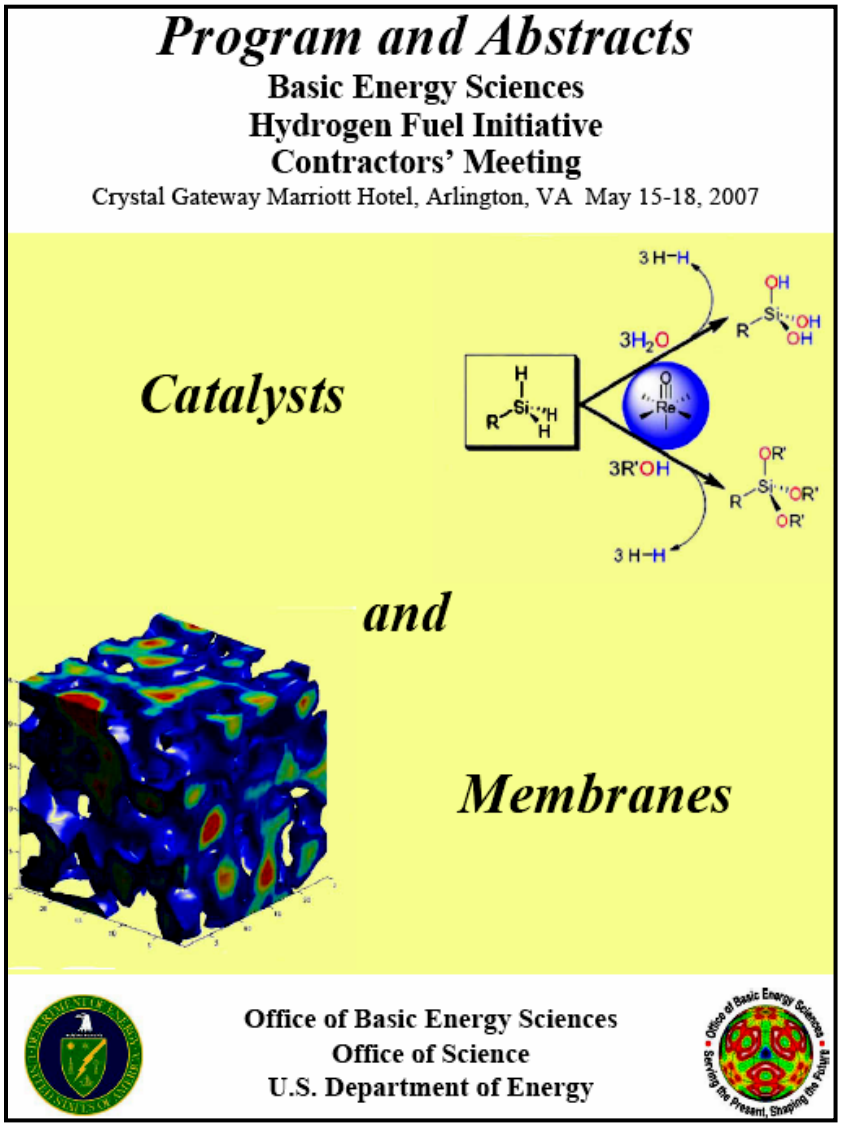
Principal Investigator			Project Title
Last Name	**First Name**	**Institution**	
Stair	Peter	Argonne National Laboratory	Structure/Composition/Function Relationships in Supported Nanoscale Catalysts for Hydrogen Generation
Rodriguez	Jose	Brookhaven National Laboratory	In-situ Studies of the Active Sites and Mechanism for the Water-Gas-Shift Reaction on Metal/Oxide Nanocatalysts
Tong	YuYe	Georgetown University	An in situ Electrode-Potential-Controlled Nuclear Magnetic Resonance Investigation of Sulfur-Poisoning Effect on Platinum Based Mono- and Bi-metallic Nanoscale Electrocatalysts
Ozkan	Umit	Ohio State University	Investigation of the Nature of Active Sites on Heteroatom-Containing Carbon Nano-Structures for Oxygen Reduction Reaction
Bullock	R. Morris	Pacific Northwest National Laboratory	New Bio-Inspired Molecular Catalysts for Hydrogen Oxidation and Hydrogen Production
Neurock	Matthew	University of Virginia	Theory-Aided Design of Active and Durable Nanoscale Cathode Catalysts

Total 6 projects with $5.6 million over three years

Coordination Between BES and EERE on the HFI

- For the EERE Solicitations
  - BES staff: (1) provided input on scientific scope of the solicitation; (2) assisted in developing the external peer review panels of experts; and (3) served as federal reviewers on the award selection panels.
- For the BES Basic Research Solicitation
  - DOE technology program offices reviewed research topical areas.
  - Staff from technology offices were part of the preproposal review process.
  - BES awards have been vetted through DOE Hydrogen Program Manager.
- BES program managers participate in the annual DOE hydrogen program review.
- The annual BES hydrogen research Contractors' Meeting will be collocated with the DOE hydrogen program review.
  - Hydrogen Storage (2006)
  - Membranes and Catalysis (2007) – See next slide
  - Solar and Bio-inspired Hydrogen Production (2008)
- BES participates in monthly meetings with EERE and other DOE program offices to formulate program management plan, operations plan, and systems integration plan.

2007 BES Hydrogen Fuel Initiative Contractors' Meeting



May 17, 8 AM – 8 PM

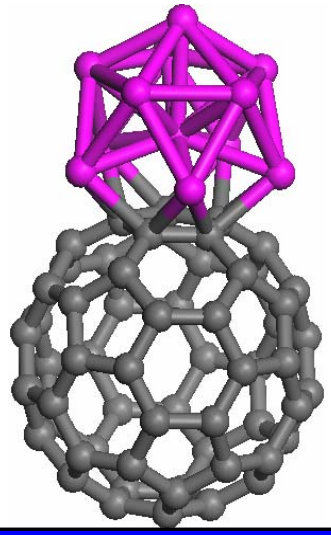
Crystal Gateway Marriott Hotel, Arlington, VA

- **45 Projects & 48 Investigators**
  - 25 Catalysis
  - 20 Membranes
- **18 Oral Presentations**
  - 9 Membranes
  - 9 Catalysis
- **30 Poster Presentations**

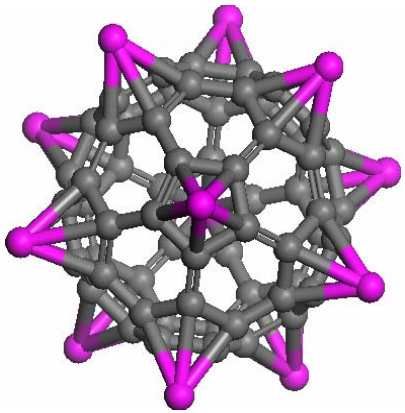
  [Joint With EERE]
  - 14 Membranes
  - 16 Catalysis

Metal decorated C_{60} fullerenes for Hydrogen Storage

$Ti_{12}C_{60}$



ΔE = 0.00 eV 24.80 eV
Wt%: 2.85
Average Binding energy per H_2: 0.5 eV



$Li_{12}C_{60}$

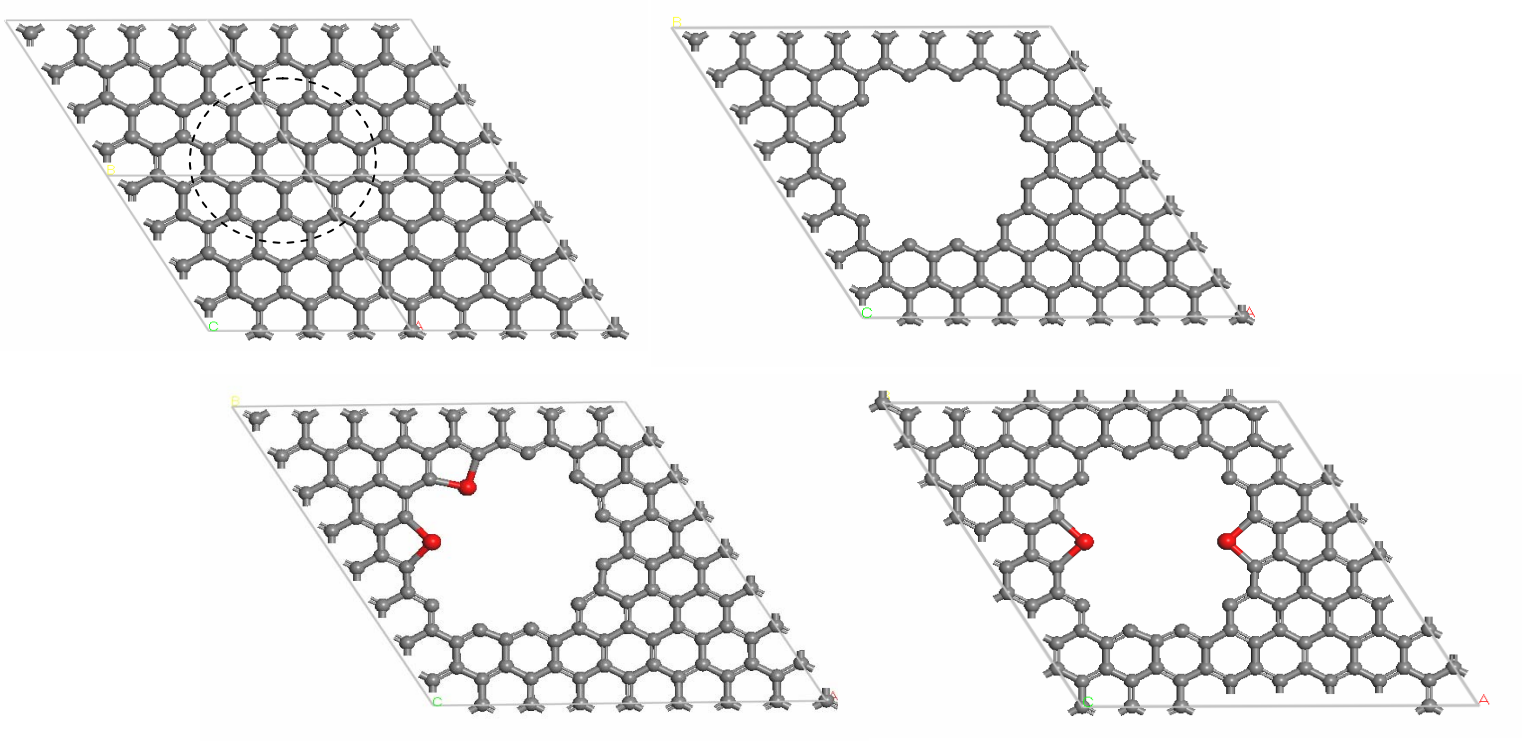
ΔE = 2.20 eV 0.00 eV
Wt%: 13
Average Binding energy per H_2: 0.075 eV

- Transition metal decorated carbon fullerenes, nanotubes, and polymers have the ideal hydrogen bonding for reversible hydrogen storage, but transition metal atoms have a tendency to cluster, thus undermining the structural integrity of the storage material for long term application.

- Li coated carbon nanostructures and polymers have the advantage that they can store large amount of hydrogen while remaining structurally stable (no clustering of Li). However, the binding of hydrogen is still weak and needs to be improved.

Q. Sun, Q. Wang, P. Jena, and Y. Kawazoe, JACS, 127, 14582 (2005); Q. Sun, P. Jena, Q. Wang, and M. Marquez, JACS, 128, 9741 (2006)
Y. Zhao, Y. Kim, A. C. Dillon, M. Heben, and S. B. Zhang, PRL, 94, 155504 (2005); B. Kiran, A. K. Kandalam, and P. Jena J. Chem. Phys. 124, 224703 (2006)
S. Li and P. Jena, Phys. Rev. Lett. 97, 209601 (2006); H. Lee, W. I. Choi, and J. Ihm, Phys. Rev. Lett. 97, 056104 (2006)

Ti Decorated Porous Carbon



E = 0 eV

E = -0.32 eV

- An ideal material is where doped transition metal atoms will not cluster and bind hydrogen molecularly with a binding energy that is intermediate between physisorption and chemisorption. In addition, such materials should be cost effective and can be synthesized in industrial scale.
- One such material currently being modeled Puru Jena and colleagues (VCU) involves porous carbon decorated with transition metal atoms. Unlike in C60 fullerene, Ti does not cluster inside carbon pores (Sa Li and P. Jena (unpublished))