
U.S. Department of Energy Hydrogen Program

Office of Science Basic Energy Sciences

**Harriet Kung
Materials Sciences and Engineering Division
Office of Basic Energy Sciences**

**2008 DOE Hydrogen Program
Merit Review and Peer Evaluation Meeting**

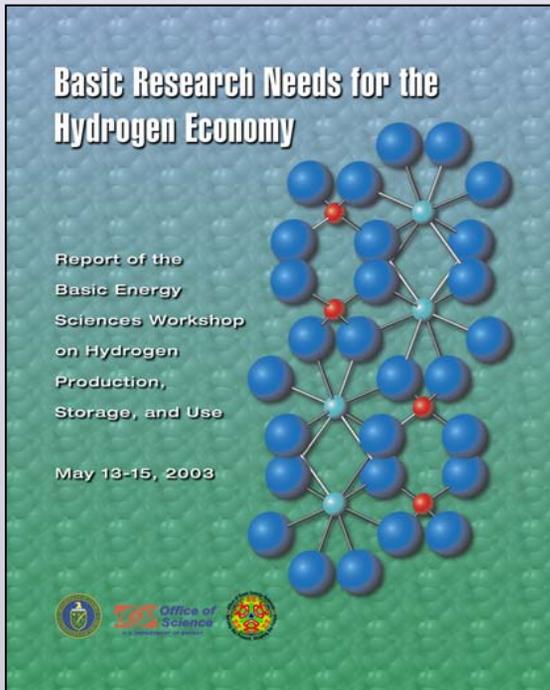
June 9, 2008





Goal and Objectives

The Office of Basic Energy Sciences within DOE held a workshop in May 2003 on Basic Research Needs for the Hydrogen Economy, which formed the scientific basis for our solicitations in 2004 and 2006.



*“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.”*

http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf



2005: BES-HFI Initiative Awards

(\$64.5M total; \$21.5M annual**)

Novel Materials for Hydrogen Storage

(17 projects, \$19.8M*)

Universities:

- MIT¹
- 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
- Illinois¹
- 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 State¹
- Purdue
- Washington
- Virginia Tech

Industry:

- Nanoptek Corp.

DOE Labs:

- Brookhaven
- Pacific Northwest
- National Renewable Energy

Bio-Inspired Materials and Processes

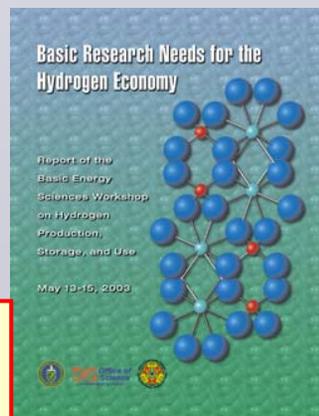
(6 projects, \$7M*)

Universities:

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

DOE Labs:

- National Renewable Energy



**This represents new funding, bringing the total BES funding of Hydrogen research to \$29.2M/yr in FY05

In 2006 a small number of additional awards were issued, bringing the BES HFI funding to a total of \$32.4M/yr

* Over three years

¹ Selected for 2 awards



2007: BES-HFI Initiative Awards

(\$12.5M total; \$3.9M annual)

Novel Materials for Hydrogen Storage

(8 projects, \$6.5M*)

Universities:

- Missouri-Columbia
- California-Santa Barbara
- Florida International
- Rutgers
- California-Davis
- South Florida
- Northwestern

DOE Labs:

- Oak Ridge

Design of Catalysts at the Nanoscale

(7 projects, \$6.0M*)

Universities:

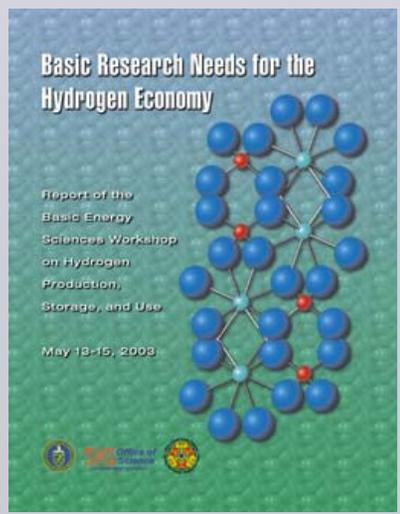
- Virginia
- Georgetown
- Ohio State
- Arizona State

DOE Labs:

- Argonne
- Brookhaven
- Pacific Northwest

In 2006 BES issued another solicitation for basic research in hydrogen. A total of 502 pre-proposals were received, 249 selected for submission of a full proposal, and 229 full proposals were received and reviewed by peer-review panels. Due to a reduction in anticipated HFI funding for FY07 only 15 new projects were initiated with a concentration in the areas of Hydrogen Storage and Nanoscale Catalysts. No additional funding for the HFI was appropriated to BES in FY08 so the remaining 214 proposals were declined.

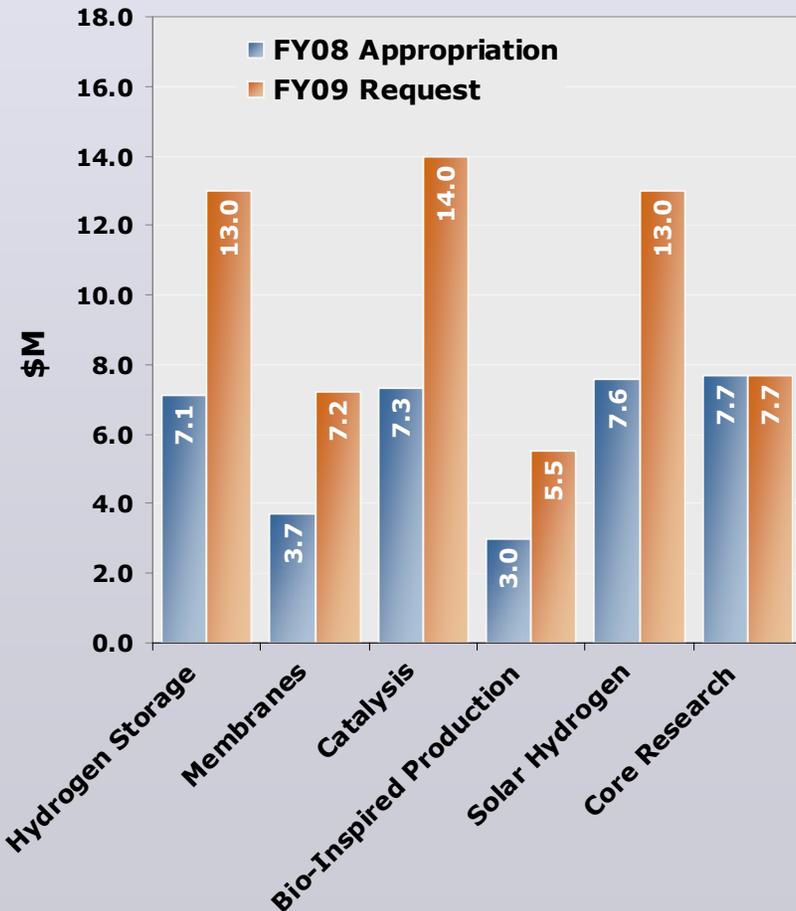
* Over three years





Budget

FY2009 Budget Request = \$60.4M
FY2008 Budget = \$36.4M



Emphasis

Continued focus on critical basic research needs for hydrogen production, storage, and use:

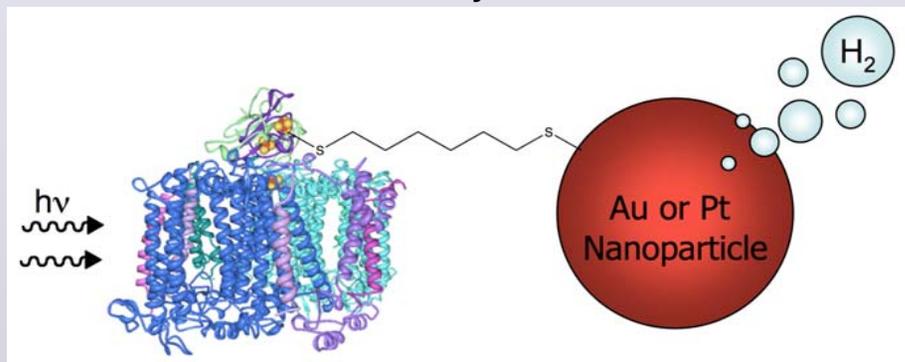
- Hydrogen Storage
- Membranes
- Nanoscale Catalysts
- Solar Hydrogen Production
- Bio-Inspired Hydrogen Production



Efficient Solar Hydrogen Production by a Hybrid Photo-catalyst System

Molecular Wire

Delivers the highly reducing electrons to the catalyst rapidly and efficiently



Photosystem I

Efficient solar absorber which generates a stable charge-separated state, a source of highly reducing electrons.

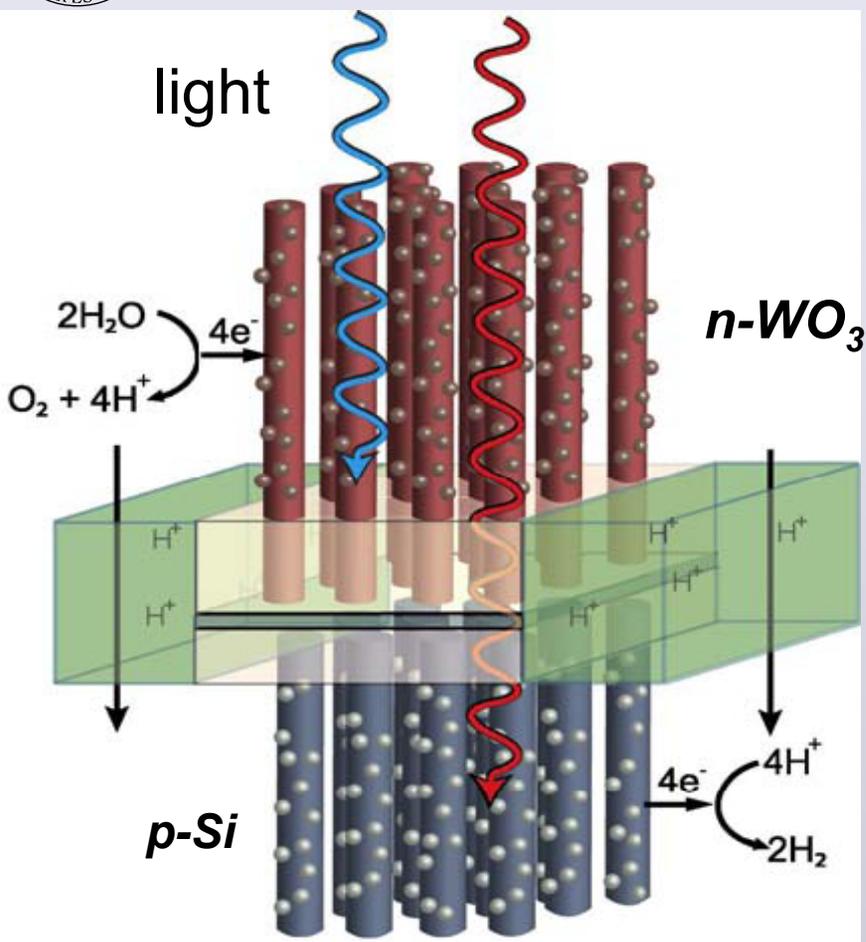
Catalyst

Uses the photo-generated electrons to reduce protons from solution into hydrogen (H_2).

- Solar energy is an attractive source for large scale hydrogen production. Robust, inorganic catalyst systems such as platinized TiO_2 have been used to generate hydrogen from sunlight, but efficiency is low because they can only use the UV portion of the solar radiation. Natural photosynthetic systems such as Photosystem I (PS I) can absorb $\sim 45\%$ of solar spectrum, but are coupled indirectly and inefficiently to a non-robust, oxygen-sensitive hydrogenase to generate hydrogen.
- In a novel strategy that combines the best of both worlds, a synthetic molecular wire, consisting of a Fe_4-S_4 cluster and an organic dithiol, is used to covalently link PS I with the Au or Pt nanoparticles. This provides a rapid, efficient pathway for shuttling photo-generated electrons to the inorganic nanocatalyst.
- Upon illumination, the PS I-Molecular Wire-Nanocatalyst hybrid system generates 8 H_2 per PS I per second over a period of 12-16 hours (with cytochrome c_6 as electron donor).
- This represents a new benchmark in the efficiency of hydrogen production by use of modified or hybrid photosynthetic systems. To compare, a genetically engineered PS I-hydrogenase gene fusion generates 0.0045 H_2 per PS I per second, and platinized chloroplasts generate 0.045 H_2 per PS I per second.



Sunlight Driven Hydrogen Formation

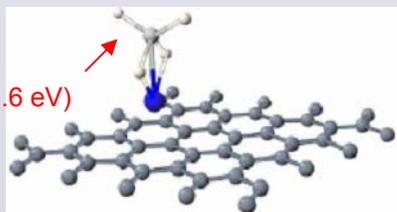
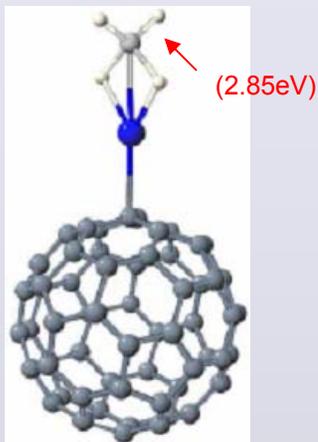
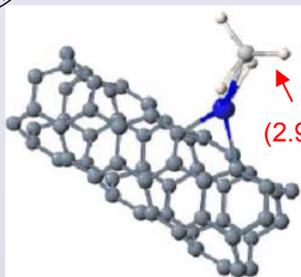


Solar powered water splitting scheme incorporating two separate semiconductor rod-array photoelectrodes that sandwich an electronically and ionically conductive membrane.

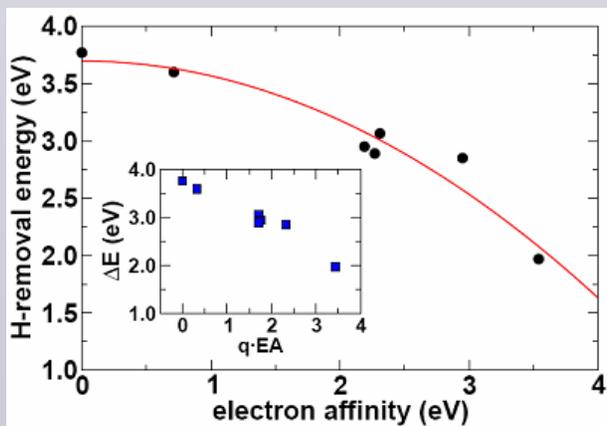
- Traditional photoelectrochemical water splitting is limited by a cumbersome planar, two electrode configuration for light absorption and H₂ and O₂ generation. Current generation of semiconductors used for absorbing visible solar spectrum are intrinsically unstable. Precious metals (Pt, Pd) are needed for H₂ evolution.
- One key constraint in photon absorbers for solar energy conversion is that the samples need to be thick enough for sufficient absorption, yet pure enough for high minority carrier length and photocurrent collection.
- New nanorod configuration was recently developed to orthogonalize the directions of light absorption and charge carrier collection, i.e. it separates longitudinal light absorption from transverse carrier diffusion to reactive surface.
- The short diffusion paths to reaction broadens usable materials to include earth abundant, resistive semiconductors. Opposing nanorod configuration with conductive ion membrane allows for compact device with inherent separation of O₂ and H₂ gas.
- High surface-to-volume ratio of nanostructure decreases current density and permits use of broad range of new metals as sites for H₂ and O₂ evolution.



Carbon Nano-structures as Catalysts for Dehydrogenation of Complex Metal Hydrides



First-principles equilibrium configurations for NaAlH_4 with CNT, fullerene and graphene. Na: Blue, Al: Gray and H: white. The hydrogen removal (energy:red) was found to be a function of the electron affinity of the substrate

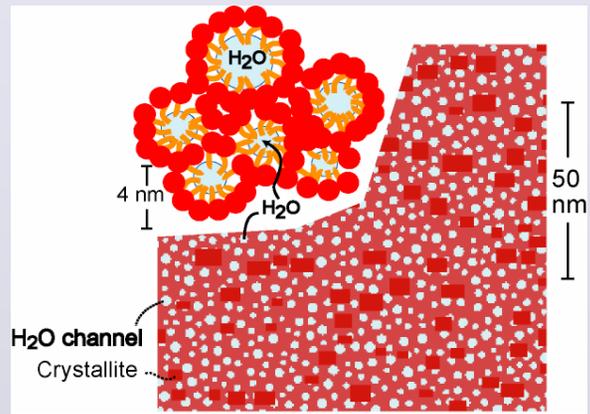


Ab-initio results for H-removal energy in NaAlH_4 as a function of the carbon substrate's electron affinity (red quadratic fit). The inset shows the linear relationship between the H-removal energy (DE) to the product of transferred charge (q) and electron affinity (EA).

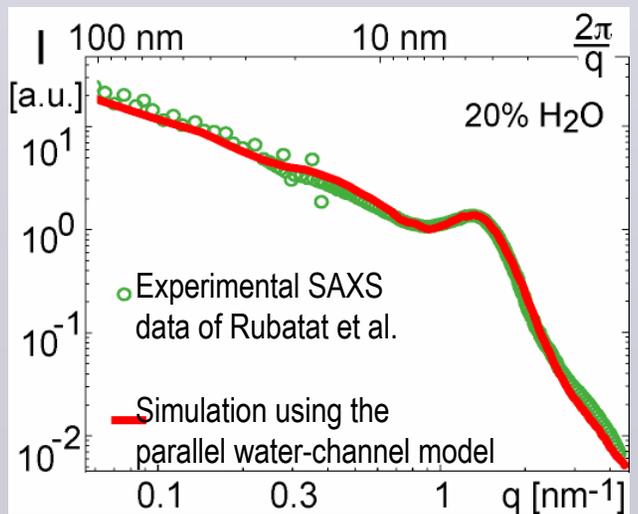
- NaAlH_4 is a good candidate for reversible hydrogen storage, but its high hydrogen desorption temperature (over 120°C) limits its usage in on-board storage applications.
- Experiments have shown that carbon nanostructures can be used as catalysts for dehydrogenation of NaAlH_4 by lowering the hydrogen desorption temperature.
- First principles calculations now confirm that substrate binding energy of NaAlH_4 depends strongly on the surface curvature (largest for C_{60}). By supporting NaAlH_4 on an electro-negative substrate such as carbon fullerene or nanotube, the ionic bond between Na^+ and AlH_4^- is modified and the ability of Na to donate its charge is compromised, thus weakening the Al-H bond and causing the hydrogen to desorb at lower temperatures.
- Theoretical calculation results also show that the hydrogen removal energy decreases as the electron affinity of the substrate increases. This is because with single hydrogen atom desorption, the remaining NaAlH_3 unit can transfer charge to the carbon support and thus bring the total energy of the system to a lower level.



The Nanostructure of Nafion® Fuel-Cell Membrane



Parallel, cylindrical water channels with ~2.4 nm diameter

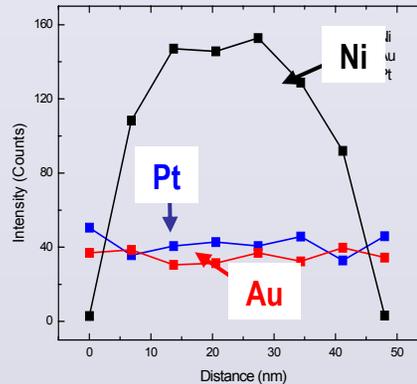
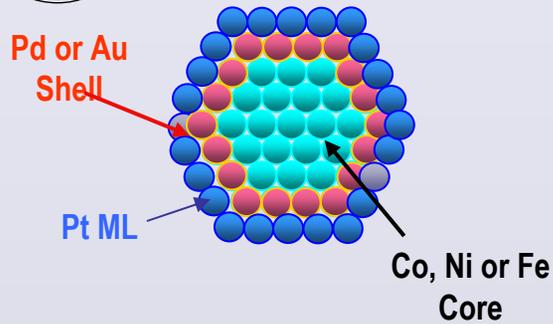


Experimental and simulated scattering curves showing agreement over the entire q-range

- Nafion® (perfluorinated polymer with ionic side groups) is the current gold standard as the proton-exchange membrane material for H₂/O₂ fuel cells.
- The long elusive nanometer-scale structure of Nafion has now been determined by a novel quantitative analysis of Small-Angle X-ray Scattering data (SAXS), based on 3D-Fourier transformation.
- This work establishes that Nafion is riddled with ~2.4 nm diameter cylindrical water channels lined by the ionic side groups.
- The channels are locally parallel and stabilized by the rigid polymer backbones, as established by novel ¹³C and ¹⁹F solid-state NMR methods.
- 12 other structural models have been ruled out.
- All previous models of Nafion contained constrictions of <1.2 nm diameter. The new model with wider channels best explains the fast transport of water and H⁺ through Nafion.
- The new structural model provides a valid target for the design of better and cheaper ionic polymers to replace Nafion.

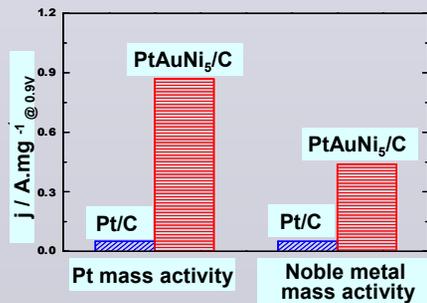
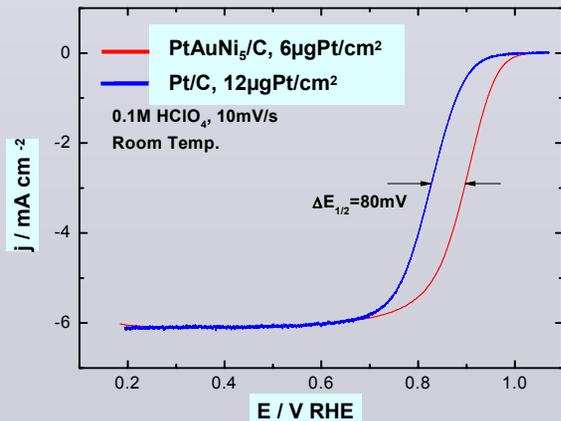


Tri-Metallic-Decorated Surface Alloys: A New Catalytic Paradigm



- A conceptual search for stable electrocatalytic alloys for both anodes (hydrogen oxidation) and cathodes (oxygen reduction) in fuel cells led to the development of novel catalyst nanostructures containing three components: a non-noble metallic core, a palladium or gold shell, and a platinum top monolayer.
- Theoretical electronic structure calculations supported the hypotheses that these new structures would present novel properties, particularly higher activity for both hydrogen and oxygen reactions. Empirical know-how projected that the stability of the tri-metallic particle would be larger than a mono or bimetallic particle, but the challenge was to synthesize and maintain the electrocatalytic functions during the cathodic reduction.
- Recent results successfully confirmed the predictions, providing evidence that the three-layered catalysts can be synthesized and that their activity is 20 times higher than that of regular Pt catalysts. The stability under cathodic reduction is better than initially expected (XANES data show a smaller extent of Pt oxidation in trimetallic particles than in monometallic ones). The concept of interlayer Au to suppress oxidation of Pt can be applied to other alloys of non-Pt electrodes, potentially eliminating in the future the need for such noble metal in electrocatalysts.

Model structure of trimetallic layered nanoparticles and energy-dispersive x-ray scan across Pt/Au/Ni nanoparticle show the radial distribution of metal constituents, evidencing a Ni core and noble metal shell.



The polarization curves (left panel) show that trimetallic particles Pt/Au/Ni are more stable to oxidation (by 80 mV potential) than monometallic Pt particles. The activity measurements (right panel) show trimetallic particles being about 20x more active than monometallic ones (on a Pt-mass basis.)

M.H. Shao, K. Sasaki, R.R. Adzic, *J. Am. Chem. Soc.* 128 (2006) 3526-3527.
M. H. Shao, K. Sasaki, P. Liu, R.R. Adzic, *Z. Phys. Chem.* 221 (2007) 1175-1190.



The Scientific Opportunities in BES

Identified in The “Basic Research Needs ...” Workshop Series

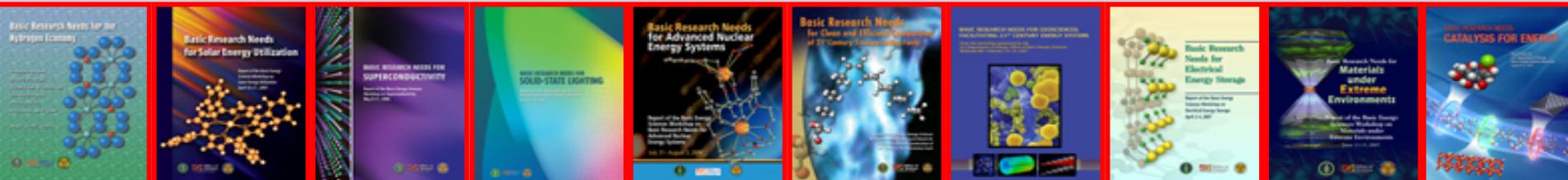
Identifying Basic Research Directions for Today’s and Tomorrow’s Energy Technologies

Basic Research Needs for a Secure Energy Future (BESAC)



http://www.sc.doe.gov/bes/reports/files/SEF_rpt.pdf

- **Basic Research Needs for the Hydrogen Economy**
- **Basic Research Needs for Solar Energy Utilization**
- Basic Research Needs for Superconductivity
- Basic Research Needs for Solid State Lighting
- Basic Research Needs for Advanced Nuclear Energy Systems
- Basic Research Needs for the Clean and Efficient Combustion of 21st Century Transportation Fuels
- Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems
- Basic Research Needs for Electrical Energy Storage
- Basic Research Needs for Catalysis for Energy Applications
- Basic Research Needs for Materials under Extreme Environments

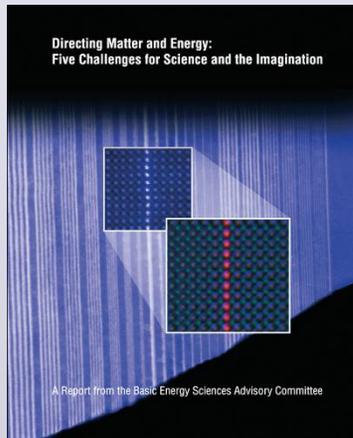




One Additional Workshop: Science Grand Challenges

How does nature execute electronic and atomic design? How can we?

Directing Matter and Energy: Five Challenges for Science and the Imagination



http://www.sc.doe.gov/bes/reports/files/GC_rpt.pdf

- **Control the quantum behavior of electrons in materials**

Imagine: Direct manipulation of the charge, spin and dynamics of electrons to control and imitate the behavior of physical, chemical and biological systems, such as digital memory and logic using a single electron spin, the pathways of chemical reactions and the strength of chemical bonds, and efficient conversion of the Sun's energy into fuel through artificial photosynthesis.

- **Synthesize, atom by atom, new forms of matter with tailored properties**

Imagine: Create and manipulate natural and synthetic systems that will enable catalysts that are 100% specific and produce no unwanted byproducts, or materials that operate at the theoretical limits of strength and fracture resistance, or that respond to their environment and repair themselves like those in living systems

- **Control emergent properties that arise from the complex correlations of atomic and electronic constituents**

Imagine: Orchestrate the behavior of billions of electrons and atoms to create new phenomena, like superconductivity at room temperature, or new states of matter, like quantum spin liquids, or new functionality combining contradictory properties like super-strong yet highly flexible polymers, or optically transparent yet highly electrically conducting glasses, or membranes that separate CO₂ from atmospheric gases yet maintain high throughput.

- **Synthesize man-made nanoscale objects with capabilities rivaling those of living things**

Imagine: Master energy and information on the nanoscale, leading to the development of new metabolic and self-replicating pathways in living and non-living systems, self-repairing artificial photosynthetic machinery, precision measurement tools as in molecular rulers, and defect-tolerant electronic circuits

- **Control matter very far away from equilibrium**

Imagine: Discover the general principles describing and controlling systems far from equilibrium, enabling efficient and robust biologically-inspired molecular machines, long-term storage of spent nuclear fuel through adaptive earth chemistry, and achieving environmental sustainability by understanding and utilizing the chemistry and fluid dynamics of the atmosphere.



Energy Frontier Research Centers

Tackling our energy challenges in a new era of science

Energy Frontier Research Centers will bring together the skills and talents of multiple investigators to enable research of a scope and complexity that would not be possible with the standard individual-investigator or small-group award.

The DOE Office of Science, Office of Basic Energy Sciences, announced the Energy Frontier Research Centers (EFRCs) program. Pending appropriations, up to \$100M will be available in FY2009 for EFRC awards that are \$2–5 million/year for an initial 5-year period. Universities, labs, nonprofits, and for-profit entities are eligible to apply.

Energy Frontier Research Centers will pursue fundamental research that addresses both energy challenges and science grand challenges in areas such as:

- **Solar Energy Utilization**
- Catalysis for Energy
- Electrical Energy Storage
- Solid State Lighting
- Superconductivity
- Bioenergy and biofuels
- Geosciences for Nuclear Waste and CO₂ Storage
- Advanced Nuclear Energy Systems
- Combustion of 21st Century Transportation Fuels
- **Hydrogen Production, Storage, and Use**
- Materials Under Extreme Environments

EFRC Funding Opportunity Announcement was published on April 4, 2008.
See: <http://www.sc.doe.gov/bes/EFRC.html>



Single-Investigator and Small-Group Research

Tackling our energy challenges in a new era of science

- Pending appropriations, up to \$60M will be available for single-investigator and small-group awards in FY2009.
- BES seeks applications in two areas: grand challenge science and energy challenges identified in one of the Basic Research Needs workshop reports.
- Awards are planned for three years, with funding in the range of \$150-300k/yr for single-investigator awards and \$500-1500k/yr for small-group awards (except as noted below)
- Areas of interest include:
 - Grand challenge science:** ultrafast science; chemical imaging, complex & emergent behavior
 - Tools for grand challenge science:** midscale instrumentation; accelerator and detector research (awards capped at \$5M over 3-year project duration)
 - Use inspired discovery science:** basic research for electrical energy storage; advanced nuclear energy systems; **solar energy utilization**; **hydrogen production, storage, and use**; other basic research areas identified in BESAC and BES workshop reports with an emphasis on nanoscale phenomena
- For full details see: <http://www.sc.doe.gov/bes/SISGR.html>





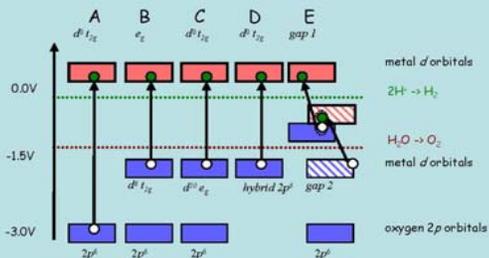
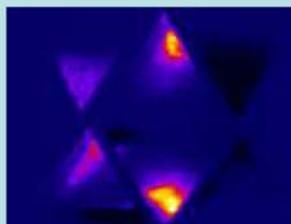
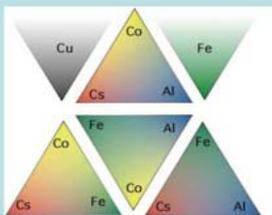
2008 BES Hydrogen Fuel Initiative Contractors' Meeting

Program and Abstracts

Basic Energy Sciences
Hydrogen Fuel Initiative
Contractors' Meeting

Crystal Gateway Marriott Hotel, Arlington, VA June 9-12, 2008

Hydrogen Production



June 11, 8 AM – 8 PM
Crystal Gateway Marriott Hotel, Arlington, VA

- 25 Projects & 36 Investigators
- 14 Oral Presentations
- 11 Poster Presentations
[Joint With EERE]



Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

