Office of Science
Financial Assistance
Funding Opportunity Announcement
DE-PS02-06ER06-17

Basic Research
for the Hydrogen Fuel Initiative

The Office of Basic Energy Sciences (BES) of the Office of Science (SC), U.S. Department of Energy (DOE), in keeping with its mission to assist in strengthening the Nation's scientific research enterprise through the support of fundamental science and the experimental tools to perform basic research, announces its interest in receiving grant applications for basic research for the Hydrogen Fuel Initiative (HFI). Areas of focus include: Novel Materials for Hydrogen Storage; Functional Membranes; and Nanoscale Catalysts. We seek to support outstanding research programs that will lead to key discoveries to make hydrogen a feasible fuel for the future. Research funded under this initiative will pursue breakthroughs in materials, chemical and physical understandings, and interdisciplinary theory-modeling-simulation- experimentation approaches in order to surpass the existing scientific and technical barriers. More information on these focus areas is provided in the SUPPLEMENTARY INFORMATION section below.

The application must contain one paragraph addressing how the proposed research will address one or more of the four BES long-term program measures used by the Office of Management and Budget to rate the BES program annually; these measures may be found at http://www.sc.doe.gov/bes/BES_PART_Performance_Measures.pdf.

PREAPPLICATIONS REQUIRED: July 6, 2006, 4:30 pm Eastern Time

Preapplication. Potential applicants are required to submit a brief preapplication containing the information specified below. Preapplications referencing Program Solicitation DE-PS02-06ER06-17, must be received by DOE by 4:30 p.m., Eastern Time, July 6, 2006. Preapplications will be reviewed for conformance with the guidelines presented and suitability in the technical areas specified in this solicitation. A response to the preapplications encouraging or discouraging formal applications will be communicated to the applicants by September 12, 2006.

Preapplication Review and Criteria

The preapplication should consist of a description of the research proposed to be undertaken by the applicant and a clear explanation of its importance to the advancement of basic hydrogen research and its relevance to the HFI. The preapplication must be submitted electronically to hydrogen@science.doe.gov as two files:

(1) A cover page in Excel format downloadable from: http://www.science.doe.gov/bes/hydrogen_preapp_cover.xls. The information to be

entered on the cover page worksheet includes: Program Announcement Number; Lead Principal Investigator name, address, email address, telephone number, and fax number; project title; selection of one submission category (see below); budget request for each project year; and total budget request for the project. On the worksheet named coPIs enter the names and institutions of all co-Principal Investigators and/or senior collaborators (excluding postdocs and graduate students). Please do not alter the overall format of the cover-page Excel file, i.e., do not move or merge cells, as this will significantly slow the processing of the preapplication.

(2) A PDF file containing a narrative section not to exceed 3 pages (including text and figures) describing the research objectives, approaches to be taken, the institutional setting, and a description of any research partnership if applicable. In addition, include brief, one-page, curriculum vitae from each Principal Investigator.

As noted above, the preapplication must also identify the primary submission topic:

(1) Novel Materials for Hydrogen Storage; or
(2) Functional Membranes; or
(3) Nanoscale Catalysts.

The purpose of this self-identification into a research topic is solely for the purposes of grouping similar applications for peer review.

APPLICATION DUE DATE: December 12, 2006, 8:00 pm Eastern Time

Applications must be submitted using Grants.gov, the Funding Opportunity Announcement can be found using the CFDA number, 81.049 or the Funding Opportunity Announcement number, DE-PS02-06ER06-17. Applicants must follow the instructions and use the forms provided on Grants.gov.

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SUPPLEMENTARY INFORMATION: Since President Bush in his 2003 State of the Union address announced the Hydrogen Fuel Initiative for a clean and secure energy future, the U.S. DOE has sponsored new research to attend to the initiative goals [http://www.science.doe.gov/bes/hydrogen.html]. The U.S. DOE Hydrogen Program, through the participation of science and technology offices, supports both basic and applied research and development toward realizing the national hydrogen vision to produce and deliver hydrogen

energy in an affordable, safe, and convenient manner. Information for applied R&D in hydrogen production, delivery, storage, fuel cell technologies, technology validation, safety, codes and standards can be found at http://www.hydrogen.energy.gov.

A workshop was sponsored in May 2003 by the Office of Basic Energy Sciences (OBES) to identify basic research needs for hydrogen production, storage and use. The workshop report, entitled *Basic Research Needs for the Hydrogen Economy* [http://www.science.doe.gov/bes/hydrogen.pdf], detailed a broad array of basic research challenges. These challenges depicted the vast gap between present-day scientific knowledge/technology capabilities and what would be required for the practical realization of a hydrogen economy. The workshop report is still a current source of information and summarizes the interests of the OBES.

In supporting the President's Hydrogen Fuel Initiative (HFI), the OBES issued its first request for proposals in 2004 under the "Basic Research for the Hydrogen Fuel Initiative," over 70 new awards were funded in 2005 and 2006 at universities and national laboratories covering the priority areas identified in the 2003 workshop report [http://www.science.doe.gov/bes/hydrogen.html]. This initial set of awards contributes to important areas addressing hydrogen production and storage and hydrogen utilization in fuel cells.

To tackle the challenges presented by the HFI, the basic research effort needs to be increased both in intensity and scope, particularly in regards to materials functionalities and structures, synthesis methods, and instrumental characterization methods, as well as with regards to new theoretical methods and simulation approaches. This Notice solicits innovative basic research proposals to significantly strengthen the scientific basis that will allow comprehensive understanding of the physical and chemical processes that lead to the extraction of hydrogen from its natural environments, storage and distribution of hydrogen, and the efficient energy conversion, all in a safe as well as economically and environmentally sustainable manner. We seek to support outstanding fundamental research programs potentially leading to discoveries and breakthroughs, focused on primarily three broad areas:

1. **Novel Materials for Hydrogen Storage**
2. **Functional Membranes**
3. **Nanoscale Catalysts**

The following provides further information under each of the three focus areas to illustrate the scope of proposals solicited under this Notice.

Novel Materials for Hydrogen Storage On-board hydrogen storage is considered to be one of the most challenging barriers to the widespread use of hydrogen because the performance of current hydrogen storage materials and technologies falls far short of vehicle requirements. Hydrogen storage is also needed for off- board uses such as for stationary power generation and for hydrogen delivery and refueling infrastructure. 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. Incremental improvements in current technologies will not be sufficient to meet the stated practical goals (see for example,

http://www.eere.energy.gov/hydrogenandfuelcells/mypp/). As indicated in the BES hydrogen workshop report, basic research is essential for identifying novel materials and processes that can provide the breakthroughs needed to meet the HFI goals. These breakthroughs may result from research at the nanoscale facilitated by new understanding derived from both theory and experiment. The advances may not necessarily come from within the boundaries of metal hydrides, chemical hydrides or carbon-based materials; instead, success may well be found at the interfaces of these classes of materials or may come from "outside-the-box" concepts. Innovative basic research in the following high priority areas is needed:

- ***Novel materials***. Research is needed to develop and examine new materials and obtain an atomic- and molecular-level understanding of the physical and chemical processes involved in hydrogen storage and release. These novel storage materials may fall outside of the hydrogen-storage materials that are currently under investigation. The innovative design and synthesis of tailored materials with high storage capacity as well as fast release times will need (a) reliable information about the structure, thermodynamic, physical, and chemical properties of novel storage materials and (b) an understanding of the interaction of hydrogen in solid-state materials.
- ***Complex hydrides***. A basic understanding of the structure, physical, chemical, and mechanical properties of metal hydrides and complex chemical hydrides is still needed. Specifically, the fundamental factors that control bond strength, atomic processes associated with hydrogen uptake and release kinetics, the role of surface structure and chemistry in affecting hydrogen-material interactions, hydrogen-promoted mass transport, degradation due to cycling, reversibility in metal hydrides, and regeneration of chemical hydrides must be understood. Innovative synthesis and processing routes need to be developed. The effect of dopants in achieving reasonable kinetics and reversibility needs to be understood at the atomic level.
- ***Nanostructured materials***. Nanophase materials offer promise for superior hydrogen storage due to short diffusion distances, new phases with better capacity, reduced heats of adsorption/desorption, faster kinetics, and surface states capable of catalyzing hydrogen dissociation. Improved bonding and kinetic properties may permit good reversibility at lower desorption temperatures. Tailored nanostructures based on light metal hydrides, carbon-based nano-materials, and other non-traditional storage approaches need to be explored with the focus on understanding the unique surfaces and interfaces of nanostructured materials and how they affect the energetics, kinetics, and thermodynamics of hydrogen storage.
- ***Theory, modeling, and simulation***. Theory, modeling, and simulation will enable (1) understanding the physics and chemistry of hydrogen interactions at the appropriate size scale and (2) the ability to simulate, predict, and design materials performance. Examples of research areas include: hydrogen interactions with surface, interface, grain boundaries and bulk defects of a particular storage material. The emphasis will be to establish the fundamental understanding of hydrogen-materials interactions so that completely new and revolutionary hydrogen storage media can be identified and designed.
- ***Novel analytical and characterization tools***. Sophisticated analytical and characterization techniques are needed to meet the high sensitivity requirements associated with characterizing hydrogen-materials interactions, especially for nanostructured materials, while maintaining high specificity in characterization. The

structure and surface properties of high-performance nanomaterials need to be identified to facilitate the modeling and provide an understanding of structure-property relationship. *in-situ* studies are needed to characterize site-specific hydrogen adsorption and release processes at the molecular level.

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. A detailed understanding of interactions between chemical species and membranes, or among species confined within membranes, is needed to develop new separation processes. 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. Often these membrane functions are closely coupled with catalytic functions such as dissociation, ionization, or oxidation/reduction. Often they must function in water environment at temperatures below the boiling point of water. These membranes may lack selectivity to prevent cross-over between electrodes or to separate selected species efficiently. Currently available oxide membranes, which are critical for ionic transport in higher-temperature fuel cells, are also inefficient. For all types of membranes, the fundamental physical and chemical processes that determine transport and separation efficiency need better understanding. Overcoming the barriers described above will require an integrated, basic research effort to enable discovery of new membrane materials, improvement in membrane performance, and integration of membrane and catalytic functions. The following are some of the high priority research directions.

- ***Integrated nanoscale architectures***. The nanoscale dimensions of catalyst particles, support materials, and ion-conducting membranes make it possible to design compact structures that facilitate transport of ions, electrons, and gases. Self-assembly or other approaches to synthesize integrated structures pose significant technical challenges but have the potential to improve catalyst uniformity and perhaps enhance endurance and overall performance. Synthesis and characterization of radically new nanoscale and porous materials are required, including but not restricted to microporous oxides, metal-organic frameworks, bioinspired structures, carbons that remove sulfur and carbon monoxide from hydrogen, etc. New approaches to the design and fabrication of integrated nanoscale architectures may enable ultra-pure hydrogen to be produced from fossil, solar, thermochemical and bioinspired processes.
- ***Fuel cell membranes***. Novel membranes with higher ionic conductivity, better mechanical strength, lower cost, and longer life are critical to the success of fuel cell technologies and other technologies that depend on ionic transport. Polymeric membranes that conduct protons and remain hydrated up to high temperatures are needed. Membranes that do not even require hydration yet meet the conductivity, durability and cost requirements are also desired. Novel oxide-ion membranes that operate at lower temperatures while maintaining selectivity and permeability, as well as membranes that are stable and durable under harshly corrosive environments are needed for efficient thermal cycles. Achieving these goals will require discovery of novel

materials, as well as better understanding and control of the electrochemical processes at the electrodes and membrane electrolyte interfaces.

- ***Theory, modeling, and simulation of membranes and fuel cells***. Fundamental understanding of the selective transport of molecules, atoms, and ions in polymeric as well as oxide membranes is emerging. The diversity of transport mechanisms and their dependence on structure over a wide temperature range requires extensive theory, modeling and simulation to discover the basic principles and develop design strategies for improved membrane performance. Significant emphasis is placed on understanding the nature of proton transport in membranes; the interaction of complex aqueous, gaseous, and solid interfaces in gas diffusion electrode assemblies; the nature of corrosion processes under applied electrochemical potentials and in oxidative media; and the origin of the performance-robbing overpotential for fuel cell cathodes.
- ***Characterization of electrochemical and buried interfaces***. Innovative techniques are needed to study the microstructure and reactivity of buried interfaces under chemical or electrical potentials. This is relevant to such applications as electrocatalyst/electrolyte interfaces in membrane-electrode assemblies, or membrane-ceramic interfaces in separation media. Understanding and controlling the structure and morphology of the membranes and their evolution during operation is crucial to maximizing performance. Therefore, *in-situ* characterization methods become particularly important.

Nanoscale Catalysts

Catalysis impacts many of the technologies for which breakthroughs are needed, ranging from production of hydrogen from traditional sources such as oil and gas, as well as underexploited sources such as coal, biomass, and water, to the low-activation-energy storage or removal of hydrogen, and to the production of electricity from fuel cells or photocells. Catalysts in many cases make possible hydrogen-related transformations that are unfeasible or impractical otherwise, by providing new reaction pathways. In other cases, catalysts increase the efficiency of hydrogen-related processes such as production, uptake and release of stored hydrogen by reduction of the energy of thermal activation. Breakthroughs in catalytic research would impact the thermodynamic efficiency of hydrogen production, storage, and use, and thus improve the economic efficiency with which the primary energy sources - fossil, biomass, solar, or nuclear - serve our energy needs. Most fuel-cell and low-temperature reforming catalysts or low-temperature combustion catalysts are based on noble metals. From a fundamental point of view, it is of interest to expand our understanding and use of non-noble metals in fuel cells, reforming and other processes. The following are some of the high-priority research directions.

- ***Synthesis-structure-function relationships of nanoscale catalysts***. The control of chemical selectivity and activity is the key to the discovery of new or more efficient hydrogen-related activation and conversion pathways. The selectivity and activity properties that arise with matter at nanometer dimensions are mostly unknown or need to be better understood. The relationship between the electronic structure of the catalyst or electrocatalyst and the support, and the catalytic activity needs to be better known. Thus, single-site catalysts with predictable chemical functionalities need to be developed. The chemical conversion of hydrogen-containing molecules with well-defined and stable

clusters of metals, oxides and other compounds needs to be understood. Such need for deeper understanding is particularly crucial for catalysts based on non-noble metals.

- ***Structural dynamics of catalysts***. It is desirable to synthesize and operate catalysts with predictable structures and compositions under reaction conditions. Catalytic structure, particularly at the atomic and electronic levels, is dynamic, and current catalyst design activities must be advanced beyond the static configurations of atomic and electronic structures. Structural changes at surfaces and interfaces are particularly of interest in addition to changing crystal phases, agglomeration, dissolution and reprecipitation. Such research should unravel the many chemical and physical events that influence catalytic behavior. It is of interest to consider fast transients, for example cationic or anionic segregation that occurs during redox cycles and leads to the formation and re-annealing of defect planes, or metal surface diffusion that is driven by chemical, thermal or electric gradients and leads to restructuring. It is also of interest to consider slow transient phenomena, for example nanoparticle sintering in electrodes, solid phase separation in mixed oxides, polymerization and phase separation of oxide species on surfaces, solid state reactions and deactivation or promotion, etc.
- ***Dynamic behavior of catalytic reactions***. Catalytic reactions of oxygen- or hydrogen-containing molecules proceed with mechanisms that can be described with classical kinetics or microkinetics models, which primarily explain the statistical behavior of reacting species. It is of interest, however, to uncover the dynamics of single events, such as bond formation and scission on surfaces or at single sites, or elemental transfer between adsorbed species, or energy transfer between reactants, products, catalytic sites and outgoing or incoming electrons, etc., by means of advanced experiments and theory. At the longer timescales corresponding to a full catalytic turnover, it is of interest to understand how macroscopic mechanisms or statistical molecular behavior correlate with the catalytic structural dynamics described in the previous bullet.
- ***Innovative synthesis techniques***. A basic challenge for catalysis in hydrogen production, storage and fuel cells is the synthesis of well-defined catalysts. Approaches are needed to tailor the molecular precursors and building blocks to yield stable quasi-equilibrium structures that retain excellent catalytic performance and robustness at extreme conditions of temperature, pressure, and potential cycling while exposed to the reaction medium. Synthesis with atomic-scale precision is necessary to produce tailored structures of catalysts on supports with controlled size, shape and surface characteristics. New, high-throughput innovative synthesis methods must be combined with theory and advanced measurement capabilities to accelerate the development of designed catalysts. In addition, novel, cost-effective fabrication methods need to be developed for the practical application of these new designer catalysts.
- ***Bio-inspired catalysts***. A fundamental understanding is needed of bio-inspired complexes that are able to perform activation of hydrogen-containing molecules. New opportunities for hydrogen reactions are sought from the discovery of synthetic analogues that operate at the high potential required for water oxidation and are able to perform a four-electron reduction, or proton-coupled redox reactions, and avoid the production of corrosive intermediates. In analogy to natural systems, bio-inspired catalysts should be able to self-repair and provide robust resilience to defects.
- ***Techniques for in-situ characterization under reaction***. Fundamental understanding of complex catalytic mechanisms in hydrogen processes requires identification of the nature

of the active sites under actual reaction conditions; the interaction of the reactants, intermediates and products with the active sites; detection of intermediate species; and quantification of the dynamics of atomic, electronic and energetic exchanges. There is a special need for ultrafast and high-resolution imaging and spectroscopic techniques to determine the interatomic arrangements, interactions and transformations in model catalysts during reaction. Such methods, in combination with advances in theory and simulation, should lead to fundamental understanding of catalytic mechanisms.

- ***Theory, modeling, and simulation of catalytic pathways***. This initiative seeks to support innovative methods to produce predictive models of catalytic reactivity relevant to hydrogen energy processes. Theoretical methods have now been developed to the point that entire reaction pathways and reactivity trends can be predicted and understood. Close coupling between experimental observations and theory, modeling, and simulation will provide unprecedented capabilities to design more selective, robust, and defect-tolerant catalysts for hydrogen production, storage, and fuel cells. This approach will enable the design and control of the chemical and physical properties of the catalyst, its supporting structure, and the associated molecular processes at the nano-, meso- and macroscopic scales.

Solar-energy related research, specifically solar production of hydrogen and photocatalytic formation of fuels, is covered under a separate notice. Please see the Office of Science Financial Assistance Program Notice DE-PS02-06ER06-15, Basic Research for Solar Energy Utilization, http://www.science.doe.gov/grants/FAPN06-15.html.

Coordination and Integration with the DOE Offices of Energy Efficiency and Renewable Energy (EERE), Fossil Energy (FE), and Nuclear Energy Science and Technology (NE) Hydrogen Program

The proposal solicitation and selection processes will be coordinated with EERE, FE, and NE's program to ensure successful integration of the basic research components with the applied technology program. Specifically, input from EERE, FE and NE have been incorporated in the formulation of this announcement, and further input will be solicited in the review of preproposals. There will also be an annual Contractors' Meeting for all participants in the BES program to help coordinate and integrate research efforts related to hydrogen research. The Annual Contractors' Meeting of BES principal investigators will be coordinated with EERE, FE and NE, and will include presentations on applied research and development needs from researchers inside and outside of the Contractors' group. Travel funds to attend this meeting must be appropriately budgeted.

Posted on the Office of Science Grants and Contracts Web Site
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