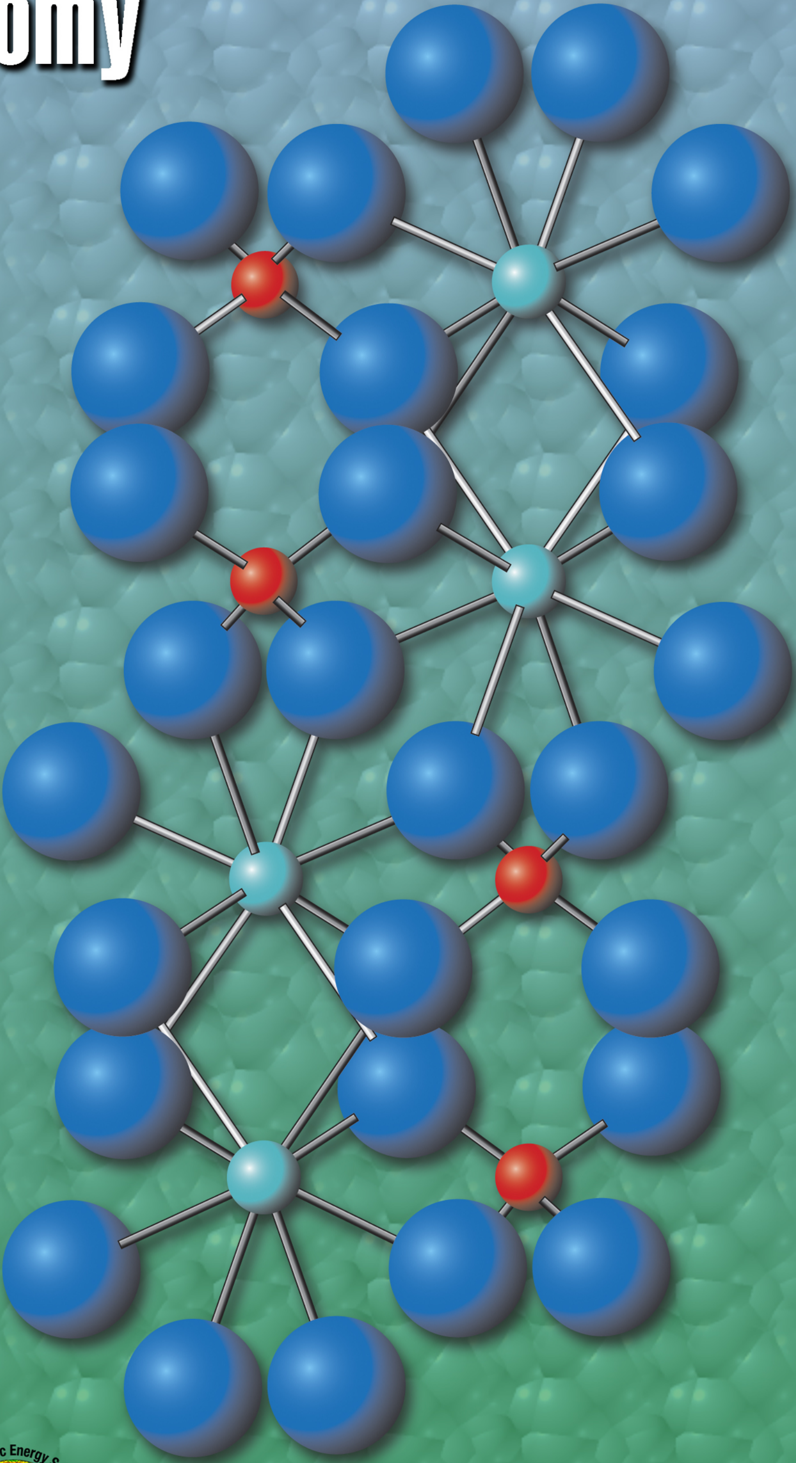
Basic Research Needs for the Hydrogen Economy



Report of the
Basic Energy
Sciences Workshop
on Hydrogen
Production,
Storage, and Use

May 13-15, 2003

Office of Science
U.S. DEPARTMENT OF ENERGY

Office of Basic Energy Sciences
Serving the Present, Shaping the Future

Second Printing, February 2004

Cover Image:

The cover shows the crystal structure of the alanate $NaAlH_4$, a new class of hydrogen storage material. Al atoms are red, Na atoms are green, and H atoms are blue. In this class of materials, hydrogen “encapsulates” Al to form a hydrogen-rich anion, AlH_4^-, whose structure resembles that of methane, CH_4. The alanate structure differs from that of the metal hydrides like MgH_2, where hydrogen is encapsulated by metal ions, and the hydrogen density is correspondingly lower. In the cover image, the diameter of the hydrogen atoms is enlarged to reflect the very high scattering cross section of neutrons for hydrogen and deuterium. This high sensitivity makes neutron scattering a natural tool for probing the interaction of hydrogen with materials. (In the report, see the sidebar, Using Neutrons to “See” Hydrogen, on page 38).

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Basic Research Needs for the Hydrogen Economy

Report on the Basic Energy Sciences Workshop
on
Hydrogen Production, Storage, and Use

Chair: Mildred Dresselhaus, Massachusetts Institute of Technology
Associate Chairs: George Crabtree, Argonne National Laboratory
Michelle Buchanan, Oak Ridge National Laboratory

Panel Chairs: Production Tom Mallouk, Pennsylvania State University
Laurie Mets, The University of Chicago

Storage Kathy Taylor, General Motors (retired)
Puru Jena, Virginia Commonwealth University

Fuel Cells Frank DiSalvo, Cornell University
Tom Zawodzinski, Case Western Reserve University

Office of Basic Energy Sciences Contact:
Harriet Kung, Basic Energy Sciences, U.S. Department of Energy

Special Assistance
Technical: Ian S. Anderson, Oak Ridge National Laboratory
Phil Britt, Oak Ridge National Laboratory
Larry Curtiss, Argonne National Laboratory
Jay Keller, Sandia National Laboratory
Romesh Kumar, Argonne National Laboratory
Wai Kwok, Argonne National Laboratory
John Taylor, Argonne National Laboratory

Administrative: Janice Allgood, Oak Ridge National Laboratory
Brenda Campbell, Oak Ridge National Laboratory
Karen Talamini, Basic Energy Sciences, U.S. Department of Energy

This report is available on the web at http://www.sc.doe.gov/bes/hydrogen.pdf.

Second Printing, February 2004

Revisions

p 9, footnote 1: In terms of energy use, 1 gigawatt (GW) of power — the output of most light-water nuclear reactors — corresponds to approximately 0.29 million tons/year (Mtons) of hydrogen. One terawatt-year (TW-yr) of energy is equivalent to 0.29 gigatons (Gtons) of hydrogen or 5.13 billion barrels (BB) of oil. The 3.3 TW use of fossil fuels in 2000 would thus correspond to approximately 0.95 Gtons of hydrogen.

p 11, paragraph 2: Natural gas resources will be sufficient for several decades to expand this capacity to support the FreedomCAR and Fuel Initiative. By 2040, it is anticipated that the use of hydrogen in fuel cell powered cars and light trucks could replace consumption of 18.3 MB per day of petroleum. Assuming that hydrogen powered vehicles have 2.5 times the energy efficiency of improved gasoline vehicles, this reduction in petroleum use would require the annual production of approximately 150 Mtons of hydrogen by 2040. If all of this hydrogen were produced by petroleum reforming, the net savings in petroleum use would be 11 MB per day (U.S. Department of Energy [DOE] 2003). The total energy used for transportation in the U.S., however, includes a substantial component of other kinds of vehicles (Figure 1a), and meeting that need poses a greater challenge to hydrogen production.

p 12 (bottom) - p13 (top): The estimated power output from 10% efficient solar cells covering 1.7% of the land area of the U.S. (an area comparable to the land devoted to the nation's highways) is 3.3 TW, equivalent to the total U.S. fossil fuel use in 2000.

The CD attached to the inside back cover contains low- and high-resolution PDFs of the report and high-resolution files of the report graphics.

PREFACE

Global energy consumption is expected to increase dramatically in the next decades, driven by rising standards of living and a growing population worldwide. The increased need for more energy will require enormous growth in energy generation capacity, more secure and diversified energy sources, and a successful strategy to tame greenhouse gas emissions. Among the various alternative energy strategies, building an energy infrastructure that uses hydrogen — the third most abundant element on the earth's surface — as the primary carrier that connects a host of energy sources to diverse end uses may enable a secure and clean energy future for the Nation.

The Basic Energy Sciences (BES) Workshop on Hydrogen Production, Storage, and Use, held May 13–15, 2003, was stimulated in part by an earlier study commissioned by the Basic Energy Sciences Advisory Committee (BESAC) to assess the basic research needs to assure a secure energy future. The charge to that study was to identify the fundamental scientific challenges of the 21st century that "… Basic Energy Sciences must consider in addressing the [DOE] missions in energy efficiency, renewable energy sources, improved use of fossil fuels, safe and publicly acceptable nuclear energy, future energy sources, science-based stockpile stewardship, and reduced environmental impact of energy production and use." The study identified 10 basic research directions in response to this charge, one of which was "Basic Research toward the Hydrogen Economy."[1]

In his State of the Union address in January 2003, President Bush unveiled the Administration's Hydrogen Fuel Initiative. The goals of this Initiative are to lessen America's dependence on imported oil and reduce greenhouse gas emissions. The President stated:

> With a new national commitment our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom, so that the first car driven by a child born today could be powered by hydrogen and [be] pollution free.

Inspired, in part, by the President's announcement, and as a follow-on to the BESAC-sponsored energy security study published in February 2003,[1] BES established the present study on Basic Research Needs for the Hydrogen Economy. The study was planned and executed in the period from March to July 2003.

Prof. Mildred Dresselhaus of the Massachusetts Institute of Technology chaired the workshop, and Drs. George Crabtree (Argonne National Laboratory) and Michelle Buchanan (Oak Ridge National Laboratory) served as the Associate Chairs. The Associate Director of DOE's Office of Science, Basic Energy Sciences, Dr. Patricia M. Dehmer, challenged the workshop chair and associate chairs to:

> Identify fundamental research needs and opportunities in hydrogen production, storage, and use, with a focus on new, emerging and scientifically challenging

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[1] "Basic Research Needs to Assure a Secure Energy Future," A Report from the Basic Energy Sciences Advisory Committee (Feb. 2003); available at http://www.sc.doe.gov/bes/besac/Basic_Research_Needs_To_Assure_A_Secure_Energy_Future_FEB2003.pdf.

> areas that have the potential to have significant impact in science and technologies. Highlighted areas will include improved and new materials and processes for hydrogen generation and storage, and for future generations of fuel cells for effective energy conversion.

Three panels were assembled to examine the charge in depth. Their topics and chairs were:

Basic Research Challenges for Hydrogen Production

Co-Chairs: Tom Mallouk (Pennsylvania State University)
Laurie Mets (The University of Chicago)

Basic Research Challenges for Hydrogen Storage

Co-Chairs: Kathy Taylor (General Motors, retired)
Puru Jena (Virginia Commonwealth University)

Basic Research Challenges for Fuel Cells and Novel Fuel Cell Materials

Co-Chairs: Frank DiSalvo (Cornell University)
Tom Zawodzinski (Case Western Reserve University)

Each panel was composed of about 15 panelists and 5 speakers with a broad spectrum of expertise from universities, DOE national laboratories, and industry. The panelists and speakers also included foreign experts, primarily from Japan and Europe. The names of the panel members and speakers, as well as the agenda for the workshop, are provided in the appendix.

Four questions were posed to the panels:

- Where are we now?
- What do we already know?
- Where do we want to be?
- What do we need to do to get there?

To initiate answers to these four questions, program officers in the DOE Office of Energy Efficiency and Renewable Energy (EERE) briefed each of the panels before the Workshop and provided a multitude of reading materials. Mark Paster briefed participants on hydrogen production and delivery, JoAnn Milliken on hydrogen storage, and Nancy Garland on fuel cell activities under the FreedomCAR and Fuel Initiative. Harriet Kung served as the BES contact throughout the study.

To set the stage for the Workshop, overview presentations were given. The panels carried out their in-depth work from the evening of the first day through the morning of the third day. The afternoon of the third day was devoted to oral reports of the findings of each panel, followed by closing remarks.

Millie Dresselhaus launched the Workshop with an overview presentation on its goals, approaches, and framework. Pat Dehmer then gave a brief overview of BES, the background for the Workshop, and her expectations. To broaden the perspective, a plenary session of five speakers reviewed the present status of knowledge and the targets, requirements, and challenges of various aspects of a hydrogen economy. Steven Chalk (DOE/EERE) addressed the Workshop on the Administration's FreedomCAR and Fuel Initiative by laying out the President's vision, as well as the plans and strategy of EERE in response to the Administration's Initiative. Specifically, a number of basic research areas in hydrogen production, storage, and fuel cells were outlined for possible collaborations between EERE and BES. The potentially most vexing problem, that of hydrogen storage, was reviewed in general by George Thomas (Sandia National Laboratories, retired). He highlighted the many scientific and technical challenges of hydrogen storage to enable hydrogen to be used as an energy carrier. Scott Jorgensen (General Motors) gave the transportation industry's perspective. He addressed hydrogen storage issues in vehicular applications with special reference to the FreedomCAR targets and goals. Jae Edmonds (Pacific Northwest National Laboratory) briefed the workshop participants on Hydrogen and Climate Change, while Jay Keller (Sandia) presented the Science of Hydrogen Safety.

Following the plenary talks, the panel chairs reviewed the current status, summarized the technology goals, and identified key fundamental scientific challenges for their panels, in the context of the background provided by the pre-workshop briefings and plenary presentations. A summary of the cross-cutting issues was presented, and Millie Dresselhaus and Pat Dehmer made closing remarks.

This Workshop Report responds to the four research challenges for the hydrogen economy outlined by Secretary of Energy Spencer Abraham in his address to the National Hydrogen Association[2]:

- Dramatically lower the cost of fuel cells for transportation,
- Develop a diversity of sources for hydrogen production at energy costs comparable to gasoline,
- Find viable methods of on-board storage of hydrogen for transportation uses, and
- Develop a safe and effective infrastructure for seamless delivery of hydrogen from production to storage to use.

The reports of the panels on hydrogen production, storage, and use in fuel cells and the high-priority research directions identified by the Workshop address these research challenges.

The focus of the Workshop was to identify knowledge gaps in the scientific and technological bases for hydrogen production, storage and use, and to identify high-priority fundamental research directions that would likely have high impact on enabling a hydrogen economy. In

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[2] Secretary of Energy Spencer Abraham, address to the National Hydrogen Association (March 5, 2003); available at http://energy.gov/engine/content.do?PUBLIC_ID=13384&BT_CODE=PR_SPEECHES&TT_CODE=PRESSRELEASE.

addition, the Workshop focused on identifying cross-cutting issues, whereby progress made in one area would significantly impact other areas, thereby accelerating the overall progress of the hydrogen initiative. The Workshop aimed primarily at defining bold new research directions to address long-term “Grand Challenges,” as well as identifying intermediate-term “show-stoppers.”

This Report is the result of a team effort by the panel chairs and Workshop chairs and is based on the presentations and discussions, as well as input from panel members. The document underwent a review process before release. Our intent is to issue a Report that accurately reflects the current scientific and technological status of a potential hydrogen economy, as well as the many great challenges that must be met for its successful implementation.

CONTENTS

EXECUTIVE SUMMARY

The coupled challenges of a doubling in the world's energy needs by the year 2050 and the increasing demands for "clean" energy sources that do not add more carbon dioxide and other pollutants to the environment have resulted in increased attention worldwide to the possibilities of a "hydrogen economy" as a long-term solution for a secure energy future. These two challenges were the focus of the Basic Energy Sciences Advisory Committee (BESAC) Subpanel Study published in February 2003,[1] in which basic research on moving toward a hydrogen economy was identified as one of the 10 general research areas of greatest urgency for a secure energy future. This Report, together with President Bush's Hydrogen Fuel Initiative, as enunciated in his 2003 State of the Union Address, led to the present more detailed study of the "Basic Research Needs for the Hydrogen Economy."

The enormous gap between our present capabilities for hydrogen production, storage, and use and those required for a competitive hydrogen economy was evident from the BESAC Energy Security Report and many other studies.[2,3] To be economically competitive with the present fossil fuel economy, the cost of fuel cells must be lowered by a factor of 10 or more and the cost of producing hydrogen must be lowered by a factor of 4. Moreover, the performance and reliability of hydrogen technology for transportation and other uses must be improved dramatically. Simple incremental advances in the present state of the art cannot bridge this gap. The only hope of narrowing the gap significantly is a comprehensive, long-range program of innovative, high-risk/high-payoff basic research that is intimately coupled to and coordinated with applied programs. The best scientists from universities and national laboratories and the best engineers and scientists from industry must work in interdisciplinary groups to find breakthrough solutions to the fundamental problems of hydrogen production, storage, and use. The objective of such a program must not be evolutionary advances but revolutionary breakthroughs in understanding and in controlling the chemical and physical interactions of hydrogen with materials.

To identify the research directions necessary to narrow the gap significantly, a Basic Energy Sciences (BES) Workshop on Basic Research Needs for the Hydrogen Economy was held in May 2003. More than 120 scientists and engineers from academia, industry, and the national laboratories attended. Participants also included research leaders from abroad and experts from the Offices of Energy Efficiency and Renewable Energy, Fossil Energy, and Nuclear Energy within the U.S. Department of Energy. A plenary session at the start of the workshop captured the present state of hydrogen research and development and the challenges posed in reaching

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[1] "Basic Research Needs to Assure a Secure Energy Future," A Report from the Basic Energy Sciences Advisory Committee (Feb. 2003); available at http://www.sc.doe.gov/bes/besac/Basic_Research_Needs_To_Assure_A_Secure_Energy_Future_FEB2003.pdf.

[2] Programmatic Publications, DOE Energy Efficiency and Renewable Energy, Hydrogen Fuel Cell Infrastructure Technology Program; available at http://www.eere.energy.gov/hydrogenandfuelcells/pubs.html#roadmaps.

[3] Secretary of Energy Spencer Abraham, address to the National Hydrogen Association (March 5, 2003); available at http://energy.gov/engine/content.do?PUBLIC_ID=13384&BT_CODE=PR_SPEECHES&TT_CODE=PRESS RELEASE.

a hydrogen economy. A closing plenary session aired the conclusions reached by the three panels, which covered detailed assessments of the most urgent research needs for hydrogen production, storage, and use in fuel cells.

The detailed findings and research directions identified by the three panels are presented in this Report. They address the four research challenges for the hydrogen economy outlined by Secretary of Energy Spencer Abraham in his address to the National Hydrogen Association[3]: (1) dramatically lower the cost of fuel cells for transportation, (2) develop a diversity of sources for hydrogen production at energy costs comparable to those of gasoline, (3) find viable methods of onboard storage of hydrogen for transportation uses, and (4) develop a safe and effective infrastructure for seamless delivery of hydrogen from production to storage to use.

The essence of this Report is captured in six cross-cutting research directions that were identified as being vital for enabling the dramatic breakthroughs to achieve lower costs, higher performance, and greater reliability that are needed for a competitive hydrogen economy:

- Catalysis
- Nanostructured Materials
- Membranes and Separations
- Characterization and Measurement Techniques
- Theory, Modeling, and Simulation
- Safety and Environmental Issues

In addition to these research directions, the panels identified biological and bio-inspired science and technology as richly promising approaches for achieving the revolutionary technical advances required for a hydrogen economy.

Many of the technical barriers to a commercially viable hydrogen economy span the functional areas of production, storage, and use. Overcoming these barriers requires an integrated approach, in which scientific breakthroughs in one area stimulate ground-breaking progress in the others. Such an integrated research approach, as outlined in this Report, emphasizes cross-cutting research directions and promotes broad interdisciplinary efforts, as well as strong coordination between the basic and applied sciences and cooperation among BES and the Offices of Energy Efficiency and Renewable Energy, Fossil Energy, and Nuclear Energy.

The need for new materials with better performance and durability is overarching, encompassing many challenges and having broad consequences on the ability to achieve a hydrogen economy. Recent dramatic advances in the controlled synthesis and self-assembly of nanostructures and composite materials and in the ability to design and tailor materials for particular applications by using modern synthetic approaches (such as combinatorial techniques) and advanced modeling and simulation approaches show promise for achieving the revolutionary progress in materials development that is needed to drive the transition to a hydrogen economy.

Nanoscience introduces a powerful and virtually untapped new dimension to the broad research directions identified in this Report. The reason is that these materials exhibit radically new properties that cannot be anticipated from their behavior in the bulk. Semiconductor nanoparticles, nanoporous solids, and organic/inorganic nanoscale composites exhibit unique properties that will enable more efficient light harvesting and product separation in solar hydrogen production. The power of nanoscale science for revolutionary breakthroughs is compellingly demonstrated by the dramatic nanoscale catalytic properties of gold. Normally an unreactive metal, gold at nanometer sizes becomes a potent catalyst comparable in activity to platinum, one of the best catalysts for hydrogen use in fuel cells. The dramatic improvements in catalytic activity that depend on nanoscale size and shape provide a powerful "knob" for the development of new, highly efficient catalysts. This Report identifies catalysis, specifically nanoscale catalysis, as being a high-payoff research direction for achieving the revolutionary breakthroughs that would lower the cost and raise the performance and reliability of technologies needed for hydrogen production, storage, and use in fuel cells.

Moreover, catalysts are central to energy conversion and will play a key role in materials synthesis and processes for the hydrogen economy. Since catalytic performance is a limiting factor for many essential elements of the hydrogen economy (including fuel cell efficiency, storage kinetics, and production capacity), the need for improved catalysts is great. A fundamental understanding of the chemical and physical processes involved in catalysis at the atomic level in any of these areas would drive collateral progress in all three, as would the development of novel and specially designed nanostructural catalytic particles and their support structures.

Biological and bio-inspired energy conversion designs have produced remarkable innovations that integrate light harvesting with charge separation and transport, charge transfer for fuel formation and stability through robust and self-healing processes into model systems. Bio-inspired supramolecular systems, particularly those that are combined with nanoscale catalysts, offer a very promising low-cost alternative to conventional, semiconductor materials for solar hydrogen production. Basic research on the fundamental molecular-level and supramolecular-level processes that underlie biological hydrogen metabolism and oxygen reduction offers an untapped high-risk/high-payoff opportunity for achieving dramatic breakthroughs that would span all phases of hydrogen production, storage, and use.

Research needed for achieving a hydrogen economy could benefit greatly from recent advances in experimental designs and instrumentation. Neutron scattering techniques that are especially sensitive to hydrogen and deuterium have enabled powerful probes of the hydride structure and hydrogen interactions with materials. The rapid development of scanning probe techniques has enabled a host of new atomic-level studies of bonding and the electronic structure of hydrogen on surfaces, of the role of nanoscale catalytic reaction chemistry, and of the often dramatic changes in materials behavior that occur at nanometer-length scales. These developments await detailed applications to the challenges of probing the interactions between hydrogen and nanostructures. Aberration-corrected transmission electron microscopes enable *in situ* atomic-level imaging of hydrogen on surfaces. The brilliance and picosecond pulse width of modern synchrotrons can resolve the time development of the surface and bulk interactions of hydrogen with materials. These sophisticated experimental approaches offer great potential for incisive studies of fundamental hydrogen behavior in materials.

Today there is a need for very high permeability and selectivity in gas separations, for high ionic conductivity with minimal fuel crossover in fuel cell membranes, and for much more durable membranes that are capable of separations at high temperatures under extreme chemical environments. Meeting these three needs calls for an intensive effort in materials synthesis, characterization, and modeling of specially designed nanostructured porous materials, robust inorganic films for high-temperature separations in corrosive environments, electronically conductive gas diffusion membranes, and low-cost, high-conductivity proton conductors.

Theory, simulation, and computation closely coupled with well-designed experiments are critical for bridging the vast gap between the present state of the art and the science and technology needed for a hydrogen economy. Recent dramatic advances in methodology (theory and algorithms) and increases in computational power have opened up new possibilities for theoretical studies of the interactions of hydrogen with materials, from catalyst design to improved kinetics of hydrogen release to controlling the hydrogen embrittlement process. All these capabilities need to be exploited in order to design new materials and associated chemical and physical processes for hydrogen production, storage, and use that have vastly improved performance and reliability, yet cost less.

The safety of a hydrogen economy is considered in this study. Safety issues are especially important because hydrogen has exceptional buoyancy, ability to migrate through very small channels, and combustion properties. Safety is not only a technological issue but is also a psychological and sociological issue. Safety concerns require the mounting of a basic research program on the transport, kinetics, and hydrodynamics of hydrogen gas in enclosed structures and on its combustion properties, as well as the development of efficient and selective sensors for detecting hydrogen leaks. In addition, a public safety education program and a suitable training program for personnel working with hydrogen will be required to ensure a safe and effective hydrogen infrastructure.

This study considers the environmental impact of a hydrogen economy, particularly with regard to assessing the degree to which a hydrogen economy would be truly environmentally friendly. In this connection, research should be carried out to address possible environmental consequences of a large potential increase in the amount of hydrogen released to the environment. High-priority research areas identified in this study focus on assessing the effect of such an increase in hydrogen on present-day geochemical, biological, and atmospheric processes.

The panels assembled to carry out this study started their investigation by focusing on the large gap between present knowledge and technology and that required by a hydrogen economy. However, as the panels carried out their work, optimism increased, as participants noted the many recent advances in chemistry, materials research, and computation that are opening up exciting new research opportunities. These opportunities have the potential to significantly narrow the knowledge/technology gap.

The hydrogen economy offers a grand vision for energy management in the future. Its benefits are legion, including an ample and sustainable supply, flexible interchange with existing energy media, a diversity of end uses to produce electricity through fuel cells or to produce heat through controlled combustion, convenient storage for load leveling, and a potentially large reduction in harmful environmental pollutants. These benefits provide compelling motivation for BES to mount a major, innovative basic research program in support of a broad effort across the applied research, development, engineering, and industrial communities to enable the use of hydrogen as the fuel of the future.

INTRODUCTION AND OVERVIEW

INTRODUCTION AND OVERVIEW

The hydrogen economy offers a compelling vision of an energy future for the nation and the world that is at once abundant, clean, flexible, and secure. We can envision the hydrogen economy as a linked network of chemical processes that *produces* hydrogen through fossil fuel reforming, biomass conversion, and electrolytic, biophotololytic, or thermochemical splitting of water; *stores* hydrogen chemically or physically; and *converts* the stored hydrogen to electrical energy and heat at the point of use. This vision of an energy stream, originating in the sun, flowing through hydrogen as a carrier to perform electrical work, and producing water as its only by-product, effectively addresses the major energy challenges of the 21st century. The biological world began developing its own hydrogen economy three billion years ago, using hydrogen, carbon, and oxygen to establish the cycle of photosynthesis and respiration that defines life on earth. The human-engineered hydrogen economy can take similar advantage of hydrogen and its chemical and physical interactions with materials to flexibly link a variety of energy sources to a multitude of energy uses.

While the hydrogen economy represents a visionary strategy for our future energy security, significant scientific and technical challenges must be overcome to achieve its implementation. The hydrogen economy spans three functional areas: production, storage, and use; each area has its special set of grand technical challenges. Recent advances in materials science, chemistry, physics, biology, computation, and nanoscience provide considerable promise for breaking through many of these current barriers. These advances underpin our vision and provide confidence that the hydrogen economy is achievable.

Before the hydrogen economy can become a reality, however, two barriers must be overcome. First, the individual technical steps that make up the hydrogen economy must be connected by an infrastructure that provides seamless transitions from production to storage to use. This infrastructure must link a range of functions and will take a variety of forms that have not yet been analyzed for their technical or commercial viability. The infrastructure needed to implement hydrogen as a primary energy carrier is equivalent to those now in place for the production and use of fossil fuels and for electricity. Hydrogen can exploit parts of these existing energy infrastructures through its production from reforming natural gas and other fossil resources and its reaction with oxygen in fuel cells to produce electricity.

The second barrier to the realization of the hydrogen economy is the demonstration in the marketplace that hydrogen as an energy carrier is economically competitive. Although hydrogen can be used for stationary generation of power, for automotive transportation, and as a battery replacement for personal electronics, it is far from being sufficiently attractive in cost, performance, and reliability to displace existing conventional technology in these areas. For hydrogen to achieve significant penetration in the marketplace, the methods of its production, storage, and use must be improved dramatically beyond their present cost, performance, and reliability levels. These gaps are enormous. For example, automotive proton exchange membrane (PEM) fuel cells can now deliver power at about $3,000/peak-kilowatt (kW) compared with $35/peak-kW for internal combustion engines. Equally large is the gap separating the performance and reliability records of fuel cell and conventional cars.

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.

The *Basic Energy Sciences Workshop on Hydrogen Production, Storage, and Use* examined the current state of the art in each of these areas, analyzed issues blocking rapid development of the hydrogen economy, and identified high-priority fundamental research directions to address these challenges. The research challenges cover every sector of the energy community, represented at the Workshop by the U.S. Department of Energy's (DOE's) Offices of Fossil Energy, Nuclear Energy, and Energy Efficiency and Renewable Energy. While each of these sectors faces its own set of challenges, very often a given research direction requires input from several sectors and returns benefit across the board. High-performance catalysts, for example, are sorely needed for reforming of fossil fuels, solar cell photolysis, and fuel cell operations. There is an extraordinary opportunity for strong cooperation among DOE's Basic Energy Sciences, Fossil Energy, Nuclear Energy, and Energy Efficiency and Renewable Energy programs in identifying basic research needs and sharing research benefits across the energy community.

Although the workshop and this Report divide the technical barriers and research needs into the three functional areas of production, storage, and fuel cells (the primary means of hydrogen use), it is clear that nearly every issue cuts across these boundaries. To present the commonality of the technical barriers and research needs across functional areas, this Report discusses cross-cutting research in each of the Panel Reports and also summarizes these research areas in a special separate section of the Report. The degree of overlap in research needs across production, storage, and fuel cells is remarkable. This strong cross-cutting feature enables global organization of research on technologies required for a hydrogen economy by research thrust, such as new materials, catalysts, or membranes, which address technical challenges in more than one functional area.

The high-priority research directions reflect the interdisciplinary needs of the hydrogen economy. Its technical barriers do not respect the traditional boundaries among chemistry, physics, materials, and engineering sciences. Rather, they span disciplines and require integrated response teams conversant with many fields. This matches a growing trend in science — to reach across traditional frontiers to address fundamental problems from several points of view. Basic research on the hydrogen economy will benefit from and reinforce this trend.

Nearly all the proposed research directions recognize an urgent need to exploit the power of modern theory and modeling. Dramatic advances in computational power, parallel processing, and numerical simulation open many previously intractable aspects of the fundamental atomic and molecular processes occurring at the interface of hydrogen with materials to theoretical analysis. Theory and modeling of these interactions have wide impacts on the problems of the hydrogen economy, from catalysis to hydrogen storage, fuel cell operation, and hydrogen-induced embrittlement of metals. Rapid advances can be made by closely coupling forefront computational methods to laboratory experiments, enabling each to guide, interpret, and stimulate the daily progress of the other.

The research needs of the hydrogen economy resonate with compelling development in another major field: nanoscale science and technology. The research needs of the hydrogen economy are quintessentially “nano.” Catalysis, hydrogen storage materials, and electrode assemblies for fuel cells all depend on nanoscale processes and architectures to achieve high performance. The advances in nanoscale materials, nanoscale assembly techniques, and nanoscale instrumentation, such as scanning probes and *in situ* aberration-corrected electron microscopy, are perfectly matched for research that will provide the breakthroughs required for a hydrogen economy. The technical barriers to the hydrogen economy all hinge on understanding and controlling the atomic- and molecular-level processes at the interface of hydrogen with materials. These processes are shaped at the nano scale, and nanoscale research has the potential to provide revolutionary breakthroughs that will make the hydrogen economy possible.

Safety and the environment are key issues affecting the viability of the hydrogen economy. Greater exposure of the public to hydrogen in everyday life requires a thorough assessment of the safety hazards for each element of the hydrogen economy and concomitant education and training in preventive and acute safety procedures. While the primary beneficial effects of the hydrogen economy on the environment are clear, we must be mindful of the possible indirect effects of additional anthropogenic hydrogen emissions on the complex dynamics of the environment. Safety and the environment are social as well as technical issues that require careful attention if the hydrogen economy is to be successful. The Workshop recognized the great importance of these two areas and identified basic research directions in safety and the environment, concurrent with fundamental research in the areas of hydrogen production, storage, and use, which are critical to achieving a hydrogen economy.

Implementing the hydrogen economy represents perhaps one of the most fundamental and wide-ranging influences on the social fabric of our times. It will lead to a reorganization of our energy culture that compares to the deployment of the fossil fuel economy in the late 19th and early 20th centuries, and the development of the electric power generation and distribution system in the mid and late 20th century. The benefits of the hydrogen economy to society are many and compelling. To realize these benefits, a strong program of innovative basic research aimed at making revolutionary advances in lowering the cost and raising the performance and reliability of the hydrogen economy is essential.

REPORTS OF THE PANELS ON BASIC RESEARCH NEEDS FOR THE HYDROGEN ECONOMY

BASIC RESEARCH CHALLENGES FOR HYDROGEN PRODUCTION

CURRENT STATUS

The Need for Hydrogen Production

Current U.S. energy systems are not sustainable. They primarily exploit limited resources and will soon accumulate unacceptable environmental impacts. Carbon dioxide (CO_2) from energy production now contributes 82% (weighted by global warming potential) of the greenhouse gas emissions in the U.S. Because the effect of CO_2 release is cumulative, the need to find alternative means of energy production is becoming increasingly compelling. Recent estimates call for the generation of more than 30% of primary power from non-carbogenic sources by 2020 in order to stabilize the global mean temperature increase due to CO_2-induced warming at 2°C (Caldeira et al. 2003). Although hydrogen is not an energy resource itself (because no natural hydrogen reserves exist), it has the potential to serve as an energy carrier at the core of a carbon-neutral system of energy production and use. Cost-effective production of hydrogen in sufficient quantities to meet growing energy demands, however, is a challenge that cannot be resolved without intensive effort in both basic research and engineering. The U.S. requires an enormous amount of energy, making this a daunting challenge. Because of the short timeline for development of large-scale hydrogen production capacity, the need to address the underlying basic science questions is immediate.

The need to develop alternative energy technology is also driven by the limited petroleum reserves in the U.S. At this time, petroleum is the major contributor to energy production. Fossil fuels currently provide 85% of the nation's energy supply, with oil accounting for 39% of that total; natural gas, 24%; and coal, 22%. By 2020, the use of fossil fuels, which totaled approximately 3.3 terawatts (TW) in 2000, is projected to increase by 32%, maintaining roughly the same proportions of oil, natural gas, and coal.[1] Transportation consumes about two-thirds of the nation's oil, and this figure is expected to remain essentially constant through 2020. In 2000, the U.S. imported 52% (net) of its oil supply; by 2020, this percentage is expected to increase to 65%. Oil imports accounted for about one-fourth of the U.S. trade deficit in goods in 2000. Clearly, as long as oil continues to be the most significant component of U.S. energy use (especially for transportation, as illustrated in Figure 1a), it will be a large contributor to trade deficits, to the cumulative effects of CO_2 emissions (Figure 1b), and possibly to geopolitical instability.

Carbon-neutral hydrogen production technologies (including technologies that use and reuse carbon but are not net producers of CO_2) could exploit many resources in sufficient supply to meet the needs of a hydrogen economy. These resources include sun-energized resources (solar, biomass, wind) and nuclear energy. Geothermal and geochemical resources could also play a role. In each case, development is needed. Substantial improvements in efficiency and reductions

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[1] In terms of energy use, 1 gigawatt (GW) of power — the output of most light-water nuclear reactors — corresponds to approximately 0.29 million tons/year (Mtons) of hydrogen. One terawatt-year (TW-yr) of energy is equivalent to 0.29 gigatons (Gtons) of hydrogen or 5.13 billion barrels (BB) of oil. The 3.3 TW use of fossil fuels in 2000 would thus correspond to approximately 0.95 Gtons of hydrogen.

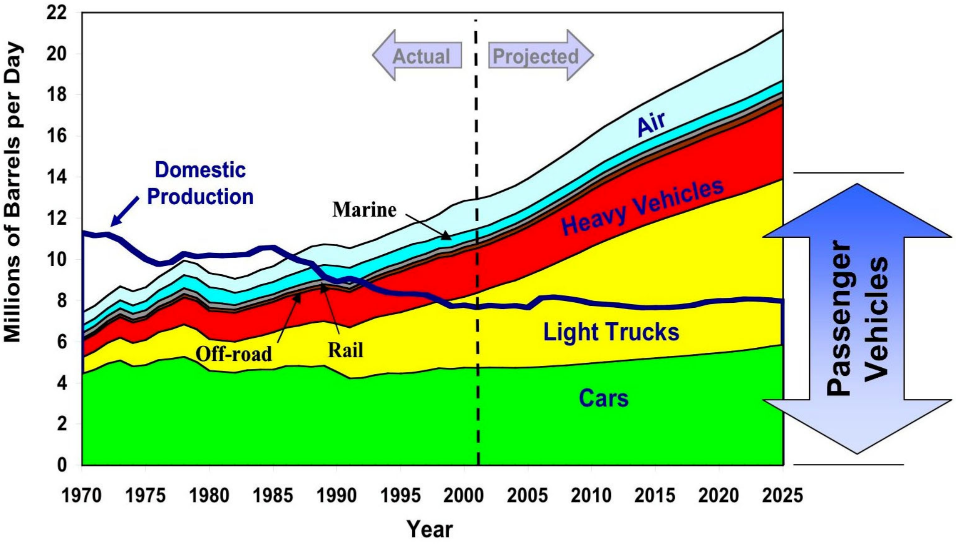


Figure 1a U.S. Consumption and Production of Petroleum Products Trend in Opposite Directions (Transportation needs are a major determinant of consumption [Source: Energy Information Administration 2003].)

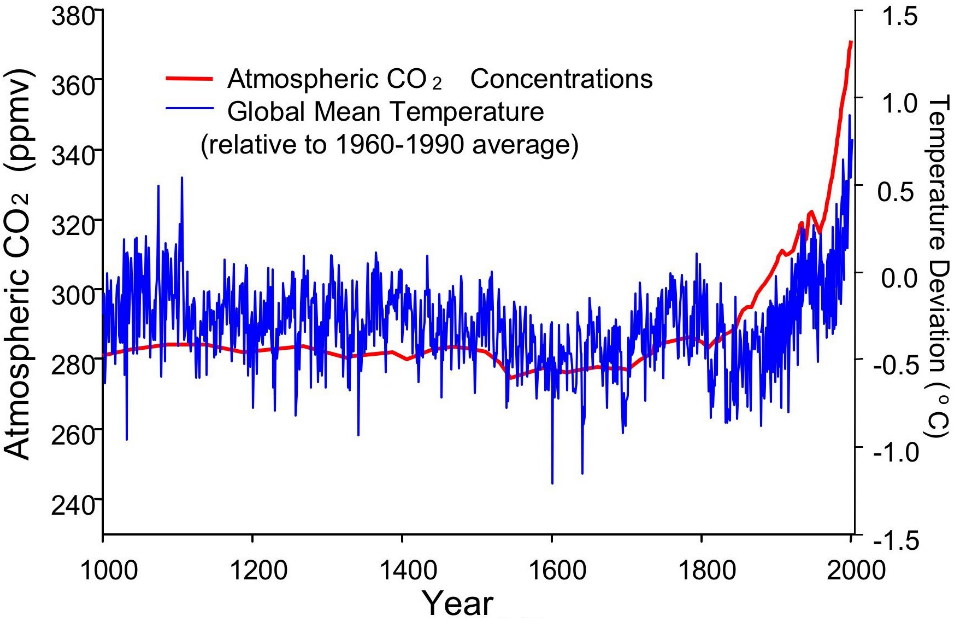


Figure 1b Increased CO_2 Emissions Causing a Rise in Atmospheric CO_2 Associated with a Rise in Global Temperature (Sources: CO_2 data from Ethridge et al. 2001, Keeling and Whorf 2002; temperature data from Jones et al. 1998, Peterson and Vose 1997)

in both capital and operational costs are needed to enable hydrogen production to meet the nation's future energy needs. Each technology faces a different set of technically diverse scientific challenges, although some of these challenges (improved chemical processes, catalysis, materials, and separations) are common to all.

Hydrogen Production from Fossil Fuels

Hydrogen is currently produced on an industrial scale (9 Mtons/yr in the U.S.) through steam reforming of natural gas. At present, most of the hydrogen made from fossil fuels is used in the fertilizer, petroleum, and chemical industries. Natural gas resources will be sufficient for several decades to expand this capacity to support the FreedomCAR and Fuel Initiative. By 2040, it is anticipated that the use of hydrogen in fuel cell powered cars and light trucks could replace consumption of 18.3 MB per day of petroleum. Assuming that hydrogen powered vehicles have 2.5 times the energy efficiency of improved gasoline vehicles, this reduction in petroleum use would require the annual production of approximately 150 Mtons of hydrogen by 2040. If all of this hydrogen were produced by petroleum reforming, the net savings in petroleum use would be 11 MB per day (U.S. Department of Energy [DOE] 2003). The total energy used for transportation in the U.S., however, includes a substantial component of other kinds of vehicles (Figure 1a), and meeting that need poses a greater challenge to hydrogen production.

Other fixed carbon reserves, such as coal or biomass feedstocks, could be used to generate hydrogen via reforming processes. Relative to natural gas, however, these resources generate approximately twice as much CO_2 per amount of hydrogen produced. This factor puts additional pressure on the development and economics of carbon sequestration (storing the CO_2 produced, rather than releasing it into the atmosphere). These feedstocks also contain variable amounts of water, sulfur, nitrogen, and nonvolatile minerals that substantially complicate reforming process engineering. Nevertheless, if an economic and safe method for CO_2 sequestration is developed, economic factors (the general availability and relatively low cost of coal) may enable coal to play a significant mid-term role in hydrogen generation. Reliance on coal as a sole source of energy for generating hydrogen for FreedomCAR transportation needs would require doubling of current domestic coal production and consumption. Two technically effective strategies for hydrogen production from coal or biomass are under development: (1) reforming under partial oxidation and (2) a combined-cycle method that uses $Ca(OH)_2$ to force the reforming reaction by adsorbing CO_2 as it is produced (Lin et al. 2002).

Although the technology is available for generating hydrogen in quantity via reforming of natural gas or possibly other carbon reserves, the hydrogen produced is not of sufficient purity for direct use in the low-temperature (<130°C) fuel cells under development for transportation applications. The last stage in current reforming processes, the water-gas shift reaction, leaves enough carbon monoxide (CO) in the product stream to poison the fuel cell anode. Current methods for removing this residual CO include pressure-swing adsorption, preferential oxidation, or catalytic methanation, all of which add cost and complexity to the fuel processing system. Basic research can supply alternative solutions to this problem, which could come in the form of more active catalysts for the low-temperature water-gas shift reaction, better gas stream separation processes and membranes, or CO-tolerant catalysts at the fuel cell anode [see section on fuel cells].

WATER ELECTROLYSIS: PROTON REDUCTION AND WATER OXIDATION

Electrolysis is a process for breaking water (H_2O) into its constituent elements (hydrogen, H_2, and oxygen, O_2) by supplying electrical energy. The advantage of this process is that it supplies a very clean hydrogen fuel that is free from carbon and sulfur impurities. The disadvantage is that the process is expensive, relative to steam reforming of natural gas, because of the cost of the electrical energy needed to drive the process.

Chemically, the electrolysis of water is simply the reverse of the electricity-generating reaction that occurs in a fuel cell. Physically, an electrolyzer is designed very much like a fuel cell, with two electrodes immersed in a common aqueous electrolyte solution. The reaction can be thought of as occurring in two “half-cells” separated by a gas-impermeable electrolyte membrane (the figure provides a schematic drawing of the electrolysis process).

In the cathode half-cell, hydrogen ions (protons) are reduced to hydrogen:

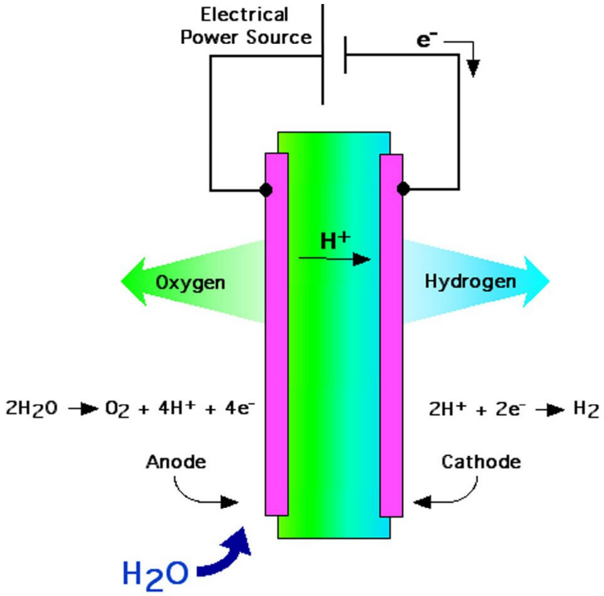
$2\ H^+(aq) + 2e^- = H_2(g)$.

On the anode side, water is oxidized to oxygen and protons:

$2\ H_2O(liq) = O_2(g) + 4\ H^+(aq) + 4e^-$.

By multiplying the first half-reaction by two and adding the two half-reactions together, we obtain the overall reaction:

$2\ H_2O(liq) = O_2(g) + 2\ H_2(g)$.



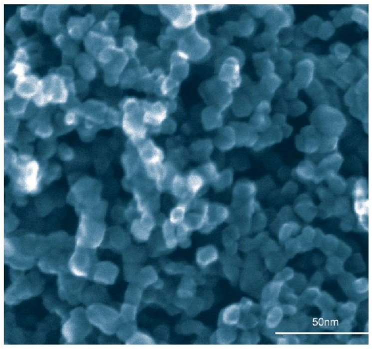
Because water is a very stable molecule relative to oxygen and hydrogen, this reaction requires input of energy. In principle, the reaction can be driven by an applied voltage of 1.23 V, which translates to a free energy input of 237 kJ/mole of hydrogen. In practice, somewhat larger driving voltages (1.55–1.65 V) are used because of slow kinetics in the two half-cells. The energy efficiency of the cell can be calculated simply as the theoretical voltage (1.23 V) divided by the applied voltage; for example, a cell operating at 1.60 V would have an efficiency of $1.23/1.60 \times 100\% = 77\%$. The process of oxidizing water in the oxygen-evolving half-cell is mechanistically and kinetically more complex than the hydrogen-evolving process because it requires four electrons and proceeds through a series of distinct oxidation intermediates. In an uncatalyzed reaction, some of these intermediate electron transfer steps require more energy than others, and some are slower than others. As a consequence, extra voltage is needed to drive the cell, primarily at the oxygen-evolving electrode, and efficiency is reduced. An ideal catalyst for water oxidation would equalize the energy required at each step in addition to equalizing the rates of each electron transfer, thus maximizing efficiency. The water oxidation complex that supports oxygen evolution in photosynthesis is one catalyst that comes close to meeting this ideal and provides a tantalizing model for building catalysts for electrolyzer anodes and fuel cell cathodes.

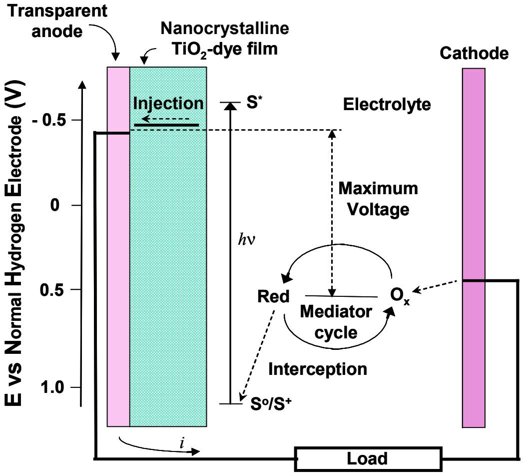
Solar Hydrogen

Solar hydrogen, which is produced by driving water electrolysis with solar cells, by direct photocatalytic water splitting into hydrogen and oxygen, by photobiological water splitting, or by solar thermal processes, represents a highly desirable, clean, and abundant source of hydrogen. Hydrogen made this way is suitable for use, without further purification, in low-temperature fuel cells and even in alkaline fuel cells, which are more efficient but more carbon-intolerant. While solar-to-electric energy conversion is an established technology, current solar cells are either too expensive or too inefficient for widespread application. However, the potential capacity for solar hydrogen is quite large. The estimated power output from 10% efficient solar cells covering 1.7% of the land area of the U.S. (an area comparable to the land devoted to the nation’s

DYE-SENSITIZED SOLAR CELLS

A promising new technology in solar energy conversion is the dye-sensitized photoelectrochemical cell, or Grätzel cell (Grätzel 2001). This cell consists of a highly porous, thin layer (~15 µm) of titanium dioxide nanocrystal aggregates (~20 nm in diameter; see scanning electron micrograph), the same material used as the pigment in white paint. The nanocrystals are coated with a dye and a liquid electrolyte that contains reactive iodide ions or other diffusible oxidation/reduction mediator, sandwiched between two conducting glass or plastic plates sealed together (schematic drawing shows the mediator cycle and electron injection). When excited by light (S_0 to S^* transition in the figure), the dye becomes oxidized (S^+ state), injecting electrons into the titanium dioxide. In the figure, oxidation/reduction potentials of the various reactants are depicted relative to the normal hydrogen electrode (left axis). The titanium dioxide layer then transmits electrons to the conducting glass electrode, which is connected to an external circuit. The reduced reduction/oxidation mediator transfers electrons to re-reduce the dye, and the oxidized form diffuses away in the electrolyte. The return path for the electrons is through the other electrode to the oxidized mediator in the solution, which completes the cycle by diffusing back to the film layer.





The energy available from the cell depends on the difference between the oxidation/reduction potential of the mediator and that of the dye/nanocrystal interface. The film surface area is huge — about 2,000 m^2/m^2 of cell surface — because of the small size of the titanium dioxide particles (the surface-to-volume ratio is inversely proportional to the particle size). Thus, the probability of light absorption is high even though the dye thickness is only a single molecular layer. While bare titanium dioxide nanocrystals can absorb photons and eject electrons to an electrode, they absorb only in the ultraviolet region of the spectrum, which is a small fraction of the solar spectrum. This is a useful behavior in such products as sunscreen and self-cleaning window coatings, but it makes the particles less than 1% efficient in converting total solar energy to electrical or chemical form. The adsorption of organic dyes onto the surfaces of the particles extends their absorption into the visible region, increasing solar conversion efficiency. It has recently been found that carbon atoms doped into the titanium dioxide nanocrystals in the place of some of the oxygen atoms can provide a similar effect (Kahn et al. 2002). The power conversion efficiency of the Grätzel cell is currently about 10%, and the cells are stable in sunlight over a period of years.

The Grätzel cell is fabricated from inexpensive materials. If its efficiency could be improved and manufacturing costs lowered further, it would be a strong candidate for solar hydrogen production via water electrolysis. Problems with the Grätzel cell that still require innovative solutions include reducing energy losses in the iodide/iodine redox cycle and at the electrode interfaces, extending the spectral response farther into the red, and reducing costs in the production of the transparent conductor-coated glass.

highways) is 3.3 TW, equivalent to the total U.S. fossil fuel use in 2000. To place this capacity in perspective, 3,300 new 1-GW nuclear power plants would need to be built — roughly 1 for every 10 miles of coastline or major waterway — to supply the same 3.3 TW of power. This capacity is more than 30 times greater than that provided by the 103 nuclear plants now in the U.S. Such growth in nuclear power is not feasible today because of the severe constraints in cost, nuclear fuel supply, site availability, safety, public acceptance, and waste disposal. Nevertheless, thermochemical cycles that use the heat from nuclear reactors to produce hydrogen by water splitting are being developed and could, in principle, play a role in the hydrogen economy on a smaller scale (see below).

The most efficient and also the most costly sources of solar electricity for water electrolysis are solid-state photovoltaic (PV) devices. Commercially available photovoltaics include single-crystal silicon and GaAs, amorphous silicon, and polycrystalline thin film materials, such as CdTe and $CuIn_{1-x}Ga_xSe_2$, which have solar-to-electric power conversion efficiencies ranging between 12% and 25% under full sunlight. Tandem photovoltaics, which are two-bandgap devices (for example, GaAs and $GaInP_2$) utilizing a greater fraction of the solar spectrum, are more efficient, but also more expensive, and are envisioned for special use in solar concentrator systems and space applications.

Current water electrolysis systems (see sidebar on water electrolysis) that produce hydrogen gas operate at about 75% energy efficiency (free energy content of hydrogen relative to input electrical energy), giving an integrated efficiency of hydrogen production from solar energy via PV/electrolysis of ~15%. This sets an efficiency standard for other technologies to meet using less costly and more abundant resources for materials. Lower-cost alternatives include photoelectrochemical cells based on polycrystalline and nanocrystalline semiconductors, dye-sensitized titanium dioxide (see sidebar on dye-sensitized solar cells), the Texas Instruments silicon microsphere system, and thin film devices based on organic liquid crystals and/or polymers (Grätzel 2001). The lower efficiency of hydrogen generation in each case arises from energy losses in electrolysis, where the most significant problem is catalysis of the water oxidation reaction. The water oxidation reaction is particularly kinetically demanding because it is a four-electron, four-proton process.

The efficiencies of different kinds of PV devices have followed similar time-efficiency development curves, which began in the 1950s for single crystal silicon; in the 1970s for amorphous silicon, CdTe, and copper-indium-diselenide and related thin film devices (CIS/CGIS); and in the 1990s for dye-sensitized nanoparticle TiO_2, organic, and photocatalytic systems. This trend is illustrated in Figure 2 (Kazmerski 2001). The newest of these systems are the least developed and offer the greatest opportunities for contributions from basic research.

Hydrogen from Biological and Biomimetic Systems

Solar energy capture based on photosynthesis can follow one of two routes: (1) storage of energy by CO_2 fixation (biomass) followed by hydrogen production via reforming or fermentation, or (2) direct water splitting to hydrogen and oxygen (e.g., using blue-green or green algae [biophotolysis]). Biological energy conversion systems use readily available materials for conversion and catalysis, and these systems are also self-maintaining. For these reasons, they might be able to compete on a cost basis with other hydrogen production systems. Biomass is currently a substantial component of global energy consumption. Of the 13 TW of global energy used in 1998, approximately 1.2 TW can be attributed to biomass. This amount, however, represents unsustainably burned, as opposed to renewably farmed, biomass. The solar-to-chemical energy conversion efficiency of current biomass crops (switchgrass and poplar) is in the range of 0.4% of total solar irradiance, and further losses would be incurred in the conversion to hydrogen. It is plausible that genetic research could improve this yield two- to three-fold, but fundamental limitations would prevent it from rising above the range of a few percent, thereby requiring use of large arable land areas to contribute significantly to the hydrogen economy. In

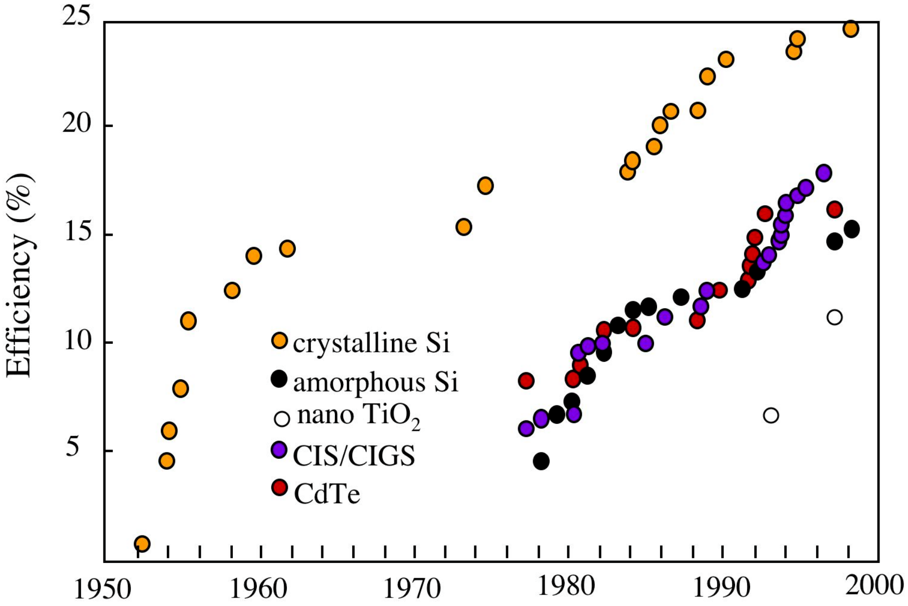


Figure 2 Power Conversion Efficiency Trends over Time for Different Kinds of Photovoltaic and Photoelectrochemical Devices (CIS = cadmium-indium-selenide; CIGS = cadmium-indium-gallium-selenide) (Source: Kazmerski 2001)

contrast, biophotolysis in natural populations of algae currently has peak yields of hydrogen in the range of 5% solar conversion efficiency, although this is only at low light intensities, about 10% of typical solar intensity in the U.S.; lower efficiency is found at higher light levels. Thus, research is needed to make these yields sustainable and to find new organisms or engineer the photosystems of existing organisms that will give similar efficiencies in full sun.

Globally, biological processes produce at a minimum of more than 250 Mtons/yr of hydrogen (see sidebar describing hydrogen in the biosphere).[2] Most of this hydrogen arises from anaerobic fermentation of carbon previously fixed by photosynthesis. Six to 17 Mtons/yr of hydrogen is produced as a by-product of terrestrial biological nitrogen fixation. This biological hydrogen is completely used as an energy carrier that fuels the growth of organisms and the maintenance of essential life processes. Much of it is consumed in CO_2 or organic acid reduction by methanogenic archaebacteria that give off methane as a by-product. On the oceanic continental shelves and in permafrost regions, this methane has accumulated in the form of extensive methane hydrate deposits, the extent of which exceeds all known petroleum, coal, and natural gas deposits. In other locales, methane is released to the environment, and a portion enters the

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[2] Assumes biogenic methane entering the atmosphere (380 Mtons/yr [Etiope and Klusman 2002]) arises 1/3 from methanogens using 4 moles of biogenic hydrogen per mole of methane produced and 2/3 from those utilizing 2 moles H_2 per mole CH_4. Ten percent of this methane arises from rice paddies, and the bulk of the remainder is from plant transpiration of methane from anaerobic sediments in fresh water and coastal wetlands. In open water, which covers much more anaerobic sediment, the methane released never reaches the atmosphere. Sulfate-reducing bacteria consume an amount of biogenic hydrogen similar to that consumed in methane biosynthesis on an annual basis. The total flux of hydrogen in the biosphere has not been directly estimated, but it is likely to exceed this minimum by at least an order of magnitude and possibly by two orders of magnitude.

atmosphere. If methane hydrates could be used, either by reforming them to make hydrogen or using them directly in fuel cells that generate electricity, they could have a large impact on the global energy economy. However, utilization of methane hydrates presents daunting technical challenges because of the depth at which they are found, because of their dispersion as ice-like crystals in ocean sediments, and because of their decomposition (to methane gas and liquid water) at ordinary pressures.

In some specific cases, details of the biological processes linked to hydrogen metabolism and of the enzymes involved as essential catalysts have been investigated and are reasonably well known. However, efforts to understand the variety of organisms and the diversity of biochemical mechanisms that participate in this extensive biological hydrogen energy economy are still at an early stage. The emergence of highly capable tools for genomic analysis of microorganisms and for dissecting the interlocking metabolic functions of microbial communities presents an opportunity for extremely rapid progress in this promising area of research (Reysenbach and Shock 2002). It is possible that exploiting and mimicking components of these natural hydrogen-producing systems, once they are better understood, will enable key improvements in efficiency and reduction in the cost of solar hydrogen production.

Thermal Energy for Hydrogen Production

Production of hydrogen from thermal energy sources is a conventional technology via the multistep route of thermal energy to electricity, and electricity to hydrogen and oxygen by electrolysis of water. The heat can be delivered from a conventional fossil energy source, a nuclear reactor, or a solar concentrator/receiver. The net efficiency (heat energy to hydrogen) is about 26%. Current hydrogen production costs, not including storage and delivery costs or the long-term costs of nuclear waste management, are \$4–\$5/kg (nuclear thermal) and \$15/kg (solar thermal). Experience with solar thermal generators is not as extensive as with nuclear plants; hence, costs for solar thermal systems are expected to drop more quickly as development proceeds.

In principle, hydrogen can also be produced by using thermal energy from solar concentrators or from nuclear reactors to drive thermochemical water-splitting cycles, the overall output of which is water splitting to hydrogen and oxygen without intervening electricity generation. These cycles need temperatures of 500°C or more, well within the range of solar concentrators but higher than can be achieved by today's light-water reactors. These temperatures are also within the range of present-day, gas-cooled reactors and designs for future nuclear power plants (Marcus and Levin 2002). The reactor operating temperature is a key factor because higher temperatures enable faster chemical reactions and higher efficiencies, at the expense of a harsh thermal and chemical materials environment. Because of the technical challenges that they raise, high-temperature reactors will also take longer to reach commercialization. High-temperature solar collector/receivers have been demonstrated and could potentially drive very efficient cycles. For example, the National Renewable Energy Laboratory has demonstrated 51% thermal collection efficiency in a 2,000°C process fluid. The potential advantages of higher operating temperatures, siting in desert locations, and lower capital cost of solar concentrators must be offset against the lower duty cycle (8 h/day) of solar power relative to nuclear reactor power.

HYDROGEN IN THE BIOSPHERE

Hydrogen gas (H_2) generated by high-temperature and radiolytic chemical processes deep in the earth's crust and vented into the oceans has been an important source of energy supporting the growth of living organisms since the origin of life some 4 billion years ago. The emergence of oxygenic photosynthesis ~3 billion years ago enabled cyanobacteria to use solar energy for the splitting of water to hydrogen and oxygen. As a consequence, biological sources of hydrogen became predominant, expanding annual global production of hydrogen by an estimated two to three orders of magnitude to the range of 250–1200 Mtons/yr of H_2 (Hoehler 2001).

In the modern biosphere, hydrogen is a ubiquitous biological energy carrier, primarily between microbes, in a wide variety of habitats — particularly in anaerobic environments like the sediments just below the soil surface. Hydrogen is produced as a product of anaerobic cellulose degradation by bacteria in termite guts and cattle rumen and in fresh water and marine sediments. Hydrogen is generated as a by-product of nitrogen fixation by cyanobacteria in rice paddies and algal mats and by nitrogen-fixing bacteria in nodules growing on the roots of peas, soybeans, and other legumes. Methanogenic archaebacteria use the hydrogen produced by anaerobic fermentation and as a by-product of nitrogen fixation by cyanobacteria to generate methane, which is transpired by the plants into the atmosphere.

Hydrogen and carbon monoxide are products of microbial methane oxidation. A number of eukaryotic algae even generate hydrogen via photosynthesis when they find themselves in anaerobic environments. Other organisms, necessarily closely associated with the producers in microbial consortia, completely consume this biogenic hydrogen within 0.1-5 sec of its production and before it can diffuse more than 0.1 mm away or accumulate to concentrations more than a few parts per million. Because of this tight cycling, very little biogenic hydrogen escapes to the abiotic environment or to the atmosphere.

These consumers are known to use hydrogen energy to support a diverse array of metabolic activities, from methane production to nitrate and sulfate reduction. About 125 Mtons of H_2 is consumed per year in the production of the fraction of biogenic methane that escapes into the atmosphere (much more methane is produced but is consumed by other bacteria before it reaches the atmosphere), and at least another 125 Mtons/yr supports sulfate reduction in the upper reaches of anoxic marine sediments. Members of this biological hydrogen energy economy inhabit all extremes of living environments, from hyperthermic (113°C) deep ocean vents to frozen tundra soils to ancient aquifers and salt deposits deep in the earth. The photochemical water oxidation reaction center that catalyzes oxygen evolution from water — photosystem II — has higher quantum efficiency than any artificial photochemical or photoelectrolytic system yet devised by humankind. One type of the known hydrogenase enzymes that catalyze the reduction of protons from water to produce hydrogen (or the reverse), the iron-only hydrogenases, has catalytic rates of more than 25,000 turnovers/second, among the highest of any known enzyme.

The biosphere uses a small fraction of total available solar energy (<0.5% of net primary photosynthetic productivity) to produce hydrogen on a scale and at a rate compatible with human energy needs. Both hydrogen production and consumption use highly selective and efficient catalysts constructed of materials readily available in the environment that operate in aqueous environments and at temperatures compatible with life. An understanding of the catalytic mechanisms and integrated energy processes of these biological systems promises insights that could revolutionize our approaches to developing human energy economies. In the past, culturing and studying these organisms has been challenging, both because of the extremes of their habitats and the complexities of their associations and interdependencies. The experimental tools provided by modern methods of genomic analysis and by *in situ* metabolic analysis on the scale of bacterial cells have finally provided an exciting opportunity for developing the necessary understanding.

Nuclear reactors, such as the helium gas-cooled reactor which has demonstrated ~900°C temperatures, have not yet been commercialized, giving them a long development horizon. Lower-temperature, gas-cooled reactors may offer nearer-term implementation of hydrogen production and a materials-friendly environment at the expense of lower production rates. The advanced high-temperature reactor concept, developed in the Generation IV reactor initiative, is proposed to match hydrogen production requirements via thermal cycles with maximum temperatures of 700–950°C. It is a more advanced reactor that would use a low-pressure molten salt coolant rather than high-pressure helium as a coolant. Further out in time, fusion energy might become an important source of high-temperature heat for driving thermochemical hydrogen production.

A related technology is the electrolysis of water assisted by heat from a nuclear reactor. By performing electrolysis at elevated temperatures using heat from a high-temperature reactor, the overall efficiency of the process can be increased relative to low-temperature electrolysis. In both cases, the energy source is noncarbogenic. A third (carbogenic) way in which nuclear energy can be used to augment hydrogen production is in nuclear-assisted steam reforming of natural gas. Here, nuclear energy replaces fossil fuel combustion as the means of driving the endothermic steam reforming reaction. Thus, less natural gas would be used to produce the same amount of hydrogen.

More than 100 different thermochemical cycles have been proposed for performing the overall water splitting reaction in high-temperature reactors (Brown et al. 2002). At present, the most promising high-temperature cycles appear to be the calcium bromide-iron oxide cycle, the sulfuric acid-hydrogen iodide (sulfur-iodine or S-I) cycle, and the Westinghouse cycle. Also, an important lower-temperature cycle, (copper-chloride [Cu-Cl]), can produce hydrogen using heat from current and near-future reactors. The Cu-Cl cycle, originally proposed in the 1970s, has recently been proven in the laboratory, and several commercially appealing variants are being evaluated. This cycle has an estimated efficiency of ~40% at its envisioned operating temperature of 550°C, not including cogeneration of electricity. A key challenge for the Cu-Cl cycle is effective catalysis of the low-temperature reactions. The calcium bromide cycle has four fixed-bed reactors, each of which performs one step of the cycle at temperatures around 760°C. Overall efficiencies of 45−49% (including cogeneration of electricity from waste heat) are projected. In this process, hydrogen and oxygen are produced at subatmospheric pressures and removed via membranes; hence, there is a major challenge for membrane technology and for compression/storage of hydrogen. In the S-I cycle, which uses all fluid reagents, a higher temperature (825–900°C) is used for the oxygen-evolving reaction, and higher efficiencies (~50% and ideally 60% with cogeneration of electricity) are possible. The individual reactions in the S-I cycle have been demonstrated, although not in a continuous process, nor at the temperatures envisioned for implementation of the technology. This cycle is being actively researched in several laboratories, including the Japan Atomic Energy Research Institute (Japan), Commisariat à l'Energie Atomique (CEA) (France), and Department of Energy laboratories (Sandia National Laboratories, Idaho National Engineering and Environmental Laboratory) and General Atomics in the U.S. Among the key challenges with this approach is the verification of durable high-temperature, chemically inert materials for fabrication of the chemical reactors needed to withstand the thermochemical cycle over economically useful lifetimes (Trester and Staley 1981). The Westinghouse cycle is a variant of the S-I process where a low-temperature, low-voltage electrolysis step (a fraction of that required for water electrolysis) replaces several chemical reactions in the S-I process.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS IN HYDROGEN PRODUCTION

Fossil Fuels

Fundamental advances in catalysis, membranes, and gas separation could enable more efficient, lower-cost fossil hydrogen technologies. Processes that combine hydrogen generation and separation in a single reactor (for example, membrane reactors for methane steam reforming) could improve conversion efficiency and thus reduce emissions. Very pure (99.999%) hydrogen is needed for some applications, in particular for current-generation proton exchange membrane fuel cells (PEMFCs); therefore, hydrogen purification technologies need further development. Advances in techniques for the removal of CO in particular, including improved gas separations and improved catalysis for the low-temperature water-gas shift reaction, are needed for both on-site reformers and centralized hydrogen production facilities. These are critical early research targets because they would affect the design of reforming plants built to meet the projected increase in hydrogen demand. Coal is also a potential source of energy for hydrogen production but poses greater challenges for obtaining high-purity hydrogen. Catalysts that resist poisoning by contaminants, which are more abundant in coal, must be developed for the water-gas shift reaction. Materials must be developed that are durable under the more acidic reforming conditions of the partial oxidation reaction that is the first reaction step in current-design, coal-based hydrogen production plants.

Because both natural gas and coal reforming processes generate CO_2 (coal generates approximately twice as much per unit H_2), their value in meeting the fundamental goals of a hydrogen economy depends on developing safe, effective, and economical methods for CO_2 sequestration. Deep ocean injection, injection into depleted oil/gas wells and saline reservoirs, and injection into unmineable coal seams are three potential sequestration technologies (Kim and Edmonds 2000).

Understanding the feasibility and safety of carbon capture and sequestration is key for the long-term use of fossil hydrogen with near-zero CO_2 emissions. This involves basic understanding of the geological processes (geoscience, flows in porous media and interactions, as well as transport of CO_2 in aqueous environments) that may be involved in CO_2 storage and release. Living organisms in deep ocean locales take up CO_2, but basic understanding of the carbon flows in those ecosystems is insufficient to enable prediction of the biological impact of deep ocean sequestration. Innovative concepts continue to be needed for CO_2 sequestration.

Two research needs in fossil-fuel-based production are considered to have high priority. These needs are discussed in the following sections.

Catalyst Development. Improved catalysts are needed to overcome kinetic constraints in all phases of the hydrogen economy, including production, storage, and utilization. A general goal involves developing catalysts that rely less on noble metals, which will become a limiting resource in large-scale hydrogen energy systems. In hydrogen production via reforming of fossil resources, high priorities include catalysts that would support a lower-temperature, water-gas shift reaction, and improved catalysts for desulfurization of feedstocks. Catalysts are needed that are more active, more specific, more stable, and less susceptible to poisoning and fouling. Recent advances in analytical tools and methods (see Figure 3), in the combinatorial synthesis of catalytic materials, and in the theoretical modeling of their active site properties at an atomic level provide an unprecedented opportunity for rapid advances to meet the needs of catalyst development. An integration of experimental and computational approaches is needed to understand and control active site structures, catalytic mechanisms, and catalyst design on the nano scale. This is particularly important for the design and discovery of cost-effective catalysts that can produce hydrogen from fossil resources of sufficient purity for use in PEM fuel cells.

Improved Gas Separations. Efficient, high-volume gas separations are needed for preparing input gas streams, separating process gases, and purifying product streams. To satisfy these needs, semipermeable membranes are an attractive option, but improvements in membrane selectivity and robustness, particularly at elevated temperatures (200–400°C), are essential.

Solar Hydrogen

For solar PV, photoelectrochemical, or photocatalytic hydrogen production to become an economically viable technology, it is necessary to dramatically reduce the cost while maintaining a high level of efficiency. The trade-off between efficiency and cost for PVs is illustrated in Figure 4. Similar considerations apply to hydrogen production by PV-driven electrolysis, although some fixed costs may be reduced by eliminating the need for inverters and power

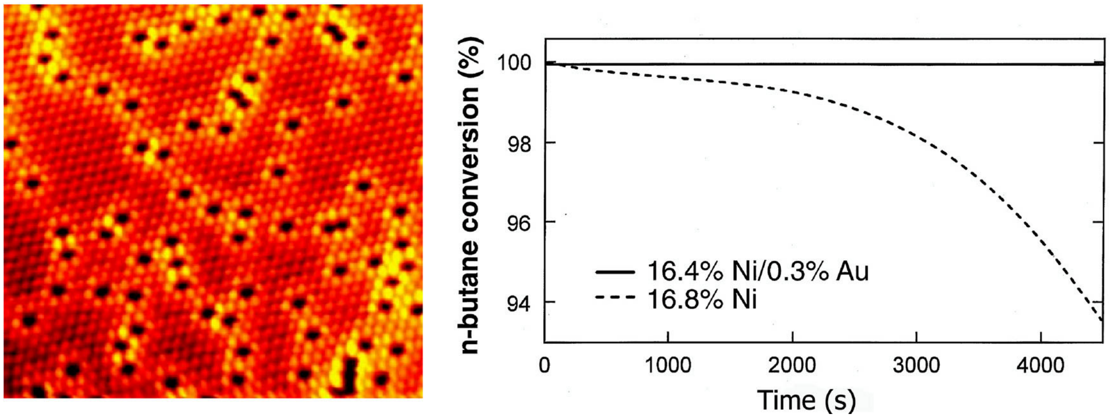

Figure 3 (Left) Scanning Tunneling Microscopy Image of a Ni Surface Alloyed with Au (The Au atoms are shown in black; the neighboring Ni atoms have a distinct electronic structure, which is different from those of Ni atoms farther away. Quantum chemical calculations show these Ni atoms to be less carbon-poisoned.) (Right) Experimental Confirmation that the Addition of Au to a Ni Catalyst Removes the Decrease in Activity with Time because of Graphite Formation (Source: Besenbacher et al. 1998)

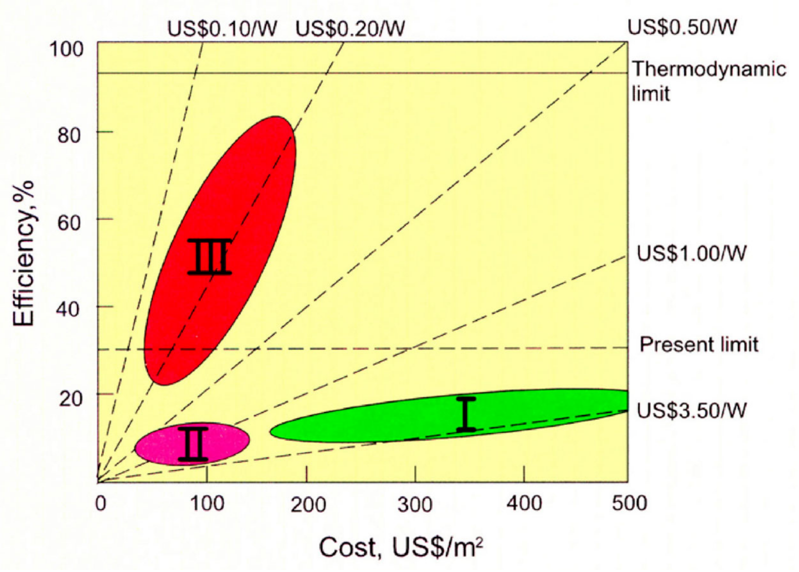

Figure 4 Efficiency Compared with Cost Per Unit Area of PV Devices (The diagonal lines show installed 2001 price of modules per peak-watt. The theoretical limit for Shockley-Queisser devices [present limit] is 32%, a figure that is approached by the best single-crystal silicon solar cells [see Figure 2]. Third-generation devices [shown in red] may exceed this limit by using multiple absorbers, hot carrier effects, or photocurrent doubling via impact ionization. The latter two phenomena are associated with quantum size effects in semiconductors and are being studied in semiconductor nanocrystals [Source: Green 2000]).

transmission lines. The real figure of merit for solar cells is the installed cost per peak-watt (dashed diagonal lines), which depends on conversion efficiency, module cost, and other baseline costs associated with connection to power grids, land use, and maintenance.

Both expensive single-crystal and less expensive polycrystalline devices follow roughly the same cost-efficiency curves in Figure 4. The efficiencies of these devices are limited by several factors. First, light of wavelength longer than the bandgap wavelength is not used, and the excess energy of shorter wavelength light is lost to heat. Second, grain boundary recombination and related losses reduce the quantum yield of light-to-electrical energy conversion. The cost/efficiency trade-off between single-crystal and polycrystalline cells is predominantly a consequence of this second factor. Third, the photovoltage is reduced by resistive losses in PVs and by the overpotentials needed to drive interfacial redox reactions at useful rates in photoelectrochemical cells.

The grand challenge for solar hydrogen is to become economically competitive with energy from fossil fuel sources. In today's market, devices that reside on the $0.20/peak-watt line would be needed. It is likely that this will be achieved only by developing new molecular-level designs and chemical processes for making very inexpensive solar cells or photocatalysts, as well as by understanding and exploiting emerging physical effects that can lead to higher efficiencies. Very low-cost solar cells ($0.20/peak-watt) could, in principle, create a “disruptive technology” (Christensen 1997) that would initially enter the energy market in low-end niche applications and eventually improve to the point of displacing high-volume legacy technologies, such as fossil fuel reforming and fossil generation of electric power. However, it is important to note that low-efficiency PV and photoelectrochemical devices (<10%) do not represent a viable solution to the problem even at very low cost because of the unavoidable baseline costs that other system components (frame, supports, wiring, inverter, land, taxes, etc.) add to the installed price.

There is now a substantial potential to leverage recent scientific advances to achieve these goals. The past 10 years have witnessed dramatic advances in our ability to control the structure of matter (semiconductor nanocrystals, supramolecular assemblies, porous inorganic solids, molecular thin films, micro-phase separated polymers) on the nanometer-length scale, which is the relevant length scale for photoinduced energy transfer, charge and redox product separation, recombination, and hot carrier thermalization. There has also been remarkably rapid progress in the maturing of closely related technologies, which include organic light-emitting diodes (OLEDs) and organic/polymer-based electronics. The physical makeup of devices in these allied technologies suggests that one could develop a reel-to-reel process for manufacturing solar cells that would be similar to the process used to make photographic film as a lamellar composite of many dye, nanoparticle, and polymer layers. Solar cells for producing hydrogen would be made from semiconductor particles, dyes, polymers, catalysts, and other components, once an understanding of the relevant physical phenomena and the necessary chemical assembly processes were in hand. The challenge is thus one of design and assembly of two- and three-dimensional photosystems, in which the optimal spatial arrangement of components achieves efficient light harvesting, charge carrier separation, and catalyzed generation and separation of hydrogen and oxygen.

Several research needs in solar hydrogen are considered to have high priority. These needs are discussed in the following sections.

Light Harvesting. New strategies are needed that will allow the solar spectrum to be used efficiently — in tandem (dual absorber) semiconductor systems or multichromophoric molecular arrays, for example, or in systems that exploit new physical phenomena, such as hot carrier injection, photocurrent doubling through impact ionization, or photon energy up/down conversion.

Charge Transport. Fundamental understanding of the phenomena that relate to energy loss mechanisms is needed. For instance, factors that control the mobility of carriers in polymers and hybrid systems, and the chemical nature and energetics of grain boundaries and surface states must be better understood. Controlling these processes should increase efficiency in PV and photoelectrochemical cells.

Chemical Assembly. Synthetic routes to organic/inorganic/polymer hybrids with controllable structure are needed, along with molecular-level understanding of the principles of their assembly. Because of their potential importance in low-cost solar devices, an important goal in this area is to make defect-free semiconductor nanoparticles with control of size, shape, and interfacial chemistry, and to understand light-induced dynamic processes involving them. Related goals are to control energy and electron transfer in supramolecular and biomimetic photoredox systems and to understand the processes that can lead to higher efficiency in multicomponent photocatalytic assemblies and in self-assembling organic photosystems, such as multilayer polymer films, molecular organic crystals, liquid crystals, and block copolymers. *In situ* characterization of multicomponent chemical systems is also of key importance to the development of efficient solar cells and photocatalysts for hydrogen production because their optimization requires a molecular-level understanding of structure.

Interfacial Chemistry. Increased understanding of electron transfer reactions at the molecule-inorganic (semiconductor and metal) and molecule-solution interfaces is needed to allow these processes to be controlled. Investigations of the processes involved in understanding semiconductor sensitization are needed to develop new sensitizers for improved dye-sensitized cells. New interface-specific investigative tools are required for studying structure and dynamic processes. These studies are important for improving the efficiency of dye-sensitized and organic solar cells because their performance depends critically on the kinetics of interfacial electron transfer reactions.

Catalysis and Photocatalysis. Improved molecular and heterogeneous catalysts, particularly for the oxidation of water to oxygen, are needed. Mechanistic studies of photocatalytic systems for direct water splitting, CO_2 reduction, and cyclic water cleavage with coupled redox catalysts will allow the development of improved photocatalysts.

Polymer and Materials Chemistry. New molecular components for PV cells are needed, including transparent conductors (particularly inexpensive polymeric conductors and p-type materials), electron- and hole-conducting polymers, semiconductors that have appropriate light-absorption characteristics and are stable in water, and corrosion-resistant coatings. Research on light-harvesting polymers, photonic crystals, and nonlinear optical materials is needed to better utilize the solar spectrum. New characterization tools are required for studying chemical, electrochemical, and photochemical processes in solid and polymeric materials. Polymer- and organic-based solar cells have the potential to convert solar energy at very low cost, if their efficiencies can be improved.

Theory and Modeling. With increased computational power and a background understanding of electron transfer in biomimetic and biological systems, theory and modeling can play an increasingly important role in our understanding and predicting the behavior of complex photosystems. The important features of these systems (such as femtosecond dynamics in sensitizer molecules and particles, and the branching of kinetic pathways in complex molecular assemblies and photoelectrochemical cells) are often at the “ragged edge” of experimental observation.

Stability. Fundamental studies are needed to understand and subsequently control parasitic processes that can degrade solar cells (particularly dye-sensitized, organic, polymer, and nanoparticle-based cells), with the goal of achieving a 10- to 15-year useful life.

Hydrogen from Biological and Biomimetic Systems

Sunlight is the primary energy source that fuels the entire biosphere, including biological hydrogen production. Like solar energy, natural biological hydrogen production is substantial on a global scale but suffers from being highly distributed and low in density compared with humankind's more concentrated energy needs, such as transportation. The energy efficiency of hydrogen production in natural populations of microorganisms and ecosystems is low in comparison with production via PV electrolysis. The efficiency limits encountered in biological energy conversion systems are related in large part to the energy needs of the living organisms themselves. Hydrogen is only one of many carriers in the energy economy of living organisms. Hence, only a portion of the solar energy acquired in photosynthesis enters into pathways that produce hydrogen, and often the hydrogen production process is many energy conversion steps removed from the initial photosynthetic reaction. Because the primary efficiency of natural photosynthetic light reactions is high (quantum yields near 1 for absorbed light, energy efficiency ~30% of total solar irradiance), direct coupling of photosynthesis to hydrogen production could, in principle, yield a highly efficient process. Achieving such efficiency, however, poses a number of basic research challenges. Recent advances in the development of tools for detailed genetic engineering of organisms capable of photosynthetic hydrogen production offer unprecedented opportunities.

Research into the fundamental mechanisms of the biological catalysts of light energy conversion, hydrogen activation, water oxidation, and intermediate electron transport, and into the design and operational principles that underlie self-assembly and self-renewal of these catalysts and energy conversion chains, holds considerable promise for developing less expensive and more efficient synthetic solar hydrogen systems. Advances in genomics and proteomics, and in the *de novo* design and biochemical synthesis of protein-based catalytic systems are strong enablers in this research. Our understanding of cofactors involved in biochemical oxidation-reduction processes and our ability to create functional synthetic mimics (Figure 5) also suggests that we are close to developing improved biomimetic catalysts for some of the most important reactions (hydrogen evolution and water oxidation) needed in hydrogen production.

Several research needs in biological hydrogen metabolism are considered to have high priority. These needs are discussed in the following sections.

Direct Production of Hydrogen Using Living Organisms. Fermentative organisms or microbial consortia could play a direct role in hydrogen production from fixed carbon energy reserves, such as biomass or natural gas, and also in removal of CO from hydrogen gas streams. Research is needed to understand the diversity and capacity of natural hydrogen production systems and to understand how to optimize their utilization in hydrogen-production processes. Photosynthetic hydrogen production could play a leading role in direct solar conversion, but research is needed

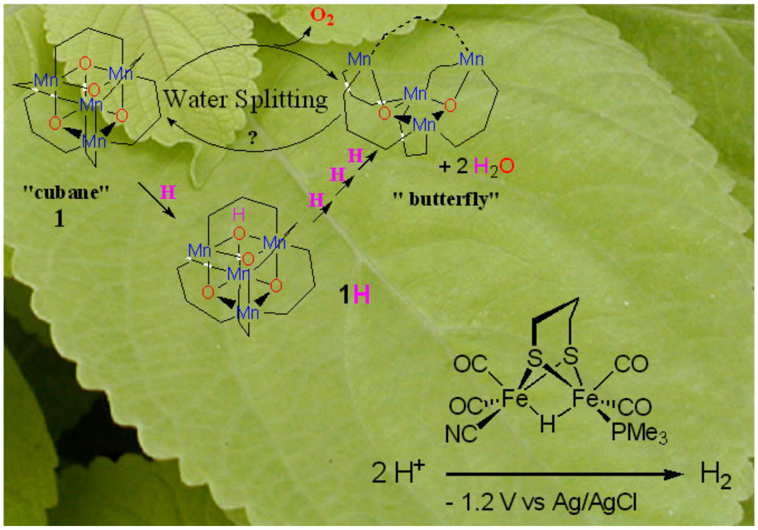

Figure 5 (Upper left) Synthetic Water Oxidation Catalysts Based on the Design of the Natural Photosystem II Manganese Cluster (Source: Maneiro et al. 2003) (Lower right) Synthetic Hydrogen Activation Catalysts Based on the Design of the Natural Reversible Iron-hydrogenase H-Cluster (Source: Gloaguen et al. 2002) (These catalysts are showing promise in mimicking many of the catalytic properties of their natural counterparts. Further advances could enable these biomimetic catalysts to play key roles in electrochemical hydrogen generation and utilization and in photochemical hydrogen production.)

to improve its efficiency, capacity, and reliability. Research is also needed in gas-separation technology for separating the mixed low-pressure H_2/O_2 gas stream that emerges from biophotolysis.

Engineered Systems Employing Biological, Biomimetic, or Bio-inspired Catalysts. The enzyme catalysts that living organisms use in both hydrogen production and consumption consist of readily available materials, such as iron, sulfur, nickel, molybdenum, manganese, and various organic cofactors in their catalytic mechanisms. Biological catalysts operate efficiently at relatively low temperatures (4–110°C) in aqueous environments. Research is needed to identify microbes and component redox enzymes and cofactors for producing/metabolizing H_2 and other fuels (e.g., CO and CH_4), understanding the mechanisms of these catalysts, and understanding how to exploit their designs in artificial systems. Research also is needed to develop and interface biological and biomimetic redox catalysts into nanostructured two- and three-dimensional complexes for hydrogen/oxygen catalysis, sensing, and energy transduction. Research is also needed for understanding the synthesis and assembly of the cofactors that participate in biological catalysis of hydrogen activation and water oxidation.

Systems Engineering Exploiting Biological Principles. The energy conversion systems of living organisms are highly organized nanoscale devices integrated into mesoscale architectures that incorporate self-repair mechanisms into their designs. An understanding of the principles governing the production of these organized systems, as well as their self-repair, may enable adoption of similar principles in the production of artificial systems with similar properties. Hydrogen is used extensively as an energy carrier between organisms that use it to energize a wide variety of different biological activities. Greater understanding of the scaling and organizational principles underlying the efficiency and stability of this diversified natural human engineered hydrogen energy economy may provide key insights that would support planning of a human-engineered hydrogen economy.

Thermal Energy for Hydrogen Production

Thermal hydrogen production places severe demands on reactor design because of the need to deliver heat at high temperatures (500−950°C). The problem of finding materials (both construction materials and membranes for separations) that resist corrosion and failure at high temperatures in extremely aggressive chemical environments is a potential roadblock for this technology. In this context, there are large incentives to reduce the temperature by 100-200°C for the S-I cycle, in which the high-temperature–controlling step is the catalytic decomposition of SO_3 to SO_2 and oxygen. Lower-temperature operation (e.g., at 725°C), however, requires cooling of unreacted sulfuric acid and reaction products, separation of components, and reheating of sulfuric acid, which results in high internal recycle with high costs and lower efficiency. There are multiple thermochemical cycles (S-I, Westinghouse, sulfuric acid-bromine) that use the same high-temperature chemical reaction (Brown et al. 2002); thus, the benefits of improving this high-temperature step accrue to several leading thermochemical cycles. The Cu-Cl cycles (Argonne Low-Temperature Cycles, ALTC-1 and ALTC-2) avoid many of the materials and reactor issues of the higher-temperature cycles by operating at a maximum temperature of 500°C. In this case, the lower operating temperature creates a new set of challenges in terms of catalysis and separations. Work is needed to assess the potential for exploiting the higher available temperatures from solar concentrators to access even more efficient thermochemical cycles. Parallel work would also be needed to identify and solve the materials and separations issues that would arise at these higher reactor temperatures.

Several research needs in thermochemical energy for hydrogen production are considered to have high priority. These needs are discussed in the following sections.

High-temperature Materials. The materials needs are severe because of the requirement to operate in a harsh chemical environment at elevated temperature. For example, in the S-I cycle, ductile and corrosion-resistant materials are needed for H_2SO_4 concentrations. Operation at very high temperatures (700–950°C) requires advances in construction materials and very efficient heat transfer.

Separations. Improved separations processes that work at high temperatures are critical to the efficient running of thermal hydrogen cycles. Opportunities for improved separations for the

S-I cycle include separation of SO_2 and O_2 from SO_3 to lower peak process temperatures, separation of H_2O and HI from $H_2O/I_2/HI$ mixtures, and removal of H_2 to shift this equilibrium. Membranes that might be used in these and related improved separation processes must have long-term stability in an aggressive chemical and physical environment. For the lower-temperature Cu-Cl cycles, efficient gas and liquid separations are also needed to shift the equilibria of component reactions and to separate the products (hydrogen and oxygen) from gaseous HCl and water.

Thermodynamic Data and Modeling for Thermal Cycles. Additional thermodynamic data (for sulfuric acid at high concentrations and for $I_2/HI/H_2O/H_2$ reactions) are needed inputs in reactor design. This involves modeling of aqueous fluids under extremely nonideal conditions. The optimum cycles for solar-matched thermal hydrogen production need to be determined.

Catalysis. Improved catalysts for the high-temperature SO_3 decomposition reaction would allow more flexibility in reactor design by enabling the cycle to run at lower maximum temperature. Reactive distillation of HI in the S-I cycle may also require catalysis.

New Thermochemical Cycles. Although much work was performed on thermochemical cycles in the 1970s and hundreds of cycles were identified, advances in nanotechnology and other areas of science may enable the development of improved cycles.

CROSS-CUTTING ISSUES

Several of the basic research needs in hydrogen production mirror those of hydrogen storage and use. These needs are discussed in the following sections.

Catalysis

Research is needed in the area of catalysis in all aspects of hydrogen production. Such research includes integrating molecular and heterogeneous catalysts into solar photoelectrochemical and photocatalytic systems, interfacing biological and biomimetic catalysts with chemical and electrochemical systems, improving catalysts for fuel processing, and developing catalysts for use in thermal hydrogen cycles. The areas of hydrogen production and use are strongly linked through catalysis because fuel cell catalysts that are not easily poisoned by CO would enable the use of reformed hydrogen with less extensive purification. Better fuel processing catalysts would reduce the need for separations processes that remove CO. Similarly, the development of intermediate-temperature fuel cells (200–400°C) that tolerate CO would greatly relax the requirements for fuel processing catalysts. Cost and scale considerations in hydrogen production and use call for the development of all of these next-generation catalysts from abundant raw materials.

Separations

Improved membranes and chemical separation processes are needed in fuel processing, in the separation of hydrogen and oxygen produced by photocatalysis and photosynthesis, and in the high-temperature chemical processes of thermal hydrogen production.

Interfacial Chemistry and Materials

Solar PV/photoelectrochemical and biomimetic hydrogen production involve electron and ion transfer at catalyst/electrolyte interfaces and present materials problems similar to those for PEM fuel cells. Corrosion-resistant materials are needed in thermal hydrogen production. For thermally assisted electrolysis, further development of high-temperature materials is needed, similar to that of solid oxide fuel cells.

Theory and Modeling

Theory has a unique role in many aspects of hydrogen production, storage, and use. In hydrogen production, theory is particularly important in uncovering the mechanisms of heterogeneous, molecular, and biological catalysis, in understanding the complex photoredox processes associated with solar hydrogen production, and in modeling the chemical processes involved in hydrogen-producing thermal chemical cycles.

CONCLUSIONS

The development of safe, sustainable, and cost-effective hydrogen production on the scale of the U.S. energy economy presents urgent and difficult challenges. The near term (5- to 10-year) goals are to improve the processes that can provide hydrogen from resources of limited capacity or sustainability. These include fossil fuels, with sequestration of CO_2, and biomass. The long-term goal (>10 years) is to develop the means to produce hydrogen cost-effectively from high-capacity, noncarbogenic resources, namely, solar and possibly nuclear energy. Meeting these goals will require a sustained effort to address a diverse set of basic scientific challenges.

In hydrogen production from fossil resources, breakthroughs in catalysis and separations, as well as an understanding of the processes involved in carbon sequestration and release, are needed. Catalysis research can leverage recent advances in nanoscale and molecular synthesis, in characterization tools that allow active sites to be probed directly, in modeling of complex chemical systems, and in high-throughput synthesis and screening methods.

The longer-term goal of developing very efficient, low-cost solar cells (solar “paint”) and photocatalysts for hydrogen production requires an understanding of light-induced dynamical processes in molecules, polymers, and semiconductor nanoparticles. There is a need to understand the rules of chemical assembly on the length scale (0.5–10 nm) of charge separation and recombination. There is also a pressing need for research on new semiconductors, polymers, supramolecular assemblies, and catalysts that will enable the synthesis of two- and three-dimensional integrated chemical systems for efficient light harvesting, charge separation, and fuel formation. These systems may integrate biological or bio-inspired catalysts. Understanding the pathways by which hydrogen is made and processed in living organisms may enable breakthroughs in this area, for example by providing nonprecious metal catalysts for water oxidation-reduction reactions and allowing fuel processing reactions to run at lower temperatures.

Thermochemical cycles (using heat from high-temperature solar and possibly nuclear sources) can in principle be used to generate hydrogen from water economically and in large quantity. The most significant challenges in this area are to (1) develop materials that are cost-effective and compatible with extreme chemical and thermal environments (e.g., aqueous sulfuric acid at 700–950°C) and (2) develop efficient separations processes and catalysts that can function in the same environment.

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BASIC RESEARCH CHALLENGES FOR HYDROGEN STORAGE

CURRENT STATUS

Effective storage and delivery of hydrogen — produced from diverse sources and intended for diverse uses — are key elements of the hydrogen economy. Flexible use of hydrogen as a carrier of energy requires a means to store excess product for later use, to transport stored hydrogen from the point of production to the point of use, and to charge and discharge hydrogen conveniently from the storage container according to need. In addition to interfacing production with use, hydrogen storage provides a load-leveling mechanism for the cyclic renewable energy production from wind and solar sources.

Two kinds of storage functions with very different requirements are needed for the hydrogen economy. Hydrogen storage systems used for such stationary applications as residential heating and air-conditioning, neighborhood electrical generation, and many industrial applications can occupy a large area, employ multistep chemical charging/recharging cycles that operate at high temperature and pressure, and compensate for slow kinetics with extra capacity. Hydrogen storage for transportation, in contrast, must operate within minimum volume and weight specifications, supply enough hydrogen to enable a 480-km (300-mi) driving range, charge/recharge near room temperature, and provide hydrogen at rates fast enough for fuel cell locomotion of cars, trucks, and buses. The hydrogen storage requirements for transportation applications are thus far more stringent and difficult to achieve than those for stationary applications. Finding onboard hydrogen storage solutions for transportation applications is one of the major challenges in achieving the hydrogen economy.

Because two-thirds of U.S. oil consumption is used to meet transportation energy needs, this sector presents not only the most difficult challenges, but it also provides the most intense driver for the hydrogen economy. Developing effective hydrogen storage for transportation is a central challenge for basic research and a key factor in enabling the success of the hydrogen economy. The operating requirements for effective hydrogen storage for transportation include the following:

- Appropriate thermodynamics (favorable enthalpies of hydrogen absorption and desorption),
- Fast kinetics (quick uptake and release),
- High storage capacity (specific capacity to be determined by usage),
- Effective heat transfer,
- High gravimetric and volumetric densities (light in weight and conservative in space),
- Long cycle lifetime for hydrogen absorption/desorption,

- High mechanical strength and durability, and

- Safety under normal use and acceptable risk under abnormal conditions.

Specific performance targets for the coming decade for a successful transition to hydrogen-fueled transportation, as specified by the Department of Energy's Office of Energy Efficiency and Renewable Energy, are presented in Table 1.

Table 1 FreedomCAR Hydrogen Storage System Targets

Targeted Factor	2005	2010	2015
Specific energy (MJ/kg)	5.4	7.2	10.8
Hydrogen (wt%)	4.5	6.0	9.0
Energy density (MJ/L)	4.3	5.4	9.72
System cost ($/kg/system)	9	6	3
Operating temperature (°C)	-20/50	-20/50	-20/50
Cycle life-time (absorption/desorption cycles)	500	1,000	1,500
Flow rate (g/s)	3	4	5
Delivery pressure (bar)	2.5	2.5	2.5
Transient response (s)	0.5	0.5	0.5
Refueling rate (kg H_2/min)	0.5	1.5	2.0

[a] Source: Milliken (2003).

A storage capacity of approximately 5–10 kg of useable hydrogen is needed, depending on the vehicle, to provide a 480-km range for a fuel cell/electric vehicle. A refueling time of less than 5 min is targeted for 2015. Current technology for hydrogen storage involves tanks in which hydrogen is stored as a compressed gas or as a cryogenic liquid. With compressed gas and liquid storage, the hydrogen is easily accessible for use. These storage methods, however, fall far short of the FreedomCAR targets because of the volume of the tanks that would be required using present technology. Solid-state storage, in which the hydrogen is absorbed in a solid material, holds considerable promise for meeting the FreedomCAR targets, but no completely satisfactory material has been identified yet.

Hydrogen storage is a crucial step for providing a ready supply of hydrogen fuel to an end use, such as a car. Without effective hydrogen storage systems, a hydrogen economy will be difficult to achieve. Hydrogen storage is considered by many to be the most technically challenging aspect of achieving a hydrogen-based economy. Current hydrogen storage materials or systems are still far short of achieving target goals set for either 2010 or 2015. For example, we need a factor of ~2 improvement in both hydrogen storage capacity and energy density, and perhaps an even higher improvement factor for hydrogen release, to achieve targeted goals within the next decade. Incremental improvements in current technologies will not be sufficient to meet the prescribed requirements for hydrogen storage. Basic research is essential for identifying novel materials and processes that can provide the revolutionary breakthroughs needed to make the hydrogen economy a reality.

Below we describe current methods of hydrogen storage, along with fundamental research issues that are needed to achieve the required hydrogen storage goals. Although this discussion focuses primarily on hydrogen storage for onboard vehicle use, hydrogen storage materials and systems developed for vehicle applications could find more general energy storage uses. One common requirement for all hydrogen storage technologies described below is the need to develop materials suitable for use in containers that house hydrogen storage media. Also, safety is a potential concern for widespread hydrogen use because of the very wide flammability range of hydrogen. Specific information on hydrogen safety and the research directions associated with the science of hydrogen safety is presented in High-priority Research Directions.

Gaseous and Liquid Hydrogen Storage

Storage of hydrogen as a gas in tanks is the most mature storage technology at present. Composite gas storage tanks are already available at 5,000 psi. Recently 10,000-psi tanks have been demonstrated and certified. These high-pressure tanks use new lightweight tank materials, such as carbon-fiber–reinforced composites. The major drawback of gaseous storage for transportation applications is the small amount of hydrogen that can be stored in a reasonable volume. Even at 10,000 psi pressures, the energy content is significantly less than that for the same volume of gasoline — 4.4 MJ/L (10,000 psi) for hydrogen compared with 31.6 MJ/L for gasoline. The energy used in compressing the gas, which depends on both the initial and final pressures, is another consideration, as is the large pressure drop during use.

Principal research needs for improved compressed gas storage include the development of novel materials that are strong, reliable, and low in cost. For example, fiber-reinforced composites for storage containers require new fiber synthesis techniques that reliably produce high-quality fibers and new binders that are strong and impermeable to hydrogen. A better understanding of the mechanisms responsible for the failure of storage container materials is also needed. Because many of the system parts exposed to hydrogen will be metallic, researchers need a better understanding of the atomic-level processes responsible for hydrogen embrittlement in candidate materials in order to develop strategies to prevent failure resulting from long exposure to hydrogen. The development of embrittlement-resistant materials will require well-coordinated basic and applied research to allow their practical application to pressurized gas storage. In addition, smart sensors that can detect hydrogen leakage and the corresponding safety feedback systems need to be fully developed to ensure safe implementation of gaseous hydrogen storage.

Storage of liquid hydrogen in cryogenic containers offers a significant advantage: more hydrogen can be stored in a given volume as a liquid than can be stored in gaseous form. For liquid hydrogen, researchers predict 8.4 MJ/L compared with 4.4 MJ/L for compressed gas (at 10,000 psi). The density of liquid hydrogen is 70.8 kg/m^3 at standard temperature and pressure. Note that these values are still less than half of those required to meet FreedomCAR goals. The automobile manufacturer BMW has been working on the development of a hydrogen-fueled fuel cell vehicle with onboard liquid hydrogen storage (Porvetto 2003). A major drawback of liquid storage is the large quantity of energy required for liquefaction — presently about one-third of the energy value of the hydrogen stored. Loss of hydrogen through evaporation is also an issue, especially with small tanks. High-pressure cryogenic tanks are also being explored to alleviate the requirement for very low temperature storage.

Basic research needs related to liquid hydrogen storage include the discovery of new lightweight, low-volume, and low-cost materials that have very low heat transfer. These materials must demonstrate strength, integrity (no leakage), and durability. There is also a need for novel, strong materials, developed through experiments and computer simulations, that minimize heat transfer and are amenable to mass production. Researchers need to identify "failsafe" methods to safely handle boil-off of hydrogen and address other safety issues associated with liquid hydrogen. New approaches are also needed that reduce the cost of liquefaction and make it more energy efficient. Finally, close coordination between basic and applied research is needed to expedite development and application of new technologies for handling cryogenic liquids.

Solid-state Storage

Solid-state storage refers to the storage of hydrogen in metal hydrides, in chemical storage materials, and in nanostructured materials. This method of hydrogen storage offers perhaps the best opportunities for meeting the requirements for onboard storage. In these materials, hydrogen can be stored both reversibly and irreversibly. Reversible storage means that hydrogen is released by raising the temperature of, for example, a metal hydride at a suitable pressure; hydrogen is subsequently replaced (stored) through the control of temperature and hydrogen pressure. Although temperature and pressure are the two typically controlled thermodynamic parameters, other types of energy (e.g., mechanical and acoustical) can be employed to control both the release and uptake of hydrogen. Ideally, storage and release of hydrogen should take place at temperatures between 0°C and 100°C and pressures of 1–10 bar and on time scales suitable for transportation applications. Some materials contain strongly chemically bound hydrogen that is not readily retrievable. Only hydrogen that can be made easily accessible will meet the hydrogen storage requirements for transportation applications.

Hydrogen is irreversibly stored in some materials, including chemical hydrides, and is released by chemical reaction with another substance, such as water. The heat released upon hydrolysis is energy that can be captured and used. The resulting hydrolysis product cannot be used again to store hydrogen without chemical reprocessing, as described in the accompanying sidebar on the supply chain of a borohyride hydrogen storage system. Hydrogen storage using recyclable hydrocarbon carriers, such as methylcyclohexane, has also been demonstrated. However, these liquid carriers store low ratios of usable hydrogen for their weight. In addition, these carriers require a long release time, because the catalyst used for dehydrogenation must first be brought up to operating temperature.

Researchers believe that metal hydrides may represent ideal storage systems. Although a database (http://hydpark.ca.sandia.gov) lists more than 2,000 elements, compounds, and alloys that form hydrides, none of these materials has yet been demonstrated to meet all of the FreedomCAR targets listed in Table 1. Conventional metal hydrides, which are well

USING SODIUM BOROHYDRIDE FOR ONBOARD HYDROGEN STORAGE

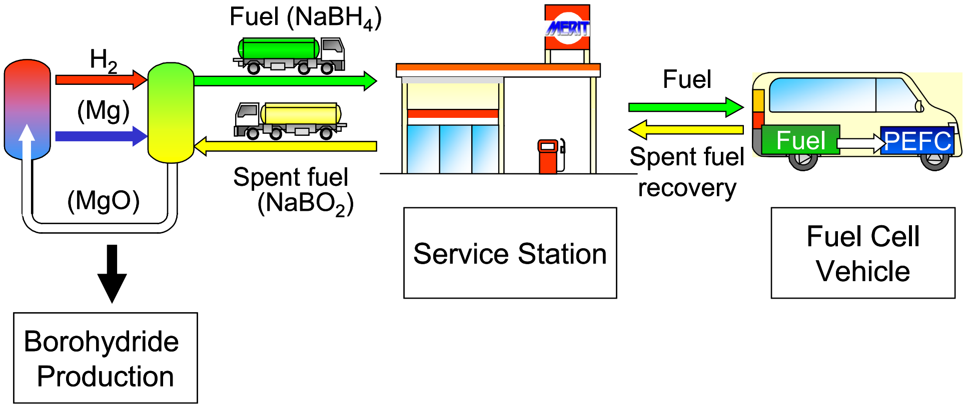
Sodium borohydride ($NaBH_4$) is a rich source of hydrogen being developed by Millennium Cell under the trade name "Hydrogen On Demand." The chemical reaction in which hydrogen is formed is as follows:

$$NaBH_4 + 2\,H_2O \xrightarrow{\text{catalyst}} 4\,H_2 + NaBO_2$$

Sodium borohydride is derived from borax, a nontoxic compound used in laundry detergents. The hydrogen storage density of $NaBH_4$ is high. A 30 wt% $NaBH_4$ fuel (30 wt% $NaBH_4$, 3 wt% NaOH, and 67 wt% H_2O) has a theoretical hydrogen content of 6.6 wt% — equal to about 66 g H_2/L, compared with 70 g H_2/L for liquid hydrogen and 23 g H_2/L for compressed hydrogen (at 5,000 psi).

The supply chain for onboard hydrogen storage and use of $NaBH_4$ is shown in the diagram. The $NaBH_4$ fuel is delivered to a service station following production. The fuel is processed onboard a vehicle by means of a catalyzed reaction with water to generate the hydrogen needed to power a fuel cell. The spent fuel (containing $NaBO_2$) is recovered from the vehicle and shipped from the service station to a central reprocessing facility, where it is reprocessed back to $NaBH_4$. Schemes for spent fuel regeneration have been demonstrated and are believed to be feasible.

Hydrogen storage materials can be divided into those that are recharged with hydrogen onboard a vehicle and those that must be removed from the vehicle for recharging or reprocessing. Total hydrogen fuel costs — including costs for hydrogen production, transportation of hydrogen or storage materials, and reprocessing — will be among the many factors that will determine the method selected for delivering hydrogen to the fuel cell onboard a vehicle.



characterized and have well-established values for interstitial hydrogen storage, include intermetallics of the types AB, AB_2, AB_5, A_2B, and body-centered cubic metals. These materials typically store between 1.4 and 3.6 wt% hydrogen. Examples of these intermetallic compounds are TiFe, $ZrMn_2$, $LaNi_5$, and Mg_2Ni. Their hydrogen storage properties are listed in Table 2; it should be noted that the hydrogen storage capabilities in general are a factor of 3 lower than FreedomCAR requirements.

Note that Table 2 provides the amounts of hydrogen that are stored, but not the amounts that are released. Furthermore, the values presented in Table 2 do not take into account the energy required to bring about the release of the hydrogen from the material. The reversible hydrogen capacity is typically 50–90% of the maximum hydrogen capacity for these intermetallics. In addition to limits in hydrogen availability, other issues need to be considered as new hydrogen storage materials are developed and characterized, such as the ease of activation, sensitivity to gas impurities, rate of hydrogen absorption/desorption, heat transfer, cyclic stability, and

Table 2 Hydrogen Storage Properties of Intermetallic Compounds

Type	Intermetallic	Maximum Hydrogen Capacity H/M[a]	wt%	Temperature (K) for 1 atm $P_{desorption}$
A_2B	Mg_2Ni	1.33	3.6	528
AB	TiFe	0.975	1.86	265
AB	ZrNi	1.4	1.85	565
AB_2	$ZrMn_2$	1.2	1.77	440
AB_5	$LaNi_5$	1.08	1.49	285
AB_2	$TiV_{0.62}Mn_{1.5}$	1.14	2.15	267

[a] H/M is the hydrogen-to-metal atomic ratio in the compound.

Source: Sandrock (1999).

physical properties (e.g., volume change and decrepitation). From an engineering perspective, the design and optimization of practical storage beds may well require at least a factor of 2 increase in the percent hydrogen mass and volume that would be necessary for use in thermal management. Thus, the materials listed in Table 2 (and related materials) presently appear to have limited potential for meeting the targets listed in Table 1.

Needed breakthroughs in hydrogen storage technology will require revolutionary new materials to meet the hydrogen storage requirements, and not simple, incremental improvements in current technologies. These breakthroughs require investments in fundamental research 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. For example, researchers have only recently learned of the improved hydrogen storage potential of many novel lightweight metal hydrides. Understanding fundamental issues about the interactions of hydrogen with these and other novel materials is critical to identifying effective materials for hydrogen storage.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS IN SOLID-STATE HYDROGEN STORAGE

Development of new solid-state materials for hydrogen storage presents many scientific and technical challenges. Fundamental research is needed to understand the interaction of hydrogen in solid-state materials in order to realize the potential of these materials for hydrogen storage. The knowledge gained from this research will allow the tailored design and synthesis of new materials that will meet the requirements for efficient hydrogen storage.

The research effort will require a multidisciplinary approach involving physics, chemistry, materials science, and engineering. Also needed is a strong integration among experiment and theory, modeling, and simulation that will not only help researchers understand the experimental data, but also allow them to identify key parameters that will facilitate major advances in hydrogen storage technology and guide subsequent experiments. This multidisciplinary, integrated research effort will lead to the discovery of new hydrogen storage materials.

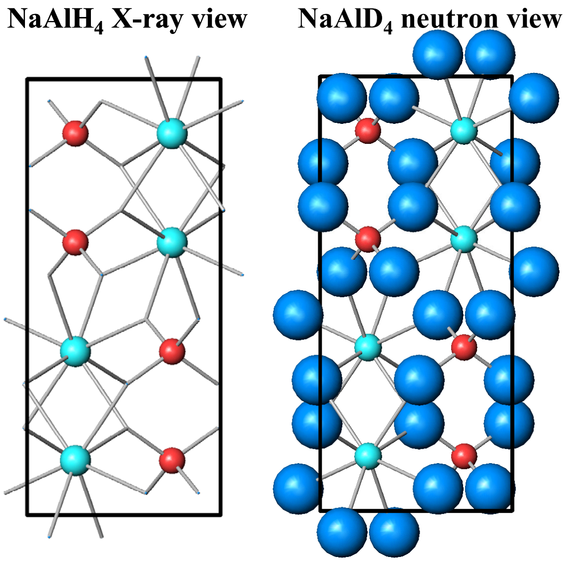
The fundamental questions that need to be asked for any potential solid-state hydrogen storage material include the following. Does hydrogen physisorb or chemisorb? Does it bind molecularly or dissociatively? Where does the hydrogen reside? What is the nature of its hydrogen diffusion? What are the activation barriers for hydrogen desorption? What adverse effect does hydrogen have on the structural and mechanical stability of the host material? What is the nature of bonding of hydrogen with host atoms — ionic, covalent, or metallic? What roles do surface morphology and defects play in hydrogen absorption and desorption? In what ways is it beneficial to store hydrogen in novel materials, such as nanostructures and porous materials? How do catalysts help in reducing the operating temperature and pressure for hydrogen uptake and release?

As we gain insight into these fundamental questions, new materials can be designed and synthetic approaches can be devised to produce tailored materials more efficiently. Reliable information about the structural, thermodynamic, physical, and chemical properties of these materials is needed. New capabilities for studying materials and chemical and physical processes at the nano scale will help us develop an understanding of how the unique surfaces and interfaces in nanostructured materials might impact the energetics, kinetics, and thermodynamics of hydrogen storage. Also, these capabilities will provide insight on how shape, curvature, and pore size affect the surface chemistry and binding that are so important for hydrogen storage.

These studies will require state-of-the-art analytical and characterization techniques, including a new generation of neutron and x-ray scattering techniques (see sidebar on neutron and x-ray scattering) and imaging tools. Researchers will also need to develop a comprehensive theoretical understanding of the interactions of hydrogen with storage materials (e.g., the nature of bonding and the role of structure and nanophase boundaries). For example, multiscale computational approaches may be applied to model absorption and desorption in hydrogen storage materials. Computational approaches should also be used — together with experimental data — to help identify mechanisms for degradation of hydrogen storage materials, which limit the lifespans of these materials, particularly with repeated hydrogen storage and release cycles. Finally, experiments on model hydrogen storage systems should be benchmarked against calculations at all length scales. Taken together, this knowledge will allow the design of novel materials for optimum hydrogen storage and release and provide a means to control and maintain the structural properties of candidate hydrogen storage materials and improve their durability. Below, these and other fundamental research needs are outlined for two key areas that hold promise for meeting the goals of hydrogen storage: metal and complex hydrides and nanostructured materials.

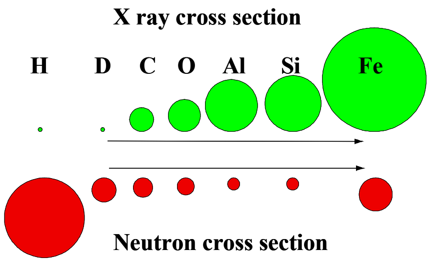
Metal Hydrides and Complex Hydride Materials

Over the past four decades, materials for solid-state hydrogen storage have been nearly exclusively metals and metallic alloys, in which the metal matrix is expanded and filled with absorbed hydrogen atoms that are usually located in tetrahedral or octahedral interstitial sites.



$NaAlH_4$ X-ray view

$NaAlD_4$ neutron view



USING NEUTRONS TO “SEE” HYDROGEN

To characterize the materials and processes involved in hydrogen production, storage, and use, researchers need atomic- and molecular-level information on structure, hydrogen diffusion, and interatomic interactions, as well as the nanoscale and macroscopic morphologies that govern their useful properties. Neutron scattering provides unique capabilities for giving this basic information. Their sensitivity to light (low-Z) atoms — such as hydrogen, lithium, and oxygen — make neutrons a valuable probe for investigations related to catalysis, membranes, proton conductors, hydrogen storage materials, and other materials and processes related to hydrogen production, storage, and use. This capability is illustrated in the figure at the right, which compares the neutron and x-ray scattering cross sections of a number of elements.

The figure at the left further illustrates how neutrons can identify the presence of hydrogen atoms in the structures of alanates used for hydrogen storage. Structural characterization using x-rays cannot reveal the site of hydrogen incorporation, which is critical to a fundamental understanding of the mechanisms of hydrogen storage. Neutrons also have a unique ability to distinguish hydrogen from deuterium, allowing isotope substitution to be used to provide additional insight into the structure of materials and into the interactions occurring between hydrogen and these materials. Another advantage of neutron-based techniques is that materials and chemical processes can be studied under realistic conditions, rather than under the high-vacuum or other controlled conditions required by other methods.

Neutron sources can provide continuous beams of neutrons (from reactor-based sources located at the National Institute of Standards and Oak Ridge National Laboratory) or pulsed beams (from spallation sources at Argonne National Laboratory and Los Alamos National Laboratory). A new generation of pulsed sources, such as the Spallation Neutron Source (SNS) currently under construction at Oak Ridge, will have advantages that are of particular interest to hydrogen studies. The intense flux of the SNS will allow samples to be studied using single-pulse, broadband techniques, which will permit neutron diffraction to determine hydrogen positions accurately and dynamically. Inelastic spectrometers allow researchers to examine diffusion processes on an atomistic level and relate them to structure. Understanding this relationship is a vital step to developing better, more affordable materials, such as membranes for selective purification of hydrogen. Similar techniques can be applied to determining diffusion paths in promising proton and ion conductors. Single-pulse determinations will allow *in situ* measurements to be made in real time during charging/discharging cycles in hydrogen storage materials and as a function of external parameters, such as pressure and temperature.

Increasing the efficiency and affordability of fuel cells requires a better understanding of the molecular-level processes involved in oxidation and reduction at electrodes, catalytic processes, and ion and proton transport, as well as the development of polymer-electrolyte-membranes and solid oxide electrolytes. The performance of these components involves several size (nm to µm) and time scales readily accessible with neutron scattering techniques. Examples of other areas that can be examined by neutrons include *in situ* studies of new catalyst materials, hydrogen-induced embrittlement in materials, uptake and release of hydrogen in metal and complex hydrides, and studies of materials used in new photovoltaic cells and coatings for solar energy devices.

Atomic hydrogen stored in these interstitial sites recombines at particle surfaces to form molecular hydrogen upon release. A major emphasis of materials-related research has been to *encapsulate hydrogen*. Capacities exceeding two hydrogen atoms per metal atom have been demonstrated by using this approach. Most metal matrices investigated to date, however, consist of relatively heavy elements, and gravimetric storage capacities usually do not exceed 2 wt% hydrogen when transition metals are major components.

Figure 6 is a van't Hoff diagram showing the dissociation pressures and temperatures of a number of hydrides (Bogdanovic and Sandrock 2002). Light elements, such as Mg, have shown promising levels of stored hydrogen (3–7 wt% hydrogen), but they release hydrogen at high temperature (e.g., 552 K at one atmosphere) (Sandrock 1999). Although improvements in the kinetics of magnesium-based alloys have been achieved by nanostructuring and adding catalysts (Oelerich et al. 2001; Barkhordarian et al. 2003), the thermodynamics remain virtually unchanged (i.e., rather modest shifts in plateau pressures/van't Hoff lines). In comparison, $NaAlH_4$, a low-temperature (LT) hydride, and Na_3AlH_6, a medium-temperature (MT) hydride, offer promise for lowering the hydrogen release temperature while attaining high storage capacity (above 5 wt%) by using both phases to provide hydrogen. Hydride formation in nearly all metal systems generally involves about a 15–25% volume change that must be accommodated in storage vessel designs. Another issue that needs to be addressed is the thermal management of the heats of absorption and desorption to (1) enhance the kinetics during filling and discharge of the hydrogen storage systems and (2) avoid degradation effects during long-life operation.

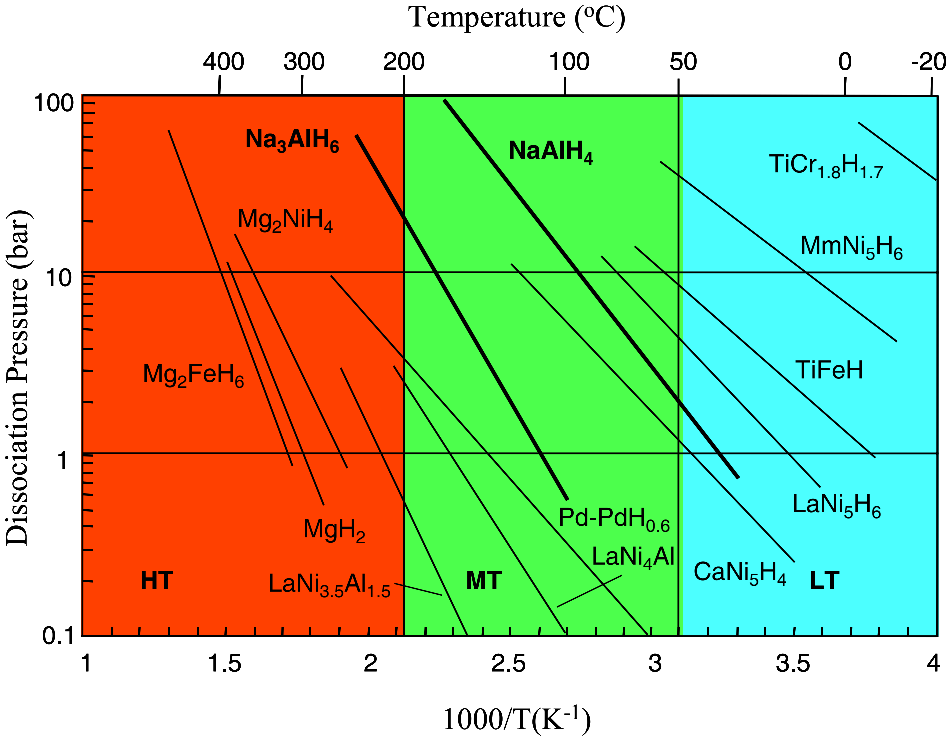


Figure 6 van't Hoff Diagram Showing Dissociation Pressures and Temperatures of Various Hydrides (Source: Bogdanovic and Sandrick 2002)

A different concept in solid-state storage of hydrogen is to *encapsulate by hydrogen*, thus opening the possibility of approaching the hydrogen content of methane. In some ways, CH_4 would seem to be the ultimate hydrogen storage compound, in which four hydrogen atoms surround a single carbon atom. However, because CH_4 is gaseous, it offers little practical benefit over storage of hydrogen itself. Further, the hydrogen-carbon bonds of methane are too strong for easy hydrogen recovery. Novel solids — such as alanates (aluminohydrides), borohydrides, and imides — in which the metal atom is surrounded by four to six hydrogen atoms forming a complex negatively charged anion, mimic the structure of methane and may provide a much-needed breakthrough in the solid-state storage of hydrogen. As shown in Table 3, their theoretical total hydrogen capacities are high (from ~7 to 18 wt%).

Solid storage materials with a high volumetric density of hydrogen (up to 100 g H_2/L) would exceed the density of a cryogenic liquid at 20 K (~70 g H_2/L). The sidebar on light hydrides compares the mass density and volume density of hydrogen for a number of hydrides. Use of these materials is critically dependent on whether (and how) the stored hydrogen can be conveniently released at a temperature that is within acceptable bounds and how the materials can be recharged with hydrogen. Mixing hydrides to make complex, multicomponent hydrides could potentially allow the synthesis of storage materials with specifically tailored properties. For example, the ionic bonding of hydrogen-rich $[MeH_n]^{p-}$ anions with various light-element cations provides a means for precise chemical substitutions in the cation sublattice, thus bridging the gap between hydrogen-poor intermetallic hydrides and hydrogen-rich LiH, BeH_2, and MgH_2 compounds. Thus, these complex hydrides have perhaps the greatest potential to provide both a high wt% hydrogen and desirable release/absorption kinetics. Reaching the potential of hydrogen storage in these complex hydrides will require fundamental research in a number of areas, as outlined in the following sections.

Table 3 Hydrogen Storage Capacities of Hydrides

Hydride	Hydrogen (wt%)[a]
$NaAlH_4$	7.5
$LiAlH_4$	10.6
$Mg(AlH_4)_2$	9.3
$NaBH_4$	10.7
$LiBH_4$	18.5
$Mg(BH_4)_2$	14.9

[a] Note that these are theoretical total hydrogen contents and not reversible hydrogen capacities.

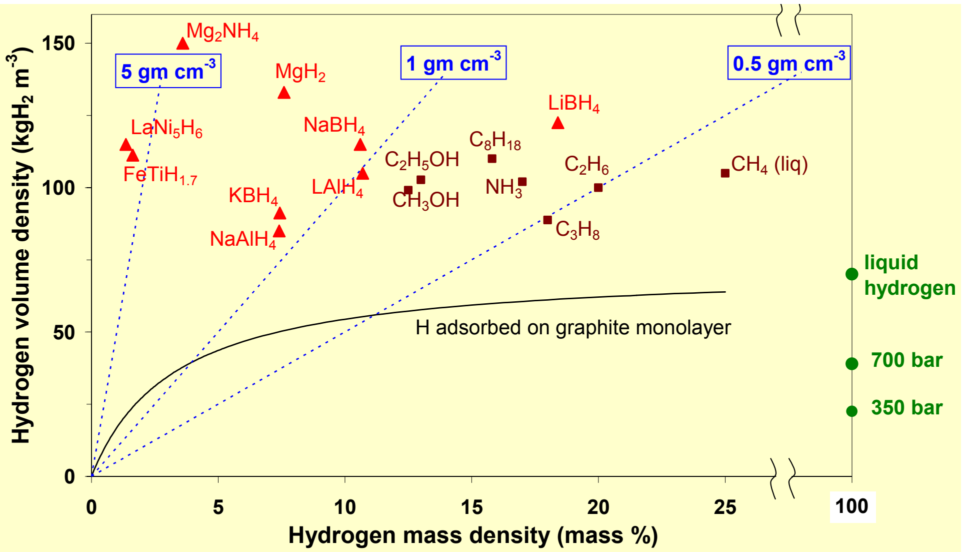
Source: Sandrock (1999).

Stoichiometric Complex Hydrides. A fundamental understanding of the physical, chemical, and mechanical properties of complex hydrides is needed, including desorption pressure, release kinetics, and chemical stability after multiple charging/discharging cycles.

Multicomponent Complex Hydrides. Basic knowledge of the structures of multicomponent complex hydrides is needed, as well as knowledge of their hydrogen storage behavior, the nature and homogeneity ranges of complex hydrides, hydrogenation-dehydrogenation kinetics and mechanisms, electronic structure, thermodynamics, and the kinetics of direct synthesis from the elements.

COMPARING MATERIALS’ HYDROGEN DENSITIES

Candidate materials for hydrogen storage will need to have high hydrogen packing density, as well as low weight. This sidebar compares these two properties — the mass density and volume density of hydrogen — for a number of different hydrogen-containing materials. The hydrogen density in the material is simply proportional to the material density through the mass fraction. Three straight-line plots are shown in the following chart for 5, 1, and 0.5 gm cm^{-3}.



The best materials for hydrogen storage applications should be in the upper-right quadrant of the chart. Intermetallic hydrides, such as $LaNi_5H_6$, have high volumetric densities, but generally are heavy — with specific gravities in the range of 5–10 gm cm^{-3}. They tend to populate the left-hand portion of the chart. Lighter compounds, with specific gravities of ~1 gm cm^{-3}, need to have high hydrogen-to-metal ratios to achieve high volumetric density. Some examples with high hydrogen content are shown in the chart. Note that the hydrogen densities in solids tend to be comparable to the densities of hydrogen in hydrocarbon fuels, alcohols, and ammonia. Furthermore, they exceed the packing density of hydrogen in its liquid state at ~1 bar pressure.

Also shown is a plot for hydrogen adsorbed on a single plane (monolayer) of graphite. The density calculation also accounts for the carbon. Density values for liquid hydrogen and for compressed gas at 350 bar (5,000 psi) and 700 bar (10,000 psi) are plotted at 100% mass fraction for comparison.

The chart is based on one published by Schlapbach and Zuttel (2001).

Synthesis and Processing. The majority of complex hydrides have been prepared via lengthy solvent-based synthesis; only a few (e.g., $LiAlH_4$ and $NaBH_4$) have been prepared without solvents. Novel materials and processing approaches need to be developed for these and other lightweight hydrides, and these materials need to be evaluated in terms of their potential for enhanced hydrogen storage performance.

Dopants. One of the most important, but least understood, findings is the critical role of dopants in achieving reasonable kinetics and reversibility of complex hydrides. For example, the addition of Ti-based compounds (such as $TiCl_3$ or $Ti[OBu]_4$ to $NaAlH_4$) was found to lower the first decomposition temperature of the hydride, so that 3.7 wt% is released at 353 K, but at the expense of lowering the hydrogen content from 5.5 wt% in the hydride without a catalyst (Bogdanovic and Schwickardi 1997; Bogdanovic and Sandrock 2002). Also $TiCl_4$-catalyzed

$LiAlH_4$ releases ~5 wt% hydrogen at ambient temperatures during mechanochemical processing and ~2.5 wt% hydrogen at temperatures below 423 K during heating. However, the reversibility of hydrogen in this material is yet to be demonstrated (Balema et al. 2000).

Nitrides and Imides. A recent report on hydrogen storage in lithium nitride of 11.4 wt% (~6 wt% cycleable) under pressure has sparked interest in the potential for nitrides and imides as hydrogen storage media (Chen et al. 2002). While the temperature required to release the hydrogen was high in this initial study, alkali metal nitrides and related compounds deserve additional study.

Nanoscale Hydrides. Studies regarding the benefits of nanoscale versions of hydride materials relative to their bulk counterparts should be undertaken over the wide range of potentially interesting hydride materials for hydrogen storage. Theoretical guidance for designing potentially interesting nanoscale hydride materials should be used.

Nanostructured Materials

Currently, there is considerable excitement about a new class of materials with unique properties that stem from their reduced length scale ($1 < d < 100$ nm). Examples of these types of materials include both carbon-based materials — such as nanotubes, nanohorns, fullerenes — and non-carbon-based nanomaterials made of other atoms (including nanoscale versions of the hydride materials discussed above). Researchers have demonstrated that at the nano scale, materials can have distinctly different properties than those observed in their bulk-material analogs. New synthesis techniques have opened the door to designing materials with specific architectures to yield desired properties. The small size of nanostructured materials strongly influences the thermodynamics and kinetics of hydrogen adsorption and dissociation by increasing the diffusion rate, as well as by decreasing the required diffusion length. The diffusion rate can also be influenced in general by changes in the phonon modes, which directly influence the transport rate. In addition, materials at the nano scale offer the possibility of controlling material parameters more independently than in their bulk counterparts. The advantages that can be realized because of nanoscale size could thus potentially minimize some of the current limitations of bulk complex hydrides, for example, and make some of these materials attractive for hydrogen storage.

Nanoscale hydrogen storage materials can be divided into two general categories. The first is "atomic" hydrogen storage materials ("dissociative" materials), which require the reversible dissociation of molecular hydrogen into hydrogen atoms and the bonding of these atoms with the lattice of the storage medium. Dissociative materials would include such storage materials as the complex hydrides discussed previously. The second category is "molecular" hydrogen storage materials ("nondissociative" materials), which, by virtue of their high surface area and microporosity, store hydrogen in the molecular state via weak molecular-surface interactions (e.g., van der Waals forces or physisorption). These materials include nanotubes, nanohorns, and non-carbon–based structures that have been tailored to have various sizes, surface areas, surface modifications, and other properties to control the physical characteristics of the materials. For example, calculations have shown advantages of curved surfaces in nanomaterials that exhibit an increase in their adsorption potential (Simonyan and Johnson 2002), and the storage of hydrogen on various carbon materials has been shown to correlate with the surface area of the material (Nijkamp et al. 2001). The hydrogen adsorbed on carbon nanotubes at 77 K is due to physisorption and is limited to 2 wt% (Zuttel and Orimo 2002).

Figure 7 shows the structures and micrographs of various carbon allotropes, including a double-wall nanotube, nanohorns, a nanotube bundle, and a cup-stacked carbon nanofiber (or multiwall nanotube) showing exposed edge planes (Eklund 2003; Endo et al. 2003). A simulation of the structure of adsorbed hydrogen in an optimized array of nanotubes at 298 K and 200 bar of hydrogen pressure is shown in Figure 8, which indicates that hydrogen atoms can adsorb both inside and on the surface of nanotubes (Johnson 2002). In addition, Figure 9 illustrates a recently reported example of hydrogen adsorption on a metal-organic nanostructure (Rosi et al. 2003). These nanostructured materials have a significant fraction of their atoms on the surface or in the adjacent subsurface of the structure. The possibility of tailoring the hydrogen storage and release properties of high-surface-area carbon materials by appropriate functionalization needs further exploration.

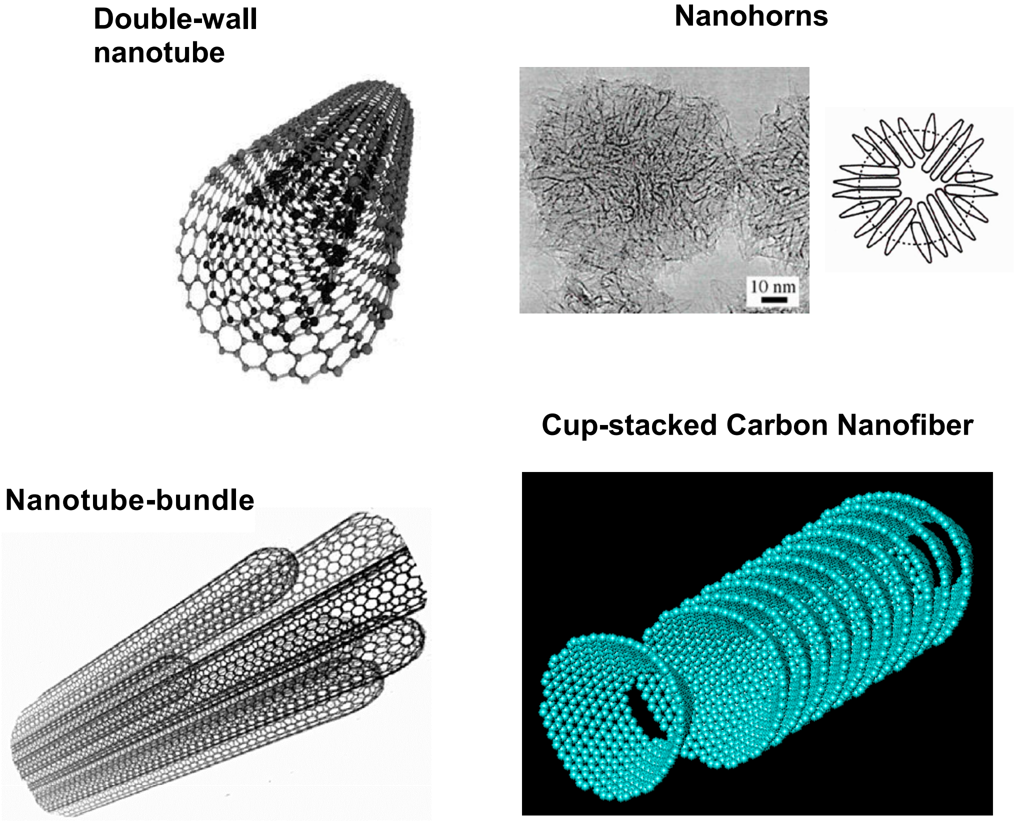


Figure 7 Structures and Micrographs of Selected Carbon Allotropes and Nanostructures (Sources: Nanohorns [upper right], Eklund 2003; nanofiber [lower right], Endo et al. 2003)

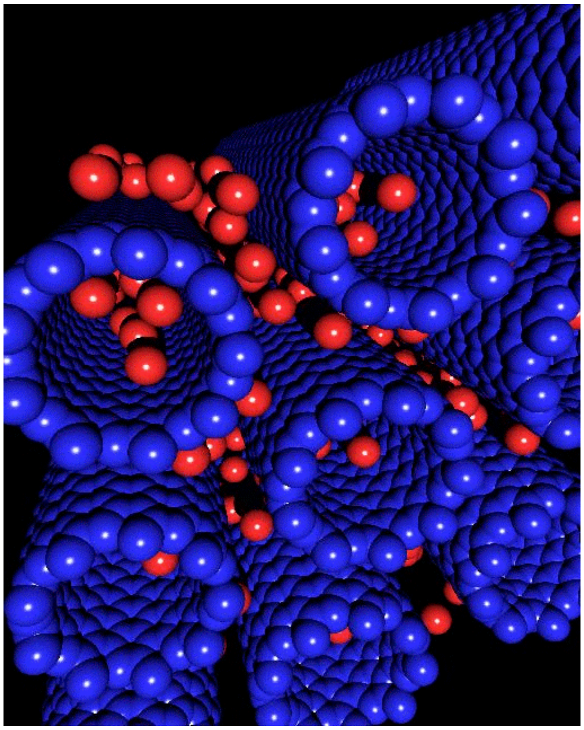


Figure 8 Simulation of the Structure of Adsorbed Hydrogen in an Array of Nanotubes at 298 K and 200 bar of Hydrogen Pressure (Source: Johnson 2002)

To learn how to design new nanomaterials for practical hydrogen storage, researchers need to gain considerable fundamental knowledge about these materials, incorporating both experimental and theoretical approaches, as discussed in the following sections.

Nondissociative Materials. For nondissociative materials, in which hydrogen is bound in molecular form, a means for increasing the hydrogen-surface interactions needs to be developed to facilitate storage at the target operational temperatures. For example, the strength of the molecular binding could be enhanced by adding suitable dopants. This will require understanding the mechanisms responsible for these interactions and the development of processes to design tailored materials that incorporate specific dopants. Theoretical guidance would be valuable in designing tailored materials.

Carbon Nanostructures. Studies of the reversible storage of hydrogen in carbon nanotubes have produced conflicting results, pointing to the need for (1) a new understanding of their synthesis and processing, (2) careful characterization of nanostructured materials, and (3) well-controlled and accurate hydrogen storage/release measurements and measurement techniques.

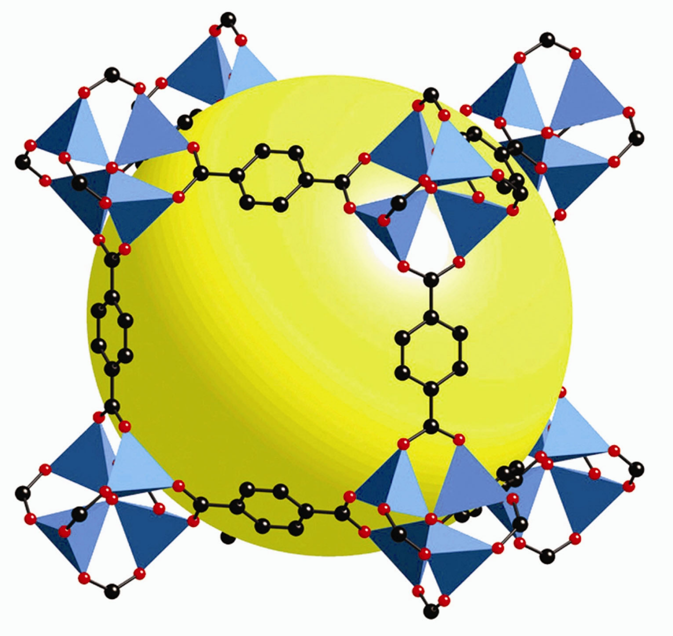


Figure 9 Schematic of a Single Crystal X-ray Structure for the Metal-organic Framework of Composition Zn_4O(1,4-benzene dicarboxylate)$_3$ Showing a Single Cube Fragment of a Cubic Three-dimensional Extended Porous Structure (This metal-organic compound adsorbed up to 4.5 wt% hydrogen at 78 K and 1 wt% at ambient temperature and 20 bar. Variants of this structure show promise for even better performances regarding hydrogen storage [Rosi et al. 2003].)

Novel Storage Concepts. Novel concepts for storage of hydrogen in nanostructured materials, such as nanoporous inorganic-organic compounds and polymers, need to be investigated. Methods for efficient synthesis of these materials are needed, as well as new tools for their nanoscale structural, chemical, and physical characterization.

High-surface Area Materials. Materials with large intrinsic specific surface area hold promise for hydrogen storage, and new materials with carefully designed architectures may meet the hydrogen storage needs for specific applications. These materials can involve physisorption or chemisorption of hydrogen on surfaces, as occurs with clathrates or zeolites. While these materials are unlikely to meet the required hydrogen density for on-vehicle storage on a gravimetric basis, they may prove suitable for stationary applications.

Nanophase Materials. Nanophase materials (e.g., nanoparticles and nanoporous media) offer promise for new classes of materials for hydrogen storage that can be effective for storing either atomic or molecular hydrogen. For example, nanoscale hydrogen storage materials might provide short diffusion distances, new phases with better capacity, reduced heats of adsorption/desorption, and faster kinetics, as well as new surface states capable of catalyzing hydrogen dissociation.

Undissociated Materials. For undissociated molecular hydrogen storage, concepts for new materials with specific surface chemical functionalities need to be evaluated, leading to the formation of intermediate-strength bonds between the surface and molecular hydrogen to permit efficient storage/release characteristics. These materials may also be designed with specific architectures, such as tunable pore size distributions, to enhance performance.

Characterization Techniques. Great care is required to characterize the structure, surface, and hydrogen storage/release properties of high-surface-area nanomaterials. Clearly, researchers need to identify the structure and surface properties of high-performance nanomaterials to facilitate modeling and provide an understanding of the structure-property relationships. Characterization of nanoscale materials presents a considerable challenge primarily because, at the nano scale, existing analytical tools lack the required detection sensitivity. Thus, new characterization tools that have increased detection sensitivity, while retaining high detection selectivity, need to be developed.

Theory and Computation

A fundamental understanding of the hydrogen interaction in materials requires a synergistic approach involving both theory and experiment. Theory and computation can be used not only to understand experimental results, but also to guide them. The large advances in methodology (theory and algorithms) and increases in computational power in recent years have opened up new possibilities for theoretical studies of hydrogen storage. Broadly speaking, four classes of theoretical approaches are available for studying these systems: (1) the quantum mechanical approach, which yields information about electronic structure and chemical bonds; (2) the empirical and semi-empirical approaches, which yield atomistic information about hydrogen trapping at vacancies and impurities; (3) the mesoscale approach, which yields information about average trapping at distributions of defects; and (4) the continuum methods, which yield information about transport through a real material.

Coupled with molecular dynamics, these approaches can predict the thermodynamic properties and time evolution resulting from thermally activated processes such as diffusion and chemical reactions. Direct simulations of time evolution can cover time scales of picoseconds (10^{-12} s) when using quantum mechanical methods to evaluate atomic forces, but up to nanoseconds (10^{-9} s) when empirical and semi-empirical potential energy functions are used. Mesoscale approaches, such as kinetic Monte Carlo, can cover much longer time scales (up to seconds), and continuum methods can cover time scales from seconds to hours. The behavior of hydrogen spans all these length and time scales and thus poses serious challenges for theory and computation. As yet, there is no general approach for integrating simulations on different length and time scales. Modeling is mainly carried out separately at each length and time scale with limited integration. Researchers need to find ways to integrate these methods in order to address the problems involving hydrogen production, storage, and use. The real challenge is to couple these approaches so that predictions of real materials behavior can be made with a solid physical and chemical basis.

Theory and computation can play two important roles in the development of hydrogen storage materials. First, each approach allows researchers to understand the physics and chemistry of the hydrogen interactions at the appropriate size scale. Researchers can use information generated at any of these levels to help choose new hydrogen storage materials. The second, and perhaps more powerful, application of theory and computation lies in the boot-strapping of information between theoretical levels. For example, the energetics data obtained from quantum mechanical calculations are used directly in the development of the semi-empirical potentials. The trapping energetics and kinetics obtained by using these potentials are used in a mesoscale calculation to determine effective properties as a function of microstructure. These results are then used directly in continuum calculations to predict the recycling properties of an engineering material. In principle, the entire process of material selection, processing, and — ultimately — material performance in service, can be accurately simulated.

To ensure that the modeling is accurate, it is critical that predictions at each size scale be compared with appropriate experimental information. Perhaps the largest contribution that theory and computation can make in the development of new hydrogen storage materials is to reduce the number of choices (and thus reduce the required development time) that researchers must investigate. Only through a multiscale approach, such as the one described above, can we expect predictions accurate enough to be useful in materials development. Examples of research areas for theory and computation are outlined in the sections that follow.

Hydrogen Interactions with Surface and Bulk Microstructures. Computational tools are needed to understand the interaction of hydrogen with surfaces and determine how hydrogen diffuses and interacts with step edges. The sites that hydrogen atoms occupy in the bulk, the energy barriers for its diffusion, its effect on the electronic structure of the host, its interaction with lattice defects (such as vacancies, voids, impurities, grain boundaries, and dislocations), and the effect of temperature and pressure on hydrogen interaction — all of these are important for a comprehensive understanding of hydrogen storage in materials.

Hydrogen Bonding. Theory can help elucidate how the ionic and covalent bonding between hydrogen and metal atoms in light complex metal hydrides can be changed by alloying. Similarly, an understanding of the role of catalysts/dopants in altering the nature of hydrogen bonding in these hydrides can be provided by theory and modeling.

Role of Nano Scale. Computational modeling can provide insight into the relationship of size and shape to the nature of hydrogen bonding and binding energies in nanostructured materials, and can thus help with the design of nanostructured versions of hydrides that may provide more efficient hydrogen storage capabilities.

Surface Interactions. In porous materials, such as clathrates, researchers need to understand how the hydrogen interacts with the surface of the materials.

Multiscale Hydrogen Interactions. A multiscale approach is needed to understand the electronic structure, dynamics, and energetics of hydrogen in materials.

Functionalized Nanocarbons. Theoretical modeling of functionalized nanocarbon materials is needed to guide the development of carbon-based nanostructures that demonstrate more desirable hydrogen storage properties than their pristine, nonfunctionalized counterparts.

CROSS-CUTTING ISSUES

Several of the basic research needs required to attain the goals for efficient hydrogen storage are similar to those needed in hydrogen production and use.

Catalysis

Catalysts can play a critical role in improving the kinetics and thermodynamics of hydrogen storage systems, allowing improved uptake and release of stored hydrogen with reduced need for thermal activation. The role of dopants in improving hydrogen release from metal and complex hydrides needs to be understood at the molecular level to facilitate development of improved storage materials.

Nanostructured Materials

A major advantage of nanostructured materials for hydrogen storage is that specific architectures can be designed into these materials to enhance the weight percentage of stored hydrogen and to control the kinetics involved in the adsorption/release of hydrogen. Incorporation of tailored nanostructures may allow dissociative hydrogen storage materials, such as the metal and complex hydrides currently used in bulk for hydrogen storage, to demonstrate substantial improvements in storage/release. Carbon nanostructures (including nanotubes and nanohorns) and the analogous non-carbon–based nanostructures show particular promise for effective nondissociative hydrogen storage. In both types of hydrogen storage, fundamental studies of the atomic and molecular processes involved in hydrogen adsorption and release are needed to enable the design of improved storage materials.

Theory, Modeling, and Simulation

As described above, close association of theory, modeling, and simulation with experiments is critical to understanding the chemical and physical processes involved in hydrogen storage and the subsequent design of improved storage materials.

Analytical and Characterization Tools

Major improvements in current analytical techniques are needed to meet the high sensitivity requirements associated with nanostructured materials, while maintaining high specificity in characterization. Ideally, researchers would like to be able to study hydrogen adsorption and release processes on individual nanotubes; such studies would include determination of the amount of hydrogen adsorbed, identification of the site of adsorption, and characterization of the physical/chemical parameters involved in hydrogen adsorption at a particular site. Many of the specialized experimental techniques available at synchrotron and neutron user facilities will be valuable for studying hydrogen storage materials. In particular, neutron scattering will provide unique capabilities for understanding the interactions of hydrogen with a storage material. These tools will also benefit from developments that will enhance the sensitivity of measurement tools to permit the detailed characterization of nanomaterials.

Safety

As with all technologies needed to achieve a hydrogen-based economy, safety issues need to be considered for technologies and materials that will be deployed for hydrogen storage devices. In particular, improvements are needed in the containers used to store gaseous and liquid hydrogen in the short term, and in solid-state hydrogen storage materials in the long term. Hydrogen presents particular challenges for the materials used for storage containers, including factors that affect container lifetime and leakage. Fundamental research will be needed to understand materials degradation and failure processes to allow design of improved materials for hydrogen storage.

CONCLUSIONS

Hydrogen storage is a key technology required for attaining a hydrogen-based economy. It represents the most challenging technical hurdle to reaching this goal. The storage capabilities of current technologies, such as gas and liquid hydrogen storage in containers or use of simple hydrides, are far from the requirements for viable onboard automotive storage. Simple, incremental improvements in these technologies will not allow researchers to meet the rigorous storage requirements. The breakthroughs needed to reach FreedomCAR targets will be attained only by fundamental research that will reveal the underlying principles in controlling hydrogen uptake and release. Understanding these chemical and physical processes will allow new, higher-efficiency, recyclable hydrogen storage materials to be designed.

Nanoscience has the potential to provide revolutionary new capabilities that will have a profound impact on hydrogen storage. Improvements in today’s metal and complex hydrides can be achieved by careful design of two- and three-dimensional nanoarchitectures that include dopants and tailored voids to improve the weight percentages of stored hydrogen and provide control of the kinetics and thermodynamics of hydrogen storage/release. Carbon and non-carbon nanostructures have shown particular promise for the storage of molecular hydrogen. New insights into the mechanisms of hydrogen uptake and release in these materials are needed to design new functionalization strategies and architectures for improved hydrogen storage.

Fundamental studies of nanomaterials used in hydrogen storage will require the availability of new highly sensitive and selective analytical tools to match the scale requirements of these nanomaterials. Finally, discovery of new hydrogen storage materials will require close coupling between experimental and computational research activities to elucidate the physical and chemical processes involved in hydrogen storage and release, while modeling and prediction of these processes are needed so that improved materials can be designed efficiently.

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BASIC RESEARCH CHALLENGES FOR FUEL CELLS AND NOVEL FUEL CELL MATERIALS

CURRENT STATUS

Fuel Cells in the Hydrogen Economy

Fuel cells provide the final step in a hydrogen economy in which chemical energy carried by hydrogen fuel is transformed into electrical energy. Fuel cells are especially well suited for this task because they operate with high efficiency, they do not produce pollution, and they provide electrical power that can be tailored to a wide variety of applications — from large stationary power plants to transportation vehicles to consumer devices like cell phones and personal computers. Fuel cells link hydrogen and electricity, two highly compatible energy carriers that embody the ideals of a sustainable energy economy: they are clean, abundant, and adapt flexibly to many sources of fuel production and to many uses. The same electrochemistry that drives the conversion of hydrogen to electricity in fuel cells also drives the production of hydrogen by electrolysis of water. These two technologies — electrolysis and fuel cells — bracket the vision of the hydrogen economy as a clean and sustainable means of energy production and use. Advances in materials, electrolytes, catalysts, and nanoscale design that benefit one of these processes automatically benefit the other.

The basic fuel cell types span a remarkable range of operating temperatures, construction materials, and performance specifications. Table 4 lists the basic types of fuel cells; the electrolyte, conducting ion, and operating temperature are indicated along with some notable features. A thorough and highly readable explanation of fuel cells in the hydrogen economy can be found in Larminie and Dicks (2003).

Fuel cells directly convert the chemical energy stored in molecular hydrogen to electrical energy. Because this electrochemical conversion does not rely on the heat of combustion, some fuel cells can have a higher limiting efficiency than the Carnot cycle that governs conventional "heat engine" power plants. Although fuel cells offer many advantages for a diverse set of applications, so far they have been introduced only on a limited scale and at high cost. The promise of high efficiency and low pollutant emissions continues to drive research and development (Vielstich et al. 2003). While several fuel cell technologies have been developed and demonstrated for use in the commercial and consumer market, significant challenges, some longstanding, must be overcome if fuel cells are to be used on a large scale.

Fuel cells currently under development consist of a variety of materials, designs, and technologies that are primarily determined by the operating temperature, from ambient to as high as 1,000^{o}C (see the sidebar for a simple description of a fuel cell). Nevertheless, there are serious and difficult obstacles to widespread implementation of fuel cell technology. Most of the challenges arise from the need for inexpensive, more-durable materials that also have better operating characteristics, especially in the case of the electrocatalysts, membranes (ionic conductors), and reformer catalysts. Reformers offer the potential for operating fuel cells by using a range of primary fuels. Some current and proposed fuel cell power systems that are

Table 4 Fuel Cell Types and Their Operating Features

Fuel Cell Type	Electrolyte	Conducting Ion	Temperature (ºC)	Features
Polymer	$CF(CF_2)_nOCF_2SO_3^{2-}$	H^+ (hydrated)	60–80	High power density, Pt catalyst, must be kept wet, poisoned by CO
Alkaline	KOH	OH^-	90	High power density, cannot tolerate CO_2
Phosphoric acid	H_3PO_4	H^+	200	Medium power density, Pt catalyst, sensitive to CO
Molten carbonate	Li_2CO_3 / K_2CO_3	CO_3^{2-}	650	Low power density, Ni catalyst, needs CO_2 recycle
Solid oxide	$Zr_{0.92}Y_{0.08}O_{1.96}$	O^{2-}	700–1,000	Medium-to-high power density, accepts CO as fuel
Direct methanol	$CF(CF_2)_nOCF_2SO_3^{=}$	H^+ (H_2O, CH_3OH)	60–120	Medium power density, low efficiency, high Pt content

[a] Source: Kumar (2003).

capable of using fuels other than hydrogen may serve as transitional technologies along the path to a full hydrogen economy. These hydrocarbon-based fuel cells may be important in increasing the efficiency of fuel use and in decreasing emissions or noise, a highly valued aspect in some military, as well as in some commercial/consumer, applications. Indeed, some of the fundamental problems in fuel cell technology are independent of the fuel source, as we discuss later.

A major use for fuel cells in a hydrogen economy is in portable and mobile applications in which compact and efficient power sources are needed. Powering transportation vehicles with fuel cells is especially attractive, because it has the potential to significantly reduce automotive pollution and the production of greenhouse gases, reduce the demand for imported oil, and conserve fossil fuel reserves. Transportation applications now drive a significant fraction of research and development (R&D) on fuel cells in industrial and government sectors (U.S. Department of Energy [DOE] 2002). DOE has established target performance specifications for demonstration and implementation of transportation fuel cell technologies. These goals point out the difficult technical challenges to the development of automotive fuel cells that are sufficiently inexpensive, effective, and durable to displace current internal combustion engines. Overcoming these challenges to produce commercially viable automotive fuel cell technologies requires innovative fundamental research on the catalysts, the electrochemistry, the membrane materials, and the nanoscale behavior governing the performance and cost of fuel cells.

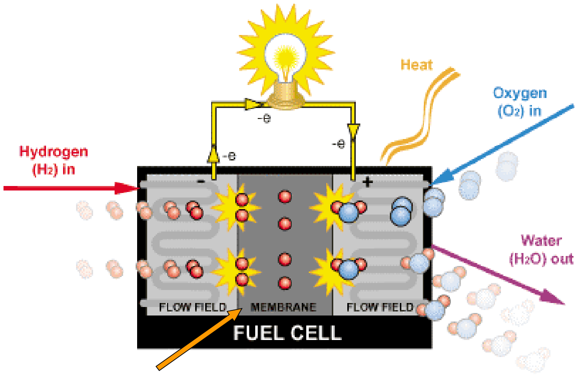
WHAT IS A FUEL CELL?

The fuel cell was invented by Sir William Grove in 1839. It was not until the 1950s, however, that the National Aeronautics and Space Administration (NASA) constructed the first practical fuel cells to produce power for space vehicles.

Fuel cells directly convert the energy released in certain chemical reactions, primarily combustion (oxidation) of hydrogen or a carbonaceous fuel, to electrical energy. Typically, combustion reactions are of interest because they release a large amount of energy per unit mass of fuel and because some of these fuels are available at relatively low cost. The reaction of hydrogen (the fuel) with oxygen (the oxidizer) to produce water is such a suitable reaction. Other fuels used in fuel cells include methane, methanol, and even gasoline. More chemically complex fuels, like gasoline, typically require pre-processing into a hydrogen-rich gas stream before introduction to the fuel cell.

The fundamental building block of a fuel cell is an electrochemical cell (see figure) consisting of two electrodes separated by an ionically conducting medium (or membrane). The ionically conducting medium can be an acid, base, or salt (in liquid, they are in polymeric or molten forms) or a solid ceramic that conducts ions; the choice of electrolyte is dependent on the nature of the fuel, the temperature of operation, and the specific application of the technology. Fuel enters the cell on the left side and oxygen enters on the right side. Any reaction products (water and perhaps carbon dioxide [CO_2] — depending on the fuel and type of cell) must also exit the cell. As fuel is oxidized, electrons are released to travel through the external load to the cathode, where oxygen consumes the electrons. The following other essential parts of a real fuel cell are omitted from the diagram: all the container and support materials that keep the fuel and oxygen flowing (but separate) and direct the reaction products out of the cell, the interconnections between a series of cells, etc.

$$2H_2 + O_2 \rightarrow 2H_2O + \text{electrical power} + \text{heat}$$



Membrane conducts protons from anode to cathode
proton exchange membrane (PEM)

The electrodes serve several functions. First, they must be electronically conducting. Second, they usually contain the electrocatalytic materials that facilitate the reaction of fuel at one electrode (the anode) and of oxygen at the other electrode (the cathode). Some catalytic materials are much better than others at facilitating the reactions and may themselves also be electronic conductors. Grove used solid pieces of platinum metal for both electrodes; platinum was both the conductor and the electrocatalyst. In most contemporary low-temperature fuel cells, platinum electrocatalysts are still used, but in highly dispersed form as nanoparticles.

The electrocatalyst is highly dispersed in order to attain large electrochemical reaction rates that result in high electrical power output. Furthermore, for the fuel cell to function properly, the electrocatalyst particles have to be easily reached by the fuel (or by oxygen on the other side of the cell), and they also must be contacted by the ionically conducting medium and by the electronically conducting medium. Consequently, current low-temperature fuel cell electrodes consist of porous composites of ionic/electronic conductors with embedded nanosize particles of the electrocatalyst in order to obtain as high an electrical power from as small an amount of precious metal as possible. The electrode contains open pores for the fuel (and any waste products) to enter or exit the electrode. Producing electrodes that offer optimal performance is challenging.

More than 150 years after Grove's discovery, fuel cells that operate near room temperature still contain the precious metal platinum. One goal of an ambitious fuel cell R&D program is to replace the expensive platinum with much cheaper materials. No one thinks this objective will be easy to attain — after all, nothing better has been found in 150 years!

Many web sites are dedicated to fuel cells and to Sir William Grove; a few of the many interesting ones are listed below:

http://fuelcells.si.edu/basics.htm (at the Smithsonian Institution)
http://science.howstuffworks.com/fuel-cell.htm
http://education.lanl.gov/resources/fuelcells/
http://chem.ch.huji.ac.il/~eugeniik/history/grove.htm
http://www.voltaicpower.com/Biographies/GroveBio.htm
http://www.eere.energy.gov/hydrogenandfuelcells/

In this Report, we discuss primarily the challenges and problems associated with low-temperature fuel cells (operating from 40 to 150°C or 200°C) and, to a lesser extent, with high-temperature (650–1,000°C) fuel cells. While there are many possible technologies, any one of which could be the optimal fuel cell for a specific (or even most) applications, much of the recent R&D effort has focused on these two technologies. They also serve as models for discussion of the many significant challenges to the large-scale implementation of fuel cell technologies. Low-temperature fuel cells, in particular, are the focus of current automotive fuel cell R&D activities that, when implemented, would be a major component of the hydrogen economy.

Low-temperature Fuel Cells

The use of fuel cells in the transportation sector could potentially provide substantial benefits and is perhaps the largest potential market for fuel cells. However, present technology cannot come close to the cost targets that will allow substitution of a fuel-cell–based "engine" for an internal combustion engine. All current designs of fuel cells for this application are low-temperature (about 80°C) technologies based on polymeric membranes as proton-conducting electrolytes. The need for low-temperature fuel cells in this sector is driven by system considerations — in particular, overall weight and volume, fuel conversion efficiency, fast start-up times, and long out-of-use periods. Current estimates of polymer proton exchange membrane (PEM) fuel cell system costs, when extrapolated to mass production, exceed $100/peak-kW. To compete economically with the internal combustion engine, however, the cost must approach $35/kW. Present-day costs for low-volume production are roughly $3,000/kW for hydrogen-based fuel cell systems. The need to reduce the costs by nearly two orders of magnitude underscores the long pathway to the goal of automotive application of fuel cells (potential stationary applications can be viable at much higher costs in terms of dollars per kilowatt-hour).

The primary difficulties in achieving the automotive cost targets lie in the materials used in the fuel cell stack. Proton exchange membranes, precious metal catalysts (typically platinum or platinum alloys), gas diffusion layers, and bipolar plates account for 70% of the cost of the system. Any two of these are projected to cost more than the target for the *full system* unless researchers can achieve significant advances in power density and materials optimization and durability.

Additional significant challenges for PEM fuel cells (PEMFCs) involve functionality and durability issues. New membranes that exhibit adequate durability and proton conduction properties at temperatures exceeding 100°C (while also maintaining these properties at low ambient temperatures) are needed because they enable the system to achieve more effective heat rejection — a must for automotive systems — as well as higher impurity tolerance in the fuel and improved overall system efficiency. Efficiency can be increased through improved thermal integration of the stack and the balance of the plant, as well as through the production of higher-quality waste heat for possible use in combined cycles. Operation in this temperature range provides a new set of challenges that are only now being addressed.

Durability of PEMFCs in transportation applications is a key issue that has been amplified in importance as fuel cell engineering has matured. Roughly 5,000 h of operating life are required, based on a simple calculation of a 250,000-km vehicle lifetime at an average speed of 50 km/h.

Performance degradation rates of the polymer membrane under the cycling conditions of automotive fuel cells can be substantial, especially as materials are pushed into higher operating temperature regimes. At present, the degradation mechanisms are only partly understood. Multiple chemical and mechanical processes undoubtedly contribute to this degradation. For stationary fuel cell applications, an even more demanding lifetime — a minimum of 40,000 h or approximately 5 yr — of continuous operation is desired.

High-temperature Fuel Cells

Solid oxide fuel cells (SOFCs) are the technology currently under most active development for applications requiring high operational temperatures (near 800°C). The solid oxide is used as the ionically conducting membrane, transporting oxygen ions from the cathode to the anode of the fuel cell. The much higher temperature of operation in SOFCs offers some advantages over most current PEM cells. A wide range of fuels, from hydrogen to hydrocarbons (especially natural gas), can be used and may enable a transition from a hydrocarbon to a hydrogen economy. In addition, in certain modes of operation, SOFCs have demonstrated the longest lifetime of any fuel cell system. For example, a 100-kW system fabricated by Siemens-Westinghouse has successfully produced power for more than 20,000 h without any measurable degradation in performance (George et al. 2002). Unlike PEMFCs for automotive applications, SOFCs in stationary applications can run for a long time without being turned off, a factor favoring long life. The waste heat production from SOFCs is at a temperature suitable for cogeneration, resulting in systems with excellent efficiencies — projected to be up to 85%. Phosphoric acid fuel cell systems operating at 200°C have demonstrated combined heat and power efficiencies in excess of 80% (Maston 1998). Until major issues such as unacceptably poor power densities and cost are addressed, however, the SOFCs that have been developed to date cannot be broadly commercialized. Many of the key barriers are materials-related. For example, materials corrosion, inability to thermally cycle, and integrity of seals are still major issues (see subsequent discussion). Targets of less than $400/kW have been set but, as in the case of PEMFCs, there are presently no obvious pathways for reaching such cost targets.

If these challenges can be overcome, SOFCs may benefit the transportation, as well as the stationary power, sector. For transportation, auxiliary power units can be used to maintain power for refrigeration and human comfort with the engine power off, providing benefits in terms of lower emissions. While SOFCs, in contrast to PEMFCs, can easily be operated with natural gas (or even gasoline) in addition to pure hydrogen, their poor durability under extended thermal cycling (heating to operation temperature and then cooling to room temperature) does not yet allow them to be used in configurations in which frequent shutdowns are required. On the other hand, in stationary applications, where shutdowns do not occur very often, extremely high efficiency can be attained for combined-cycle and cogeneration systems.

Many of the engineering challenges in design of the electrode assembly, the fuel-oxidizer-water-waste flows, etc., have been met in both the low- and high-temperature fuel cells to at least a first approximation. Major challenges that remain (i.e., cost, durability, efficiency, insensitivity to impurities) can be addressed only by developing new and better materials in conjunction with continued (and in some cases, accelerated) advancement in both our fundamental understanding of fuel cell processes and engineering to incorporate new approaches. The proportions of this challenge are immense, and the need to address fundamental scientific questions associated with fuel cells is immediate.

These challenges represent a significant opportunity for a broad range of R&D in chemistry, nanoscience, and materials sciences. The primary needs are addressed more specifically in the following pages.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS IN HYDROGEN FUEL CELLS

The heart of the fuel cell is formed from two electrocatalytic electrodes separated by an ionically conducting membrane — the so-called membrane electrode assembly (MEA). Although the specific challenges are different for different fuel cell technologies, the underlying key materials issues are similar: cost, performance, and durability.

Cathodes

In all fuel cell technologies, independent of the fuel and operating temperature, oxygen is reduced at the cathode. In all cases, independent of the particular material used as the cathode electrocatalyst, the overpotential for the reduction of oxygen at operating currents is too high. This overpotential is caused by the slow electrochemical kinetics of oxygen reduction, and it represents an additional driving force needed to obtain significant currents in the cell. The result is a decrease in cell voltage, with a corresponding loss in efficiency. The problem is especially severe in near-ambient-temperature fuel cells, in which the only cathode catalysts that are currently acceptable and used are Pt or Pt-based alloys. The high overpotential results in a loss of 300 to 400 mV out of a Nernst voltage of 1.23 V per cell. Furthermore, the activation overpotential for oxygen reduction at Pt is high even at very low currents, as illustrated in Figure 10. Thus, cheaper materials with lower overpotential are sorely needed.

Platinum is generally used in the cathode as carbon-supported nanoparticles. Mass-specific power densities range from 5–10 gPt/kW (i.e., \$125–\$250/kW) for direct methanol fuel cells (DMFCs) to 0.5–1 gPt/kW (i.e., \$12.5–\$25/kW) for the others. The lower mass-specific power densities observed for DMFCs arise mainly from poor anode kinetics and even poorer cathode performance caused by methanol crossover, requiring much higher noble metal loadings compared with hydrogen-fueled PEMFCs. While noble metal cost is less critical for applications in which small power sources (in the 1-W range) are needed, Pt cost and Pt supply constraints for large-scale automotive applications require mass-specific power densities in the range from 0.1 to 0.2 gPt/kW (see Figure 11) (Gasteiger and Mathias 2002). Dramatic improvements in overall performance, efficiency, and cost can be achieved by reducing the overpotential. The high overpotential for oxygen reduction, however, is a long-standing problem and, so far, research on the fundamental processes of oxygen reduction and catalysis has not yielded a breakthrough. Clearly, new insights from theory and modeling, new creative ideas, and (most likely) new materials are needed.

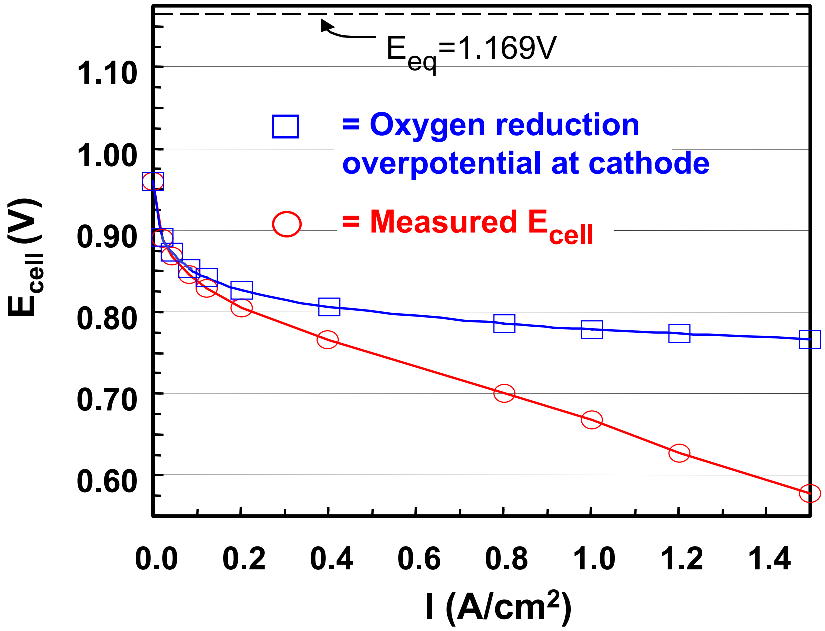


Figure 10 (Lower curve) Cell Voltage (E_{cell}) of a State-of-the-art H_2/Air Membrane Electrode Assembly Operated at 80°C versus the Current Drawn from the Cell (in amp/cm^2) (Gasteiger and Mathias 2002) (The equilibrium [theoretical] cell voltage [1.169 V] is shown by the dashed line at the top of the figure.) (Upper curve) Reduction from the Theoretical Value Caused by the Oxygen Reduction Overpotential at the Cathode Alone (Note that the overpotential is large at all but the very lowest currents. The remaining loss in potential at a given current is caused by internal resistance in the cell and to O_2 gas transport limitations through the air in the porous cathode composite.)

The oxygen reduction overpotential often increases as the hours of operation increase. Depending on the exact operating conditions, voltage degradation rates of 1–100 μV/h are typical. System requirements (heat rejection, performance) generally drive the system temperature to the upper limit of the specific fuel cell system (e.g., greater than 80°C for automotive PEMFCs), where degradation rates are highest. Current automotive PEMFCs operating at >80°C show degradation rates of >50 μV/h; <10 μV/h are required (5,000-h life). Stationary PEMFC systems operate at ≤80°C, with degradation rates from 10 to 20 μV/h, while <1 μV/h is required (40,000-h life). Researchers believe that these degradation phenomena are caused by chemical or structural changes in the catalysts or their supports that are intrinsic or driven by the presence of various impurities; however, fundamental studies of the mechanisms of degradation are sorely needed.

The state of understanding in this area is improving, and several Pt alloys have been shown to provide higher oxygen reduction rates. A promising way of reducing Pt loading, and perhaps increasing reduction activity, may involve a metal nanoparticle surface "decoration" by using a submonolayer-to-monolayer amount of Pt. This approach showed promising results with the

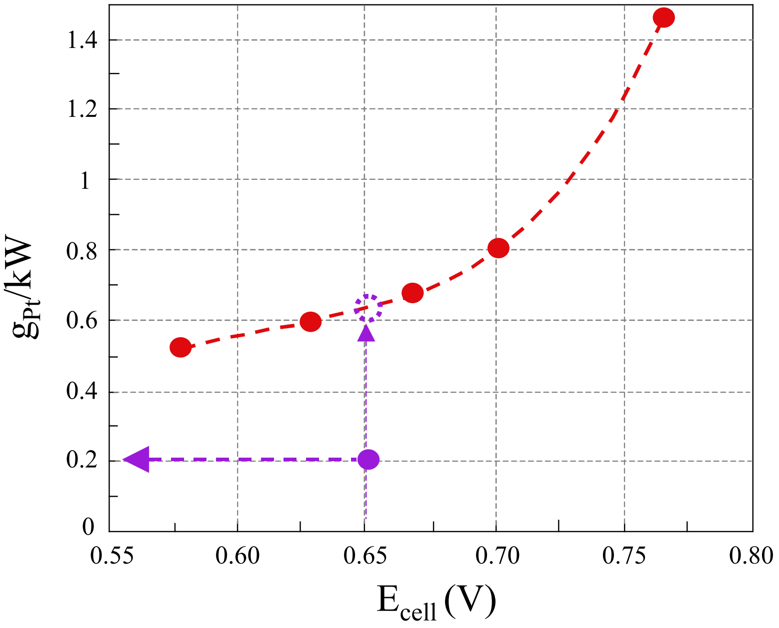


Figure 11 Mass of Pt Used in the Fuel Cell — a Critical Cost Issue (This plot shows the power density per gram of Pt that can be obtained in a state-of-the-art H_2/air membrane electrode assembly operated at 80°C at different operating cell potentials. The present design is to operate at a cell potential of 0.65 V, which must use about 0.65 g of Pt nanoparticles to attain a power output of 1 kW. For cost, weight, and volume reasons, the Pt loading must be decreased to about 0.2 g of Pt/kW output [Gasteiger and Mathias 2002].)

Pt/Ru anode catalyst (Brankovic et al. 2001). However, the long-term stability of these systems in the PEMFC environment and at cathode potentials is still unproven. It is therefore critical to understand the fundamental principles underlying both the performance and corrosion stability of Pt alloys at all particle sizes and coverages and, of course, of any new materials that are proposed or invented.

Finally, the currently used carbon supports for Pt (either fully or partially graphitized materials) corrode under certain system-imposed operating conditions (e.g., idle operation, start/stop) and thus limit fuel cell system durability. More durable support materials are needed. Recent advances in nanostructured carbons, such as cup-stacked carbon nanofibers, have been introduced for use in fuel cell and lithium (Li) battery applications in Japan (Endo et al. 2002). Such materials might be useful for fuel cell cathodes.

Some biological enzymes apparently reduce O_2 at a high rate and low overpotential (Katz et al. 2003). These enzymes are unlikely to be directly useful in fuel cells for many reasons, including their instability at fuel cell operating temperatures. We know the stoichiometry and structure of the inorganic core of the enzyme. The challenge lies in mimicking this property in more robust materials by understanding the operation of the enzyme — whether properties of the organic part, such as flexibility and stereochemical blocking, also play an important role. These enzymes hint that there may be a solution to the long-standing challenge of the efficient electrochemical reduction of oxygen — a solution suitable for fuel cell applications. Clearly, considerable research is required to determine whether bio-inspired materials that are significantly cheaper and more efficient than Pt can be used as cathode electrocatalysts in low-temperature fuel cells.

A conducting perovskite, such as strontium-doped lanthanum manganate (LSM) (e.g., $La_{0.84}Sr_{0.16}MnO_3$), is normally employed as the cathode electrocatalyst in SOFCs. At typical operating conditions (800°C and 0.5 A/cm^2), the overpotential is 100–300 mV. There is a major push to reduce fuel cell operating temperatures to replace some of the ceramic components with metals, which have lower manufacturing costs. The metal components that would be used in a reduced-temperature fuel cell would serve as interconnects between individual fuel cells in a fuel cell stack. As the temperature is reduced, there will be a need for a higher-conductivity electrolyte other than zirconia. Current materials under development include $(La,Sr)(Ga,Mg)O_3$ (LSGM) and doped ceria as oxide ion conductors and various oxide proton conductors (Doshi et al. 1999). The real challenge to reduced-temperature operation is the cathode material. $(La,Sr)MnO_3$ is only moderately effective at high temperatures and has unacceptable performance at lower temperatures. Alternatives that have been considered are $(La,Sr)(Co,Fe)O_3$ (LSCF) and $(Sr,Sm)CoO_3$ (SSC). While these materials exhibit potentially higher performance than LSM cathodes, they are difficult to process due to chemical reactivity and thermal mismatch with the electrolyte.

Anodes

In most fuel cells, the main issue is “poisoning” or fouling by impurities in the hydrogen feed stream such as sulfur, hydrocarbons, and carbon monoxide (CO) (CO is only a problem in low-temperature cells). The overpotential for the oxidation of high-purity H_2 is quite small. In fact, for Pt electrodes used in H_2-operated PEMFCs, the anode overpotential is on the order of 10–50 mV, while the cathode overpotential ranges from 300 to 500 mV (Gasteiger et al. 2003). Impurities that react with the anode, however, can substantially increase the overpotential. The same situation occurs in high-temperature SOFCs when hydrogen is the fuel and Ni is used as the anode electrocatalyst. A higher tolerance of impurities would allow the use of less-pure H_2, reducing the cost of hydrogen production. Lower-temperature fuel cells also use precious metals as the anode electrocatalyst; a higher impurity tolerance would reduce the amount of precious metal needed. CO tolerance of available catalysts is marginally acceptable at present but could be improved. Sulfur tolerance is quite low (in the 10-parts-per-billion [ppb] range). The best tolerance to CO has been achieved by combining catalysts with passable tolerance (especially Pt/Ru alloys) with air injection to remove CO from electrode surfaces (Tada 2003). However, the air injection can lead to durability problems.

Anode catalysts that can use fuels other than hydrogen may also be important for several reasons. They may be useful in the transition from hydrocarbon fuels to hydrogen fuel. Pt/Ru alloys have been used for some time as the catalyst in near-ambient–temperature methanol fuel cells. Although the use of Pt/Ru alloys in such cells is not without problems, its performance is considerably better than that of pure Pt. Recently, reports of other materials, such as ordered intermetallic PtBi, which are potentially useful catalysts for the oxidation of formic acid, methanol, etc. (Casado-Rivers et al. 2003), suggest that these materials will be tolerant of at least hydrocarbon and CO impurities. Studies of the sulfur tolerance of these new materials have yet to be undertaken. To make real headway, such catalysts should be significantly more tolerant of impurities than Pt/Ru. Researchers have not yet identified catalysts that operate near ambient temperature and can completely oxidize fuels that contain more than one carbon atom, but such catalysts would be very desirable for using ethanol or other fuels that are not as poisonous as methanol. Finally, if such catalysts can be found, they are likely to be very useful for catalyzing a variety of industrial organic processes, particularly oxidation reactions. So the discovery of novel anode catalysts may impact many other technologies, not all of them directly related to fuel cells.

The situation is similar in SOFCs, in which the poor ability of Ni to catalyze hydrocarbon electroreduction at reduced pressure (carbon deposition is catalyzed instead) and the susceptibility of Ni to oxidation are important problems. High-priority electrode research needs are discussed in the following sections.

Low-temperature Cathode Catalysts. In PEMFCs, improvement of cathode catalysts would not only increase efficiency, but would also lower the mass (and cost) of precious metals and result in system improvements (e.g., less heat rejection). If this challenge can be met, higher-temperature membranes (120°C or so) may not be required for automotive applications. This is, however, a monumental challenge; electrochemists have been working on it for half a century.

In the short term, researchers need to develop materials processes for low-temperature electrodes that reduce the precious metal content in order to reduce cost. These processes could include depositing precious metals only on the *surface* of nanoparticles or using alloys or intermetallic compounds that contain less expensive elements but maintain (or even enhance) the catalytic activity of Pt. Precious metal that is not at the surface of the electrocatalytic nanoparticles is inactive. Reducing Pt content might be achieved via Pt-skin catalysts, Pt-decoration of other nanoparticles, and/or improved support materials; however, the long-term structural and chemical stability of such surface coatings is not known. Another alternative to platinum cathode catalysts is Pt alloys (Thompsett 2003), but their long-term durability has not yet been demonstrated. If the catalyst is supported on a second material, there is also a need to develop catalyst supports that are more resistant to corrosion at high voltages (i.e., idle fuel cell conditions) and transient operation (i.e., start/stop) to improve system durability.

In the long term, the discovery of oxygen reduction catalysts containing much less (or no) precious metal is highly desirable. The breakthroughs may come from materials that are bio-inspired — mimicking those that are as efficient as some enzymes — and from exploiting combinatorial synthesis and analysis methods to rapidly and efficiently search large phase spaces to identify materials with potentially improved catalytic activity. These complex materials may be produced as nanoparticles, which could facilitate high reaction rates and high-power output. Indeed, if the catalysts are active only as nanoparticles (as is the case for gold cathodes in alkaline cells), we can design synthesis strategies to prepare such particles as part of a combinatorial synthesis approach. Theory and modeling of oxygen reduction processes at different catalytic surfaces could guide the synthesis of new cathode materials or otherwise help in the search. Finally, theory could support the effort by helping researchers to understand experimental results for known catalysts.

High-temperature Cathode Catalysts. The main impediment to longer life of SOFCs is the high operating temperature. Lowering the operating temperature by several hundred degrees could significantly improve their lifetime, as well as lower the cost. Two factors currently prevent lower-temperature operation: the poor activity of present cathode materials at lower temperatures and the low oxygen ion conductivity of known, durable solid oxide membranes. Clearly, inventing and developing new materials to address these needs is critical. As with low-temperature cells, combinatorial synthesis and analysis methods may be able to more rapidly and efficiently identify new materials candidates. Also, as with low-temperature cells, modeling and theory could play an important role.

Anodes. The need here is for considerably improved impurity tolerance, especially to sulfur, hydrocarbons, and CO (the last in low-temperature fuel cells only). Improved impurity tolerance would allow the use of less pure hydrogen and perhaps hydrocarbon-based fuels, a potentially useful transition technology. Ordered intermetallic compounds are one potential class of materials that have recently been shown to be tolerant of CO and hydrocarbons, even at room temperature. In fact, such materials may be suitable ambient-temperature electrocatalysts for simple fuels such as methanol (Casado-Rivers et al. 2003). Whether such materials would be similarly effective as anode catalysts in high-temperature fuel cells remains to be demonstrated. In addition, based on earlier results using Cu, researchers believe that Ni in SOFC anodes may be replaced by other inexpensive materials to eliminate the coking problems, boost catalytic activity, and tolerate (or even use) C_2 to C_{10} hydrocarbons. In both cases, sulfur-tolerant anodes would be very desirable.

Understanding Electrocatalysis at the Atomic Level. Well-defined fundamental experiments (e.g., using single crystals) to understand oxygen reduction mechanisms at the surfaces of known materials (Pt, Pt-alloys, Au) and novel materials are needed. Such experiments should not be limited to acid environments. For example, work in alkaline environments may improve our fundamental understanding of why a gold catalyst is active in alkaline and not in acid electrolytes. Breakthrough catalysts for alkaline fuel cells would make such fuel cells attractive for many diverse applications. It is also important to expand this understanding to include interfaces that mimic the conditions at real electrodes that are only partly hydrated so that gases have access to the same surface.

At the same time, improved methods of modeling experimentally realistic electrode phenomena are sorely needed. For example, modeling and simulation have progressed to the point that studies of the dissociation of oxygen on electrocatalyst metal surfaces in the presence of an electrolyte and as a function of potential could be carried out at a high enough level of accuracy to be useful (see Figure 12). Such calculations may provide insights that can be translated into the development of new materials.

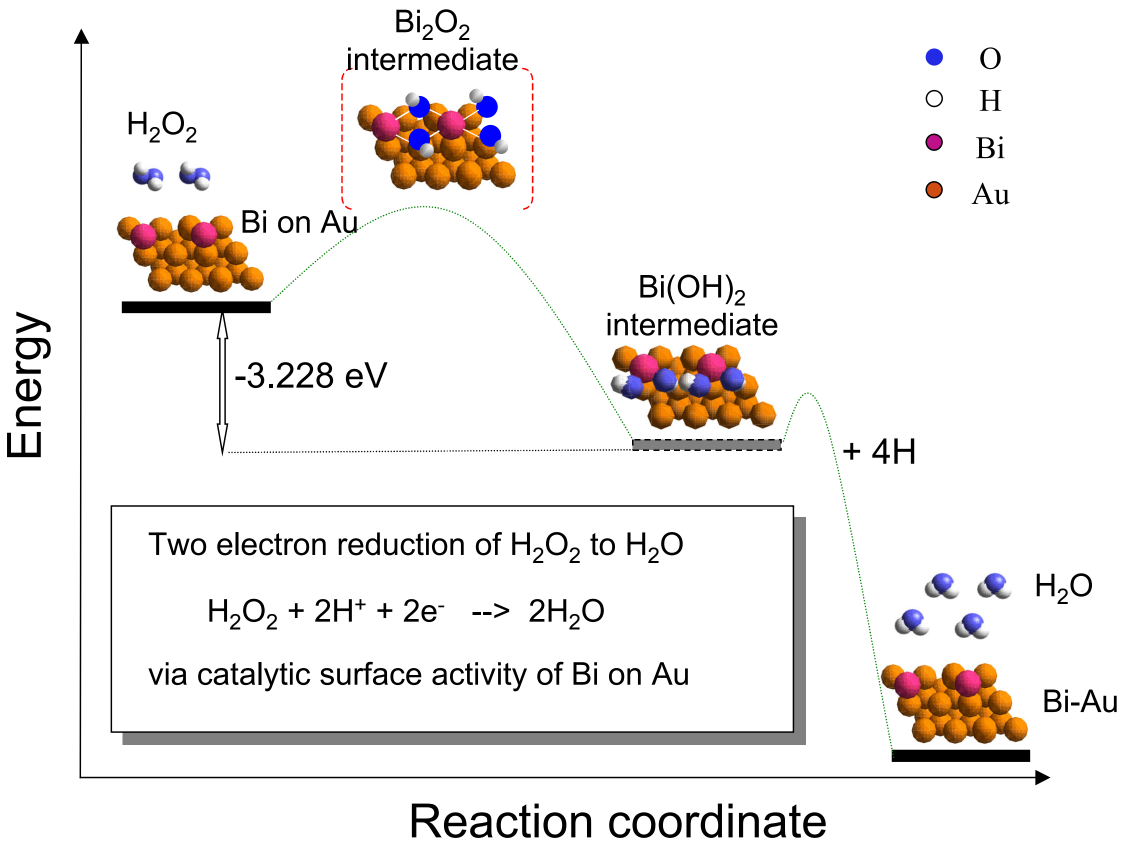


Figure 12 Simulation of the Hydrogen Peroxide Reduction Mechanism by Catalysis on the Bi/Au (111) Surface (The 2 × 2 structure of Bi on Au is a key factor driving the dissociation of the peroxide O-O bond [Sources: Gewirth 2003; Li and Gewirth 2003].)

Membranes

Higher ionic conductivity, better mechanical strength, lower cost, and longer life are all important issues for fuel cell technologies. For near-ambient temperature cells, polymer electrolytes (Nafion is the commercial membrane) must be hydrated to operate. Without complex high-pressure systems, hydration is lost above 80°C; fuel cells ideally should operate at 120°C for heat dissipation reasons (Gasteiger and Mathias 2002; Masten and Bosco 2003). It appears that polymer membranes are easily degraded under high power and on/off cycling. Macroscopic holes can appear even after relatively short-term use. The membranes are also sensitive to ionic impurities produced when the metal components of the fuel cell corrode. Clearly, polymer membranes need considerable improvement.

The polymer membranes presently available for fuel cell applications can be divided into two general classes. Perfluorosulfonic acid (PFSA)-based membranes (e.g., Nafion) have long been the standard. Membranes based on aromatic sulfonic acid moieties have been the primary class of materials investigated as alternatives to PFSAs. The latter class includes a wide range of materials, including sulfonated poly(phosphazenes), sulfonated poly(sulfones), sulfonated poly(ether ketones), and sulfonated poly(trifluorostyrenes), among others. An additional wrinkle to the membrane theme is the inclusion of the proton-conducting phase within a network. Examples include materials prepared by Gore and by Foster-Miller R&D scientists. Advantages of the Foster-Miller approach include (1) the excellent mechanical properties of the membranes, which enable the preparation of very thin (and thus low-resistance) films, and (2) the resistance to swelling of such films, leading to small-dimensional variations with changes in water content. The swelling resistance is highly desirable for fabrication purposes.

Available PFSAs have most of the necessary properties for a good fuel cell membrane. The most significant drawbacks of the PFSA membranes are their relatively high cost, their dependence on water for conduction, and their limited stability at temperatures substantially in excess of 100^{o}C. These last properties are particularly unfortunate because recent work has suggested that substantial improvements in fuel cell performance, either in the presence of CO or when using DMFCs, can be achieved by operating at temperatures above 150^{o}C. Much of the development of aromatic-based membranes has focused on the demonstrated improved thermal stability of the membranes. These membranes, however, are still vulnerable to the loss of conductivity upon loss of water. It is thus at least as difficult to maintain adequate conductivity for these materials. In fact, the conductivity drop is especially severe for aromatic-based membranes because the water loss is associated with membrane swelling, and the acid sites on sulfonated aromatics are less acidic than those of PFSAs.

Water in current proton-transporting membranes is conveyed via two primary mechanisms: electro-osmotic drag of water by protons transported from anode to cathode and diffusion of water along any concentration gradients. In a proton exchange membrane fuel cell (PEMFC), these two mechanisms balance to produce the water distribution in the membranes: electro-osmotic drag and the oxidation reaction tend to create an excess of water in the vicinity of the cathode, while back-diffusion tends to flatten the water concentration profile in the membrane. Generally, researchers want to maximize proton conduction at all water contents and minimize electro-osmotic drag.

To understand water management and the conductance of a fuel cell membrane, researchers need to determine the protonic conductivity, water diffusion coefficient, and electro-osmotic drag coefficient — all as functions of water content in the membrane.

Various approaches to novel polymeric membranes arise from simple (and often simplistic) pictures of the necessary elements of proton conduction in polymer electrolytes. Such pictures need to be replaced with a sophisticated set of guiding principles that are based on carefully designed and executed experimental and theoretical studies. A thorough understanding of proton conduction in electrolyte membranes at the molecular level is still lacking. Such an understanding is likely to aid synthetic chemists in designing new membrane materials.

Another possible approach is to develop low-temperature electrolytes that transport protons in the absence of water. Some research indicates that such a solution may be possible, but many problems, including low conductivity and water solubility, remain (Haile et al. 2001). If solid or polymeric electrolytes that transport other ions such as hydroxide (OH^{-}) could be found, novel fuel cell technologies could be developed (see subsequent section on Alternative Fuel Cell Technologies).

The electrolyte most commonly employed in SOFCs is yttria-stabilized zirconia (YSZ). As noted above, there has been a move to develop SOFCs that operate at reduced temperatures, primarily for reasons of corrosion resistance and cost and secondarily for reasons of thermal cyclability. Attaining sufficiently low electrolyte resistance at temperatures of ~500°C requires either considerably reducing the YSZ membrane thickness (but so far this is only practical down to thicknesses of about 5–10 μm) or pursuing alternative electrolytes. Materials currently under development include $(La,Sr)(Ga,Mg)O_3$ (LSGM) and doped ceria as oxide ion conductors, as well as various oxide proton conductors, such as $Ba(Zr,Y)O_3$. The doped lanthanum gallates have been demonstrated to have ion conductivities at least ten times better than those of YSZ (Feng and Goodenough 1994), and doped ceria has an even higher conductivity (Steele 1994).

Ceria is generally unsuitable for high-temperature applications because of the electronic conductivity caused by the reduction of Ce^{4+} to Ce^{3+} and associated losses in efficiency. At reduced temperatures (~500 °C), electronic conductivity decreases to negligible levels, enabling high open-circuit potentials and, in principle, good efficiencies can be achieved (Huang et al. 2001). A second challenge associated with the reduction of ceria is the volume expansion under low oxygen partial pressures. The result of such expansion is the generation of significant internal stresses across the electrolyte, exposed to oxidizing conditions on one side and reducing conditions on the other. One strategy for alleviating these stresses is fabrication of very thin electrolyte membranes, which would be desirable in any case to enhance fuel cell performance.

In the case of LSGM, challenges arise from the reaction of this material with the anode electrocatalyst (Ni). The most common solution to this problem has been to incorporate ceria interlayers between the electrolyte and anode (Huang et al. 2001), but this introduces significant fabrication challenges and uncertainties for long-term thermodynamic stability. Moreover, LSGM and related materials undergo structural transformations after prolonged use, and these transformations lead to decreases in the conductivity. A large number of research groups in Japan and Europe are focusing on addressing the challenges facing samaria-doped ceria (SDC) and LSGM-based fuel cells and finding materials with even higher oxygen-ion conductivity. In contrast, not much work in this area is being carried out in the U.S. Because the potential payoff for developing better electrolytes is so great, this area is one that clearly requires serious investigation. High-priority research needs for membranes are discussed in the following sections.

Better, More Durable Membranes. This is a high-payoff area for fuel cell systems. Polymeric membranes that conduct protons (or other ions, such as hydroxide or even oxide) and remain hydrated to 120–150°C are sorely needed to reduce the purity requirements of the hydrogen fuel and enable the use of non-precious−metal catalysts. Of course, such materials also need to have mechanical and structural integrity, as well as improved durability. These goals can likely only be achieved by development of new polymeric, inorganic/ceramic, or hybrid materials. Perhaps nonhydrated proton conductors can be designed to have high conductivity in this temperature regime and even up to 200–300°C. While such high temperatures are less likely in automotive applications, they can easily be tolerated in stationary applications. In SOFCs, stable oxide ion conducting materials with higher conductivities than YSZ — especially at lower temperatures — are badly needed to enhance fuel cell reliability by decreasing corrosion and causing less thermal stress in all the SOFC components. Severe limitations in thermal cycling are related to thermal expansion differences between electrodes and the electrolyte, while interfacial reactions at higher operating temperature limit component lifetimes.

Better Understanding of Electrodes and Electrolytes. Understanding and controlling the structure and morphology of the electrodes and electrolytes and their evolution during operation is crucial to maximizing fuel cell performance. Modeling the electrochemical processes at the electrode-electrolyte interface is essential for optimizing fuel cell electrodes. As theory and modeling become more sophisticated and more widely applied to understanding ion transport, we hope that some guidance for the materials synthesis community may be forthcoming to illuminate the atomistic characteristics that need to be included in new materials.

Membrane-electrode Assemblies

Electrocatalysis in fuel cells requires the efficient interconnection of the array of catalyst particles with transport pathways for electrons, protons, and gases. These three interpenetrating nanoscale percolation networks must be optimized to produce acceptable performance of the electrode. Mass transport limitations within the cathode catalyst layer are a fundamental limiting factor in fuel cells today. If and when better catalysts become available, improving this aspect of membrane-electrode assemblies (MEAs) will become the next important target.

In present-day PEMFCs, for example, the necessary functionality is achieved by the formation of “thin-film composite” electrodes with interpenetrating networks of Pt-coated carbon, ion conductors, and pores. Nonetheless, access to the Pt is not ideal, and mass-transport–related voltage losses occur at high current densities; these losses are often driven by “flooding” of the electrodes and the diffusion medium caused by less-than-optimal management of by-products, especially water. A process or materials system that “self-assembled” these interpenetrating networks into an optimal geometry would be a seminal advance. Hints that such “self-assembled” structures could be prepared are found in the beautiful sequence of ordered phases that have been discovered in multiple component block copolymers (Bates and Fredrickson 1999). Perhaps these can be exploited to produce a more rational design for MEAs. Control of nanostructure in materials systems has advanced substantially in recent years (Garcia et al. 2003), and the preparation of functionalized systems using these concepts could be a highly fruitful path for future research.

One often-overlooked component of the PEM-based MEA is the gas diffusion layer (GDL), which mediates the flow of gases and water between the flow channels into the cell and the catalyst layer. Present-day materials used in this application are based on either carbon cloth or carbon paper macroporous substrates, usually wet-proofed with polytetrafluoroethylene (PTFE, or Teflon™) and sometimes filled with carbon-blacks and/or graphite particles (Mathias et al. 2003). Generally, these diffusion media substrates are coated with a so-called “microporous layer,” which facilitates the removal of water from the electrodes. The GDL (i.e., the diffusion medium substrate and a suitable microporous layer) attempts to control water droplet formation via structure and hydrophobicity controls, thus maintaining water balance in the cell. Understanding the details of mass transport and its relation to structure in these materials is in its infancy, and further improvements will require detailed fundamental understanding and materials characterization, as well as modeling of the two-phase transport phenomena in this component. High-priority research needs for MEAs are discussed in the following section. Also, a brief explanation of neutron imaging of fuel cell operation is provided in the sidebar.

Understanding and Controlling Nano- and Micro-scale Structure. Both materials advances and new concepts are needed in this area. Understanding and controlling by design the three-part percolation network for the electrodes is critical. Each network is structured on the nano scale (for example, the catalyst particles in low-temperature electrodes are 3–5 nm in size). Experimental and modeling approaches to this problem are needed and must be integrated. Developing new methods for characterizing the "buried" electrochemical interfaces is also necessary, and an understanding of the local environment surrounding catalyst particles could lead to a better definition of the desired features in optimized materials. Finally, studies of the compatibility and bonding behavior of the electrodes to the membrane will be necessary for each promising set of anode-membrane-cathode assemblies.

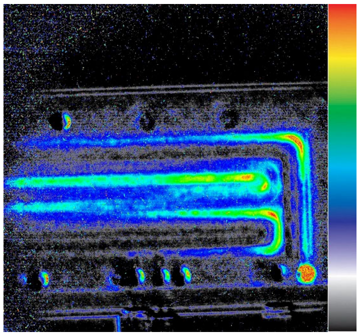
Recent advances in the controlled preparation of organized nanostructures, for example by exploiting the self-organization of di- and tri-block copolymers (Bates and Fredrickson 1999), could provide a pathway to prepare and control the three interpenetrating percolation pathways,

NEUTRON IMAGING OF FUEL CELL OPERATION

The electrochemical conversion of hydrogen and oxygen to water and electricity in a fuel cell occurs at electrode interfaces buried deep within its interior. The reaction takes place over a large surface area with the reactant gases directed to the electrodes through channels in the gas diffusion layer that also collect and drain the water produced. At the heart of fuel cell operation is water; it directly reflects the activity of the basic chemical reaction and can also disable the fuel cell by flooding the gas diffusion channels. Monitoring the ebb and flow of water throughout the fuel cell provides a powerful diagnostic for fuel cell operation.

Because fuel cells are not transparent to visible light, other forms of penetrating radiation must be used to view their internal workings. Neutrons can easily penetrate the metal casing of the fuel cell and still be highly sensitive to hydrogen. This capability makes neutrons a valuable probe for looking at the water distribution and dynamics inside a working fuel cell. Water in quantities less than 1 μg can be detected, corresponding to a spatial resolution of about 100 μm. A neutron image of water inside a fuel cell is shown in the figure.

The neutrons easily penetrate the fuel cell when dry. As the fuel cell runs, water builds up and appears as a darker shadowed region. Digital image analysis allows the representation of the dry cell to be removed from the image, revealing water formation at the cathode and its motion through the gas diffusion media and flow channels. In the image, the gas distribution system of the fuel cell appears as serpentine racetracks, and color enhancement represents the water density increasing from black to red. Images taken every second show the real-time operation of the fuel cell. They can pinpoint regions of high and low chemical activity, as well as identify flooding due to water buildup in the flow channels. This remote observation of water dynamics in the operating fuel cell provides precise space- and time-resolved diagnostics and enables targeted design improvements.



Neutron image of a working fuel cell, showing the distribution of water increasing in density from black to red as indicated in the color bar. The density of water reflects the local activity of the fuel cell reaction and can reveal blocking of the gas diffusion channels by flooding. This image (7.5- × 7.5-cm^2 field of view) shows a fuel cell after 1,000 sec of normal operation. (Courtesy of David Jacobson, National Institute of Standards and Technology Center for Neutron Research) as required. Expanding this research to functionalize the nanostructures to yield conductive and/or electrochemically active materials will be important. The same research emphasis should be placed on understanding, designing, and modeling of GDLs, the effectiveness of which largely controls PEMFC performance at high current densities.

In SOFCs, the MEA is structured on the meso- rather than the nano scale. Here, it is necessary to address the prevention of particle size growth in the electrodes, the changes in morphology, the reaction between components, and the changes in open porosity, among other effects. These are challenging issues because of the high operating temperatures. New methods or new materials that are resistant to such effects are needed.

Bipolar Plates

In practically all applications of fuel cells, individual cells must be stacked (connected in series) to obtain useful voltages. Many designs employ a single conducting plate to connect the cathode of one cell to the anode of the adjacent cell. The plate must then be stable and durable under both oxidizing and reducing conditions and potentials (hence the name “bipolar plate”). However, the durability and stability of the bipolar plate material are serious issues. For example, in the case of metallic bipolar plates (e.g., stainless steel), corrosion products from these plates (e.g., iron and chromium ions) shorten the life of the membrane and the cell electrodes considerably. New materials or corrosion-resistant surface coatings with low contact resistance between the GDL and the plate coating are sorely needed to address this problem.

Bipolar plate materials currently under study for use in low-temperature cells include lightweight metals, graphite, and carbon-thermoset composites. Each of these has limitations in durability or manufacturability. In SOFCs, lower-temperature operation would enable the use of metals or alloys, rather than the currently used conducting oxide materials, as interconnects and bipolar plates. Here, stainless steels might serve as possible interconnect materials, but the chromium has high enough volatility at the higher temperatures to react with the electrode/electrolyte components, causing degradation.

New materials are clearly needed to serve as interconnects, and the possible classes of materials that could be used will be determined by fuel cell operating conditions (such as temperature) and engineering needs (such as weight and volume constraints). High-priority research needs for bipolar plates are discussed in the following section.

New Materials and Novel Interconnect Designs. Even if researchers can make all the desired advances in electrodes and membranes, the success of fuel cells is not assured. In most applications, including automotive applications, the cells must be connected together in series (and possibly in parallel as well). While such connections can be made outside of each cell, a more efficient (especially on a weight basis) connection can be made using a single bipolar plate to connect the cathode of one cell to the anode of another. Because of the different electrochemical environments, however, most materials corrode in such an environment. Corrosion-resistant, electrically conducting materials are needed for this application. Perhaps surface coatings will solve the problem, but there is a lack of research even addressing which materials may be suitable. Reactivity between interconnect materials, gases, and other fuel cell components (containers and seals) has been identified as strongly limiting fuel cell performance and lifetime. Fundamental studies in corrosion science are required. Novel stack designs that mitigate difficulties with seals and interconnects should be investigated. There is a clear need and opportunity for innovative basic research to address cell interconnect issues.

Materials Durability

All materials in every type of fuel cell system degrade, decay, corrode, or otherwise fail under medium- to long-term operating conditions, as mentioned briefly in the sections above. This issue is discussed in greater detail in the following sections.

Low-temperature Cells. For PEMFCs, membrane degradation, electrode structure degradation, plate corrosion, and reformer catalyst lifetime are all issues. The longevity of catalyst-coated membranes, GDLs, and bipolar plates in operating PEMFCs is currently an Achilles' heel for the entire field. Performance degradation is a serious challenge that must be overcome if fuel cells are to realize their widely recognized market potential. Durability problems are typically studied by simply running fuel cells for long periods. Data are then analyzed after the fact to assess the failure modes. Conclusions are based on limited real data concerning the materials used and with less-than-optimal insight into probable failure mechanisms. Although some claims are occasionally made to the contrary, there is no fully validated accelerated life test for fuel cells. Fundamental and applied research into PEMFC degradation modes and new diagnostics are required to underpin efforts to improve materials. Degradation mechanisms in cells of all types are poorly understood. There is an urgent need for rational validated accelerated testing, as well as new materials systems that are themselves robust or possess enhanced durability.

High-temperature Cells. In SOFCs, microcracking and material deformation in response to thermal cycling are key factors driving degradation. Another important contribution to degradation is corrosion, which is enhanced by the high operating temperatures in present systems. Recent advances in materials and system design of solid oxide fuel cells offer hope that these degradation issues can be addressed (Kendall 2000). New electrolyte and electrode materials are becoming available, as are new cell designs and new fabrication methods to produce cells with thin electrolytes and engineered interfaces; however, many large challenges remain. Most are associated with durability and the high reactivity of materials at high temperatures. At this time, our understanding of the electrochemical and diffusion reactions that occur at the interfaces between the electrode and the electrolytes is very limited. The development of even better materials and better ways of using them could significantly decrease operating temperatures in SOFCs, allowing the use of cheaper materials and improving durability. Furthermore, the fuel flexibility offered by some electrode designs could allow the use of hydrocarbons or hydrogen as fuels.

Materials properties affect the performance of SOFCs in many crucial ways. Each of the materials aspects of the anode, electrolyte, cathode, seals, and interconnects can serve as a showstopper because of tendencies toward microcracking, thermal expansion mismatch, and corrosion. To produce inexpensive, high-performance SOFCs, further improvements are needed in each of these system components, along with a fundamental understanding and control of the interaction of the various parts.

New materials in both fuel and air electrodes can be as important as the electrolyte in improving performance and lowering operating temperatures. On the cathode side, a number of new materials with potential for improved performance have been discovered (Xia et al. 2002). On the anode side, there have also been exciting developments using alternative materials. For example, conductive ceramics (Tao and Irvine 2003) have been shown to allow reasonable cell performance and provide redox stability, an important factor in applications in which the anode may need to be cycled from low to high temperatures. SOFC anode formulations that do not contain Ni, such as Cu/CeO_2, lanthanum-chromium-manganese oxides and lanthanum-strontium-titanates, exhibit much greater sulfur tolerance (>1,000 ppm) than Ni anodes. Further work needs to be performed to optimize non-nickel anode materials and to evaluate their long-term suitability in solid oxide fuel cells. Similarly, it has been demonstrated that replacing Ni with Cu enables the use of alternative fuels (Park et al. 2000).

Finally, the structure of the interfaces between the various cell components, which can be controlled by synthesis procedures, can have a huge impact on performance. For example, the traditional anode (Ni-YSZ cermet), cathode (lanthanum-strontium-manganate [LSM]), and electrolyte (YSZ) materials can be designed to achieve higher cell performance at 650°C (Kim et al. 1999) than is normally achieved at 950°C (Pross et al. 2003). While a fraction of this enhancement can be explained by the use of a slightly thinner electrolyte (10 µm compared with 40 µm), the major factor in enhancing the low-temperature performance comes from engineering the electrode-electrolyte interface (Virkar et al. 2000). At the present time, this “tailoring” of the structure is largely performed by trial and error. A basic understanding of the needed interfacial structures could simplify the design and manufacturability of such interfaces, especially as new materials are introduced.

In all fuel cells, durability is a system issue. Often, interactions occur between components, either at contacting interfaces or by corrosion products from one component interacting unfavorably with another component. For example, providing a new membrane that operates well at high temperature will often demand modifications to other materials in the fuel cell system. Such membranes must not only be stable in both oxidizing and reducing atmospheres, but they also must be nonreactive with the electrode materials. The poor long-term stability of interfacial connections between components, including issues of electrical connectivity and adhesion, often lead to operational difficulties.

Alternative Fuel Cell Technologies

While the preceding discussion has focused primarily on PEMFCs (and, to a lesser extent, on SOFCs), it is possible that other fuel cell technologies could be enabled by discoveries of novel materials. For example, intermediate-temperature electrolytes (200–500°C) would allow the use of low- or non-precious metal catalysts and fuels containing substantial amounts of CO (thereby eliminating the need for low-temperature water-gas shift and preferential oxidizer [PROX] cleanup of reformed hydrogen). The candidate material would likely be an inorganic proton and/or oxide-ion conductor or even a hybrid or composite membrane structure and would need to provide mechanical durability, high ionic conductivity, and robustness in the fuel cell environment.

Oxygen reduction under basic conditions occurs at smaller overpotentials than under acidic conditions. In fact, alkaline cells are used by the National Aeronautics and Space Administration (NASA) in its space program, where very high-purity hydrogen and oxygen are available onboard. These cells are known to be very efficient and robust. Currently, alkaline cathodes cannot use air as the oxygen source, because the CO_2 in the air reacts with the electrolyte. If there were an efficient and inexpensive way to remove CO_2 from the air, and if carbon-free hydrogen produced by water electrolysis were available, alkaline fuel cells might become practical in transportation applications.

Membrane-free fuel cells have been demonstrated in very low power, short-term use in biological environments (Mano et al. 2003). One question is whether membrane-free concepts can be developed for use in higher-power, long-life systems. Such a system would need electrodes that are very specific and discriminating in their catalytic function. For example, the anode must oxidize only the fuel, even in the proximity of oxygen, and the cathode must only reduce oxygen and not the fuel. In such systems, the formation of stacks of individual fuel cells is a much smaller engineering challenge. Of course, such mixed fuel/oxidizer systems could present substantial safety challenges. The point is not so much that this particular idea is a good one (or not) but that it may encourage the research community to think in entirely new directions.

A broad, long-range research program aimed at finding novel materials for fuel cells would encourage "out of the box" approaches to novel fuel cell concepts.

Fuel Processing

If more efficient means of hydrogen storage are not found for transportation applications — means that allow 6 wt% hydrogen storage or greater (counting the weight of the storage system, containers, etc.) — hydrogen will need to be efficiently extracted from a hydrocarbon source. Potentially, the hydrogen source might even be a recyclable carbon-containing molecular carrier. In that case, an efficient catalyst to remove the hydrogen from the carrier would be needed. Currently, hydrogen is produced by the reaction of hydrocarbons (like methane) with steam; the process also produces CO_2 and CO. For all current PEMFC applications, the CO concentration has to be less than 100 ppm to avoid anode poisoning.

Proposed automotive fuel processing involves several steps, primarily steam reforming and water-gas shift. The first is typically carried out at high temperatures (650°C and above) over an Ni catalyst, and the second is typically carried out at lower temperatures (200–500°C) over Cu- and Fe-based catalysts. Steam reforming cannot be carried out at much lower temperatures because of unfavorable changes in equilibrium, but the Ni catalyst could be improved. The Ni catalyst has problems with "coking" — the formation of carbon deposits on the surface, blocking its active sites. The output gas from the steam reformer contains 3–10% CO. The water-gas shift reactor is currently needed to reduce the CO level to perhaps 2,000 ppm, and then a

PROX device reduces the CO content to about 100 ppm. This shift reactor/PROX unit is large — accounting for more than one-third of the mass of the hydrogen-producing plant in current automotive systems — all because of the slow reaction kinetics over the Cu catalyst. Much-improved catalysts and operation at lower temperatures could greatly reduce the size of this component and could enhance prospects for onboard fuel processing. This entire scheme is only sensible if the overall fuel processor/fuel cell system is more efficient than competing power sources, like internal combustion. Otherwise, even higher CO_2 production would result, without any gain in efficiency.

Known catalysts that are efficient in reforming operate at temperatures of $600^{o}C$ or above. This is a serious drawback because both the energy required for heat-up and the heat-up time for the reformer are substantial (on the order of 10 min). Furthermore, the reformer and water shift reactors add engineering complexity. If impurity-tolerant (no sensitivity to sulfur at the 200-ppm level or to CO at 3–10%) anodes are found, reformer technology would be much more attractive. The 200-ppm requirement for sulfur comes from the current average sulfur content in gasoline. This requirement is scheduled to be reduced to 30–50 ppm in 2005. Other sources, such as methane, can contain much less sulfur. Such anodes would ideally not only be “tolerant,” but would actually oxidize the CO to CO_2 and any sulfur to SO_2. Such anodes would reduce the purity requirements for the fuel, independent of its source.

We should emphasize, however, that if the challenges in hydrogen production, and especially storage, can be overcome, fuel processors will not be needed for hydrogen-based fuel cells. High-priority research needs in reformer catalysts are discussed in the following section.

Improved Catalysts. New catalysts need to be explored that will enable water-gas shift chemistry at lower temperatures or with faster kinetics. These catalysts would not only potentially be useful for providing hydrogen from hydrocarbons to vehicular fuel cells, but they also would be a welcome improvement to current hydrogen production processes and other chemical transformations. Catalysts that avoid coking in the steam reformer would likewise be useful to current hydrogen production technologies.

CROSS-CUTTING ISSUES

Several of the basic research needs in fuel cell work mirror those of hydrogen storage and production. These cross-cutting issues are discussed in the following sections.

Catalysis

Clearly, electrocatalysis is a central aspect of fuel cell research. As in the production and storage areas, heterogeneous catalysis and biomimetics are core disciplines for potential advancement. It should be stressed that fuel cell electrocatalysis is a rather unique subfield of heterogeneous catalysis, in that a large variable electric field is generally present at the interface.

Membranes

Membranes that permit the flow of one species (molecules or ions) while blocking the flow of other species are crucial, especially for production of fuel cell technologies. They may also play an important role in storage technologies, depending on which technologies progress to implementation.

Interfacial Chemistry and Materials

Understanding, controlling, and improving materials and material interfaces throughout the multilayer system characteristic of a fuel cell are central to achieving the qualitative improvements in performance and cost required for a successful hydrogen economy. Advances in adhesion, interfacial science, and characterization are equally central to breakthrough progress in fuel cell technologies.

Theory and Modeling

Theory and modeling of electrochemical reactions, catalysis, ionic conduction in membranes, and surface interactions of hydrogen could provide a strong driving force in understanding, controlling, and enhancing the fundamental phenomena that govern the operation of fuel cells and related chemical sciences.

CONCLUSIONS

The development of efficient and cost-effective fuel cell technology solutions for automotive and stationary applications presents a grand challenge that will take a substantial and sustained effort in chemical and materials research, combining both near- and long-term strategies. The major needs are all based on improved or new materials. Meeting this challenge will take a major effort by many scientists and engineers, experimentalists as well as theorists, in an interdisciplinary and collaborative effort. A basic, exploratory research program of significant size is needed to produce these enabling discoveries.

Near-term goals include lowering costs and improving the durability of materials and components sufficiently to enter selected markets. Long-term thrusts include large-scale introduction of fuel cells in vehicles and in a broader hydrogen economy — the desired end-game. Breakthrough advances are needed in electrocatalysis, membranes, and interconnect materials to realize the full potential of these devices for improved efficiency and cleaner power generation. Perhaps even novel fuel cell technologies, based on as-yet undiscovered electrode/electrolyte materials, will need to be discovered to take full advantage of the promise of affordable, high-efficiency power sources based on fuel cells.

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HIGH-PRIORITY RESEARCH DIRECTIONS

LOW-COST AND EFFICIENT SOLAR ENERGY PRODUCTION OF HYDROGEN

SCIENTIFIC CHALLENGES

Solar energy is the only renewable energy source that has sufficient capacity to meet fully the global energy needs of the next century without potentially destructive environmental consequences. In most respects, similar considerations apply to the economic viability of solar hydrogen and solar electricity: while many kinds of solar cells exist and some are made from abundant elements (such as silicon), their present cost/efficiency ratio is too high for widespread use. The present efficiencies of solar cells range between about 3% and 25%. At the high end of this range are single-crystal silicon photovoltaic (PV) cells, which approach the theoretical energy conversion limit of 32% for single-bandgap devices in sunlight.[1] Single-crystal solar cells are expensive and have been optimized over many years (and hence are unlikely to improve substantially in the future). The low-end cells (organic, dye-sensitized, and semiconductor nanocrystalline cells) are made from inexpensive materials and have not yet been extensively optimized. These technologies are most likely to (1) benefit from advances in basic science and (2) meet the cost constraints of widespread use.

Two basic strategies are available for creating a cost-competitive solar technology for hydrogen production:

- Development of emerging physical phenomena and novel synthetic techniques to achieve ultra-high conversion efficiency (>40%) at moderate cost per unit area, and/or

- Development of novel materials and chemical processes leading to ultra-low-cost per unit area with moderate efficiency (at least 10% efficient solar to stored hydrogen energy).

Both of these practical goals are rooted in basic scientific questions connected to materials synthesis, chemical self-assembly, dynamic photo-redox processes, and catalysis.

RESEARCH DIRECTIONS

This research has three goals: (1) understand the basic science that would lead to a disruptive high-efficiency solar technology, (2) learn to exploit new physical phenomena in quantum-size semiconductor particles and new synthetic techniques for the organization of matter on the nanometer-length scale in order to exceed present limits, and (3) develop analytical tools and theoretical methods for understanding relevant photoprocesses and catalytic chemical reactions. Promising research directions are discussed in the following sections.

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[1] The Shockley-Quiesser limit of solar-to-electric energy conversion efficiency for a single-bandgap device is 32%. The theoretical limit for multigap cells matched to the solar spectrum is approximately 65%. For a review of multigap semconductor/electrolyte cells, see Licht (2001).

Organic-based PV Systems

Organic photovoltaics coupled to electrolyzers, and organic photoelectrochemical cells that produce hydrogen directly, are strong candidates for very low cost solar cells if their efficiencies can be increased to more than 10%. Because the solar-to-electric efficiencies of these cells are typically less than 3%, major advances in basic understanding and new design concepts are needed. Some of the problems of organic solar cells are generic to other kinds of low-cost solar cells. A number of these are discussed below.

Light Harvesting. New strategies are needed to efficiently use the entire solar spectrum. These strategies could involve research on molecular photon antennas, junctions containing multiple absorbers, and physical techniques for up- and down-conversion of light to the appropriate wavelengths.

Photoprocesses in Organic Solids and Thin Films. Research is needed to understand the effects of structure on energy transfer and energy loss, exciton dissociation, and charge carrier recombination.

Self-assembly. Organic and hybrid organic-inorganic systems that spontaneously develop ordered nanostructures are of interest in the design of thin-film organic solar cells. These systems include, for example, di- and tri-block copolymers containing light-absorbing and electron- or hole-conducting segments, liquid crystals, and layer-by-layer assembled thin films.

Chemical Components. New low-cost alternatives are needed for transparent conductors and precious metal catalysts. Research is also needed to make better electron- and hole-conducting polymers. New design concepts are needed to achieve more efficient charge separation in liquid crystal and organic thin-film devices.

Characterization Tools for Understanding Dynamic Processes at Interfaces. Light-induced charge separation often occurs at interfaces in solar cells, and it involves dynamic processes that span many time scales. These time scales encompass hot carrier thermalization (femtoseconds), electron transfer and electron-hole recombination (femtoseconds to seconds), and catalytic water oxidation-reduction (milliseconds to minutes). Better tools are needed to study these processes, which determine the efficiency of photoconversion, particularly on short time scales. High sensitivity is needed to obtain information from specific interfaces or from individual molecules in complex assemblies.

Novel Frameworks for Assembly of Multicomponent Solar Cells and Photocatalysts

Photocatalytic water splitting represents a potential low-cost alternative to photovoltaics, because it generates hydrogen directly from water without the need for wiring, electrolyzers, and other system components. At present, visible-light water splitting has been demonstrated only with a few materials and is very inefficient. Integrated chemical systems, in which light-absorbing and photo-redox components are properly juxtaposed on the nano scale, have the potential to increase this efficiency. Researchers need to learn to control light-induced charge separation, charge recombination, and coupling to hydrogen- and oxygen-evolving catalysts in these systems. The four-electron oxidation of water to oxygen is a major challenge for these systems because of slow kinetics for all known molecular, colloidal, and solid-state catalysts; research is needed to develop better catalysts. Research is also needed on artificial photosynthetic systems, which are supramolecular photo-redox assemblies organized by microporous solids, membranes, and other nanophase media. Chemical assembly principles that lead to better photocatalysts probably would be useful for increasing the efficiency of organic and semiconductor nanoparticle-based PV cells.

Solar Cells Based on Inorganic Semiconductors and Nanoparticles

Inorganic nanoparticle-based solar cells hold the potential to exceed the Shockley-Quiesser limit of conversion efficiency by exploiting novel physical effects, including hot carrier injection and impact ionization. Recent ultrafast spectroscopic studies show that dye-sensitized nano-TiO_2 cells — one of the most interesting new concepts in solar PV design — function by hot carrier injection from the dye to the semiconductor. Research is needed to understand and exploit these effects in new solar cell designs. Recent advances in semiconductor nanocrystal synthesis suggest that it may be possible to design multicomponent crystals that contain more than one absorber (e.g., as core-shell structures, stripes in nanowires, or branches in dendritic crystals). The challenge is to learn to assemble and wire these nanocrystals into solar cells in useful ways. Much of what has been learned about making very expensive but efficient photovoltaics by using molecular beam epitaxy to define quantum well and multi-bandgap structures might be translated to inexpensive solar cells in nanocrystals.

Theory

Theory and modeling are needed to develop a predictive framework for the dynamic behavior of molecules, complex photo-redox systems, interfaces, and photoelectrochemical cells. As new physical effects are discovered and exploited, particularly those involving semiconductor nanoparticles and supramolecular assemblies, challenges emerge for theory to accurately model the behavior of complex systems over a range of time scales.

POTENTIAL IMPACTS

The payoff from successful research in solar energy would be the production of very pure hydrogen that is cost-competitive with fossil fuels as an energy source. Inexpensive, high-purity hydrogen would greatly accelerate the implementation of fuel cell technology by eliminating some of the costly purification systems currently used. It would also enable the widespread use of proven technologies (such as alkaline fuel cells) that are not useful with carbon-containing fuels. Solar energy is readily available in sufficient supply to enable solar hydrogen to be the dominant global energy source if the cost/efficiency ratio of PV cells can be decreased by a factor of 10 or more.

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NANOSCALE CATALYST DESIGN

SCIENTIFIC CHALLENGES

Catalysis in many forms is vital to the success of hydrogen energy technology. It is essential for the development of more efficient, cost-effective ways of producing hydrogen from reforming fossil fuels, and it is key to the development of photoelectrochemical and photochemical approaches. It is also the cornerstone of fuel cell technology and is important in the activation of hydrogen for storage in solid form. Catalysts with higher activity are needed for reducing kinetic barriers and increasing the thermodynamic efficiency of many different reactions in hydrogen production, chemical storage, and fuel cells. More highly specific catalysts are needed for reducing energy and material losses to parasitic and corrosive side reactions. Many of the currently available catalysts are subject to poisoning, fouling, or corrosion in the presence of reactants or their contaminants. These problems have led to a heavy reliance on platinum and other noble metal catalysts, but the supply of these materials is too limited and the cost too high to support the scale-up of current catalyst-dependent processes needed to meet the demands of a hydrogen energy economy. The replacement of platinum with less expensive and more generally available non-noble metal catalysts emerges as a critical challenge that cannot be met without intensive research into catalytic mechanisms, structures, and fabrication.

Although catalyst development has been based largely on trial-and-error methods, new approaches are critically needed to provide a substantial jump in the ability to design, characterize, and test new catalysts. Several lines of basic research are converging to provide an unprecedented opportunity for developing a robust catalysis science that could lead to revolutionary advances to meet these challenges. These areas of research include advances in nanoscience and nanofabrication, theory and modeling of catalytic properties, nano- to atomic-scale characterization methodologies, and high-throughput combinatorial synthesis. Research strategies are needed that would bring several or all of these advances together for working on problems in catalysis.

Recent developments in nanotechnology have opened new opportunities for the controlled synthesis of nanomaterials with tailored structures. These new materials have several properties important to catalysis, including high surface areas and a large, controllable concentration and organization of the kinds of crystal defect sites that are involved in forming catalytic "active sites." The concepts, technologies, and synthetic capabilities arising from nanoscience provide an entirely new avenue for the controlled production of novel categories of catalysts. These nanocatalysts have potential to provide great improvements in catalytic activity and specificity. In addition, improved capabilities for experimental and theoretical studies of surfaces and nanostructured materials are needed to elucidate atomic and molecular processes involved in catalysis.

Theoretical methods based on electronic structure calculations and on molecular dynamics and Monte Carlo-type simulations have developed to the point that entire reaction pathways can be identified; the basic trends in reactivity from one system to the next are understood for simple reactions. There are also new developments in the treatment of the thermodynamics of surfaces and kinetics of catalytic reactions based on combinations of electronic structure calculations and statistical and kinetic methods. Methods to better understand adsorption and diffusion in molecular sieves and other porous solids are also being developed.

A number of new experimental methods have been developed that allow a detailed analysis of correlated geometric and electronic structure of surfaces. Scanning probe methods now provide unprecedented insights into the structure and composition of surfaces and nanoparticles. In particular, they allow the first detailed analysis of defects and of their effects on surface chemistry. This capability is extremely important because defects are often the active sites for catalytic processes. New *in situ* experimental methods for characterizing real, nanostructured catalysts during turnover have been developed. Recently, it has become possible to use electron microscopy under high-pressure conditions to obtain the first direct images of the structure and dynamics of catalysts in a reactive environment. *In situ* methods have also been extended to spectroscopic techniques that require synchrotron radiation or neutrons. Spectroscopic methods based on synchrotron radiation now provide a very detailed picture of the bonding at surfaces; several new methods allow characterization of surfaces under high pressures of gases or in liquids. Neutron-scattering methods, such as inelastic neutron-scattering spectroscopy, also provide structural and bonding information at high temperatures and pressures. These methods are particularly important for understanding electrocatalysis.

New high-throughput combinatorial synthesis methods are emerging that can be exploited in combination with theory and advanced measurement capabilities to accelerate the development of designed catalysts, including nanocatalysts. The importance of this capability is underscored by the recent development of a novel nonplatinum catalyst for hydrogen production via reforming of reduced carbon (Huber et al. 2003). The ability to rapidly generate and characterize a wide range of compositions provides practical access to extensive experimental feedback into models of catalytic processes. This interplay between theory and experiment forms a recursive process that will accelerate the development of models with the predictive power needed for supporting development of optimized catalysts for specific steps in hydrogen energy processing. An essential issue in this connection is the development of informatics methods that allow rational use of large amounts of data. Better tools are needed for both analyzing and visualizing this multiparameter space.

All of these recent experimental and theoretical developments provide a new basis for uncovering the detailed atomistic processes underlying catalysis and for identifying the active catalytic sites. Once it is understood how alterations in the structure and composition of a catalyst can change the chemical properties and stability of the active site, it will be necessary to control the synthesis of the material with atomic-scale precision. Development of such synthetic methods will be an important part of testing models and advancing the understanding of the critical properties of catalysts and of their supporting structures. In addition, cost-effective fabrication methods will be vital for the practical application of these new designer catalysts.

A combined experimental-theoretical approach is needed to provide a new platform for the design of more selective, robust, and impurity-tolerant catalysts for hydrogen technology. This new platform will enable design and control of physical and chemical properties of the catalyst particles, as well as the properties of their supporting structures at the nano and atomic scales.

RESEARCH DIRECTIONS

The basic research effort in catalysis should provide new methods for catalyst design, synthesis, and characterization. Some fundamental issues, however, need clarification, including:

- Understanding catalytic activity from one system to the next;
- Understanding selectivity and trends in selectivity;
- Understanding deactivation mechanisms;
- Defining and understanding the chemical and structural state of the active site during catalysis;
- Understanding metal-support interactions;
- Understanding size effects in catalysts;
- Understanding metal-metal interactions in bi- and multimetallic catalysis; and
- Finding ways to design novel micro- and mesoporous solids.

Goals for catalysis research as a basis for hydrogen technology should include:

- More efficient, carbon-resistant reforming catalysts;
- More active, low-temperature–shift catalysts;
- Better electrolysis catalysts;
- Better photocatalysts;
- More efficient removal of contaminants, including sulfur and carbon monoxide (CO);
- More CO-resistant anode materials for proton exchange member (PEM) fuel cells;
- Better cathode materials with lower overpotentials for PEM fuel cells;
- Development of hydrogen activation catalysts that depend less on noble metals; and
- Multifunctional catalysts.

POTENTIAL IMPACTS

Developments in catalysis hold important keys to the economic viability of hydrogen energy systems. More active, specific, and durable catalysts would mean that a given amount of hydrogen could be produced or used in a given period of time with smaller, longer-lived production and utilization plants. Hence, the scale-up of hydrogen systems would require less capital investment. Improved catalysts would increase the thermodynamic efficiency of hydrogen production, storage, and use and also improve the economic efficiency with which the primary energy source — fossil, solar, or nuclear — serves our energy needs.

At this time, platinum is the preferred catalyst for many of the processes of interest for hydrogen technology. Unfortunately, this element is very limited in supply. Unless catalysts are found that consist of more readily available and less expensive materials, the strategic goal for the hydrogen economy of relieving dependence on imported resources for our national energy needs will be defeated by the development of a strategic dependence on platinum. A rational strategy for developing such catalysts depends on improved basic nano- and atomic-scale understanding of catalytic mechanisms and on improved methods for formulating catalysts and their supports with properties that are controlled on the nano- and atomic scales. This research direction would fill critical gaps in gaining the necessary understanding.

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BIOLOGICAL, BIOMIMETIC, AND BIO-INSPIRED MATERIALS AND PROCESSES

SCIENTIFIC CHALLENGES

Hydrogen production on a scale necessary for supporting energy needs for humankind faces kinetic constraints that must be solved either by thermal activation or catalysis. Living organisms use hydrogen as an energy carrier on this scale, solving the kinetic constraints with enzyme catalysis adapted to the organisms' thermal environment, which ranges in specific cases from 0°C to more than 100°C. These biological catalysts support integrated energy conversion processes that parallel those needed for most aspects of current or contemplated industrial processes, including ambient catalysis of the water-gas shift reaction, the full equivalent of natural gas reforming (Thauer 1998), and the complete anode reaction of a methane fuel cell optimized for low temperatures (0–20°C) (Nauhaus et al. 2002). Many green algae are capable of utilizing solar energy to energize the photolysis of water into hydrogen and oxygen, a process known as biophotolysis. The supporting enzyme catalysts for all of these activities are synthesized from materials readily available to the organisms from their environments. In spite of the apparent promise of adapting biological materials and principles to produce efficient and cost-effective engineered hydrogen energy systems, the current understanding of many aspects of the biological processes is too limited to support immediate application. Not enough is known about the molecular mechanisms and diversity of the enzyme catalysts, how they are assembled with their cofactors, how they are assembled into integrated systems, how potentially wasteful or destructive side reactions are controlled, how components and systems are maintained in the face of damaging side reactions, or how energy flows are regulated. Because of the central role of kinetic constraints in governing the practical utility of hydrogen energy systems in general, basic research into the fundamental principles underlying biological hydrogen metabolism could lead to crucial breakthroughs toward development of human-engineered hydrogen energy systems.

RESEARCH DIRECTIONS

Research is needed for understanding the mechanisms that underlie the biogenesis, maintenance, and integrated activity of the enzymes and cofactors that support biological hydrogen metabolism. It is an important goal to test this understanding through the development of biomimetic or bio-inspired synthetic catalysts and systems, because these extensions of biological systems may lie along the route toward practical applications in human-engineered hydrogen energy systems. Some promising research directions are discussed in the following sections.

Biomimetic Catalysts for Hydrogen Processing

The future of practical systems for solar energy conversion and storage depends critically on understanding the fundamental principles that determine how molecular systems carry out photochemical charge separation, transport, and storage. Although natural photosynthesis serves as a useful model for designing these systems, we need to go beyond that model to (1) synthesize photoconversion molecules and assemblies that build on these principles and (2) develop general methods to assemble mesoscale photofunctional engineered architectures.

Biomimetic photosynthesis catalyzed by synthetic complexes and assemblies offers a clean way of producing high-purity hydrogen (or other fuels) from solar energy and water. Research in artificial biomimetic photosynthesis is at an early stage and has not yet reached the point that production of integrated, practical systems is feasible. Progress has been promising in demonstrating synthetic catalysts of light-harvesting and photochemical conversion, controlled intermolecular electron transfer, water oxidation, and proton reduction to generate hydrogen. Each of these areas needs additional research; methods must be developed for assembling these biomimetic components into functional assemblies.

Production of hydrogen or other fuels using biomimetic photosynthesis requires a source of reducing equivalents. In oxygenic photosynthetic organisms, water is the source of the reducing equivalents needed for carbon fixation. Because water is readily available, oxygenic photosynthetic organisms predominate in the biosphere. It is highly beneficial to use water as the source of reducing equivalents for biomimetic photosynthesis. Splitting of water into protons and oxygen is energetically demanding and chemically difficult. The manganese-containing, water-splitting catalytic site in natural photosystem II (PSII) complexes performs this reaction at close to thermodynamically limited efficiency (<0.2 V overvoltage), at a high turnover rate ($\sim 10^3\ s^{-1}$), and under mild external but low effective internal pH conditions. In spite of promising recent progress in developing mimetic complexes based on the water oxidation complex of PSII, research is still needed to develop efficient artificial water-oxidation catalysts. A catalyst must be developed that can operate at the very high potential needed for the water-oxidation reaction; can perform a four-electron reaction so as to maximize the energetic efficiency; and can avoid production of corrosive intermediates, such as hydroxyl radicals, and mediate proton-coupled redox reactions.

The biomimetic chemistry involved in the reduction of protons to hydrogen is at an early stage of development. Efficient enzymes called hydrogenases catalyze reactions in which protons are reduced to molecular hydrogen using electrons from different substrates. Three known types of hydrogenases are known: iron (Fe)-centered, Fe-nickel-centered, and metal-free. Functional biomimetic Fe-hydrogenases have recently been demonstrated. They require strong reducing conditions and have low catalytic turnover but hold great promise for the future. The natural reaction centers of hydrogenase enzymes are poisoned by oxygen; methods must be developed for engineering oxygen-insensitive synthetic catalysts or sequestering the catalytic sites from oxygen while allowing access to protons and electrons and release of the hydrogen product.

Research is needed for:

- Understanding the structure and mechanism of the natural biocatalysts for water splitting and all aspects of hydrogen processing,
- Understanding the origin of oxygen-inactivation of hydrogenases and creating oxygen tolerance,
- Translating this understanding into efficient biomimetic catalysts,

- Integrating light absorption capability with catalytic hydrogen and oxygen production, and

- Developing a modular approach based on biomimetic photovoltaics for the direct anodic catalytic oxidation of water and cathodic reduction of protons to hydrogen.

Exploitation of Biodiversity for Novel Biocatalysts and Determination of Mechanisms of Assembly

It is becoming increasingly clear that the diversity of organisms that exploit hydrogen as an energy carrier is immense. Exploration of this potentially rich source of key catalysts for hydrogen production and use is at a very early stage. Moreover, while metals play intrinsic fundamental roles in catalysis and electron transfer (as well as in enzyme structure), very little is known at the molecular level regarding how different types of metal-containing enzymes and proteins are assembled inside a cell, how their assembly is regulated, how assembly mechanisms vary in different organisms, or how metalloprotein assembly might be mimicked in the test tube. Understanding the mechanisms involved would have a major impact on biomimetic technologies. High-throughput technologies specifically directed toward identifying photosynthetic and hydrogen-metabolizing organisms must be developed. Many of the microorganisms that are key players in hydrogen metabolism participate closely with others in complex consortia and are not independently culturable. Methods for discovering and studying these organisms *in situ* must be developed.

Current knowledge of the metabolism of hydrogen and biological solar energy conversion is based almost entirely on traditional biochemical and genetic approaches. Information is available for only a few model photosynthetic and hydrogen-metabolizing organisms. Similarly, our knowledge of metal metabolism has been gleaned from a few selected enzymes, and bioinformatic approaches to define potentially important catalysts on genome-wide scales are currently limited by the incompleteness of the comparative data.

Research is needed for:

- Developing and applying high-throughput methods for screening novel hydrogen-metabolizing and water-splitting components in new organisms from diverse environments;

- Developing biochemical, analytical, and computational tools to define the metallo- and redox-proteome;

- Identifying the factors and pathways involved in the expression, synthesis, function, and regulation of the metal cofactors, redox enzymes, and proteins involved in hydrogen metabolism and photolytic water splitting;

- Developing molecular and genomic tools for the construction and evolution of novel hybrid organisms capable of using light to split water and to generate hydrogen or other energy-containing compounds readily convertible to hydrogen; and

- Developing methods to interface redox enzymes and proteins into complex two- and three-dimensional architectures for catalysis, sensing, and energy transduction.

Coupling between Electrode Materials and Light-driven Catalytic Water Oxidation and Hydrogen Production Components

Investigations into natural light-activated and electron transfer proteins reveal empirical engineering guidelines based on fundamental principles of energy and electron transfer theory that can be applied to the abiotic reproduction of natural activity and function using synthesis and self-assembly. A wide range of donor-acceptor molecules have been produced over the past 20 years that mimic the multistep charge separation scheme of natural photosynthesis reasonably well. In some cases, these artificial reaction centers have been coupled to artificial antenna arrays to increase the cross section for absorption of solar energy. Far less work has been performed on how the charge separation created by these systems can be coupled to electrodes or practical chemical systems for energy storage. Very little work has focused on the interfacial chemistry necessary to produce workable solid-state devices analogous to common silicon-based solar cells or photochemical cells.

Attachment chemistries for electrode-protein-lipid constructions are a well-developed art, but application to redox chemistry has been successful with only the simplest systems and with only modest success with larger protein complexes. On the other hand, many chemical methods are available to attach small molecules to diverse surfaces such as metal oxides and gold. The availability of these methods makes it possible to chemically attach more complex biomimetic assemblies to surfaces; however, investigation of the electronic nature of these spacers and how they promote coupling of charges between the surface and assembly is in its infancy. Also, many molecular recognition strategies result in the self-assembly of complex molecules on surfaces. Once again, biomimetic systems with sufficient complexity to carry out photocatalytic production of hydrogen and water splitting have not been explored.

Research is needed for:

- Developing strategies for the assembly of synthetic photochemical and catalytic units that have fast electronic communication with the surface, controllable orientation, and long-term stability or self-repair; and

- Developing methods for the direct characterization of structure and mechanism of catalyst function on surfaces.

Biomimetic Nanostructures to Separate the Catalytic Functions of Water Oxidation and Hydrogen Production

The presence of oxygen at the catalytic site for hydrogen production inactivates the currently known catalysts. Moreover, it is likely that hydrogen will also react with the catalytic site for water oxidation. Biomimetic nanostructures are required to spatially separate and provide locally controllable environments for the catalytic centers for the production of hydrogen and oxygen. Ways to achieve this include building nanostructured surfaces that isolate key catalytic components, preparing biomimetic diffusion barriers that serve to encapsulate the individual photochemical and catalytic systems, synthesizing oxygen and hydrogen molecular traps and channels for controlling accessibility, and developing multilayered functional structures that achieve three-dimensional spatial separation.

Natural structures have evolved to spatially separate and compartmentalize reducing and oxidizing species on a 4- to 10-nm length scale. In photosynthetic systems, this includes the use of the membranes to separate charge and remove the oxygen product. Enzyme active sites are designed for high specificity and are often protected by the surrounding protein to prevent side reactions. The nature of the electronic coupling of the sites linked by chains of redox cofactors is reasonably well understood.

There is a good working knowledge of the construction of chemically integrated redox cofactor chains as well as self-assembled model proteins. However, further integration of photochemical systems, electron transfer chains, and compartmentalized catalytic systems has yet to be accomplished. There is also the advantage afforded by extensions to hybrid constructions involving inorganic and organic frameworks.

Research is needed for:

- Designing, preparing, and characterizing integrated nanoscale constructs to isolate and compartmentalize photochemical water oxidation and hydrogen formation;
- Establishing connections between components that permit electron and proton flow between these components;
- Developing methods to extend nanoscale functional catalytic units into the 100-nm to 1-μm mesoscale; and
- Developing strategies to efficiently harvest hydrogen and to separate out oxidative by-products.

POTENTIAL IMPACTS

Biological hydrogen metabolism and production processes and catalysts promise inexpensive materials for overcoming kinetic constraints in hydrogen energy systems. Their potential practical utility is essentially unexplored in spite of their clear importance in global energy flows in the biosphere. It is plausible that biological, biomimetic, or bio-inspired components and systems could make critical contributions to all aspects of human-engineered hydrogen energy systems. The scale of the necessary research is challenging, but steady investment could yield important practical results in the long run.

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COMPLEX HYDRIDE MATERIALS FOR HYDROGEN STORAGE

SCIENTIFIC CHALLENGES

Transportation applications require compact, lightweight, responsive, and affordable hydrogen storage onboard the vehicle. A 480-km (300-mi) driving range requires 5–10 kg of usable hydrogen, depending on the size of the vehicle. Basic research is needed to identify new storage materials and to address a host of associated performance and system issues. Such issues include operating pressure and temperature; the life cycle of the storage material; the requirements for hydrogen purity imposed by the fuel cell; the reversibility of the storage; the refueling conditions (rate and time); the hydrogen release rate, time, and delivery pressure; the stability of the system and hydrogen loss through permeation; and overall safety, toxicity, and system-efficiency issues. No material available today comes close to meeting all the needs for onboard storage of hydrogen for fueling a fuel cell/electric vehicle.

Hydrogen can be stored onboard vehicles in its pure form as compressed gas or cryogenic liquid in tanks or in the solid state as a chemical compound. The commercial sector is developing storage for the gaseous and liquid forms of hydrogen, but development is far from meeting the transportation storage targets set by the Department of Energy for 2015. Indeed, some of the requirements for onboard hydrogen storage seem unattainable with simple gaseous and liquid confinement methods. Storage of hydrogen in chemical compounds offers a much wider range of possibilities to meet the transportation requirements, but no single material investigated to date exhibits all the necessary properties. Several compounds of hydrogen with light metals have been identified that contain a high content of hydrogen on a mass basis, namely, sodium, lithium, boron, and aluminum. The performance of these metals for practical systems is severely limited by the high temperatures required to desorb hydrogen and their limited reversibility for storage. For example, $LiBH_4$ contains 18 mass% of hydrogen, but the resulting material cannot be recharged with hydrogen onboard the vehicle. For sodium alanate, the use of $TiCl_3$ as a dopant improves the release kinetics, but at the expense of a dramatic reduction in storage capacity (from 7.5 to 3.7 wt% of hydrogen at 80°C). Physical methods applied to enhancing hydrogen storage that have shown promise include ball milling and other processes that decrease particle size and increase surface area.

Finding effective hydrogen storage materials is one of the most difficult challenges facing hydrogen-powered transportation. The solution requires breakthroughs in materials performance that come from innovative basic research that looks beyond the storage materials currently known. The exacting demands on storage capacity, charge and discharge conditions, recycling lifetime, and cost span the traditional disciplines of chemistry, physics, and materials science. The fundamental factors that control bond strength, desorption kinetics, degradation due to cycling, and the role of nanosize and nanostructure in bonding and kinetics must be understood. For example, small amounts of heavier elements could be effective in tuning the lattice spacing or altering the chemical and physical properties of hydrogen storage compounds. The strong bonds typically formed by light elements with hydrogen need to be weakened with suitable dopants to improve their kinetics of absorption and desorption. An appropriate bond strength lies between covalent bonds and physisorption. The role of dopants in regulating the reversibility of storage materials at reasonable temperatures and pressures needs to be understood.

Nanostructuring is a potentially promising approach for controlling bond strength, kinetics, and desorption temperatures and pressures. Sophisticated theory and modeling of chemical bonding and kinetics can reveal key factors that control materials performance and guide the search for new materials and for modification of their performance. The search for viable hydrogen storage materials requires high-risk/high-payoff basic research that incorporates exploration of new materials, sophisticated experiments probing their behavior using cutting-edge facilities and instrumentation, and advanced theory and modeling of chemical and physical bonding and kinetics as a function of composition and particle size.

RESEARCH DIRECTIONS

Research in hydrogen storage materials needs to focus on (1) understanding the fundamental factors governing bond strength, kinetics, absorption and desorption behavior, and degradation with cycling; (2) applying these principles to modify the performance of known hydrogen storage materials; and (3) identifying new materials and new classes of materials whose properties can be tailored to meet the transportation and other demands of the hydrogen economy. Of the 2,000 storage materials known, most have not been explored in doped or nano form (Hydride Information Center 2003). Promising research directions are discussed in the following sections.

Fundamental Research

Fundamental research is needed that focuses on understanding the structural, thermodynamic, physical, and chemical properties of light-metal hydrides, such as $NaAlH_4$, $LiBH_4$, $NaBH_4$, $LiAlH_4$, LiH, BeH_2, and Li_3N. Experimental techniques for the development of solvent-free synthetic approaches should be explored. It is necessary to understand lifetime degradation issues, the fundamental atomic processes in absorption and desorption of hydrogen, the role of surfaces and surface catalysts in hydrogen storage, the role of hydrogen-promoted mass transport on phase transformations, and thermophysical properties of the potential metal hydride hydrogen storage materials.

Nanophase Structures

Many of the intermetallic compound-based hydrides form nanophase grain structures and particle sizes on charging and discharging hydrogen. While this capability can be desirable in minimizing the hydrogen diffusion path and enhancing the rate of charging and discharging, it may also have disadvantages in increasing the susceptibility to corrosion and reducing stability. Control of particle and grain size can enhance other desirable properties. Methods for controlling the particle size and grain size by thermal management during the charging and discharging cycles need to be explored. Theory and modeling of nanophase-grain and particle-size effects may point to fruitful research directions that exploit this degree of freedom for enhancing storage performance.

Transition Metal Dopants

A fundamental understanding of the role of transition metal dopants and processing on the ability to store and release hydrogen in light-metal hydrides at desired temperatures and pressures is needed to control their kinetics on storage and release and their related thermophysical properties.

Surface Barriers

Surface barriers to hydrogen transport can often be decreased by alloying and by the formation of surface phases. Disproportionation of the alloys is an issue during charging and discharging of hydrogen, particularly as high hydrogen concentrations greatly increase the diffusivity of the substitutional alloy elements. Fundamental understanding and effective control of these phenomena need to be developed.

Complementary Theory and Experiment

Close collaboration between theory and experiment aimed at understanding experimental data on structural, thermodynamic, physical, and chemical properties of metal-hydrogen systems should pave the way for the design and synthesis of new hydrogen storage materials. It should be possible to influence the absorption energy by manipulating the electronic and physical structures of the absorbent. Adjusting the lattice parameters and strains, grain structure, Fermi level, polarization, and charge distribution of the absorbents should allow tuning of the absorption potential and hence the thermodynamics of absorption. Experimental data should be generated with an emphasis on state-of-the-art characterization tools and establishment of standards for comparison of data from various laboratories.

Novel Materials

Researchers need to look vigorously for new materials and new classes of materials that deliver dramatically better hydrogen storage performance. Innovative basic science, high-risk/high-payoff research, and breakthrough materials discoveries are needed if the demanding storage requirements for hydrogen-powered transportation are to be achieved.

Comprehensive Database

The catalog of 2,000 potential hydrogen storage compounds represents a potentially fruitful knowledge base for guiding the search for new materials (Hydride Information Center 2003). Although this catalog covers many compounds, its level of information varies widely among materials. A systematic effort to bring a consistent set of data on the hydrogen charge and discharge behavior of the listed materials would be very helpful. Such a comprehensive database would be a valuable resource in stimulating and testing creative new approaches for finding materials with dramatically enhanced storage performance.

POTENTIAL IMPACTS

Developing effective hydrogen storage materials is a necessary prerequisite for viable fuel cell transportation and a versatile hydrogen economy. Currently known storage materials do not have the capacity, charge/discharge rate, or life cycle to allow fuel cell transportation to be a competitive alternative to the internal combustion engine. Beyond transportation, inexpensive and effective hydrogen storage is needed for load-leveling renewable, nuclear, and other energy production cycles that do not match demand cycles, and for interchangeably linking the point of hydrogen production with the point of use. Storage is a key component for nearly every aspect of the hydrogen economy. It is vital not only for transportation but also as an integral part of the production cycle and in nontransportation uses ranging from neighborhood power generation to consumer electronics.

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NANOSTRUCTURED AND OTHER NOVEL HYDROGEN STORAGE MATERIALS

SCIENTIFIC CHALLENGES

Extensive research over the last two decades with more than 2,000 hydrogen storage materials has not produced a viable candidate for onboard storage of hydrogen for automotive transportation. The simultaneous requirements for high storage capacity, fast and full charge and discharge cycles, and long life cycle have not benefited from traditional materials discovery and development techniques. The rapidly developing science of nanoscale materials enables dramatic changes in atomic structure, bond strength, and reaction kinetics, as the length scale for particle size and internal structure decreases. Nanoscale materials science is an innovative and promising approach for creating new functionality from traditional materials. It is the natural direction to search for breakthroughs in hydrogen storage materials that will enable the hydrogen economy. Large surface-to-volume ratios, unique size-specific chemistry and short bulk diffusion lengths favor enhanced hydrogen storage performance. Encouraging possibilities include nanostructures of bulk hydrides that have shown promise (e.g., light-metal hydrides), materials with nanopores such as carbon nanotubes, nanohorns, and fullerene derivatives, organic-inorganic composites, aerogels, and metal-organic frameworks.

The development of a suitable hydrogen storage system for a fuel-cell–powered vehicle is a major challenge. From a research perspective, the focus must be on three basic requirements: high storage capacity, a facile way to remove (desorb) the hydrogen from the material, and a way to quickly and economically recharge (adsorb and/or absorb) the material with hydrogen. The finite size of nanoscale materials positively influences the thermodynamics and kinetics of hydrogen adsorption. This fact is one reason that these materials promise to exhibit fast sorption and desorption of hydrogen. Nanosize adds a degree of freedom for tailoring material properties. The length scale and the curvature of these materials influence the thermodynamics of storage materials. The nanostructured materials that have received the most attention in the literature for hydrogen storage are carbon-based materials. A systematic investigation is needed that explores the hydrogen storage characteristics for nanoporous light elements and a wide range of nanoporous structures. While materials such as carbon nanotubes, carbon nanohorns, and porous carbon have shown promise, the experimental results have been controversial. Target adsorbents need extremely high surface areas to approach the hydrogen storage target; if hydrogen adsorbs on high-surface–area carbon as a single monolayer, however, the maximum storage is only 4.1 wt%. Multilayer adsorption is therefore necessary, and researchers do not yet know how to perform this process. Overall, fundamental principles learned to date provide encouragement that the unique properties of nanosize materials relative to their bulk counterparts will enhance hydrogen storage performance.

Researchers need to focus on understanding the unique surface and interfaces of nanocomposites and how they affect the energetics, kinetics, and thermodynamics of hydrogen storage. Advantages and disadvantages of storing hydrogen atomically and molecularly need to be explored. New methods need to be developed for synthesizing nanostructured materials of known and uniform dimensions for use in experimentation. The role of catalysts in hydrogen storage, uptake, and release in nanomaterials is an important area that can have potential impact.

Good characterization of materials and control of synthesis processes needs to be key requirements. Significant research on materials characterization at the nano scale is needed, using scanning probe microscopy, transmission electron microscopy, and electron diffraction. Developing the experimental techniques to probe nanoscale behavior in the presence of hydrogen is a leading scientific challenge.

RESEARCH DIRECTIONS

The goal of this research is to use fundamentally different physical and chemical properties that are available at the nano scale in the design of new hydrogen storage materials. By changing the structure of a given chemical compound at the nano-level, materials with different properties are obtained, and properties determined by material structure can be controlled. Promising areas of research are discussed in the following sections.

Size and Curvature of Nanomaterials

A systematic investigation of the effect of size and curvature of nanomaterials on the thermodynamics of hydrogen storage is needed. In addition, the influence of finite size on the electronic and atomic structure of materials with promise in their bulk form needs to be explored to see how they can be improved in their nanoforms for enhanced hydrogen storage. One example is to understand the influence of pore size and curvature on the hydrogen interaction that determines the range of the plateau pressure (the pressure at which the hydrogen is released at a given temperature). A complementary approach would be to understand the influence of particle size on the same parameters.

New Classes of Hybrid Hydrogen Storage

By combining different materials with suitable catalytic and thermodynamic properties, new classes of hybrid hydrogen storage materials would emerge. For example, a core material could be selected with respect to its thermodynamic properties, and the mantle could be chosen for its catalytic activity. The combination of functional materials in a layered fashion could open up completely new routes for optimizing the overall performance of such an absorption material. Thin films could be studied as a model system prior to three-dimensional layering in a particle form.

Chemical and Mechanical Stability of Dissociative Storage Materials

The chemical and mechanical stability of dissociative storage materials is of great importance because hydrogen storage materials must withstand repeated absorption and desorption cycles. Work is needed to develop suitable nanoparticles that are chemically stable (resistant to poisoning and oxidation), resistant to segregation, and stable in terms of structure (resistant to sintering and decrepitation). Heat transport in nano-based materials, especially across grain boundaries, needs to be explored as part of this work.

High-surface−area Nanoporous Materials for Hydrogen Adsorption

High-surface−area nanoporous materials, where hydrogen can be adsorbed on internal surfaces in an ordered or disordered structure, need to be explored. There are many examples of such materials, such as metal-organic frameworks, aerogels, and intercalation compounds whose potential for storing hydrogen is only now being appreciated. An integrated theoretical and experimental approach to this problem would be especially fruitful, because many possible stable structures could be searched effectively through modeling and simulation techniques.

Storage of Hydrogen at Various Temperatures and Pressures

In view of the mixed results reported so far with carbon-based materials, researchers need to determine if more than 1% storage is possible at normal temperatures and pressures using pure, well-characterized nanocarbon materials. Alternatively, the possible temperature and pressure conditions for multilayer adsorption and the kinds of carbon structures in which this might occur need to be explored. Carbon systems, when functionalized, might have additional potential for hydrogen storage and release. Hybrid materials might be synthesized that combine the surface properties of nanoporous carbon with the bulk properties of other storage materials.

POTENTIAL IMPACTS

The rational design of hydrogen storage materials that exploit the unique structures and size-specific chemistry of nanomaterials could lead to the successful development of hydrogen storage systems.

THEORY, MODELING, AND SIMULATION OF MATERIALS AND MOLECULAR PROCESSES

SCIENTIFIC CHALLENGES

A comprehensive theoretical plan is needed to complement experimental efforts in fundamental scientific research in the design and synthesis of new materials for hydrogen production, storage, and use. The challenges for theory and modeling lie in three related areas: (1) understanding of fundamental chemical and physical processes, (2) understanding of catalytic reaction mechanisms, and (3) design of new materials. Such a plan needs to focus on basic research that helps to create a fundamental knowledge base in these critical research and development areas. Successful efforts in these areas would significantly enhance our ability to meet the key technical challenges of the hydrogen economy.

Understanding of Fundamental Chemical and Physical Processes

Many complex chemical and physical processes are critical to the development of hydrogen production, storage, and use. The challenge for theory is to develop synergistic approaches with experiments to attain a fundamental understanding of these processes. For hydrogen storage, it is desirable to develop an accurate theoretical understanding of how hydrogen (either atomic or molecular hydrogen, depending on the material) reacts with the surface, interface, grain boundaries, and bulk defects of a particular material (Mergalli and Parrinello 2001; Zuttel and Primo 2002). In fuel cell research, fundamental insight into the ionic transport properties of polymer electrolytes (Paddison and Zawodzinski 1998) used in membranes and electron conductivity mechanisms in electrode materials is essential for developing improved electrode and electrolyte materials. Understanding electron transfer processes at interfaces is needed for enhancing the photocatalysis and electrocatalysis processes involved in fuel cells and hydrogen production.

Understanding of Catalytic Reaction Mechanisms

In the catalysis area, the challenge for theory is to develop a fundamental understanding of the controlling factors of catalytic reaction mechanisms from quantum chemical, kinetics, atomistic, and continuum modeling. While few examples exist where theory has led to the actual development of a new catalyst, substantial gains have been made in understanding catalytic reactions. With improved methodologies, theory should be able to contribute significantly to the development of new catalysts and the improvement of existing catalysts. Computations of the controlling factors can help find catalysts with higher activity, higher specificity, higher stability, and less susceptibility to impurities that cause poisoning and fouling. Included are catalysts for hydrogen production (e.g., photovoltaic cells, reforming catalysts) (Erickson and Goswami 2001), fuel cells (electrocatalysts) (Anderson and Albu 2000), and hydrogen storage catalysts (for efficient uptake and release of stored hydrogen with reduced need for thermal activation).

Design of New Materials

The synthesis and design of new materials for hydrogen production, storage, and use would utilize the knowledge base from the fundamental theoretical and experimental studies of chemical and physical processes and catalytic mechanisms. The challenge is to use this knowledge to predict trends (i.e., changes in functionality of a catalyst, storage, or fuel cell material as the composition and structure are varied). This approach can speed up the search for better materials and ultimately make it possible to design new materials with better performance from first principles.

Computational Challenges

Recent advances in theoretical and computational methods and tools have enhanced the ability to use these methods and tools to study fundamental processes, catalytic reaction mechanisms (Kroes et al. 2002), and materials. Four classes of computational methods are available. These methods span the length scales from 0.1 to 10 nm (quantum mechanics), 1 to 1,000 nm (statistical mechanics), 0.1 to 100 μm (mesoscale), and 1 mm to 10 m (continuum mechanics). Traditionally, modeling has been carried out separately for each length scale; only recently have efforts been directed toward integration across length scales. Time scales for quantum mechanical methods are on the order of 1 femtosecond (fs; 10^{-15} sec), whereas continuum methods range from seconds to hours. The challenges for theory in hydrogen research span all these length and time scales, thus posing a serious challenge for theory and computation.

RESEARCH DIRECTIONS

Theoretical understanding and effective modeling of the interaction of hydrogen with materials in all phases of the hydrogen economy research programs are needed. In production, molecular-scale theory and models of the chemistry and catalysts are needed for extracting hydrogen from fossil fuels, water, and biomass. In storage, molecular-scale theory and models are needed for the chemisorption and physisorption of hydrogen on surfaces, its chemical binding with light-metal and complex hydrides in bulk and nanoscale form, its physical and chemical interaction with carbon nanotubes, and the molecular phenomena governing the rate of hydrogen absorption and desorption. In fuel cells, theory and models are also needed for specific electrocatalysts for the oxidation of hydrogen and reduction of oxygen at the electrodes, the mechanisms of proton and oxygen ion conduction in organic and oxide membranes, and the mechanism of degradation of electrode and membrane materials with cycling and use. Beyond the description of phenomena in particular cases, a more demanding and useful goal is the prediction of trends (i.e., the changes in functionality of a catalyst, storage material, or membrane as the composition is varied). This can speed up the search for better materials and ultimately make it possible to design new materials with better performance in hydrogen production, storage, and use from first principles. Promising research directions are discussed in the following sections.

Integration of Experimental and Computational Approaches

In hydrogen production via reforming of fossil resources, an integration of experimental and computational approaches is needed to understand and control active site structures, catalytic mechanisms, and catalyst design on the nano scale. Integration of approaches is particularly important for the design and discovery of cost-effective catalysts that can produce hydrogen of sufficient purity for use in proton exchange membrane fuel cells.

Complex Photosystem Behavior Associated with Hydrogen Production

Theory and modeling are needed to help understand and predict the behavior of complex photosystems associated with solar hydrogen production. With increased computational power and understanding of electron transfer, theory can provide insight into important features of these systems (such as femtosecond dynamics in sensitizer molecules and particles, and the branching of kinetic pathways in complex molecular assemblies and photoelectrochemical cells) that are often at the "ragged edge" of experimental observation.

Modeling of Aqueous Fluids

Modeling of aqueous fluids under extremely nonideal conditions is needed to provide thermodynamic data (for sulfuric acid at high concentrations and for $I_2/HI/H_2O/H_2$ reactions) for input in reactor design for thermal hydrogen production.

Verification of the Accuracy of Theoretical Models

Experimental data are needed on well-characterized storage systems, including measurement of adsorption isotherms, isosteric heats of adsorption, and diffusion and reaction rates as a function of temperature. Once the accuracy of theoretical models has been verified by comparison with such experiments, theory should be able to provide experimental guidance by predicting how to modify materials to obtain better performance.

Effect of Size and Shape on Nanoparticle-Hydrogen Interaction

At the nanostructure level, a fundamental understanding is needed as to how the size and shape of nanoparticles affect their interaction with hydrogen. Understanding this concept can be accomplished, for example, by synergistic experimental and theoretical studies on atomic clusters (where size and composition are known at the atomic level), mimicking the composition of complex metal and chemical hydrides.

Mimetic Methods for Producing Nanoporous Materials

New mimetic methods, which mimic at the molecular level the method by which the material was made at the macroscopic level, are needed for producing computationally molecular-level instances of catalytic and adsorptive materials that are nanoporous but not regular. Such mimetic materials can be used in studies of adsorption and reaction at the molecular level.

Compositional Changes from Binding and Diffusion of Hydrogen

Computational studies of the nature of binding and diffusion of hydrogen in light-metal and chemical hydride storage materials are needed for understanding and predicting the effect of compositional changes. For example, the bonding between hydrogen and some of the light-metal solids, such as magnesium, appears to be ionic, whereas the metal-metal bonding in the host crystal is metallic. This suggests that the ionic or covalent bonding between hydrogen and the host metal lattice in the lightweight alloys might be changed to metallic bonding by alloying with elements. Similarly, an understanding of how catalysts affect the nature of hydrogen bonding is important.

Hydrogen-interface Interaction

Calculation of the interaction of hydrogen with interfaces, such as boundaries between nanocrystals, is needed to understand why and in what cases the presence of such interfaces can increase the magnitude and rate of absorption and desorption of hydrogen in storage materials.

Design of Improved Storage Materials

Atomistic simulations of hydrogen adsorption and diffusion into mimetically produced adsorbent materials will provide molecular-level insight into designing improved storage materials.

Theoretical Approaches to Hydrogen Storage

It is important to bring several layers of theoretical approaches to bear on the hydrogen storage problem. First-principle calculations of binding, diffusion, and the effect of defects in small systems need to be performed. Results from these calculations need to be fed into methods that can be used to study larger samples, such as potential energy functions or tight binding approaches. Furthermore, the results of such simulations need to be fed into mesoscopic (such as kinetic Monte Carlo) or continuum models that can be used to study longer time and larger length scales.

Scanning of New Materials for Use in Hydrogen Storage

Fast computational methods are needed for scanning new materials for their potential for use in hydrogen storage. For example, simplified density functional theory, combined with genetic algorithms, can be used to search for stable crystal structures. Techniques from informatics could also prove useful. In some cases, better functionals for density functional theory are needed. Linear scaling of first-principle algorithms for metals would be useful in studies of defects and disordered materials.

Hydrogen-induced Failure Mechanisms

Calculation of hydrogen-induced failure mechanisms — both at the atomic level and on larger-length scales — can help in the understanding of the durability of these materials.

Hydrogen Interaction in Nanostructured and Porous Storage Materials

Computational studies of hydrogen interaction in nanostructured and porous storage materials, such as carbons and metal organic frameworks, are needed. Theory can be used to investigate fundamental questions regarding whether hydrogen binds molecularly or dissociatively, where the hydrogen resides, where the activation barriers for hydrogen desorption reside, and how the material can be modified to increase hydrogen adsorption. Such knowledge will make it possible to design the geometric and electronic structure so as to improve the selective adsorption and release of hydrogen from these materials.

Modeling of Experimentally Realistic Electrode Phenomena

Modeling of experimentally realistic electrode phenomena is needed. Studies of the dissociation of oxygen on electrocatalyst metal surfaces in the presence of an electrolyte and as a function of the electrode potential can provide insights that can be translated into new materials. Also, fundamental experimental and theoretical studies of molecular reactions on model systems (e.g., using single crystals) of both known materials (e.g., platinum, platinum alloys, gold) and novel materials can provide mechanistic insight and help to assess the reliability of theoretical predictions.

Combined Methodologies for Improving Proton-conducting Membranes

A combination of experimental and theoretical methods to probe proton dissociation and transport in pores of polymers is essential to find improved proton-conducting membranes. Theory can provide insight into key active molecular fragments in the polymer electrolyte, most notably the sulfonic acid (or other acid) moiety; water solvation and proton dissociation phenomena at the fixed acid site; and transport processes in short segments of polymer electrolytes "pores" as well as in complete models of macroscopic transport.

Effects of Confinement and Catalytic Activity on Reaction Rates in Nanoporous Materials

Careful theoretical studies are needed to separate the effects of confinement (in nanoporous materials) and catalytic activity on reaction rates in nanoporous catalytic materials, since nanoconfinement alone can impact reaction rates by orders of magnitude. Indeed, it is likely that simulation is the only way in which these effects can be studied independently.

Transport and Chemical Reactions during Adsorption and Desorption of Hydrogen in Storage Materials

Calculations of both transport and chemical reactions during the adsorption and desorption of hydrogen in storage materials are needed. Consistent coupling between calculations on different length scales is required.

Hydrogen Lattice and Hydrogen-Hydrogen Interactions that Limit Storage Capacity

Investigation is needed as to the nature of the hydrogen lattice and the particular hydrogen-hydrogen interactions that limit the hydrogen storage capacity to a much lower amount than would be available if more of the interstitial sites could be occupied by hydrogen.

POTENTIAL IMPACTS

Theory, modeling, and simulation have the capability to substantially impact all areas of hydrogen research. Specifically, it is anticipated that computational tools will be increasingly applied to understanding real catalysts for hydrogen production, that they will be a driving force in the rational design of a high-density hydrogen storage material, and that they will play a key role in the development of new electrocatalysts and proton-conducting membranes for more cost-effective fuel cell systems.

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LOW-COST, HIGHLY ACTIVE, DURABLE CATHODES FOR LOW-TEMPERATURE FUEL CELLS

SCIENTIFIC CHALLENGES

Current composite cathodes in low-temperature fuel cells contain a significant amount of platinum (Pt) in the form of very small particles (3 to 5 nm) to catalyze the reduction of oxygen from the air. Even though Pt metal is the best-known catalyst for that application, low-cathode catalyst activity leads to 25–33% efficiency loss (i.e., a loss of about 0.3–0.4 V) over the majority of the operating range of low-temperature fuel cells (10–100% of power [Gasteiger and Mathias in press]).

Enhanced cathode catalysts would not only improve the overall fuel cell system efficiency (well-to-wheel), but it would also significantly reduce the heat rejection load of the system. For example, increasing full-power E_{cell} by 100 mV (from 650 to 750 mV) would reduce the heat-rejection load by 30%. Next to cost, heat rejection is currently a major impediment to automotive fuel cell applications (Masten and Bosco 2003), driving the need for high-temperature membrane research and development.

Cost

Mass-specific power densities for the Pt catalyst range from approximately 0.5–1 gPt/kW (i.e., $12.5–25/kW) for proton exchange membrane fuel cells (PEMFCs) using hydrogen as the fuel. In low-temperature fuel cells that use other fuels, such as methanol, the Pt loading is much higher (ca. 5-10 gPt/kW; that is, about. $125–$250/kW) due to problems caused by methanol leaking through the membrane from the anode to the cathode. While noble metal cost is less critical for applications in low-power applications (1-W power range), Pt cost and supply constraints for large-scale automotive applications require mass-specific power densities in the range from 0.1 to 0.2 gPt/kW or less.

Durability

Cathode performance typically degrades with time; that is, the overpotential for oxygen reduction increases with use. Voltage degradation rates range from 1 to 100 μV/h, depending on the operating conditions. System requirements (heat-rejection, performance) generally drive the system temperature to the upper limit of the specific fuel cell system (e.g., more than 80°C for automotive PEMFCs), where degradation rates are largest. Current automotive PEMFCs at >80°C show degradation rates of >50 μV/h, while much less than 10 μV/h is needed (for 5,000-h life). Stationary PEMFC systems operate at less than 80°C, with degradation rates between 10 and 20 μV/h, while an even more demanding 1 μV/h or greater is required (for 40,000-h life). Because the system operating temperature is generally driven by heat-rejection requirements (Masten and Bosco 2003), more active cathode catalysts (i.e., higher cell voltage and thus improved conversion efficiency) would lead to durability improvements.

Furthermore, the Pt nanoparticles are supported on larger conducting carbon particles. Currently used carbon supports (either fully or partially graphitized carbon-black) also corrode (or oxidize) under certain system-imposed operating conditions (e.g., idle operation, start/stop) and thus limit fuel cell system durability. More durable support materials are desirable. Recent work in Japan suggests that carbon nanotubes show considerable improvement in this regard (Endo et al. 2003). The use of Pt alloys in place of pure Pt improves efficiency and reduces cost (Thompsett 2003), but the stability of Pt alloys in the PEMFC environment is still unproven.

Much of the current development work is hampered by poor electrochemical testing and analysis methods, so that poor catalysts are being pursued for decades, while novel catalysts may be missed. Education in catalyst test methods is badly needed, and test methods need to be developed and communicated so that they can be used by a wider community (e.g., standard electrochemical testing methods in liquid electrolytes rather than full-blown membrane electrode assembly [MEA] testing; also, simplified MEA preparation and testing methods).

Furthermore, determining the activity of cathode catalysts requires some rather detailed knowledge of electrochemistry. Clearly, broad collaborations and joint interdisciplinary research are sorely needed and would enable the "out of the box" thinking that is required for the needed revolutionary advances. Enabling and supporting such activity should be a priority.

RESEARCH DIRECTIONS

Improved Activity of Noble-metal–based Catalysts

Development of cathode catalysts with improved activity, that is, higher voltage at a given mass-specific current density ($A/mg_{catalyst}$, or A/mgPt), is needed. This addresses three critical issues: efficiency, cost, and system improvements (heat rejection). If solved, the need for high-temperature membranes would also be lessened or eliminated, increasing durability and again decreasing cost. Catalysts are currently known to have mass activities superior to Pt and Pt alloys (e.g., PtCo, PtCr), but their long-term stability is not clear. Long-term electrochemical studies clearly are needed (Thompsett 2003).

Even when the Pt particles are as small as 3 to 4 nm, only 25–40% of the Pt is active in electrocatalysis, since only that fraction of the Pt atoms is at the particle surface. Improved dispersions would reduce the cost of Pt. Cost reductions might be achieved via Pt-skin catalysts, Pt decoration of other nanoparticles, and improved support materials.

Platinum-free Catalyst

Ideally, a catalyst that contains no precious metals is desirable on the basis of cost. Such a catalyst, however, must have at least 10% of the activity of the current Pt catalysts; otherwise, the system volume or weight becomes too large, even if the catalyst is free (current Pt catalysts — 50 wt% Pt/carbon — achieve ~1,000 $A/cm^3_{electrode}$ at 0.8 V in H_2/O_2 PEMFCs at 80°C [Wagner et al. 2003]). New catalysts, with higher activity than Pt but containing no precious metal, would clearly be one of the most highly sought high-risk/high-payoff discoveries in catalysis research for the hydrogen economy. The catalyst has to be produced as nanoparticles and integrated into a membrane electrode assembly; that is, it must be compatible with other fuel cell materials and processes. Finally, these materials must have long-term stability in the fuel cell environment and in use. Clearly, this challenge is daunting, since no better material than Pt has been discovered in the more than 150 years since the invention of the fuel cell.

Fundamental Experimental Understanding of the Activity of Known Catalysts

Such research may provide the insight necessary to design, modify, or invent materials with improved oxygen reduction performance. Research should include studies of well-defined single crystals and surfaces and changes that occur when such materials are in the form of nanoparticles. Researchers should understand the oxygen reduction reaction mechanisms on Pt, Pt alloys, gold, decorated nanoparticles, and other known and recently suggested catalysts. Furthermore, these investigations should not be limited to the acid environment, since work in salt and alkaline environments might improve basic understanding and perhaps lead to unforeseen breakthroughs. For example, these studies might elucidate the unexpected activity of gold in the oxygen reduction reaction in alkaline electrolytes (Ross 2003). These experimental studies should be supported, and perhaps guided, by a rigorous computational and theoretical effort.

Novel Catalysts

Studies of the oxygen reduction reaction on new materials should be undertaken. Possible systems should include ordered phases (such as intermetallics), mixed oxide-metal phases (e.g., $PtSnO_x$) (Swider-Lyons and Bouwman 2003), and supported inorganic and perhaps even organic compounds. This latter category should include bio-inspired systems (Katz et al. 2003), transition-metal macrocyclics, and other likely candidates. Exploiting the synergy between catalyst and support could also be promising. An important goal is the development of catalysts selective for the oxygen reduction reaction, resistant to poisoning, and stable in the fuel cell environment. Computational and combinatorial methods might well play a useful, even central role in catalyst discovery.

Durability of Cathode Catalysts

The stability of carbon-based catalyst supports should be examined by establishing the mechanisms of degradation under open-circuit and transient conditions. Novel carbon materials, such as nanotubes or other substances that are thermodynamically or kinetically stable at anodic potentials and operating conditions, should be explored. These studies should lead to the selection of new electrochemically stable supports to provide solutions for the support corrosion problem. Novel support materials with enhanced corrosion stability, possibly including Nb-doped TiO_2 (Chen et al. 2002), tungsten-bronzes, stable carbons, and other materials should be examined. Again, combinatorial approaches may prove effective.

Corrosion, sintering (Tada 2003), de-alloying and other mechanisms that deactivate cathode catalysts should be investigated.

Atomistic Modeling of Reaction Pathways

Modeling of experimentally accessible phenomena associated with the goals discussed above should be undertaken. These efforts could begin with realistic models of the oxygen reduction reaction mechanism on Pt surfaces, including effects of the solvent and electric fields, and the effects of the base metal in Pt-X (X = Co, Ni, Fe, Cr, etc.) alloys. One recent effort to understand the reduction of peroxide on modified Au surfaces demonstrates that such calculations are feasible (Gerwith 2003). Such a theoretical program might be able to make predictions of relevant properties of prospective novel catalysts, or even to propose specific catalyst compositions and structures, and to model catalyst corrosion or dissolution under control of the applied potential for elucidation of durability issues.

POTENTIAL IMPACTS

The discovery of novel low-cost and abundant catalysts that could enhance cathode activity, improve durability, and withstand the cathode environment is key to large-scale deployment of low-temperature fuel cells for hydrogen-based transportation. The high-priority research direction leverages cross-cutting developments in areas of nanocatalysis, combinatorial chemistry, and atomistic modeling and provides an interdisciplinary research strategy toward attaining this goal.

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MEMBRANES AND SEPARATION PROCESSES FOR HYDROGEN PRODUCTION AND FUEL CELLS

SCIENTIFIC CHALLENGES

Membranes and separation technologies are key determinants of efficiency and economy in hydrogen production and use. Ideally, membranes for fuel cells and electrolyzers should be highly permeable to protons (or oxide ions) but impermeable to hydrogen and oxygen. Very highly selective permeability is needed for both process and product gas separations in reformers and storage systems. High ionic conductivity over broader temperature ranges is needed in fuel cell electrolyte membranes. Membranes that can perform separations at high temperatures in extreme chemical environments are essential for efficiently producing thermochemical hydrogen and for improving the efficiency of reformers. Knowledge of membranes with these combinations of properties is limited, as is the basic understanding necessary for their design. These needs for improved separation membranes call for an integrated effort in new materials synthesis, characterization, and modeling.

Low-temperature PEMFCs require expensive catalysts and fuel processing systems because of residual carbon monoxide (CO) in the hydrogen that is made by steam reforming. Residual sulfur in the hydrogen derived from fossil fuels causes catalyst poisoning. Developing advanced membranes or other gas separation methods that can efficiently remove impurities from steam-reformed hydrogen could solve these problems.

Ionically conducting membranes are critically important components of low-temperature (less than 200^{o}C) and high-temperature (greater than 600^{o}C) fuel cells. In PEMFCs, there is a need for proton-conducting membranes that retain conductivity at higher temperatures. Perfluorosulfonic acid (PFSA)-based membranes, such as Nafion, lose conductivity as they begin to dehydrate above 100^{o}C. Proton-conducting polymeric, inorganic, or hybrid membranes that could function above 200^{o}C would represent a true breakthrough for fuel cells, because they would enable the use of inexpensive catalysts and lower-purity hydrogen. Similarly, the utility of solid oxide fuel cells (SOFCs) is largely limited by the lack of inorganic oxide-ion-conducting membranes that function at 600^{o}C and below. In both PEMFCs and SOFCs, the electrolyte membrane, catalysts and gas diffusion layers are part of an integrated system that determines reactivity at a three-phase (catalyst, electrolyte, fuel or oxidant) interface. Learning to control and characterize these nanostructured interfaces is important for developing fuel cells that economize on catalysts and function more efficiently.

The least expensive implementations of photochemical and biophotolytic systems for generating hydrogen from water and solar energy produce mixtures of hydrogen and oxygen. Development of energy-efficient methods for separating the hydrogen from these mixtures requires new approaches. Palladium membranes that are widely used for hydrogen purification in a number of applications cannot be used in this case, because they catalyze the recombination of hydrogen with oxygen. Alternatively, membranes that are gas-impermeable and proton-permeable could be developed as hosts for inorganic or biomimetic photochemical reaction centers that generate pure hydrogen on one side of the membrane and oxygen on the other.

Separation technologies could also play a key role in enabling the production of hydrogen from solar thermal or thermonuclear chemical cycles. In the proposed water splitting cycles, efficient separations are needed to isolate hydrogen and oxygen from other compounds and to shift the equilibria of reactions in the cycle. In some cases, these cycles involve separations under extremely corrosive conditions (e.g., separation of water, sulfur dioxide, and oxygen from unreacted sulfuric acid at 750–900°C in the sulfur-iodine cycle), and thus would require membranes or sorbents made from unusually stable materials.

RESEARCH DIRECTIONS

The goals of the research on membranes include (1) enhancing the efficiency of gas separations for the production of ultra-pure hydrogen, including those involved in both process and product gas separations during production and also for point-of-use (in fuel cells) repurification of hydrogen that is not sufficiently pure (e.g., that made by steam reforming); (2) improving gas-impermeability while retaining high proton conductivity of membranes for PEMFCs and of membranes for hosting nanoscale photochemical reaction centers; (3) enabling novel intermediate- and high-temperature fuel cell designs by means of advanced polymeric and inorganic-ion-conducting membranes; and (4) developing robust inorganic membranes to enable thermal water splitting cycles as a viable means of hydrogen production. Promising research directions are discussed in the following sections.

Nanostructured Porous Materials for Gas Separations in Hydrogen Production

The design and construction of porous materials has recently become quite sophisticated, and a promising opportunity exists to create new materials for improved gas separations. Microporous oxides, metal-organic frameworks, and carbons may be particularly useful sorbents for the removal of sulfur-containing compounds and carbon monoxide from hydrogen. Advances in this area will be driven by the synthesis of new porous materials and their physical characterization as sorption media.

Chemical Assembly of the Catalyst-electrolyte-vapor, Three-phase Interface

Both synthetic advances and an increased understanding of structure-property relationships are needed to create more efficiently functioning electrocatalyst-electrolyte percolation networks for membrane electrode assemblies. The characteristic dimensions of catalyst particles and of pores that transport fuel, ions, and oxygen are in the nanometer regime; this suggests that self-assembling systems on this length scale (e.g., di- and tri-block copolymers, mesostructured inorganic solids, thin films assembled layer by layer) should be studied as a means of organizing these networks. New concepts should be pursued with the goals of enhancing catalyst utilization and reducing resistive losses in fuel cells.

Characterization of Electrochemical and Buried Interfaces

Better techniques are needed to study the microstructure and reactivity of the electrocatalyst/electrolyte interface in membrane-electrode assemblies. *In situ* characterization methods are particularly important because the structure of the interface depends on the local potential gradient and changes with time.

Modeling of Sorption and Transport in Porous Materials and Membranes

Theoretical models are needed to understand a number of phenomena associated with sorption and transport. In membranes, these include atomic-level processes (e.g., the coupled motions of polymer chains, water, and protons in polymer electrolytes), transport in pores, and the relationship between macro-scale conductivity and the structure of pore networks.

Electronically Conductive, Selectively Permeable Gas Diffusion Membranes for Purifying Anode (Hydrogen/Carbon Monoxide) Streams in PEMFCs

The purity requirements for hydrogen in fuel cells would be relaxed if gas diffusion layers could selectively transport hydrogen and not carbon monoxide to the catalyst surface. This would require electronically conducting membranes (such as microporous carbons or hydrogen-permeable metals), or perhaps novel gas diffusion layer/catalyst architectures, with selectively high hydrogen permeability.

Membranes for Hosting Nanoscale Catalytic or Photochemical Reaction Centers

Membranes are needed as substrates for organizing oriented two-dimensional arrays of nanoscale catalytic centers. Such catalytic centers could enhance the selectivity of membrane permeability, and conversely the proximity to a selectively permeable barrier could enhance the net activity of integrated catalytic devices. For example, nanoscale photochemical reaction centers embedded and co-oriented within a gas-impermeable membrane immersed in water could generate trans-membrane light-driven electron transfer coupled to pure hydrogen production on one side and oxygen production on the other.

Low-cost, High-conductivity Proton Conductors for Use in Low- (<200^{o}C) and Intermediate-temperature (200-400^{o}C) Fuel Cells

Alternatives to PFSA-based membranes are needed for low-temperature (<200^{o}C) and intermediate-temperature (>200°C) PEMFCs, in particular, materials that retain water and proton conductivity at higher temperatures and have lower gas permeability. These could include new polymers and composite materials with higher thermal stability, and preferably lower cost, than Nafion. Access to the intermediate-temperature regime would significantly improve carbon monoxide tolerance, reduce the need for precious metal catalysts, and improve heat rejection in fuel cell stacks.

Lower-temperature (500-600^{o}C) Fast Oxide-ion Conductors for Solid Oxide Fuel Cells

The discovery of lower-temperature oxide-ion conductors would be an important enabler of SOFC technology, because most of the problems of SOFCs (corrosion, differential thermal expansion) are associated with high-temperature operation. Understanding oxide-ion conductivity in these materials is important for the development of improved electrolyte membranes.

High-temperature Separations Processes and Membranes for Use in Corrosive Environments

Thermal water splitting cycles involve the use of corrosive materials, such as sulfuric acid, hydrohalic acids, and water, at high temperatures. Sorbents and membranes that are stable in such environments will be needed if these thermal cycles are to be run efficiently.

POTENTIAL IMPACTS

Improved gas separation in hydrogen production and use would lower the cost of PEM fuel cells by reducing the need for or eliminating some of the most expensive fuel processing components (water-gas shift and preferential oxidation [PROX] units). Selectively permeable membranes with integrated nanoscale catalytic sites could yield efficient, inexpensive solar-to-hydrogen energy conversion devices as well as efficient electrode interfaces for fuel cells. Increasing the operating temperature of hydrogen/air fuel cells, by developing membranes that are good ionic conductors above 200^{o}C, would allow the use of inexpensive, non-noble metal catalysts and relatively low-purity hydrogen. An ability to conduct efficient separations at high temperatures and in corrosive environments is one of the advances needed for realizing the high efficiencies proposed for solar or nuclear thermochemical water splitting cycles.

ANALYTICAL AND MEASUREMENT TECHNOLOGIES

SCIENTIFIC CHALLENGES

Development of improved methods for hydrogen production, storage, and use requires a fundamental understanding of the structure and properties of new materials and the chemical processes that occur at the interfaces with these materials. New capabilities are needed to study these materials and associated processes directly under realistic environmental conditions, rather than in high vacuum. Furthermore, measurements need to be taken with high temporal resolution, allowing changes to be monitored dynamically. New techniques are also needed that enable multiple analytical measurements to be made simultaneously on the same system. For example, in fuel cells, the three percolation networks (proton, electron, and gaseous) need to be monitored simultaneously to assess new membrane designs. While many techniques are capable of characterizing materials composed of elements with high atomic number (Z), far fewer allow the study of lower-Z elements, particularly hydrogen. This lack of capability is particularly true at high spatial resolution. Such capabilities, for example, would allow fundamental understanding of hydrogen interactions at nanophase boundaries. Emerging capabilities in nanoscience present many exciting possibilities to revolutionize our ability to design and probe tailored materials and selective chemical processes. To fully realize this potential, however, researchers require new tools to characterize these nanoscale materials and associated chemical processes. Working at the nano scale presents many challenges for analytical and measurement science. For example, the curvature, length, shape, and pore size of nanotubes need to be reproducibly measured to assess the effects of these parameters on hydrogen-binding characteristics of these materials. More important, these measurement techniques need to be standardized so that results can be compared among laboratories. Studies of materials and processes at the nano scale also require analytical tools and sensors capable of providing specific chemical and physical information at very high resolution. The advantage of studying catalytic processes of nanostructured clusters, for example, would be realized if we could study the chemical processes occurring at individual nanoclusters characterized for size, shape, crystallinity, etc., rather than on large ensembles of heterogeneous nanoclusters.

RESEARCH DIRECTIONS

Multimodality, In Situ Characterization

In general, spectroscopic tools and sensors monitor a single process at a time. Recent studies, however, have shown that catalytic processes involve more than just a simple interaction of the reactant and the catalytic site. Combinations of analytical techniques and sensors with fast time response are needed to monitor these processes simultaneously and to fully elucidate the chemical transformations; changes in nanoscale structure; reaction kinetics; and other processes involved in hydrogen production, storage, and use. In addition, computational methods are needed to integrate information obtained from multiple sensors measuring different properties on different length scales and time scales.

Electrochemical Process Monitoring

New capabilities are needed for measuring ion and electron transfer processes and chemical transformations that occur at the interface with surfaces, such as nanostructured materials, electrodes, and bio-inspired materials that are used in hydrogen production and fuel cells. Of special interest are techniques that would measure proton conduction in low- or zero-water environments.

Neutron-based Techniques for Studying Hydrogen Reactions

Neutron-based techniques have unique capabilities for studying low-Z atoms. Because of the differences in the scattering of neutrons by hydrogen and deuterium, neutrons show particular promise for examining reactions involving hydrogen, such as understanding the role of surfaces and materials structure in hydrogen storage, catalysis, and membranes. In addition, because of their penetrating nature, neutrons can be used to study reactions at surfaces under high-pressure conditions.

Sensors to Support Hydrogen Infrastructure

Economy-wide deployment of hydrogen as an energy source will demand new sensors and detection capabilities to ensure safe production, storage, and use. Inexpensive and sensitive detectors of hydrogen leaks will be needed to monitor storage devices and pipes. Sensors will be needed to monitor degradation of materials, including weld failures and embrittlement of materials.

Dynamic, High-spatial-resolution Environmental Electron Microscopy

Fundamental research in hydrogen production, storage, and use places additional demands on state-of-the-art electron microscopy to monitor atomic-level processes that occur in materials. Observing these processes under realistic environmental conditions will be valuable for understanding atomic-level changes that occur during catalysis, corrosion, and hydrogen charging and discharging cycles for hydrogen storage. Furthermore, new computational tools are needed to increase the speed at which images are collected so that changes in the structure can be monitored dynamically.

Chemical Microscopes

Observing reactions at the nano scale requires new tools that can monitor chemical processes with high spatial resolution. While electron microscopes can provide insight into high-Z elements used as catalysts, electrodes, and other materials, few high-spatial resolution tools can monitor chemical reactions at these surfaces. These “chemical microscopes” would also be able to study nonconducting materials, which are difficult to study with electron microscopes.

Micro- and Nanoscale Sensors

Revolutionary advances in sensitivity are being achieved by scaling down analytical devices to the micro and nano scale, as demonstrated with micro-electromechanical system (MEMS) and nano-electromechanical system (NEMS) devices. For example, microfluidic lab-on-a-chip devices, nanocantilevers, and others have already exhibited femtomole and lower detection sensitivities in materials. Further developments in MEMS and NEMS technologies are needed to provide sensors that can monitor an experiment continuously, providing detailed information on atomic-level and molecular-level processes. Furthermore, these devices have low power requirements, making them amenable to long-term and remote monitoring scenarios.

High-throughput Characterization

With the incorporation of large-scale combinatorial synthesis techniques, new characterization methods will be required to rapidly screen synthesized materials with respect to chemical and physical properties, reactivities, and other benchmarking parameters.

High-sensitivity Measurements for Nanoscale Materials

To realize the full potential of nanoscale science, new analytical and characterization tools are required to measure the chemical and physical processes of very small amounts of materials. Achieving this goal will require increasing measurement sensitivity, while maintaining the selectivity of analytical techniques.

POTENTIAL IMPACTS

Reliable sensors, characterization, and measurement techniques are essential for the implementation of all aspects of a hydrogen economy. Fundamental research to elucidate the atomic- and molecular-level processes involved in hydrogen production, storage, and use will require a new generation of analytical tools that provide high spatial and temporal resolution to capture the multiple chemical and physical processes that occur within materials and at their interfaces. Together with computational tools, the results of these experimental measurements can provide understanding and predict the full range of chemical and physical parameters required for the development of materials and processes needed for efficient hydrogen production, storage, and use.

IMPACT OF THE HYDROGEN ECONOMY ON THE ENVIRONMENT

SCIENTIFIC CHALLENGES

The development of a large-scale hydrogen economy is motivated in part by its beneficial effects on the environment, including a reduction of the anthropogenic emission of carbon dioxide and other greenhouse gases and of atmospheric pollutants associated with the present fossil fuel economy. These beneficial effects are easy to foresee; however, our ability to anticipate the potential of harmful environmental effects from increased emissions of hydrogen itself to the atmosphere is more restricted. Although hydrogen is neither a greenhouse gas nor a toxic substance, it influences the dynamics of atmospheric methane, water vapor, and ozone, and it actively interacts with the biosystem of the soil. The transition to a hydrogen economy may lead to a substantial increase in the amount of hydrogen entering the atmosphere — from a current ~75 Mtons/yr (Novelli et al. 1999) to as much as ~120–180 Mtons/yr, based on estimates of the possible rates of leakage from hydrogen generation, storage, and transport sites (Tromp et al. 2003). In the current steady state, it is hypothesized that the bulk of the hydrogen entering the atmosphere is taken up by microbiological hydrogen metabolism in subsurface soils (Novelli et al. 1999). It is unknown whether this biological sink has the capacity to accommodate the expected increased hydrogen flux, or if the net concentration of hydrogen in the atmosphere will increase. Preliminary modeling indicates that an increased atmospheric concentration has the potential to:

- Affect the oxidizing capacity of the atmosphere,
- Impact the stratospheric ozone layer by moistening the stratosphere,
- Alter the pace of climate change by indirectly increasing the lifetime of methane, and
- Change the balance of hydrogen-consuming microbial ecosystems in subsurface soils.

To reliably quantify the potential impacts of large-scale increases of hydrogen releases to the atmosphere, we need to improve our understanding of the global biogeochemical cycles of atmospheric hydrogen. This research would also provide an engineering constraint on the environmentally acceptable amount of 'leakage' from a large-scale hydrogen infrastructure — information that is urgently needed by those industries seeking to develop a safe and efficient hydrogen infrastructure.

Hydrogen is a naturally occurring atmospheric trace gas. The National Oceanic and Atmospheric Administration Climate Modeling Diagnostics Laboratory has collected observations of hydrogen as an atmospheric trace gas at sites around the world on a regular basis. The global average tropospheric concentration is ~500 parts per billion. The two main sinks for H_2 are believed to be reaction with OH radicals and deposition at the earth's surface through the activities of terrestrial microbes, with the latter sink predominating. The primary sources of H_2 to the atmosphere are from oxidation of methane, oxidation of nonmethane hydrocarbons, fossil fuel combustion, and biomass burning. Our understanding of the processes governing the sources and sinks of atmospheric H_2 is limited, and the magnitudes of the fluxes are poorly constrained.

RESEARCH DIRECTIONS

The goal is to develop a fundamental understanding of the processes involved in the global biogeochemical cycling of atmospheric H_2. This knowledge will make it possible to perform a comprehensive assessment of the environmental impact of the release of H_2 to the atmosphere from a developing global H_2 economy.

New Modeling and Simulation Tools

Models of the sources and sinks of atmospheric hydrogen need to be developed and incorporated into global three-dimensional coupled chemistry-climate models. Long time series of observations of atmospheric H_2 are available for testing and comparing models.

Biological and Technological Sources and Sinks of H_2

The H_2 inventory is biologically mediated both as a source and as a potentially major sink. At least two routes lead to the release of H_2. One route to H_2 production is through wetlands fermentation of photosynthetically produced biomass (Schlesinger 1997). Mats of photosynthetic cyanobacteria also generate molecular hydrogen as a by-product of nitrogen fixation at concentrations well above atmospheric (Hoehler et al. 2001). A modest fraction of this biogenic H_2 probably escapes utilization by other microbes and enters the atmosphere. Biogenic hydrogen emanating in one way or another from biological solar energy conversion is thought to have had a profound effect on the evolution of the earth's atmosphere (Hoehler et al. 2001). Much of this impact arises from the role of hydrogen as a source or reductant in the synthesis of methane from carbon dioxide by methanogenic archaebacteria in subsurface soils. Our understanding of the spatial and temporal distribution, magnitude, and intensity of the soil sink for atmospheric H_2, as well as of the fates of the reductant once the hydrogen is consumed, needs to be expanded. The possible effect of increased atmospheric H_2 on soil uptake, fertilization, warrants study.

Importance of H_2 in Determining the Oxidative Capacity of the Atmosphere

Atmospheric H_2 is reactive and first affects the lower atmospheric layer, called the troposphere. It reacts with the trace OH radicals to form water. The trace OH radical inventory is critical to the cleansing of the atmosphere. Hence, any additional stress on OH radicals is a problem. Prinn et al. (2001) recently reported a potentially dramatic variation in the atmospheric inventory. Increasing the stress on the OH radical concentration through the deployment of a hydrogen economy that is leaky would have to be viewed as deleterious. Global atmospheric chemistry models can be used to study the impact of H_2 releases on the oxidizing capacity of the atmosphere.

Role of H_2 Releases on the Stratospheric Ozone Layer

H_2 releases significantly impact the chemistry of the troposphere and the stratosphere, particularly with regard to the long-term stability of the stratospheric ozone layer. Stratospheric chemistry models can be used to study the impact of H_2 releases on the long-term stability of the ozone layer.

Likely Source of H_2 to the Atmosphere from a Hydrogen Economy

It is almost certain that international agreements will be developed that limit the emissions of H_2 to the atmosphere at an environmentally sustainable level as we go forward with the development of a hydrogen economy. The OH radical inventory in the troposphere and ozone depletion in the stratosphere provide constraints on how "tight" the hydrogen economy must be. Estimates show that a 1% leak rate from a hydrogen economy would double current anthropogenic H_2 emissions. Leakage rates much greater than 1% are likely if no action is taken to engineer systems in advance to minimize hydrogen leakage. To quantify the potential impacts of large-scale releases of hydrogen to the atmosphere, we need to develop precise systems-based engineering models of the likely H_2 release arising from a developing global hydrogen economy infrastructure.

Comprehensive Impact Assessment

Ultimately, we must perform a series of simulations to quantify the effects of an increasing H_2 release as a consequence of the large-scale development of a hydrogen economy. Such simulations must be able to assess the impact of these releases on the oxidative capacity of the atmosphere, the long-term stability of the ozone layer, the impact on climate, the impact on microbial ecosystems involved in hydrogen uptake, and the role of those biological impacts in causing indirect effects on the atmosphere and climate. This information can be used to provide a reliable estimate of the maximum leak rate that can be tolerated from an environmental standpoint from large-scale H_2 systems that might be deployed in the future.

POTENTIAL IMPACTS

Improvements in our understanding of the global biogeochemical cycles of atmospheric H_2 will provide essential anticipatory guidance in developing hydrogen energy technologies that minimize environmental impacts. Large-scale implementation of hydrogen energy systems does not seem prudent in the absence of these critical assessments.

- Improving our understanding of the global biogeochemical cycles of atmospheric hydrogen would lead to a reliable quantification of the potential environmental impacts of large-scale releases of hydrogen to the atmosphere.

- This research would also provide an engineering constraint on the environmentally acceptable amount of leakage from a large-scale hydrogen infrastructure — information urgently needed by industries seeking to develop a safe and efficient hydrogen infrastructure.

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SAFETY IN THE HYDROGEN ECONOMY

SCIENTIFIC CHALLENGES

The large-scale use of hydrogen as an energy carrier for stationary, automotive, and portable power generation will result in close contact between hydrogen and the public. In a well-designed hydrogen infrastructure, gaseous hydrogen would remain confined in storage devices and delivery lines as it moved from production to use. The everyday presence of large quantities of hydrogen, however, demands that we understand fully its behavior and danger if significant quantities were to leak into the open environment or into enclosed spaces. Hydrogen is significantly different from today's common fuels because of its tendency to embrittle metals and other containment materials, its rapid leaking behavior, its fast diffusion through the atmosphere, its high buoyancy, and its combustion behavior. These differences in properties and behavior require that special research be done in order to understand and control the safety hazards that a hydrogen economy would pose.

Hydrogen can leak through tiny orifices 2.8 times faster than methane and 3.3 times faster than air because of its small molecular size (Larminie and Dicks 2003). It is flammable over a wider range of compositions in air than is methane, propane or gasoline, and its detonation range is similarly broad (Larminie and Dicks 2003; Ogden 2002). Hydrogen's unusually high diffusion and buoyant velocities in air, however, somewhat compensate for the danger posed by its fast leak rate and wide range of combustible compositions. In the open environment, hydrogen quickly disperses up and away from the source of a leak, rather than concentrating in low-lying areas, as do propane and gasoline vapors. If hydrogen does catch fire, it burns with a nearly invisible flame that is hard to detect. Its ignition energy is lower than methane or propane at most compositions, enabling self-ignition of high-pressure leaks.

Because the combustion behavior of hydrogen differs from that of other fuels, it presents another set of hazards and requires diverse safety precautions. In the open air, for example, the high buoyancy and diffusivity of pure hydrogen make it very unlikely to accumulate to its threshold of flammability, which gives hydrogen an intrinsic safety feature. In enclosed spaces, however, combustible compositions can build up, and precautions such as ventilation and careful monitoring are needed.

The basic kinetics and explosion limits of hydrogen/air are well known (Lewis and von Elbe 1987) because very few chemical species are involved. The ignition step in pure hydrogen/air mixtures (i.e., $H_2 + O_2 \rightarrow H + HO_2$), however, is essentially never involved in accidental explosions. Rather, an external heat source (e.g., a spark from static electricity) or an impurity-assisted lower energy dissociation reaction (e.g., the thermal dissociation of a lubricant or organic film) in the presence of hydrogen initiates the production of radicals and triggers a subsequent runaway chain reaction. Beyond kinetics, the hydrodynamics of hydrogen mixtures in oxygen and nitrogen are complex because of the very different masses and the broad range of transport properties (e.g., diffusivities, viscosities, and buoyancies) of the constituent gases. When chemical combustion is added to the picture, modeling and predicting flame and explosion behavior become more complex, because the relatively unknown transport properties of the airborne neutral radicals (e.g., H and OH) are important in modeling the turbulent characteristics of the explosion. Nevertheless, a thorough understanding of the hydrodynamics and combustion of hydrogen in the open atmosphere and in enclosed spaces as a function of mixing ratio, wind speed, and ventilation rate is needed if we are to recognize and control the safety hazards presented by the hydrogen economy.

An obvious precaution against fire is the prevention of leaks in the hydrogen infrastructure through careful construction, sensing, and maintenance. Hydrogen presents special difficulties, however, because of its tendency to embrittle metallic container materials like stainless steel and its welded joints. Embrittlement arises from hydrogen’s ability to diffuse through metals readily, perhaps using grain boundaries as easy flow channels, and weakening internal metal-metal bonds by combining locally with host atoms. Because embrittlement occurs slowly and can cause catastrophic failures of hydrogen storage containers, it creates a basic materials science challenge that must be overcome if the hydrogen economy is to be successful.

The safety hazards of hydrogen in everyday life can be significantly mitigated by simple knowledge of its presence. Hydrogen is largely invisible to human senses, such as sight and smell. Sensors that selectively reveal the presence of hydrogen are needed to provide early warning of leaks before the flammability threshold is reached. Beyond human safety, such sensors would be useful for monitoring, optimizing, and controlling the technical operation of the hydrogen economy, such as fuel cell operation, the charge/discharge cycle of hydrogen storage devices, and hydrogen production by the water splitting or hydrocarbon reforming routes.

Education and training in safe hydrogen practices are important factors in reducing the hazards of a hydrogen economy. Hydrogen-powered cars would expose the public to hydrogen during the refueling process and would release hydrogen to enclosed spaces during maintenance and repair operations. Repair technicians, professional drivers, and the driving public should receive instructions in the safe handling of hydrogen and in emergency procedures, should an accidental release of hydrogen occur. The institutional training and safety procedures for handling hydrogen in the fertilizer and petroleum industries provide one set of models for establishing an appropriate culture of safety as part of a hydrogen economy.

RESEARCH DIRECTIONS

The goal of research on safety in the hydrogen economy is to (1) develop predictive models of the hydrodynamic behavior of hydrogen/air mixtures in open environments and in enclosed spaces; (2) develop predictive models of the combustion and detonation of hydrogen in open and enclosed spaces in the presence of other gases and other materials; (3) develop a basic understanding at the atomic level of hydrogen embrittlement of materials; and (4) identify, discover, and develop inexpensive and effective sensors that selectively and sensitively monitor the presence and concentration of hydrogen. Promising research directions are discussed in the following sections.

Improved Understanding of Ignition Sources for H_2/Air Explosions

Experimental and theoretical studies can help to identify low-energy heterogeneous and homogeneous sources of radicals that can initiate chain branching and consequent explosions in H_2/air mixtures. Resonance-weakened bonds in certain organic lubricants, oils, and films or metal-catalyzed chemical transformations at imperfections or ruptures in metallic containers can be a potential source for generating radicals under external conditions of heat, shock, or stress. Ignition of mixtures of hydrogen with gases other than air needs to be studied. The risk of ignition of commonly occurring mixtures of hydrogen with methane, gasoline, benzene, and other volatile liquids is not well understood.

Improved Modeling of the Hydrodynamics of H_2/Air Explosions

Hydrodynamics modeling capabilities suited to handling H_2/air turbulence explosions in confined spaces need to be developed. Such developments would include a more secure experimental and/or theoretical database of the transport properties of airborne neutral radicals such as H and OH under explosive conditions.

Understanding of the Basic Physics of Hydrogen Transport in Metals and Hydrogen-assisted Damage Mechanisms

Corrosion and hydrogen embrittlement of materials are closely connected to details of their microstructure, and, in particular, to the segregation and diffusion processes that occur at internal interfaces and associated defects, such as dislocations. Although it is well known that the segregation of common solute impurities, such as sulfur and phosphorus, to grain boundaries can promote decohesion of these boundaries, the suspected synergistic role of hydrogen in this process is not well understood. The dependence of interfacial segregation on the nature of the grain boundary is also unclear. Filling this gap would help in designing an optimal microstructure that might, for example, minimize the connectivity of fracture-susceptible boundaries. We need to improve our understanding of the mechanisms and activation barriers for intergranular diffusion, in particular because grain boundaries can act as fast diffusion pathways. Diffusion and bonding of hydrogen in the microstructure of bulk materials are key factors that control hydrogen embrittlement and corrosion. An integrated approach uniting experimental studies with sophisticated theory and modeling is required.

Preventing hydrogen embrittlement by coating exposed surfaces with a self-sealing barrier should be explored. Such a barrier can be created by surface segregation of a dissolved element that reacts with hydrogen to form a protective layer. Breaches of the surface layer are automatically sealed by reaction of hydrogen with freshly exposed surface. Research is needed to identify suitable alloys with components that surface-segregate and form barriers upon reaction with hydrogen.

Sensors for Hydrogen

New concepts for hydrogen sensors are needed to detect the presence of dangerous levels of hydrogen in refueling stations, repair garages, passenger cabins in hydrogen-powered cars, and other situations where the public is exposed to hydrogen. These sensors need to be reliable, highly specific, and low cost, and they need to have low power requirements. For example, resistive sensors could be developed from nanowires or ultra-thin films, where a thin layer of hydride forming at the surface significantly alters the bulk resistivity. Adsorption of hydrogen on carbon nanotubes produces a distinctive signature in the transport properties, especially in the thermopower. Highly selective detection of H_2 can also be achieved with various spectroscopic approaches. For instance, the high reactivity of hydrogen enables chemical sensing, where a hydride forming on the surface of a reactive film can be detected spectroscopically or through its optical reflectivity.

POTENTIAL IMPACTS

Safety is a prime requirement for the success of the hydrogen economy. The development of predictive models for the dynamics of free H_2 in air in open and enclosed spaces would allow the assessment of risk and establishment of safety procedures for specific activities of the hydrogen economy, such as hydrogen vehicle refueling, driving in partially enclosed tunnels, indoor parking, and vehicle repair. Models of hydrogen ignition and detonation in the presence of vapors from common volatile liquids would enable new standards for their use in proximity to hydrogen. Fundamental knowledge of hydrogen embrittlement of metals and welded joints would enable the setting of standards for the materials used in building a hydrogen infrastructure. Sensitive, selective sensors for detecting hydrogen would warn against the danger of fire or explosion in sheltered or enclosed areas.

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CROSS-CUTTING RESEARCH DIRECTIONS

CROSS-CUTTING RESEARCH DIRECTIONS

During the workshop, several recurring basic research needs surfaced that were common to hydrogen production, storage, and use. These "cross-cutting issues" included six areas: (1) catalysis; (2) nanomaterials and nanostructured assemblies; (3) membranes and separation; (4) characterization and measurement techniques; (5) theory, modeling, and simulation; and (6) safety and environmental issues. These cross-cutting issues are described separately below; however, they are actually interdependent in many cases. For example, the combination of new characterization tools with theory, modeling, and simulation can be applied to achieving an understanding at the molecular level of chemical and physical processes that occur at the surface of well-defined nanostructured catalysts. Advances in one cross-cutting area can also impact another area; therefore, care must be taken to evaluate the entire process of hydrogen production, storage, and use as a system. For instance, as new catalytic materials are developed that are more tolerant to impurities, the requirements for separation of impurities from feedstocks are reduced, and, conversely, as new methods for separating impurities are developed, the stringent purity requirements for new catalysts are reduced. Finally, safety and the environment were identified as cross-cutting issues because, ultimately, safety and environmental concerns will impact the large-scale utilization of hydrogen as a reliable energy resource. In the following, each of these cross-cutting issues is discussed in more detail.

CATALYSIS

Overview

Catalysis is broadly recognized as a critical issue in hydrogen production, storage, and use. Catalysts are essential for converting solar energy to chemical energy. Reforming catalysts, which are used to convert fixed carbon resources (from natural gas, petroleum, coal, or biomass) into hydrogen, can provide hydrogen resources that can be distributed across a supply grid. Electrocatalysts — which are catalysts having large voltage gradients at the surface and which thereby affect chemical processes — are employed in photovoltaic (PV) cells and are also integrated into fuel cells for onboard hydrogen generation in automobiles. Catalysts also play a critical role in improving the kinetics and thermodynamics in hydrogen storage systems, allowing more efficient uptake and release of stored hydrogen with reduced need for thermal activation. General needs across these many application areas include catalysts with higher activity, higher specificity, higher stability, and less susceptibility to impurities that cause poisoning or fouling. An additional requirement for catalysts is the use of metals that are less costly and more abundant than platinum and other precious metals.

New catalytic materials need to be identified to meet the demanding requirements outlined above — both catalytic materials based on improved conventional and novel materials and those that take inspiration from biological processes. New catalytic materials, such as organometallics or nanostructured materials, that reduce or eliminate the need for noble metals will reduce the cost associated with catalysts. New materials for catalysis may also be inspired by nature. Natural photoconversion systems, such as those used by nature to perform photosynthesis, use non-noble metals to make high-purity hydrogen. Furthermore, these photoconversion systems often incorporate self-repairing mechanisms to enhance the longevity of catalytic systems in the face of corrosion, fouling, or poisoning of the catalytic sites. These self-regulating characteristics are also found in the design of automotive exhaust catalysts, where multiple catalysts are combined into a single system.

Research Issues

To improve catalytic processes involved in hydrogen production, storage, and use, a fundamental understanding of the molecular-level processes involved in catalysis is required. Achieving this knowledge involves detailed characterization of the active site, the interaction of the reactants (such as fuel or water) with the active site, full characterization of the chemical intermediates formed, and the dynamics of the entire catalytic process. This will entail the production of well-defined (at the atomic level) materials that can be characterized under realistic operating conditions. Emerging techniques that allow synthesis at the nano scale will open up new approaches for producing tailored structures with controlled size, shape, and surface characteristics. These structures can be produced with specific multielement-, organometallic-, and even stable biological and bio-inspired catalytic sites. For example, nanoscale clusters of mixed metals or even metal spheres coated with thin layers of catalytically active metals could improve the efficiency of the catalytic process, while reducing the need for costly noble metals.

By controlling the functionality and morphology of the catalytic materials, it may be possible to improve selectivity and efficiency of a catalyst by design. Designing catalysts with specific mesoporous structures, for example, can increase the selectivity of the catalyst by restricting the interaction of materials with the catalytic surface. A well-designed nanostructured support can also play an important role in tailoring a catalyst’s activity, selectivity, and stability, as well as generating a more homogeneous distribution of active sites. Furthermore, hybrid catalytic structures with both inorganic and organic functionalities could be made to provide a high degree of control over the catalytic process.

Indeed, broad new classes of catalysts need to be synthesized and characterized to discover new processes that will allow the goals of the hydrogen economy to be achieved. An understanding of the fundamental principles that underlie an effective catalytic process, developed through a synergistic combination of theory, modeling and simulation, and experimental evaluation and exploration, would support the directed design and discovery of new catalysts.

New analytical techniques are needed to rapidly characterize novel catalysts and their activities under realistic conditions. For example, high-resolution microscopes and scanning probe techniques are required to characterize the structure of catalytic sites at the atomic level. Improved spectroscopic probes are also needed to elucidate the interaction of reactants and intermediates with the catalytic site. This information can reveal the mechanisms responsible for the generation of hydrogen products and allow the dynamics of the catalytic process to be studied.

Impact

Advances in catalysis will be critical to providing the revolutionary breakthroughs needed for meeting the technical goals outlined for hydrogen production, storage, and use. In fact, kinetic constraints lie at the heart of most of the major problems that must be solved in order to develop a full-scale hydrogen economy. Catalysis is a multidimensional process, and the resulting complexity can present formidable challenges for improving current technologies by merely using a simple empirical approach. The needed breakthroughs for improvements in catalysis will be achieved only with basic research, to study the molecular processes with well-characterized materials, under realistic conditions. Information obtained in these studies will allow the design of catalysts with highly defined selectivity and higher stability, durability, and efficiency. Computational methods combined with experiments will guide the rational design of new catalysts and will help to predict their catalytic activities.

Specially designed catalysts can also minimize the need for purification of feedstocks or products. New nanoscale materials that incorporate novel structures or special catalytic centers containing hybrid organic/inorganic/biological features could also greatly decrease the cost of the catalytic process by reducing the need for using precious metals as catalysts. A well-designed nanostructured support can also play an important role in tailoring a catalyst's activity, selectivity, and stability, as well as in generating a more homogeneous active site distribution.

Addressing these and other fundamental issues can provide the critically needed insight that will help to develop entirely new concepts for catalysis. These new concepts could provide revolutionary enhancements in catalyst performance, at greatly reduced costs. The challenge is immense. Only through basic research is there a chance to make headway.

NANOSTRUCTURED MATERIALS

Overview

Many of the current limitations in hydrogen production, storage, and use are imposed by materials performance. Nanoscience has the potential to provide entirely new classes of materials with capabilities that transcend these limitations and generate the performance breakthroughs required for a viable hydrogen economy. Nanoscale materials often have distinctly different properties than their bulk material counterparts. Emerging nanoscale synthetic capabilities allow the design of materials with structures tailored for specific physical and chemical properties. Nanoscale probes, such as transmission electron microscopy and scanning probe microscopy, allow the atomic-level characterization of nanoscale structure of surfaces and interfaces that is key to the catalytic activity, molecular dissociation, and ionization that underlie the operation of fuel cells and hydrogen storage materials. This knowledge, coupled with theory, modeling, and simulation techniques, allows deeper understanding of these processes and guides experiments and synthesis of materials with improved properties.

New materials are needed across all aspects of hydrogen production, storage, and use. While metal and composite hydrides have demonstrated capabilities for hydrogen storage, new materials are needed that will increase the weight percentage of stored hydrogen and improve the kinetics associated with hydrogen uptake and release. Improvements are needed in fuel cell materials to achieve higher performance, greater flexibility in the use of fuel sources, and lower cost. New dyes and semiconductor materials are needed to enable light absorption across the entire solar spectrum for use in PV cells for electrolytic hydrogen production. Nanomaterials are central in the development of more efficient and tailored catalysts. For example, in a nanostructured material, the atoms at the surface have varying coordination numbers, all of which are lower than in bulk systems. In some systems, surface atoms with the lowest coordination numbers tend to be more reactive; in other systems, specific surface geometry is required. Furthermore, it has been observed that the reactivity of some atomic clusters can be changed by several orders of magnitude by small changes in cluster size.

Research Issues

Although our knowledge of nanostructured materials is just emerging, these materials have already shown potential for providing needed breakthroughs to achieve a hydrogen economy. The large surface/volume ratios of nanostructured materials produce chemical and physical properties that can be dramatically different from their bulk counterparts. Decreased size leads to quantum confinement effects that may enhance reactivity. Fundamental research is needed to identify the size and structure relationships that determine the catalytic activity, altered bonding strength, and kinetics in nanophase materials. For example, considerable promise for hydrogen storage has been demonstrated by a totally new approach that exploits various nanostructures: nanotubes, nanohorns, nanoribbons, nanostructured and nanoporous materials, zeolites, and clathrates. Improvements in understanding the processes that control the adsorption of hydrogen could improve the performance of these materials. This knowledge would allow the geometric structure — shape, surface area, pore size, and curvature — and surface-molecule interactions to be designed to improve the selective absorption and efficient release of hydrogen from these materials. Functionalizing their surfaces to catalyze the release of hydrogen and to improve the selectivity and weight percentages of hydrogen absorption could also enhance the hydrogen storage properties of these materials. Nanomaterials also may be exploited to produce novel properties that are dominated by surface interactions rather than bulk behavior. For example, it may be possible to make lower thermal conductivity materials for tanks for liquid hydrogen storage, using nanostructured constituents with many interfaces.

More traditional hydrogen storage materials, such as metal and complex hydrides, would also benefit from new capabilities provided by nanoscience. Specific nanoscale architectures may be designed into these materials to increase surface area and incorporate dopants to enhance the percentage of stored hydrogen and to improve the kinetics and thermodynamics of hydrogen uptake and release. At present, there is little understanding of the fundamental processes involved in hydrogen storage with bulk metal and complex hydrides. This includes knowledge of the atomic and molecular processes responsible for the interaction of hydrogen with the hydrides, the kinetics of hydrogen uptake and release, and the mechanisms for associated degradation mechanisms responsible for the limited durability of these materials. Fundamental research on nanostructured hydrides may also provide insight into the mechanisms responsible for the recently reported improvements in storage and kinetics of hydrides when dopants are added to these materials. Similarly, improvements in the lifetimes of hydride-based storage materials may be possible if we examine nanostructured materials to elucidate the mechanisms for associated degradation processes and sensitivity to impurities. This knowledge, when combined with computational modeling, is expected to allow the directed design of new, higher-efficiency, recyclable hydride-based materials.

Fuel cell electrodes require inhomogeneous structure on the nano scale, with mutually interpenetrating networks for ionic, electronic, and chemical transport. A fundamental understanding at the atomic level of the dissociation, ionization, and ionic conduction at the electrochemically active interface region is critical to improving fuel cell operation. Once these processes are understood, catalytic nanomaterials could be designed with the appropriate physical and chemical characteristics to improve performance, such as better chemical and thermal stability, increased tolerance to impurities, and lower cathode overpotentials for oxygen reduction. In the last case, bio-inspired catalysts that reduce oxygen with little overpotential offer an exciting new approach for dramatic improvements in fuel cell cathode performance. To achieve these gains, new approaches for synthesizing nanoscale hybrid materials are needed to incorporate the essential features of naturally occurring oxygen-reducing catalysts into robust, synthetic hosts. Hybrid materials have high potential for dramatic improvements in materials performance by taking advantage of nanoscale interfaces between dissimilar materials, such as inorganic/organic or conducting/insulating, to build specialized functionalities and architectures for specific applications.

The field of nanoscience is moving rapidly as basic research discovers new features in nanosize structure/property relationships. Nanoscale structures can be varied widely, for example, by size, morphology, ordered or disordered assembly and composition, and interfacial structure, resulting in properties that may be changed profoundly from those of the parent bulk material. Rapid advances in nanoscale synthesis and processing allow us to control and tailor these structures and properties. Key materials properties for application to hydrogen production, storage, and use will benefit from these advances. While the challenges to achieve a hydrogen economy are great, nanomaterials offer an unusually promising opportunity to discover and develop tomorrow’s hydrogen technology.

Impact

Ultimately, hydrogen production, storage, and utilization processes must be embodied in efficient physical devices with practical durability. Discovery of new materials with unique properties resulting from nanostructured design could provide critical breakthroughs with broad impact. Understanding and controlling the synthesis and processing of materials will allow the design of materials tailored to optimize performance in a particular end application. Materials could also be designed that incorporate multiple features, such as nanostructured fuel cell electrodes with three interpenetrating networks of catalyst/electrical conductor, ionic conductor, and open porosity, all designed to optimize electrochemical performance and reduce sensitivity to impurities.

MEMBRANES AND SEPARATIONS

Overview

Many of the processes involved in exploiting hydrogen as an energy carrier involve separating gases (e.g., separating hydrogen, produced by natural gas reforming, from contaminating carbon monoxide) or selectively controlling gas or ion transport between reaction compartments (e.g., allowing protons but not hydrogen or oxygen to cross between the chambers of a fuel cell). For kinetic reasons, selectively permeable membrane barriers are often the best design for meeting these requirements. Today's membrane materials are often insufficiently selective to eliminate critical contaminants or to prevent leakage transport between compartments in a fuel cell that robs efficiency. For instance, carbon monoxide that normally contaminates hydrogen produced in reforming processes requires several other complex, large, and heavy purification stages to reduce the carbon monoxide to below the 20 parts per million (ppm) level, which is sufficient to poison the anode of low-temperature proton exchange membrane fuel cells (PEMFCs). A simple membrane that would exclude carbon monoxide but not hydrogen would greatly simplify hydrogen purification. The Nafion™ membrane material that is presently the best available for separating PEMFC chambers is not only expensive, it also allows enough gas transport to reduce efficiency. Oxide ion transport, which is necessary for higher-temperature fuel cells that are less sensitive to poisoning by carbon monoxide, is inefficient in membranes that are currently available and operate at the lower temperatures that would be needed for use in transportation. Finally, separation membranes that could operate in the rigorous chemical environment of a thermal cycle hydrogen generator (i.e., gaseous H_2SO_4 at temperatures above 700°C) would be of substantial value but are essentially unknown at present. In general, membranes with improved selectivity, transport rates, and stability under various operating conditions could improve the efficiency and feasibility of many key steps in hydrogen production, storage and use. Developing these membranes will require improvements in membrane materials, in understanding and design of permeation catalysts, and in technical strategies for constructing membranes with hybrid organic and inorganic composition and with nanostructured features.

Research Needs

Advances in membrane separations will be driven by the synthesis and functional analysis of new nanoporous materials and the characterization and modeling of the molecular phenomena associated with sorption and transport. A fundamental understanding of these chemical and physical processes would allow both the selectivity and the kinetics of the separation process to be enhanced by design. This selectivity could potentially be achieved by using novel synthetic techniques to produce tailored two- and three-dimensional materials incorporating oriented nanocatalytic domains. Improvements in fuel cells as well as in electrolytic and photocatalytic hydrogen generator performance will require improved control over the three-phase reaction surface in which electrons at the electrode surface, liquid (e.g., water and solvated protons), and gas reactants (hydrogen and oxygen) interact. Self-assembling systems, such as di- and tri-block copolymers, mesostructured inorganic solids, and thin films assembled layer-by-layer, have the potential to organize these networks effectively. Membranes that incorporate nanocatalysts and nanocatalyst supports could provide the key for developing efficient, selective transport functions, such as the faster oxide ion conductors needed to enable solid oxide fuel cells to function at the lower operating temperatures (500–600°C) required for transportation applications. Proton-conducting membranes that operate essentially in the absence of water (at temperatures above 100°C) would enable the design of intermediate-temperature fuel cells that potentially combine advantages and avoid the disadvantages of PEMFCs and solid oxide fuel cells. Robust inorganic membranes with high selectivity and high transport rates are needed to enhance the efficiency of high-temperature separations, as required for hydrogen production via thermal water splitting cycles.

Impact

Fundamental advances in membrane separation technologies could reduce the high cost of meeting the hydrogen purity requirements of PEMFCs. This is an important near-term objective that stands in the way of commercializing hydrogen energy systems with current hydrogen generation, storage, and fuel cell technologies. The potential for combining membrane materials with catalytic materials in nanostructured architectures opens the possibility of entirely new approaches to hydrogen production, such as membranes containing embedded photocatalytic reaction centers that produce high-purity hydrogen when immersed in water and exposed to sunlight. Similarly, new membrane/electrode assemblies designed to improve ionic, electronic, and chemical conduction at the surface of electrodes can improve both the energy efficiency and economic performance of fuel cells.

CHARACTERIZATION AND MEASUREMENT TECHNIQUES

Overview

Insight into both the chemical and physical characteristics of materials at the nano scale can enable revolutionary new capabilities for hydrogen production, storage, and use. An especially challenging need is to increase the sensitivity of analytical tools to permit characterization and measurement of processes involving nanophase materials. For example, new analytical techniques will be needed to determine how much hydrogen is adsorbed on a nanostructure, such as a nanotube or a nanohorn. In addition to improved sensitivity, new analytical tools are needed that provide high selectivity and resolution in order to fully satisfy the need to study nanoscale materials and processes at the atomic and molecular levels. Novel sensors will also be needed for sensitive and specific detection of hydrogen and other chemical elements and compounds, especially in support of meeting safety-related concerns, such as those arising from hydrogen leaks and materials failures.

Research Needs

New tools are needed to allow chemical and physical characterization of nanostructured materials with atomic-level resolution. Reactions that occur at interfaces with these nanostructured materials require characterization techniques with both enhanced spatial and multidimensional spectral resolution to characterize interactions and reaction dynamics occurring at these surfaces. Furthermore, characterization and analysis tools are required to study reactions under realistic conditions, with reactants and products present at concentrations, temperatures, and pressures employed in specific applications. These conditions may also include use of extreme temperatures, corrosive/reactive chemicals, and high pressures that are not typically compatible with today's analytical techniques. Tools are also needed to understand ion and mass transport, thermophysical, mechanical, and other chemical and physical properties at the nano scale. Also, techniques are needed for measuring proton conduction in low- or zero-water environments. With the incorporation of large-scale combinatorial synthesis techniques, new characterization methods will be required to rapidly screen synthesized materials with respect to chemical and physical properties, reactivities, and other benchmarking parameters. Sensors for micron- and submicron-length scales with fast time response will be needed to monitor processes at various length and time scales. In addition, entire systems of sensors will be needed to integrate information from multifunctional processes.

Along with new characterization tools, standards will be needed to assure the ability to compare results across the research community. An especially challenging need is to increase the sensitivity of analytical tools to permit characterization and measurement of processes involving nanophase materials. Advances in scanning probes and electron microscopy will make it possible to characterize materials at the atomic level; these sensitive techniques have, for example, been used to study novel nanocatalysts. Revolutionary advances in sensitivity are being achieved by scaling down analytical devices to the micro and nano scales, as demonstrated with micro-electromechanical system and nano-electrochemical system devices. Devices, such as microfluidic lab-on-a-chip devices, nanocantilevers, and others, have already exhibited femtomole and lower detection sensitivities in materials. This technology can provide sensors that can monitor an experiment continuously, providing detailed information on atomic- and molecular-level processes.

Impact

Reliable characterization and measurement techniques, including hydrogen-specific sensors, are essential in the implementation of all aspects of a hydrogen economy. Sensitive new tools are needed that can provide atomic and molecular information at the nano scale to support fundamental research that has promise to ultimately yield the new materials and processes required for establishing a hydrogen-based economy. Together with computational tools, the results of these experimental measurements can provide an unprecedented understanding of the full range of chemical and physical parameters required for the prediction and development of materials and processes needed for efficient hydrogen production, storage, and use.

THEORY, MODELING, AND SIMULATION

Overview

Theoretical modeling, including computational simulation and analysis, will impact all research areas essential for the development of effective hydrogen energy systems. A strong, synergistic relationship between theory and experiments on well-defined systems will provide insight into mechanisms, predict trends, identify promising new materials and reaction processes, and guide new experiments. Successful efforts in these areas will significantly enhance our ability to meet the key technical challenges of the hydrogen economy in hydrogen production, storage, and use.

Research Needs

New computational approaches are needed to integrate across disparate time and length scales that are important for hydrogen production, storage, and use. For example, modeling has traditionally been carried out separately for increments of length scales using quantum mechanics (0.1 to 10 nm), statistical mechanics (1 to 1,000 nm), mesoscale (0.1 to 100 μm), and continuum mechanics (1 mm to 10 m). Time scales range from quantum mechanical methods (10^{-15} s) to continuum methods (1 to 10^5s). There is a critical need for theoretical modeling and simulation to span all these length and time scales seamlessly to meet the needs of hydrogen research. New first-principle algorithms are required to simulate and model condensed-phase phenomena with higher accuracy. This will enable experimental measurements to be assessed for the identification of trends that will aid in the development of new materials and processes for specific applications. For example, computational tools could aid in the identification of elements or compounds that could be added to nanostructured hydrogen storage materials to help improve the rate of hydrogen release. Simulations could then be used to understand the molecular-level processes responsible for the observed improvements.

Computational methods can be used in the design of novel biologically inspired components for catalysis, for example, and to predict the structure and mechanisms of these processes. Computational methods are also needed to understand the structure of materials and interfacial regions, interactions in composites, and ionic and electronic transport within and across phase boundaries. Predictive modeling will be required to provide an atomic-scale understanding of catalytic sites and of the mechanisms involved in catalysis to allow tailored design of catalysts on the nano scale. For hydrogen storage, computational methods are needed to understand how hydrogen reacts with the surface, interface, grain boundaries, and bulk defects of a particular storage material. In fuel cell research, fundamental understanding of ionic transport properties of electrolytes used in membranes and the detailed reduction processes of oxygen at the cathode electrocatalyst-electrolyte interface, for example, are needed to develop improved electrode and electrolyte materials. Understanding electron transfer processes at interfaces is needed to enhance photocatalysis and electrocatalysis processes involved in fuel cells and hydrogen production.

Impact

Coupled with new characterization techniques that will yield unprecedented amounts of detailed information about atomic and molecular processes, new computational methods for theory, modeling, and simulation have the potential to revolutionize the design of materials at the nano scale and to expedite the discovery of molecular-level processes critical for hydrogen energy systems. Development of these novel materials and processes is critical for attaining the full suite of technologies necessary for a hydrogen economy. The time horizon for the development of practical hydrogen energy systems is short and cannot be met without a strong investment in theory and modeling in parallel with a significant investment in basic experimental research.

SAFETY AND ENVIRONMENTAL ISSUES

Overview

Safety and environmental issues impact all aspects of hydrogen utilization. Moving toward a hydrogen economy will require production, storage, and utilization of large quantities of hydrogen under various operating conditions. The accidental release of hydrogen poses significant risks that differ from those associated with fossil fuels. Hydrogen ignites more readily than propane, and a high-pressure leak can be self-igniting, burning with an invisible flame. Its high diffusivity and buoyancy normally prevent the buildup of flammable concentrations in the open air, but in enclosed spaces, the risk of fire or explosion can be serious. With large quantities of hydrogen in everyday use, we must be able to predict the behavior of hydrogen under many conditions, including enclosed garages, covered parking structures, enclosed or partially ventilated cars, and windless or windy open air. In each case, we should understand the hydrodynamics well enough to predict the threshold of flammable or explosive concentrations, and understand the combustion dynamics well enough to predict the magnitude of the released heat and blast. Of paramount importance to the safe handling of hydrogen is the training of skilled personnel and extensive public education. In addition, improved materials are needed that address issues related to hydrogen exposure, such as embrittlement, weld failures, and general materials compatibility. Developed technologies must also incorporate safeguards and processes that protect the environment from hydrogen leaks and potentially hazardous by-products of hydrogen production, storage, and use.

A large part of the interest in adopting hydrogen for use as an energy carrier arises from its potential for reducing the negative environmental impacts of our energy systems. However, in planning the development of any technology system that is intended to be implemented on a large scale, it is prudent to anticipate potential deleterious environmental impacts as well. If hydrogen were to become established as the primary carrier in the worldwide energy economy, the additional amount of hydrogen cycled each year would exceed the known amount cycled by all present-day geochemical, biological and atmospheric processes. If 10% of the hydrogen in use were to escape to the atmosphere, the amount of hydrogen entering the atmosphere from all sources would more than double. Hydrogen is rapidly mixed into the atmosphere and has a relatively short turnover time (~2 yr), being consumed in atmospheric processes and by soil microorganisms. The potential consequences of doubling the annual inputs into these processes need careful scientific study.

Research Needs

The need to understand the behavior of hydrogen under a wide variety of conditions demands better theory and modeling of its hydrodynamics and combustion dynamics. Such models would allow predictive capability for assessing the risk of fire or explosion under the many possible leak and failure scenarios that would be found in the hydrogen economy. These predictive models of hydrogen accumulation, ignition, and combustion will form the basis for establishing comprehensive safety standards and procedures. The fundamentals of the interactions of hydrogen with specific materials need to be understood, as well as the mechanisms involved in materials failure. Embrittlement in metals, the role of grain boundaries and other microstructure in promoting or retarding materials degradation, and the effect of hydrogen in weakening welds and joints need to be examined to anticipate catastrophic failures in the hydrogen infrastructure. Studies are needed to fully assess requirements for materials compatibility. Sensors are needed to detect trace amounts of hydrogen escaping into public places and to warn of potential flammable accumulations in enclosed spaces. Such sensors should be highly selective and highly sensitive to hydrogen, providing quantitative as well as qualitative information.

The fate of hydrogen that escapes to the atmosphere needs to be studied in greater detail so that the consequences of increased releases can be accurately modeled and projected. The capacity of soil and various aqueous microbial ecosystems to take up the increased hydrogen flux must be assessed. To make an accurate assessment, the properties of hydrogen-metabolizing organisms and microbial consortia need to be much better understood. The impact of any increased microbial uptake on the diversity and stability of their ecosystems and of increased accumulation of their metabolic by-products, such as methane, must also be assessed. These data are needed for projecting whether or not the net content of hydrogen in the atmosphere would rise. The consequences of increasing atmospheric hydrogen must be carefully studied, including an assessment of its impact on other atmospheric processes.

Impact

The ability to model the hydrodynamics and combustion dynamics of hydrogen in the open air and in enclosed spaces will enable reliable risk assessment of the many potential hydrogen-human contact situations that would occur in a hydrogen economy. Understanding the causes and evolution of hydrogen embrittlement of metals and weld joints at the atomic level will enable prediction and prevention of mechanical failures within the hydrogen infrastructure and the accidental release of hydrogen to the environment. Development of inexpensive and effective sensors for the presence and concentration of hydrogen will provide early warning of dangerous hydrogen concentrations before they reach the ignition point. Data concerning potentially deleterious environmental impacts of hydrogen energy systems are critically needed for developing rational hydrogen emission standards so that the costs of containment are known *before* the technology is adopted on a large scale.

CONCLUSIONS

CONCLUSIONS

The hydrogen economy offers a grand vision for energy management in the future. Its benefits are legion, including an ample and sustainable supply, flexible interchange with existing energy media, a diversity of end uses to produce electricity through fuel cells or heat through controlled combustion, convenient storage for load leveling, and freedom from harmful environmental pollutants. These benefits provide compelling motivation for a broad effort across the research, development, engineering, and industrial sectors to implement hydrogen as the fuel of the future.

The challenges to reach a hydrogen economy, however, are enormous, considering today's state of knowledge and technical capabilities. The hydrogen economy consists of many physical and chemical processes linked in an interdependent network that connects production, distribution, storage, and use. Hydrogen in its various forms flows throughout the network, linking primary sources like hydrocarbons or seawater to storage media like alanates to end-use functions like fuel cells. Many of the processes in the network have been demonstrated in laboratory or prototype tests at some level, but nearly all of these processes remain to be proved in competitive environments against existing technology for cost, performance, and reliability.

The gap between present-day technology and commercial viability is vast. To be economically competitive with the present fossil fuel economy, the cost of fuel cells must be lowered by a factor of 10 or more, the cost of producing hydrogen by a factor of 4, and the performance and reliability of hydrogen technology for transportation and other uses must be improved dramatically (Abraham 2003). This gap cannot be bridged by incremental advances of the present state of the art. Bridging the gap requires not only creative engineering, but also revolutionary conceptual breakthroughs in understanding and controlling the physical and chemical processes that govern the interaction of hydrogen with materials. Such breakthroughs can only come from comprehensive basic research focused on the behavior of hydrogen at the atomic level, exploiting the remarkable recent advances in materials synthesis capabilities, forefront characterization tools, and creative theory and modeling. The best scientists from universities and national laboratories and the best engineers and scientists from industry must work in interdisciplinary groups to find breakthrough solutions to the fundamental problems of hydrogen production, storage, and use. The formulation of such a basic research program must be coordinated with the needs of applied research and development and have coupled experimental and theoretical components for maximum impact. The hope is that these discoveries and related conceptual breakthroughs from basic research will provide a foundation for the innovative design of materials and processes that will produce qualitative improvements in the performance, cost, and reliability of the production, storage, and use of hydrogen so that an economically competitive hydrogen economy can eventually be realized.

Secretary of Energy Spencer Abraham outlined four research challenges for achieving the hydrogen economy in his address to the National Hydrogen Association (Abraham 2003):

- Dramatically lower the cost of fuel cells for transportation,
- Develop a diversity of sources for hydrogen production at energy costs comparable to gasoline,

- Find viable methods of onboard storage of hydrogen for transportation uses, and

- Develop a safe and effective infrastructure for seamless delivery of hydrogen from production to storage to use.

The findings of the three panels and the high-priority research directions presented in this Report address these challenges.

As we ponder the benefits of a hydrogen economy, we also must consider other factors. The time scale required to develop the technology and the infrastructure needed to produce the amount of hydrogen required for a hydrogen economy is significant. In recognition of this long-term focus, we must consider complementary routes for achieving significant energy savings and environmental benefits in the near term, such as internal combustion/electric hybrid vehicles. This Report, however, focuses on the long-term context of the hydrogen economy and the high-priority basic research directions needed to achieve it.

The technical challenges of the hydrogen economy consist of a microcosm of modern interdisciplinary basic science. Fuel cells require electrocatalysts, ionic membranes, and electrical conductors in complex and demanding architectures. Hydrogen storage materials involve special bulk structures, complex surface chemistry, and special catalysts to achieve high storage capacity simultaneously with rapid kinetics. Production of hydrogen from water using either solar photocatalytic and photochemical reactions or heat from nuclear reactors requires nanoscale semiconductor/metal/dye hybrids or complex chemical cycles with sophisticated separation membranes. The specific challenges described in some detail in this Report cannot be met by research within a single field of knowledge; rather, they require coordinated research efforts at the intersection point of traditional chemistry, physics, biology, materials science, and engineering science.

The preceding chapters not only go into some detail about the great technical challenges of the hydrogen economy, but also consider high-priority research directions that offer promise for addressing these challenges. Looking across these high-priority research directions, several broad themes emerge: materials and nanoscale architectures, catalysis, membranes, bio-inspiration, modeling and simulation, and advanced measurements techniques. These themes capture both the technical limitations of current hydrogen technology and the promise for revolutionary conceptual innovations that would enable significantly higher performance at reduced cost. Comprehensive efforts in each of these broad areas will impact key issues across the hydrogen economy, as well as other needs for long-term energy security (Basic Energy Sciences [BES] Advisory Committee 2003).

The basic research that will help to realize a commercially viable hydrogen economy requires an integrated approach, connecting progress in the critical areas of hydrogen production, storage, and use. Major advancement toward the goal of a hydrogen economy can be achieved only with concomitant scientific breakthroughs in each of these critical areas. The integrated research approach emphasized in this Report not only identifies key barriers to success in each of the critical areas, but also promotes broad interdisciplinary efforts, cross-cutting solutions, strong coupling and coordination between basic and applied science, and cooperative efforts among

Basic Energy Sciences and the Energy Efficiency and Renewable Energy, Fossil Energy, and Nuclear Energy Program Offices of the U.S. Department of Energy. Each of these offices will play a decisive role in a future hydrogen economy; the research needs of each office must be folded into the formulation of the basic research program.

Materials discovery, performance, and design are identified in this Report as overarching areas of a grand challenge with opportunities for broad impact on enabling the transition to a hydrogen economy. The success to date, the current limitations on performance, and the prospect for dramatic advances in achieving the hydrogen economy all center on materials behavior. Basic research understanding of the mechanisms for proton and oxygen ion conduction, of gas separation, and of surface behavior at interfaces is fundamental to the design of new approaches to hydrogen production, storage, and use. A key materials issue is the integration of functions in hybrid materials, such as gas permeability with catalysis and electron and ion mobility in fuel cells. Another fertile area for research is the self-assembly of polymer and/or inorganic materials into complex composite structures that could enable and optimize many of the processes needed for production, storage, and use of hydrogen. These complex materials open sweeping horizons for variations of structure and function with high potential for revolutionary advances.

Nanoscience introduces a powerful and virtually untapped new dimension to the broad research directions identified in this Report because of the radically new properties that materials exhibit at the nano scale. This theme permeates nearly all the materials and process issues of the hydrogen economy. The dependence of catalytic activity on size and shape of some nanoparticles may provide a powerful knob for increasing the reaction rate and selectivity, while decreasing the cost of catalysts. The intimate interaction of electrons, ions, catalysts, and gases in fuel cells requires complex nanoscale architectures for effective control. In storage media, large surface areas with catalytically enhanced absorption and desorption rates are a key element in obtaining reasonable kinetics and storage densities. These are fundamentally nanoscience phenomena requiring atomic and nanoscale understanding and control to achieve the qualitative advances needed for a viable hydrogen economy. This Report identifies nanoscale science and technology as a high-payoff research direction with the potential for revolutionary breakthroughs in lowering the cost and raising the performance and reliability of technology for hydrogen production, storage, and use in fuel cells.

Present catalytic performance limits many essential elements of the hydrogen economy, including fuel cell efficiency, storage kinetics, and production capacity. Fundamental understanding of the catalytic process at the atomic level in any of these areas would drive collateral progress in all three. Major effort needs to be expended to synthesize less expensive, nonpoisoning, robust catalysts with much higher activities, selectivities, impurity tolerance, and capabilities for operating under extreme environments. These research directions should exploit newly emerging capabilities in the synthesis of size-controlled and patterned nanostructures and composite assemblies. Catalysis research should seek guidance from state-of-the-art modeling and simulation calculations to point the way to the selection of promising approaches to the design of catalysts for specific applications. Catalysis cuts across all areas of hydrogen research. It has high potential for the revolutionary breakthroughs in hydrogen production, storage, and use that will enable a viable hydrogen economy.

Biological and bio-inspired energy conversion designs have produced remarkable innovations that integrate light harvesting, charge separation and transport, and charge transfer for fuel formation and stability into model systems. Particular microbes have been identified for biophotolysis, along with component redox enzymes, proteins, cofactors, and regulatory pathways for producing and metabolizing hydrogen and other fuels (e.g., carbon monoxide, methane) using inspiration from nature's evolutionary prowess. Biomimetic catalysts devoid of noble metals and protein-modeled maquettes designed for electron tunneling and proton exchange offer promise for incorporation into fuel cell electrodes. Furthermore, these novel bio-like structures can be bonded onto nanoengineered surfaces to amplify their effectiveness through self-assembly and enhanced surface area. Since kinetic constraints severely limit the practical utility of present hydrogen energy systems in so many ways, basic research into the fundamental principles underlying biological hydrogen metabolism and oxygen reduction could lead to crucial breakthroughs along the path toward development of large-scale, hydrogen-based energy systems. In this vein, research is needed for understanding the mechanisms that underlie the bio-genesis, maintenance, and integrated activity of the enzymes and cofactors that support biological hydrogen metabolism and oxygen reduction, as well as to transform this understanding to the development of biomimetic or bio-inspired synthetic catalysts. Nature chose hydrogen as the energy carrier for development of the biosphere some three billion years ago. Through evolution, nature has developed powerful and clever approaches for manipulating hydrogen in the natural environment. Basic research into biological and bio-inspired energy conversion is an untapped high-risk/high-payoff opportunity for dramatic breakthroughs spanning all phases of hydrogen production, storage, and use.

Separation technology is a key determinant of efficiency in both hydrogen production and use. The needs for very high permeability and selectivity in gas separations, high ionic conductivity with minimal fuel crossover in fuel cell membranes, and membranes with much improved durability that are capable of separations at high temperatures under extreme chemical environments call for an intensive effort in materials synthesis, characterization, and modeling. Basic research is sorely needed to enhance the efficiency of separations for the production of ultra-pure hydrogen and for direct use in fuel cells of hydrogen made by steam reforming, to enable novel intermediate- and high-temperature fuel cell designs by means of advanced polymeric and inorganic ion-conducting membranes, and to develop robust inorganic membranes to enable thermal water splitting cycles as a viable means of hydrogen production. Research that is likely to have high impact will seek advances in nanostructured porous materials; robust inorganic membranes for high-temperature separations in corrosive environments; electronically conductive gas diffusion membranes for PEM fuel cell applications; low-cost, high-conductivity proton conductors for higher-temperature use; and fast oxide-ion conductors for solid oxide fuel cells.

Sensitive tools are needed for the detection, characterization, and measurement of hydrogen as it interacts with materials, particularly with nanostructures, under a wide range of realistic operating conditions of temperature, pressure, and chemically reactive environments. Included are imaging tools like scanning probes and transmission electron microscopes, as well as scattering tools like neutron and synchrotron diffractometers and spectrometers. The development of novel, low-cost, and selective sensors for hydrogen gas will also be needed for safety-related applications connected with the detection of hydrogen leaks and for the prevention of hydrogen-embrittlement–related materials failures.

Theory, simulation, and computation are critical for bridging the vast gap between the science and technology necessary for a competitive hydrogen economy and our present capability for implementing hydrogen production, storage, and use. To bridge this gap, it is necessary to couple theory and experiment in basic research to gain a fundamental understanding of the basic interactions of hydrogen with materials. Theory and computation can be used not only to understand experimental results, but also to guide them. The first step in this direction is to understand the interaction of hydrogen with surfaces and associated step edges and crystal defects, and how hydrogen diffuses on the surface. The sites that hydrogen atoms occupy in the bulk; the energy barriers for its diffusion, including their effect on the electronic structure of the host and their interaction with lattice defects (e.g., vacancies, voids, impurities, grain boundaries, and dislocations); and the effect of temperature and pressure on phenomena are all important for a comprehensive understanding of hydrogen in materials. It is important to understand how alloying can change the bonding between hydrogen and metal atoms in light complex metal hydrides. Similarly, an understanding of the role of catalysts and dopants in altering the nature of hydrogen bonding in these hydrides is needed. In nanostructured materials, it is important to study the effect of size and shape on the nature of hydrogen bonding and binding energies. In porous materials, one needs to know whether hydrogen remains in molecular form or if it bonds atomically. A multiscale approach is needed to understand the electronic structure, dynamics, and energetics of hydrogen in materials. Recent advances in methodology (theory and algorithms) and increases in computational power have opened up new possibilities for theoretical studies of the hydrogen-materials interaction over a wide range of length and time scales. This study sees great promise for theory/simulation/calculations to make major headway in bridging the gap between present capabilities and the needs of a hydrogen economy.

This study paid special attention to safety in the hydrogen economy, because of the high diffusivity, buoyancy, and inflammability of hydrogen. Hydrogen embrittlement of materials after extended exposure, together with possible explosive scenarios for hydrogen accumulation in enclosed spaces, is a concern. It is concluded that the study of hydrogen embrittlement; the hydrodynamics of the combustion of hydrogen in enclosed spaces and when mixed with other gases; and the development of sensitive, selective sensors for hydrogen gas are important research areas. Public education about the safe use of hydrogen and suitable training of personnel working with hydrogen are both needed in planning for a hydrogen economy.

Attention is also given to environmental issues — in particular, assessing to what degree a hydrogen economy would be truly environmentally friendly. Because of the large potential increase in atmospheric hydrogen, high-priority research was identified for assessing the effect of such an increase in hydrogen on present-day geochemical, biological, and atmospheric processes.

The panels assembled to carry out this study started their investigation by focusing on the large gap between present knowledge and technology and the requirements of a hydrogen economy. As the panels carried out their investigations, however, optimism increased, indicating that the many recent advances in chemistry, materials research, and computation have opened exciting new research opportunities with the potential for having a significant impact on diminishing the gap between knowledge and technology. At the same time, concerns about possible safety and environmental risks led the panels to propose additional research agendas in these areas that should be pursued.

Whereas others have emphasized the huge knowledge and technology gap (Davis et al. 2003; Weiss et al. 2003) separating us from the hydrogen economy, this Report takes the position that a serious long-range basic research effort could have a large impact on significantly narrowing this gap. Furthermore, most of the research directions identified in this Report are expected not only to make progress in achieving a hydrogen economy, but also to have a dramatic impact on many other aspects of the DOE efforts to provide the nation with a secure energy supply for the future (BES Advisory Committee 2003).

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APPENDIX

Workshop on Basic Research Needs for the Hydrogen Economy

Doubletree Hotel and Executive Meeting Center
Rockville, Maryland
May 13–15, 2003

Agenda for Plenary Sessions

Tuesday Afternoon, May 13

Time	Topic	Speaker or Location
1:00 - 1:15 pm	Welcome and Introduction	Mildred Dresselhaus, Workshop Chair, Massachusetts Institute of Technology
1:15 - 1:30 pm	Overview of the Office of Basic Energy Sciences	Patricia Dehmer, Director, Office of Basic Energy Sciences
1:30 - 2:15 pm	President's Hydrogen Initiative	Steven Chalk, Program Manager, DOE/EERE Hydrogen, Fuel Cells and Infrastructure Technologies Program
2:15 - 3:00 pm	Hydrogen Storage: State of the Art	George Thomas, Consultant, Sandia National Laboratories
3:00 - 3:30 pm	Onboard Hydrogen Storage: Who's Driving and Where Are We Going?	Scott Jorgensen, Manager, Energy Storage Systems Group/General Motors R&D
3:30 - 3:45 pm	Break	
3:45 - 4:15 pm	Hydrogen and Climate Change	Jae Edmonds, Senior Staff Scientist, Pacific Northwest National Laboratory
4:15 - 5:00 pm	Science of Hydrogen Safety	Jay Keller, Department Manager, Sandia National Laboratories/Combustion in Engines and Hydrogen Energy
5:00 - 5:15 pm	Overview of Hydrogen Production Breakout Session	Tom Mallouk, Penn State University, and Laurie Mets, The University of Chicago
5:15 -5:30 pm	Overview of Hydrogen Storage and Distribution Breakout Session	Kathy Taylor, General Motors (retired), and Puru Jena, Virginia Commonwealth University
5:30 - 5:45 pm	Overview of Fuel Cells and Novel Fuel Cell Materials Breakout Session	Frank DiSalvo, Cornell University, and Tom Zawodzinsky, Case Western Reserve University
6:00 - 7:00 pm	Reception (cash bar)	Plaza Ballroom Foyer
7:00 pm	Working Dinner	Plaza I

Agenda for Plenary Sessions (Cont.)

Wednesday, May 14, and Thursday Morning, May 15

No Plenary Sessions; see Agenda for Breakout Sessions.

Thursday Afternoon, May 15

Time	Topic	Speaker or Location
1:30 - 1:45 pm	Concluding Remarks	Mildred Dresselhaus, Workshop Chair Massachusetts Institute of Technology
1:45 - 2:30 pm	Summary of Hydrogen Production Breakout Session	Tom Mallouk, Penn State University Laurie Mets, University of Chicago
2:30 - 3:15 pm	Summary of Hydrogen Storage and Distribution Breakout Session	Kathy Taylor, General Motors (retired) Puru Jena, Virginia Commonwealth University
3:15 - 3:30 pm	Break	
3:30 - 4:15 pm	Summary of Fuel Cells and Novel Fuel Cell Materials Breakout Session	Frank DiSalvo, Cornell University Tom Zawodzinsky, Case Western Reserve University
4:15 - 4:45 pm	Cross-cutting Issues and Summary	Workshop Associate Chairs: George Crabtree, Argonne National Lab Michelle Buchanan, Oak Ridge National Lab
5:00 pm	Adjourn	

Agenda for Hydrogen Production Breakout Session

Wednesday, May 14

Time	Topic	Speaker or Location
8:30 - 9:00 am	Solar Production	Allan Bard, University of Texas, Austin
9:10 - 9:40 am	Biological and Biomimetic Production	Charles Dismukes, Princeton
9:50 - 10:10 am	Bio/inorganic Interfaces	Leonard Tender, Naval Research Lab
10:20 - 10:50 am	Break	
10:50 - 11:20 am	Fossil Production	Jennifer Holmgren, UOP
11:30 am - 12:00 pm	Nuclear Production	Ken Schultz, General Atomic
12:10 - 1:30 pm	Working Lunch	Executive Dining Room
1:30 - 3:30 pm	Panel Discussions	
3:30 - 4:00 pm	Break	
4:00 - 7:00 pm	Meetings of Subgroups to Draft Reports	
7:00 pm	Working Dinner	Regency
Evening after Dinner	Meetings to Assess Progress	

Thursday Morning, May 15

Time	Topic	Speaker or Location
8:30 - 10:00 am	Meetings of Subgroups to Finalize Reports	
10:00 am - 12:00 noon	Consolidation of the Reports/Preparation for Presentation	
12:00 - 1:00 pm	Working Lunch	Executive Dining Room

Agenda for Hydrogen Storage Breakout Session

Wednesday, May 14

Time	Topic	Speaker or Location
8:30 - 8:45 am	General Objectives	Kathy Taylor, General Motors (Retired)
8:45 - 9:20 am	Key Issues	Scott Jorgensen, General Motors
9:20 - 9:55 am	Metal and Compound Hydrides	Robert Bowman, Jet Propulsion Laboratory
9:55 - 10:30 am	Theory and Computation	Karl Johnson, University of Pittsburgh
10:30 - 11:00 am	Break	
11:00 – 11:35 am	Nanostuctured Hydrides	Thomas Lassen, GKSS-Research Center
11:35 am - 12:05 pm	Carbon-related Materials	Peter Eklund, Penn State University
12:05 - 1:30 pm	Working Lunch	Executive Dining Room
1:30 - 3:00 pm	Panel Discussions	
3:00 - 3:30 pm	Break	
3:30 - 5:30 pm	Meetings of Subgroups to Draft Reports	
7:00 pm	Working Dinner	Regency
Evening after Dinner	Meetings to Assess Progress (tentative)	

Thursday Morning, May 15

Time	Topic	Speaker or Location
8:30 - 10:00 am	Meetings of Subgroups to Finalize Reports	
10:00 am - 12:00 noon	Consolidation of the Reports/Preparation for Presentation	
12:00 noon - 1:00 pm	Working Lunch	Executive Dining Room

Agenda for Fuel Cells and Novel Fuel Cell Materials Breakout Session

Wednesday, May 14

Time	Topic	Speaker or Location
8:00 - 8:30 am	Loading of Presentations onto Computer, Check of Audio-Visual Equipment	All Speakers
8:30 - 8:45 am	Introduction and Welcome	Frank DiSalvo and Tom Zawodzinski
8:45 - 9:15 am	Overview: The Fuel Cell Prospect	Shimshon Gottesfeld, MTI
9:15 - 9:45 am	Bio-fuel Cells	Adam Heller
9:45 - 10:15 am	SOFC	Ray Gorte
10:15 - 10:45 am	Break	
10:45 - 11:15 am	Fuel Processing	Levi Thompson
11:15 - 11:45 am	Electrocatalysis and Auto Needs	Hubert Gasteiger
11:45 am - 12:15 pm	Polymers in Fuel Cells	Jim McGrath
12:15 - 1:30 pm	Working Lunch	Executive Dining Room
1:30 - 2:00 pm	Status of Theory for Fuel Cell Processes	Woods Halley
2:00 - 3:30 pm	Panel Reflections, Summaries, Additions	15 min from Member of Each Panel
3:30 - 4:00 pm	Break	
4:00 - 7:00 pm	Meetings to Draft Reports	Low-T Fuel Cells, High-T Fuel Cells, Reformers
7:00 pm	Working Dinner	Regency
Evening after Dinner	Meetings to Draft Reports	

Thursday Morning, May 15

Time	Topic	Speaker or Location
8:30 - 10:00 am	Meetings to Draft Reports, Joining Sections When Possible	
10:00 am - 12:00 noon	Preparation for Presentation	
12:00 noon - 1:00 pm	Working Lunch	Executive Dining Room

Workshop on Basic Research Needs for the Hydrogen Economy

Doubletree Hotel and Executive Meeting Center
Rockville, Maryland
May 13-15, 2003

Invited Participants

Workshop Chair	Mildred Dresselhaus, Massachusetts Institute of Technology
Associate Chairs	George Crabtree, Argonne National Laboratory Michelle Buchanan, Oak Ridge National Laboratory

Pre-Workshop Briefing Presenters

Mark Paster, Department of Energy/Energy Efficiency and Renewable Energy
JoAnn Milliken, Department of Energy/Energy Efficiency and Renewable Energy
Nancy Garland, Department of Energy/Energy Efficiency and Renewable Energy

Plenary Session Speakers

Steve Chalk, Department of Energy/Energy Efficiency and Renewable Energy
George Thomas, Sandia National Laboratories - California
Scott Jorgensen, General Motors
Jae Edmonds, Pacific Northwest National Laboratory
Jay Keller, Sandia National Laboratories - California

Hydrogen Production Panel Chairs

Tom Mallouk, Pennsylvania State University
Laurie Mets, The University of Chicago

Speakers

Allen Bard, University of Texas, Austin
Charles Dismukes, Princeton University
Jennifer Holmgren, UOP
Ken Schultz, General Atomics
Lenny Tender, NRL

Panelists

Michael Adams, University of Georgia
Les Dutton, University of Pennsylvania
Charles Forsberg, Oak Ridge National Laboratory
Heinz Frei, Lawrence Berkeley National Laboratory
Tom Moore, Arizona State University
Jens Nørskov, Technical University of Denmark
Arthur J. Nozik, National Renewable Energy Laboratory
K. Lee Peddicord, Texas A&M University
Tom Rauchfuss, University of Illinois
John A. Turner, National Renewable Energy Laboratory
Luping Yu, The University of Chicago

Hydrogen Storage Panel

Chairs

Kathy Taylor, General Motors, retired
Puru Jena, Virginia Commonwealth University

Speakers

Robert Bowman, Jet Propulsion Laboratory
Karl Johnson, University of Pittsburgh
Peter Eklund, Pennsylvania State University
Scott Jorgensen, General Motors
Thomas Klassen, GKSS-Research Center, Germany

Panelists

Mike Baskes, Los Alamos National Laboratory
Björgvin Hjörvarsson, Uppsala University, Sweden
Hannes Jonsson, University of Washington
Vitalij Pecharsky, Ames Laboratory
James Ritter, University of South Carolina
Seiji Suda, Kogakun University, Japan
George Thomas, Sandia National Laboratory, (Retired)
John Wolan, University of South Florida

Fuel Cells and Novel Fuel Cell Materials

Chairs

Frank DiSalvo, Cornell University
Tom Zawodzinski, Case Western Reserve University

Speakers

Joel Christian, Osram/Sylvania
Hubert Gasteiger, General Motors
Ray Gorte, University of Pennsylvania
Shimshon Gottesfeld, MTI Micro Fuel Cells
Woods Halley, University of Minnesota
Adam Heller, University of Texas, Austin
Jim McGrath, Virginia Polytechnic Institute and State University
Levi Thompson, University of Michigan

Panelists

Zachary Fisk, Florida State University
Fernando Garzon, Los Alamos National Laboratory
Sossina Haile, California Institute of Technology
John Lannutti, Ohio State University

Additional Contributors

Andrew Gewirth, University of Illinois
Radoslav Adzic, Brookhaven National Laboratory
Marvin Singer, Department of Energy
David Ginley, National Renewable Energy Laboratory
Giselle Sandi, Argonne National Laboratory

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