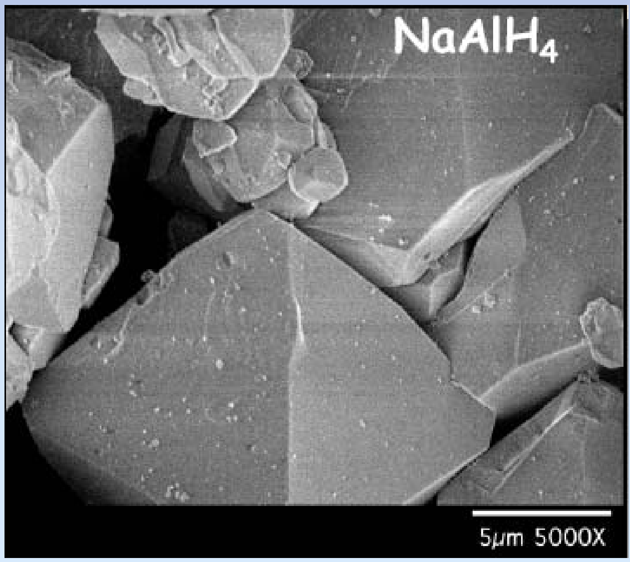
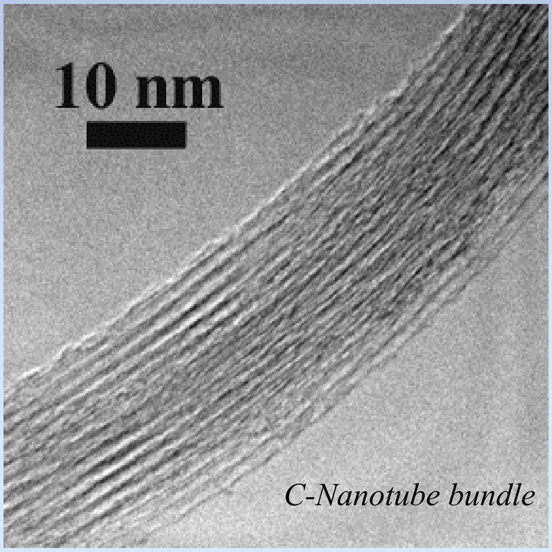
Hydrogen Storage "Think Tank"

Report

March 14th, 2003
Washington, DC

Sponsored by the
U.S. Department of Energy
Office of Hydrogen, Fuel Cells and Infrastructure Technologies





Executive Summary

To identify potentially new and promising hydrogen storage technologies, a team of distinguished scientists was assembled to provide a forum for innovative and non-conventional brainstorming on this critical issue. This "Think Tank" meeting was held in Washington, D.C. on March 14, 2003 and was organized and sponsored by the U.S. Department of Energy (DOE) Office of Hydrogen, Fuel Cells and Infrastructure Technologies. .

The group identified and discussed a number of specific materials concepts that may provide improved storage properties over existing approaches. These included:

- Nanotechnology
- High surface area materials
- Synthetic metals
- Chemical and metal hydrides, clathrates
- Modeling and experimental approaches

The team also recommended some overall strategies. Briefly, these were:

- Issue a "Grand Challenge" to communicate the problem to the scientific community and to generate interest and innovative ideas.
- Establish integrated teams (virtual centers) of universities and industrial laboratories, coordinated and integrated by a national laboratory. These teams would provide a mechanism for collaboration and multi-disciplinary research.
- Explore novel concepts through small projects in which technical feasibility would be demonstrated during the first one or two years.
- Educate the scientific community about the technical challenges and educate the public about hydrogen technologies.

Introduction

A major goal for establishing a hydrogen energy economy is to gain consumer acceptance for fuel cell powered vehicles in the transportation sector. Hydrogen storage is a “critical path” technology that will facilitate the commercialization of fuel cell powered vehicles. Research on gaseous and liquid methods to inexpensively store hydrogen on-board vehicles in a safe, compact and lightweight package has been ongoing for more than a decade. The U.S. DOE’s Hydrogen, Fuel Cells & Infrastructure Technologies Program has been instrumental in developing state-of-the-art compressed hydrogen tanks. The future focus, however, will be on solid-state materials allowing low-pressure storage, including adsorption on high surface area materials like carbon nanotubes; absorption in metal hydrides, such as the sodium alanates; and hydrogen binding in chemical compounds such as sodium borohydrides. Despite tremendous advances in recent years, no approach currently meets on-board storage density and/or charge-discharge requirements. On-board storage of hydrogen is more challenging than off-board storage, and is therefore the primary focus of the DOE program; however, the program is also developing technologies for off-board hydrogen storage.

To identify potentially new and promising hydrogen storage technologies, a team of distinguished scientists was assembled to provide a forum for innovative and non-conventional brainstorming. This “Think Tank” meeting was held in Washington, D.C. on March 14, 2003 and was organized and sponsored by the U.S. Department of Energy (DOE) Office of Hydrogen, Fuel Cells and Infrastructure Technologies. The meeting began with a plenary session, where DOE speakers provided the participants with the motivation behind hydrogen storage development, followed by a facilitated brainstorming session in which the participants discussed a wide range of issues and concepts.

Motivation for Hydrogen Development

The U.S. currently imports 54% of its petroleum, and this value is projected to rise to 68% by 2025; the transportation sector is the major consumer of petroleum imports. U.S. DOE analysis shows that, even if CAFE standards were raised by 60% immediately and 11 billion barrels of oil per day were produced in the Arctic National Wildlife Refuge, we would still be dependent on imported oil. Use of hydrogen as a fuel offers the opportunity to shift the energy requirements for transportation from imported oil to diverse, domestically available resources. Hydrogen-powered fuel cell vehicles are a tremendously attractive alternative to gasoline and diesel powered automobiles as they emit only water with essentially no criteria pollutants. The hydrogen fuel itself may be generated by several different means, including thermochemical processing of primary energy sources such as coal, oil, or biomass, or generated by electrolysis using electricity derived from nuclear energy, wind power, or photovoltaics. Producing hydrogen at central locations will enable pollutants and greenhouse gases to be contained and more easily remediated. The high efficiency of fuel cells will make hydrogen a cost effective, energy efficient, and environmentally friendly alternative to current fuels when considering the full lifecycle. Thus, the concept of a hydrogen-based transportation system offers energy resource flexibility and the potential for energy independence, as well as the elimination of net carbon dioxide emissions.

During his 2003 State of the Union address, the President proposed to accelerate the research and development required to solve technical challenges to hydrogen production, delivery, storage, and distribution, and to establish the necessary safety-related codes and standards. The FreedomCAR and Hydrogen Fuel Initiative will develop the technologies needed for the mass production of safe and affordable hydrogen-powered fuel cell vehicles, and accelerate the demonstration of both vehicles and infrastructure under real world conditions. By pursuing fuel cell vehicle and hydrogen infrastructure activities in parallel, the FreedomCAR and Hydrogen Fuel Initiative will enable the automotive and energy industries to make a commercialization decision in 2015, rather than in 2030 as previously anticipated. Through partnerships with the private sector, the FreedomCAR and Hydrogen Fuel Initiative will develop technologies to make it practical and cost-effective for large numbers of Americans to choose to use hydrogen-powered fuel cell vehicles by 2020.

PLENARY SESSION

Energy, Economic, and Environmental Drivers: David Garman, Assistant Secretary - DOE Energy Efficiency and Renewable Energy

Mr. Garman discussed the energy and environmental drivers for DOE's energy efficiency programs and the President's FreedomCAR and Hydrogen Fuel Initiative. Mr. Garman mentioned that, in his many conversations with the President leading up to the State of the Union announcement, discussion often centered on the technical issues, and hydrogen storage was identified as a critical path research area that had to be solved, through innovation.

Asked by the participants if the Department and the Program were ready to push for a "Man on the Moon" level of effort, Mr. Garman opined that this problem might be harder than the Moon Mission or even the Manhattan Project, because our customer is the American consumer, not the U.S. Government. The FreedomCAR and Hydrogen Fuel Initiative will develop hydrogen and fuel cell technologies that will work on a number of different platforms to fit the varying needs of American consumers.

In an exchange of quotable quotes, "vision without money is a hallucination" was countered with an analogy similar to the popular MasterCard commercials: "commitment of the President and national resolve are priceless."

Program Overview: Steven Chalk, Program Manager- Hydrogen,

Fuel Cells and Infrastructure Technologies

Mr. Chalk described the President's Freedom CAR and Hydrogen Fuel Initiative, including the planned budget. The Hydrogen, Fuel Cells and Infrastructure Technologies Program has identified a number of critical challenges that need to be addressed aggressively. Whereas the current limitations of hydrogen production and fuel cell technologies are likely to be solvable with incremental or evolutionary improvements, the storage challenge requires revolutionary improvements and breakthroughs.

Mr. Chalk mentioned that heightened international interest and activity related to hydrogen and fuel cells has benefited the U.S., particularly through our interactions with member countries in the International Energy Agency. In addition, the Department has entered into an international agreement with the European Union on hydrogen and fuel cell research and development.

Cooperation with Office of Basic Energy Sciences: JoAnn Milliken, DOE Hydrogen Storage Team Leader

Dr. Milliken discussed the importance of the historical and existing cooperation between the DOE Office of Basic Energy Sciences and the Office of Energy Efficiency and Renewable Energy. The implementation of hydrogen and fuel cell technologies depends on progress in both fundamental and applied research, and the challenges require interdisciplinary and multi-disciplinary approaches.

State of the Art of Hydrogen Storage: George Thomas, Sandia National Laboratory

Dr. Thomas pointed out that the low volumetric density of gaseous fuels such as hydrogen requires a storage method that compacts, compresses or otherwise densifies the fuel. In addition, containment and balance-of-plant equipment result in additional weight and volume above that of the fuel - all of these components must be considered. The chief technical challenge for hydrogen storage is to achieve adequate stored energy in an efficient, compact, safe and cost-effective system.

The DOE program managers have worked with industry to develop technical targets for on-board hydrogen storage. The focus for this meeting was on the key technical targets of gravimetric energy density and volumetric energy density. These targets (shown in Table 1) were developed by the FreedomCAR Hydrogen Storage Technical Team. Achieving the 2010 targets will result in a system that is suitable for large-scale commercial production on a limited number of the least demanding platforms. The 2015 targets represent mass production of a full spectrum of vehicles.

Table 1. FreedomCAR System Targets

	2005	2010	2015
specific energy (MJ/kg)	5.4	7.2	10.8
weight percent hydrogen	4.5%	6.0%	9.0%
energy density (MJ/liter)	4.3	5.4	9.72
system cost ($/kg system)	9	6	3
operating temperature (°C)	-20/50		
cycle life (cycles)	500	1000	1500
Minimum full flow [(g/sec)/kW]	0.02	0.027	0.033
delivery pressure (bar)	2.5	2.5	2.5
transient response (sec)	0.5	0.5	0.5
refueling rate (kg H_2/min)	0.5	1.5	2.0
loss, permeation, leakage, toxicity, safety			

There was some discussion of the targets and whether or not they needed to be so stringent, i.e. why not give up something on the automobile like weight or range. Scott Jorgensen of General Motors and co-chair of the FreedomCAR Hydrogen Storage and Vehicle Interface Technical Team briefly discussed the basis for the targets. He explained that the automobile manufacturers must provide a product that U.S. consumers want to buy. That means producing vehicles that are equivalent to today's automobiles in terms of safety, performance, reliability, and range.

Figure 1 provides a summary of the status of current hydrogen storage technologies relative to the DOE/FreedomCAR 2015 targets.

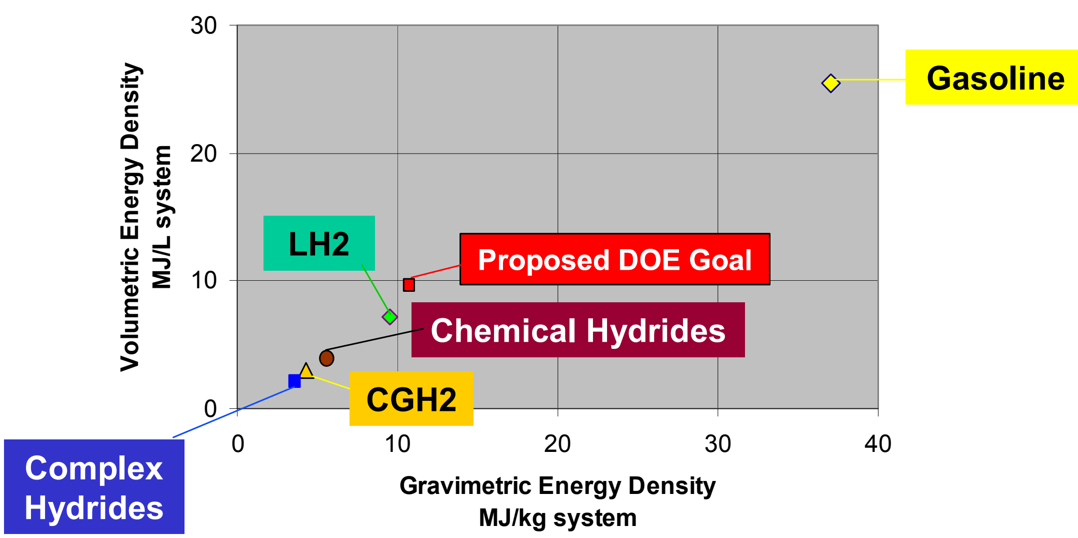


Figure 1. Status of current hydrogen storage technologies relative to the DOE/FreedomCAR 2015 targets.

BRAINSTORMING SESSION

Generation of Ideas

Participants were asked to describe their ideas on innovative concepts to solve the storage challenge and meet the stringent targets. These are listed in no particular order, and all related discussion is included under the appropriate subject. Attribution of ideas is not included.

The group believes that while the problem is challenging, potential solutions exist that do not violate the laws of chemistry and physics. There are materials and structures that offer promise for hydrogen storage at higher capacities. While the discussion was mainly focused on transportation applications, ideas that would be useful for stationary systems were considered. The ideas discussed at the meeting included:

1. Nanotechnology

Using a "nanotechnology" or "miniaturization" approach to material properties, the participants suggested that thermodynamic properties (or behavior) of materials might be "changed" by reducing the particle size to a point where surface activity (surface free energy) could actually drive the reaction. Keeping the particles small in a system might be difficult, as they are likely to have an affinity to re-assemble. Effects of particle size on the hydrogen capacity of metal hydrides should be investigated, i.e. do hydrogen storage properties, e.g. capacity, kinetics, energetics, improve with decreasing particle size?).

Substituting atoms at defect sites in solids might provide binding locations for hydrogen. Defect sites, themselves, might additionally provide binding sites for hydrogen. Surface modification of nano-scale materials with organic molecules could be an interesting research area. Another interesting area might be hydrogen storage accompanied by biological conformation changes.

2. High Surface Area Materials, including Carbons

Materials with extremely high surface-to-volume ratios such as nano- or mesoporous materials have significant potential as storage materials. The materials would need to be "designed" and "tailored". There is a stronger binding of H atoms in high-surface-area materials, therefore, catalysts may be needed for reversibly binding hydrogen.

Coating of high-surface materials with highly reactive materials, such as platinum, that can reversibly bind hydrogen with small temperature excursion was also suggested.

The storage capacity of activated carbon was discussed, focusing on the non-porous skeletal volume limiting available surface area. Heterogeneity of structure and binding sites renders optimization of the material difficult. The discussion also covered the possibility of optimizing adsorption energies and capacities with other forms of carbon, including fullerenes, nanographites, and nanotubes. The production and purification processes and the activation (tube opening) methods were discussed, focusing on the need for close control.

Manipulation of carbon nanotubes, including incorporation of heterolytic catalytic materials on the ends of the tubes, was suggested as a potential area of research. Tubes with specific diameter and chirality would be needed, pointing again to the need for understanding and control of the production process. A fundamental understanding of the hydrogen-carbon interaction is needed (is it physisorption, chemisorption, or some combination?).

The group agreed that the controversy over the storage capacity in carbon nanotubes needs to be resolved. The conditions (purity, size, type) under which they store hydrogen must be identified. Reproducible results that can be repeated independently by multiple research groups are needed. The group also discussed the implications of the (weak) interaction between hydrogen and carbon.

The discussion turned to the selection criteria for this class of materials. High surface area alone will not lead to an effective hydrogen storage system. For example, when evaluating the promise of a given porous material, there must be evidence or reasons to expect a higher binding energy than would be expected for simple physical adsorption. Additionally, there must also be space within the adsorbent to accommodate high capacities of hydrogen on both a per-volume and a per-weight basis. Characteristics that might affect hydrogen adsorption performance include the structure of a material (crystalline or amorphous); it is not completely clear which structure is ideal.

3. Synthetic Metals

Synthetic metals (conducting polymers), such as polyaniline and polypyrrole have recently been reported to exhibit storage capacities of around 8 wt% hydrogen. These materials should be investigated – it was pointed out that their electronic properties can be altered by applied electric fields. The reference cited on this work is: S.J. Cho, K.S. Song, J.W. Kim, T.H. Kim, and K. Choo, "Hydrogen in HCl-Treated Polyaniline and Polypyrrole; New Potential Hydrogen Storage Media", ACS Fuel Chemistry Division Preprints, Vol. 47, Issue 1, (2002).

4. Chemical and Metal Hydrides, Clathrates

Borohydrides were suggested as an interesting class of compounds with high hydrogen capacities and varying physical properties, ranging from solids (B_4H_{12} – rocket fuel) to liquids or waxes ("lower" borohydrides) at room temperature. These compounds could also be stabilized (in solution or as mixtures) at slightly elevated pressures or moderately low temperatures. A quick literature search of the thermodynamic properties of these compounds would be helpful.

Materials that change phase at the desired temperature should be explored for specific applications (a systems approach to storage integration is required). Lightweight metal and alloy hydrides should be considered, even if they do not meet the storage weight criteria, if there are unique physical and chemical mechanisms that could be applied to the design of other systems to achieve higher capacities and better performance.

Ammonia as a hydrogen carrier was suggested as an area that should be revisited. Although the synthesis process requires a catalyst, there are low temperature systems in nature (nitrogenase) that synthesize ammonia efficiently. However, some pointed out that much research has been devoted to replacing the Haber process for ammonia production by attempting to mimic nature.

There was also a discussion of the use of chemical cycles (such as benzene-cyclohexane). These systems have been looked at previously and were found to be lacking in terms of catalyst needs, as well as the pressure and temperature excursions required for charging and discharging. New approaches having new strategies to overcome these limitations would be attractive. The overall energy requirements for the generation/regeneration cycles must be evaluated to determine the overall energy efficiency of these systems.

The characteristics of methane clathrates (methane molecule is trapped in a cage-like ice structure at high pressure and low temperatures) might also be applicable to hydrogen storage. Searching for similar combinations of compounds that could "trap" hydrogen could be an interesting area for exploration.

Another suggestion was to try to mimic nature by integrating hydrogen production, storage, and utilization, e.g. a "direct-hydride" fuel cell, to reduce mass and increase efficiency. Nature has apparently recognized the problem of hydrogen storage and devised a system that converts hydrogen into chemical energy almost immediately. Nature's "micro hydrogen economy" stores very little hydrogen in hydrophobic cavities or channels that are adjacent to hydrogen production and hydrogen uptake sites - a system worth exploring as we seek a breakthrough for hydrogen storage at the macro scale.

5.Modeling and Experimental Approach

It was commonly recognized that new theoretical methods are required for discovering and modeling interactions between hydrogen and materials. For example, the strength of interaction energies required for room temperature, atmospheric pressure storage fall in an intermediate range between physisorption and chemical bond formation, and current theoretical methods are not well suited for the required computational simulations. Systems of interest are also typically multi-component and may involve synergistic interactions that are difficult to handle with current theoretical methods.

High through-put methods, i.e. combinatorial approaches, of experimentation and evaluation are also needed.

Recommended Strategy

The group believes that hydrogen storage presents a difficult, but interesting, challenge. In their view, however, most scientists are not familiar with the problem and how intriguing it is in terms of the chemistry, physics, and materials science challenges. They recommended that DOE issue a "Grand Challenge" to communicate the problem to the scientific community and to generate interest and innovative ideas. Two approaches to structuring the R&D activities were suggested:

1) Establish integrated teams (virtual centers) in which several institutions collaborate and pursue multi-disciplinary research. The team would include universities, small businesses, and industry laboratories, but would be coordinated/integrated by a national laboratory to keep the research focused on the DOE goals and to facilitate transfer of technology. Team proposals would be evaluated both in writing and in person - at the lead laboratory - based on criteria such as group cohesiveness and commitment, analytical capabilities, creativity, and theoretical approaches, in addition to scientific and technical merit.

2) Explore novel concepts through single investigator or small group projects in which technical feasibility would be explored during the first one to two years, followed by a down-selection process and continued development of the most promising ideas.

Finally, the group stressed the importance of educating the scientific community about the technical challenges and educating the public about hydrogen technologies.

Additional information on this meeting, including the presentations, and information about DOE hydrogen and fuel cell activities can be found on the website at http://www.eere.energy.gov/hydrofgenandfuelcells.

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