Hydrogen Production and Storage Research & Development Activities at the U.S. Department of Energy

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Introduction

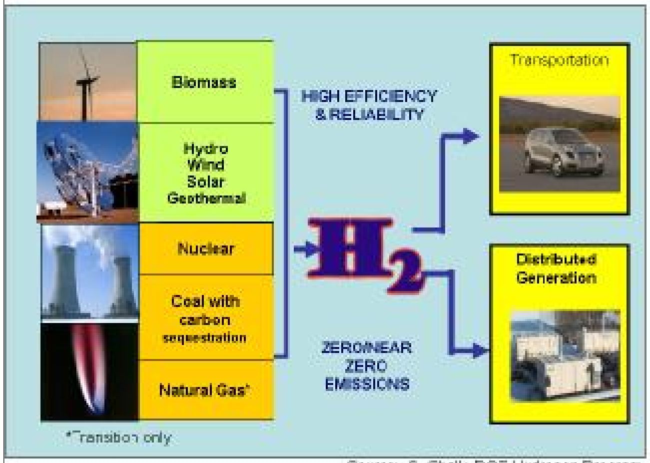
The potential of hydrogen as an energy carrier is one of many parallel strategies within the U.S. Department of Energy's (DOE) research and development portfolio. Active programs are underway on hydrogen, biomass, solar, wind, geothermal and nuclear energy, as well as on improved use of fossil fuels, carbon sequestration, and advanced hybrid vehicle technologies. In this presentation, I will focus on the DOE Hydrogen Program and two of the critical areas of investigation- hydrogen production and hydrogen storage. Following a brief overview of hydrogen production strategies, the status and challenges of hydrogen storage will be presented in detail.

U.S. petroleum dependence is driven by transportation, which accounts for two-thirds of the 20 million barrels of oil our nation uses each day.[1] The U.S. imports 55% of its oil, and this is expected to grow to 68% by the year 2025 under a status quo scenario.[1] The public has few options for transportation fuel as nearly all of our vehicles currently run on gasoline or diesel. To promote national energy security, alternative energy carriers need to be developed.

Molecular hydrogen, the simplest diatomic molecule known, with the highest gravimetric energy content of all known fuels, has the potential to be an attractive alternative energy carrier. It can be clean, efficient, and derived from diverse domestic resources: biomass, hydro, wind, solar, geothermal and nuclear energy resources, as well as coal with sequestration and natural gas for limited applications in the near-term (see Figure 1). Hydrogen can then be employed in high-efficiency power generation systems, including internal combustion engines or fuel cells for both vehicular transportation and for distributed electricity generation. In addition to its value for energy security, pure hydrogen used in fuel cells produce only water and heat as byproducts. Carbon dioxide emissions and criteria pollutants (e.g. NO_x, SO_x, CO, etc.) can be essentially eliminated from the point of use. Control of such emissions can then be much simpler at the point of generation, rather than from the tailpipes of 200 million vehicles on the roads. However, though molecular hydrogen is abundant in the universe, it is not plentiful on earth and, to reiterate, it is not a primary fuel source. How does one efficiently produce and safely deliver, store and use hydrogen to reap the benefits of reduced emissions, higher energy efficiency and improved energy security?

Figure 1

Hydrogen production strategy: To produce hydrogen from renewable, nuclear, and coal resources with technologies that will yield virtually zero criteria and greenhouse gas emissions

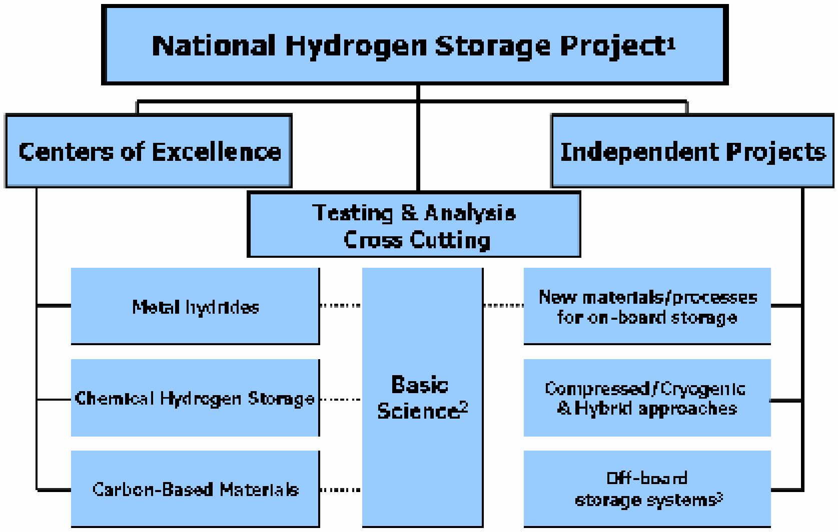


Source: S. Chalk, DOE Hydrogen Program

The Hydrogen Fuel Initiative, announced by President Bush in 2003, commits $1.2 billon over 5 years for accelerated research, development, and demonstration programs that will enable an industry decision in 2015 on commercial viability of hydrogen and fuel cell technologies. Should industry decide to proceed, a full transition to a hydrogen economy would clearly take decades and strong government industry partnerships. However, the key point is that research and development to address the feasibility of hydrogen needs to occur now.

A brief overview of hydrogen production and the key technical challenges under investigation through the DOE Hydrogen Program will be given. Once you produce hydrogen, a critical technical challenge is how do you safely and efficiently store it? In 2003, DOE launched a “Grand Challenge” to the global technical community on hydrogen storage, culminating in the formation of a “National Hydrogen Storage Project” (see Figure 2). For the first time, Centers of Excellence[2], dedicated to hydrogen storage, were formed with multiple university, industry and national laboratory partners, leveraging expertise and capabilities to tackle this difficult problem. In addition, seventeen new projects on the basic science of hydrogen storage were selected in 2005, funded at roughly $20 million over 3 years through DOE’s Office of Science. Detailed examples will be given on the key issues in hydrogen storage, the National Hydrogen Storage Project and progress in the search for the ‘holy grail’ of hydrogen storage.

Figure 2: Based on the ‘Grand Challenge’ launched by DOE in 2003, the National Hydrogen Storage Project was planned at roughly $150 million in federal funding over 5 years, subject to appropriations. An additional ~$20 million over 3 years is planned for 17 new projects selected by the Office of Science in 2005.



Summary of Hydrogen Production Research & Development Activities

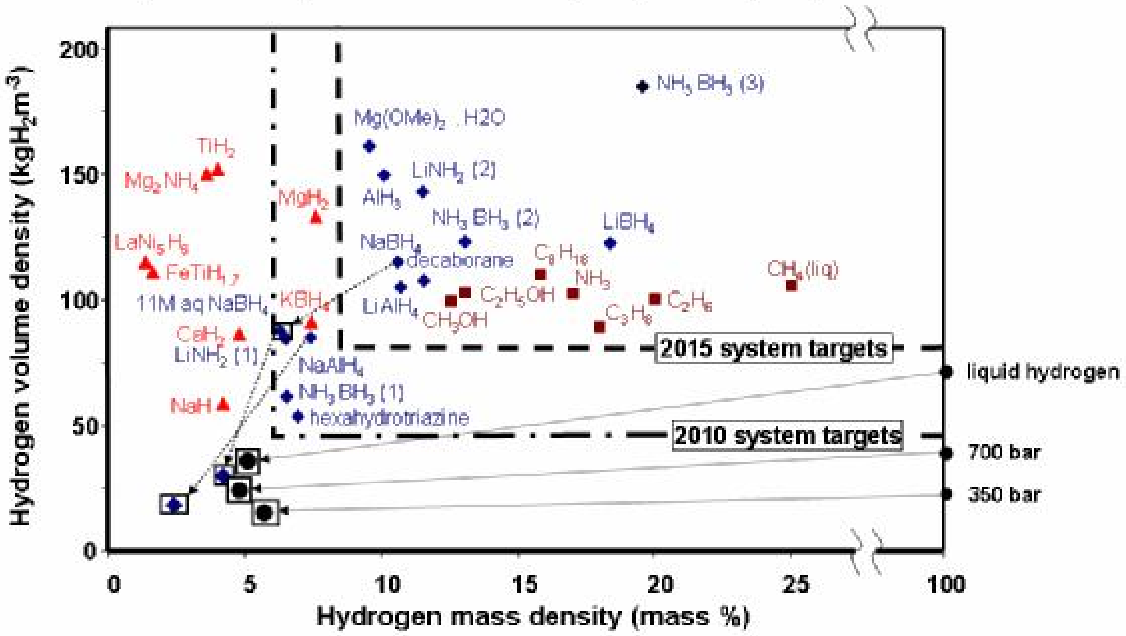
To meet the needs of a hydrogen economy while enabling energy security and environmental benefits, hydrogen must be produced from *diverse* resources and with minimal life cycle cost, energy efficiency and environmental impact. In the near term, to reduce large capital investments in infrastructure, small-scale distributed hydrogen production is likely, including distributed natural gas reforming or electrolysis at the fueling station. The key challenge is to reduce cost to meet the DOE goal of $2 to $3 per gallon gasoline equivalent (gge) by 2015, which is independent of the pathway to produce hydrogen. Recent results show that the cost of hydrogen produced from natural gas in a distributed system is approaching $3 per gallon gasoline equivalent (gge), reduced from about $5 per gge (delivered, untaxed).[3] More work is required to improve cost, durability and energy efficiency, and active research is underway on areas such as catalysts, membranes for separation and purification, water gas shift reactors, and hydrogen compression technology. Reforming of biomass and renewable liquids is also under investigation and many of the same issues apply. The long term strategy is to produce hydrogen using renewables, nuclear, and coal with sequestration (via gasification, not coal-based electricity) to achieve carbon-neutral or zero carbon technologies.

Water electrolysis is another approach under consideration and the key issues are capital cost and electricity cost. Research is underway on materials to increase electrolyzer durability and energy efficiency, while addressing the competing challenge of reducing cost. Another approach under investigation involves high temperature thermochemical reactions that can use heat from nuclear power plants or high temperature solar energy. Key issues are efficiency, cost and durability and several research areas are under study such as the development of more robust materials for high temperature operation, lower cost solar concentrator technology and optimized thermochemical reactions, to name a few. Finally, exploratory research for long-term approaches such as photobiological or photoelectrochemical production of hydrogen is underway. In all these areas, hydrogen purity is a key issue with 99.99 % purity required for polymer electrolyte membrane (PEM) fuel cells.

The "Grand Challenge" of Hydrogen Storage

On a weight basis, hydrogen has nearly three times the energy content of gasoline (120 MJ/kg for hydrogen versus 44 MJ/kg for gasoline). However, on a volume basis the situation is reversed (8 MJ/liter for liquid hydrogen versus 32 MJ/liter for gasoline). On-board vehicular hydrogen storage is a critical challenge to meet customer expectations for a greater than 300 mile driving range within the weight, volume, safety and cost constraints of a marketable vehicle. Through the FreedomCAR & Fuel Partnership, between DOE and leading automotive and energy industries, technical targets were set in the U.S. for commercially viable vehicular hydrogen storage systems. Examples of some of these system-level targets (by 2010) are: gravimetric capacity of 6 wt.% (= 2.0 kWh/kg), volumetric capacity of 1.5 kWh/L (= 0.045 kg hydrogen/L) and a cost of \$4/kWh.[4] Figure 3 shows various material capacities and the total system capacities for a limited number of systems built, illustrating that both fundamental properties and system engineering issues need to be addressed to meet the targets.

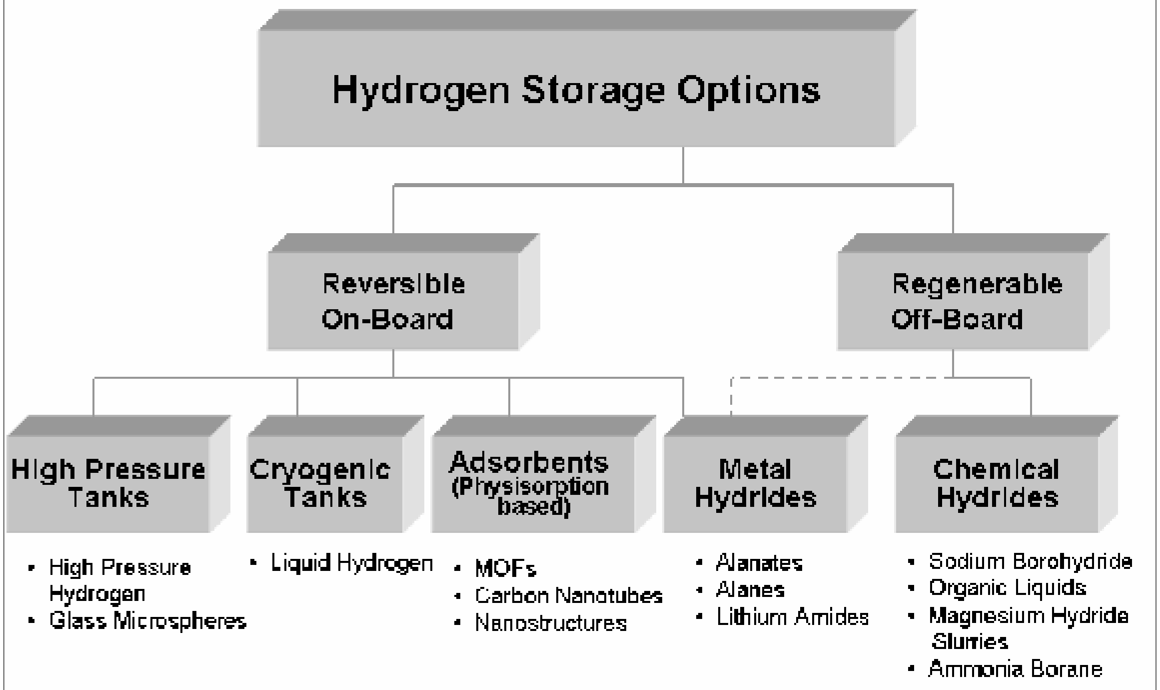
Figure 3: Examples of materials and hydrogen storage capacities.



Source: G. Thomas, S. Satyapal, DOE Hydrogen Program Annual Program Review, May 2005

Current hydrogen storage technologies include: high-pressure tanks, cryogenic storage, metal hydrides, chemical hydrides, and high surface area sorbents such as nanostructured carbon-based materials. High pressure and cryogenic tanks, high surface area sorbents and many metal hydrides fall in the category of “reversible” on-board hydrogen storage, since “refueling” with hydrogen can take place directly on-board the vehicle. For chemical hydrogen storage and some high-temperature metal hydrides, hydrogen regeneration is not possible on-board the vehicle and thus these systems must be regenerated off-board (see Figure 4).

Figure 4: Options for vehicular hydrogen storage.



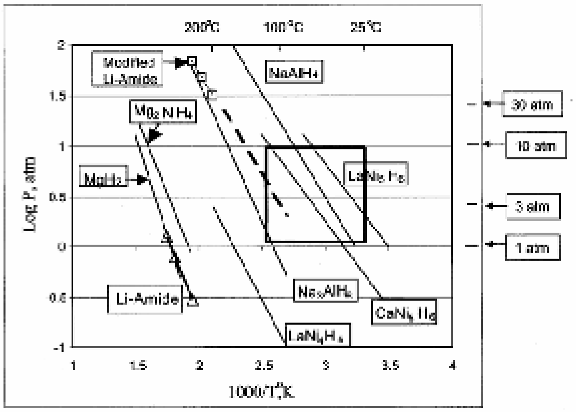
Source: S. Satyapal et al. DOE Hydrogen Program

High pressure and cryogenic tanks meet some of the near term DOE targets and are already in use in prototype vehicles. The state-of-the-art in high-pressure tanks is 10,000 psi (or about 700 atm), as developed by Quantum and others.[5] Key challenges are volumetric capacity, issues with high pressure and cost. Refueling times, compression energy penalties and heat management requirements during compression also need to be considered as the mass and pressure of on-board hydrogen are increased to meet a driving or range of over 300 miles.

Cryogenic or liquid hydrogen (LH_2) tanks can, in principle, store more hydrogen in a given volume than compressed tanks, since the volumetric capacity of liquid hydrogen is about 0.07 kg/L (compared to roughly 0.04 kg/L even at 700 atm). Key issues with LH_2 tanks are hydrogen boil-off, the energy required for hydrogen liquefaction (typically 35% of the lower heating value of hydrogen), insulation requirements and cost.

Metal hydrides function by ***dissociatively*** adsorbing (or absorbing) hydrogen into their metal lattice, thereby allowing for higher energy densities than liquid hydrogen. Figure 5 shows that the optimum “operating P-T window” for PEM fuel cell vehicular applications is in the range of 1-10 atm and 25-120 ^{o}C.[6] A simple metal hydride such as $LaNi_5H_6$, that incorporates hydrogen into its crystal structure, can function in this range, but its gravimetric capacity is too low and its cost is too high for vehicular hydrogen storage applications. However, at the present time, $LaNi_5H_6$ is one of the few metal hydrides commercially available.

Figure 5: Equilibrium pressure-temperature curves for various metal hydride materials. The "P-T window" for PEM fuel cell vehicular applications is indicated by the highlighted box.



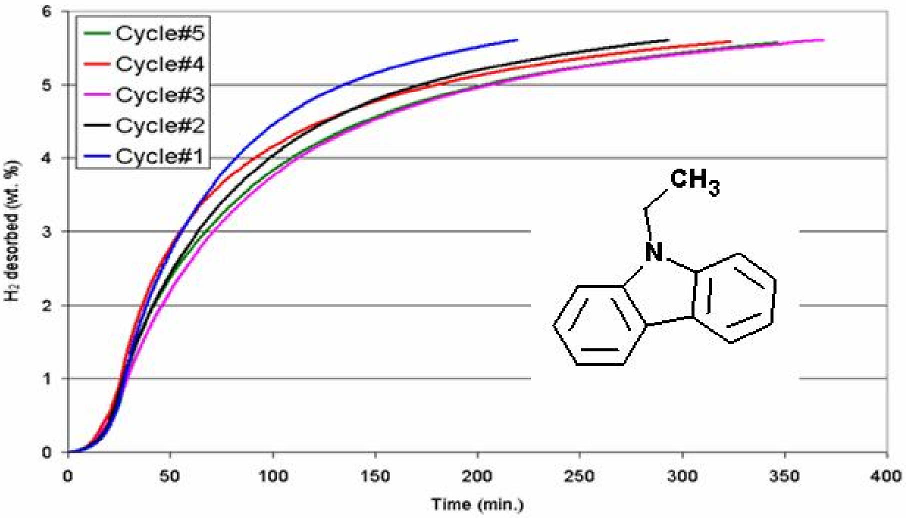
Source: Wang et al., U.S. DOE Hydrogen Program Annual Progress Report (2004)

Metal hydrides have been studied for decades and Sandrock has compiled a database of metal hydride properties to help guide the development of improved materials.[7] Because most metals in traditional metal hydrides are heavy, the gravimetric capacity of such systems is unacceptable. However, in 1997, a breakthrough by Bogdanovic and coworkers[8] identified that titanium species could act as a catalyst in reversibly storing hydrogen in ‘complex’ metal hydrides (e.g. $NaAlH_4$). Such systems, with light elements (in this case Na and Al), can achieve much higher gravimetric capacities without compromising volumetric capacities. Although $NaAlH_4$ will not meet the DOE targets, this recent discovery spurred a range of activities around the world on complex metal hydrides. New systems, such as $Li_2NH + H_2 = LiNH_2 + LiH$ have recently been discovered.[9] Substitution by light metals like Mg is an active area of research to tune the operating temperatures and pressures and improve kinetics.

One of the main issues with metal hydrides is that the heat of reaction is typically 30 to 40 kJ/mol. This means that to meet refueling time targets (~ 3 min. for 5 kg H_2), close to 0.5 MW needs to be rejected while charging typical metal hydride systems. Thus, certain metal hydrides such as AlH_3 appear to be more suitable for off-board regeneration. Significant engineering challenges lie ahead, such as thermal management and reactor design optimization to meet weight, volume and cost targets. Examples of other issues with metal hydrides include low gravimetric capacity and slow uptake and release kinetics.

Chemical hydrogen storage refers to chemical reactions, such as the hydrolysis of sodium borohydride ($NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$), demonstrated by Millennium Cell[10] and others; or the dehydrogenation of organic compounds such as methylcyclohexane or decalin, studied for decades, particularly in Japan. In 2004, a new type of liquid phase hydrogen storage material was demonstrated.[11] This liquid, based on N-ethylcarbazole, can attain over 5.5 wt.% and 0.05 kg/L of hydrogen storage, with several dehydrogenation/hydrogenation cycles of N-ethylcarbazole recently shown (Figure 6).[11]

Figure 6: Several cycles demonstrated for the dehydrogenation of N-ethylcarbazole



Source: A. Cooper et al, U.S. DOE Hydrogen Program Annual Progress Report, p. 210 (2004).

Another exciting recent discovery is that by combining ammonia borane (NH_3BH_3) in a mesoporous scaffold structure, the hydrogen release reaction can be tailored in terms of byproduct release and temperature, with roughly 6 wt.% hydrogen storage demonstrated.[12] The most significant issue with chemical storage is that the covalent bonds broken to release hydrogen, cannot be easily replaced on-board a vehicle. The 'spent' fuel must be reclaimed from the car and regenerated off-board at a central plant or at the fueling station. The energy requirements and total life cycle analysis, including environmental impact, are issues under study.

Finally, high-surface area sorbents, such as nanostructured carbon materials or metal organic frameworks (MOFs) and perhaps clathrates can be used to physically adsorb hydrogen[13] There is still some controversy as to how much hydrogen some of these materials can store. Although there is potential for high gravimetric capacity, the fact that these are high surface area materials (e.g. ~ 4,000 m^2/g) means that the volumetric capacity for hydrogen storage will likely be low. However, one advantage is that the binding of hydrogen is weak so the release of hydrogen should require low temperatures and heat rejection during refueling may not be as much of an issue. Engineering issues like reactor design as well as tuning fundamental material properties must be addressed.

With improved theoretical modeling, combinatorial/high throughput screening techniques and understanding at the nanoscale, future work worldwide aims at "tailoring" materials to meet the targets for hydrogen storage. In addition to U.S. activities, the DOE is supporting the mission of the International Partnership for the Hydrogen Economy (IPHE), formed in November, 2003, to help accelerate global activities towards a hydrogen economy. Along with other countries, DOE co-organized IPHE conferences on hydrogen storage, hydrogen production and other research areas to effectively identify, evaluate and coordinate multinational research, development and demonstration programs related to hydrogen and fuel cell techologies.[14]

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14. See details under www.iphe.net.