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Materials Go/No-Go Recommendation Document

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EXECUTIVE SUMMARY

The DOE Hydrogen Sorption Center of Excellence (the Center) was formed in FY2005[2] to research and develop hydrogen storage materials mainly for the application of light-duty vehicles. However, sorbent materials may find use in other hydrogen storage applications such as stationary power generation, portable power, back-up power, and niche, early-market vehicles. For transportation applications, sorbent materials offer tremendous advantages. These include fast hydrogen fill-up and discharge rates, nominal thermal management requirements during refueling, ease of engineering, ability to provide required pressures, and favorable system energy efficiencies (which affect costs). In addition, use of sorbent materials may significantly reduce the volume and weight of storage systems compared to 350- and 700-bar high-pressure tanks.

When the Center was established, the main issue for sorbent materials revolved around the relatively low binding energies with hydrogen, and thus the need to use cryogenic temperatures (e.g., 77K, -193°C, liquid nitrogen temperature at 1 bar). The Center's critical goals included the original FY2010[3] hydrogen storage system targets: net available capacity of 45 g/L and 6 wt%, and system cost of \$133/kg H_2. From the outset during proposal formulation, Center partners were chosen to provide the specific expertise and capabilities necessary to develop sorbent materials that could be used to meet the DOE hydrogen storage system targets. The virtual Center includes development activities at more than 20 different institutions throughout the United States, and direct collaborations with institutions around the world.

This document provides: an overview of the work performed by the DOE-funded Center; specific recommendations to DOE for materials development efforts that should, and should not, be continued; and a list of key research priorities remaining to be resolved. The Center is led by the National Renewable Energy Laboratory (NREL), with partners at other U.S. national laboratories and universities, and at Air Products and Chemicals, Inc (our corporate partner). To ensure that the development activities were performed as efficiently as possible, the Center formed four complementary, focused research clusters based on one of four different sorption-based hydrogen storage mechanisms. By focusing on specific mechanisms, the Center leveraged appropriate materials and synthetic capabilities and expertise of the different partners to create: optimized pore size and high specific surface-area materials; heterogeneous materials with enhanced dihydrogen binding; materials with coordinated metal centers; and spillover or chemisorbed hydrogen materials.

Since the Center's inception, substantial progress has been made in developing sorption hydrogen storage materials. This progress includes down-selecting of numerous specific materials, but more importantly, entire material classes. Thus, the Center recommends that no further development efforts be performed on these materials/classes.

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[2] Awarded from the FY2003 EERE Hydrogen Storage Grand Challenge Solicitation, Funding Opportunity Announcement DE-PS36-03GO93013, September 2003.

[3] Note that in FY2009, DOE revised the hydrogen storage system targets for light-duty vehicles (see Appendix I). Thus, all DOE targets discussed in the remainder of this document will reference the revised DOE hydrogen storage system targets.

In addition, the Center has identified clear development paths for constructing sorbent materials that have the potential to meet DOE's revised 2015 and Ultimate Full-Fleet targets for light-duty vehicles (see Table ES-1). The Center recommends that development efforts for specific materials/classes be continued where there are viable routes for synthesizing sorbents that can be used to meet DOE's targets.

For example, after substantial efforts, it has become clear that only certain materials will meet the DOE 2015 targets. Specifically, among the materials that rely only on relatively weak physisorption where cryogenic (e.g., <100K) temperatures will be required, only those materials with very high specific-surface areas (>3,000 m^2/g) and optimized pore sizes in the range of ~0.7 to 1.2 nm have the potential to achieve at least the 50 g/L (bulk density) and 7 wt% excess material capacities that will be needed to meet the DOE 2015 targets. Thus, the Center recommends that physisorption-based materials that do not have these attributes be down-selected and not pursued in future development efforts. As demonstrated by this example, by investigating a specific class of materials, the Center is able to select materials based on their specific characteristics for a given hydrogen storage mechanism, thus enabling the elimination of dozens of materials with limited or no effort. However, the Center recommends that physisorption materials with the requisite attributes be investigated further for hydrogen storage systems.

Improving sorbent properties for hydrogen storage beyond that attained with weak physisorption materials will require substantial increases in binding energy that improves capacities at higher temperatures, towards ambient. In the select few cases where binding energies can be increased, the stringent specific surface area and pore size distribution criteria applied to weak physisorbents will be different, even though material optimization will still be important. Since its inception, the Center has investigated several methodologies and material systems to increase the intrinsic binding energy of dihydrogen molecules or H_2. Based on these efforts, numerous materials have been down-selected, and a select few materials/material classes have been identified with the potential to be used to meet DOE system targets. For example, almost all lightweight elements (e.g., Li, N, O, and F) substituted in a carbon matrix do not significantly increase dihydrogen binding. Only beryllium (Be) and boron (B) will substantially increase dihydrogen binding energy when substituted in carbon in the appropriate coordination.

Similarly, metal centers in metal-organic frameworks (MOFs) or equivalent materials bind dihydrogen in the 10–15 kJ/mol range, which is sufficient for near-ambient temperature (150 to 220K) storage. The main issue with all of these types of materials is the need for a high number of these binding sites to be uniformly dispersed and accessible in order to have the enhanced dihydrogen adsorption properties available for a significant fraction of the material storage capacity. Thus, the Center recommends that future efforts should only develop these types of materials with demonstrated higher binding energy sites, and the focus should be on creating materials with the appropriate chemical/electronic structures, sufficient composition, and specific-surface areas needed for these materials to meet, at a minimum, DOE's 2015 targets.

In addition to higher dihydrogen binding, the ability to adsorb multiple-dihydrogens on designed sites will probably be required to meet DOE's Ultimate targets. Several inexpensive material systems and synthetic pathways (e.g., Calcium [Ca] integrated with graphene and other framework materials) have been identified that may be used to meet DOE's Ultimate targets. Such systems and pathways, however, will require substantial applied development efforts to achieve the breakthroughs necessary to form the novel structures that have enhanced dihydrogen binding for the entire capacity range. Even so, the basic principles of forming multiple-dihydrogen bonding on these sites with 15 to 40 kJ/mol binding energies have been demonstrated experimentally. Because these sites have higher binding energies, development efforts will most likely require airless and dry processing, and material stability and contamination issues will have to be fully addressed. However, the potential to store H_2 at ambient temperature and nominal pressures between 10 and 50 bar with theoretical densities greater than twice that of liquid hydrogen make these development efforts highly promising.

The Center has also investigated methodologies to store dissociated hydrogen molecules (e.g., hydrogen atoms). Unlike the work discussed previously to increase binding for dihydrogen, the key issue was actually developing ways to store dissociated hydrogen with binding energies substantially lower than what is typically observed for hydride formation. Among the more promising material classes, the Center demonstrated that catalyzed hydrogen molecule dissociation followed by "spillover" onto lightweight receptor support materials enabled ambient temperature storage with binding energies in the range of 10 to 25 kJ/mol. Although the phenomenon of spillover has been known for many decades, Center partners demonstrated that this material class could be used to store substantial (> 30 g/L and 4 wt%) amounts of hydrogen at near ambient temperature and at nominal pressure. The Center demonstrated spillover both experimentally and by thermodynamic principles as a process for ambient temperature, reversible hydrogen storage. However, the materials have tended to be very sensitive to synthetic processing conditions, resulting in substantial irreproducibilities.

Furthermore, the intrinsic nature of the spillover storage mechanisms makes hydrogen refill rates, material stability/durability, and intrinsic material costs challenging issues that must be adequately resolved. Nonetheless, once these issues are addressed, initial analyses indicate that storage systems with more than 75% of the material capacities could be achieved. Because the potential spillover material storage limits are ~80 g/L and ~8 wt%, and ultimately fill rates, materials costs, and durability are tractable issues, it should be possible to construct spillover-material based hydrogen storage systems that meet DOE's 2015 targets.

As mentioned previously, the Center's focused development efforts identified a substantial number of materials/material classes that should not be investigated further based on a number of considerations, including a detailed selection criteria developed specifically for sorption materials. Based on the nature of the Center's development of hydrogen storage mechanisms (rather than specific materials), the exact number of materials down-selected is difficult to identify. Through these efforts, the Center was able to quickly identify the few selected material classes and their required properties and stress them for present and future development. For example, regardless of the specific elements used, a pure physisorption material needs to have more than 3,000 m^2/g specific surface area. This requirement alone eliminates hundreds of elements that are just too heavy to be able to meet this requirement if only a physisorption-based hydrogen storage mechanism is used. Furthermore, through calculations and a limited number of specific experimental investigations, it became clear that only correctly coordinated boron-substituted in graphitic carbon is a viable route to improved hydrogen storage for substituted carbon materials, and thus the use of other lightweight elements should not be investigated. In terms of carbon materials, this eliminated the need to perform experimental investigations on hundreds of potential element/process combinations for this material class. Similarly, the Center has focused on identifying in Table 1 the material classes and their corresponding properties that should be investigated in present and future development efforts.

With currently demonstrated bulk material packing densities and hydrogen storage properties, sorbent materials will substantially decrease the volume and pressure now used for high-pressure (350 to 700 bar) compressed tanks, and thus could significantly reduce overall system costs. Future selection criteria should focus further on identifying materials that can be used to meet DOE Ultimate targets. In addition to the specific performance issues for each material class discussed previously, developing material synthetic processes and pathways that are scalable, inexpensive, and reproducible—and produce materials that can meet the DOE system cost targets—remains a challenge that must be aggressively pursued in all cases.

Again, in general, the main issues for sorbents are the relatively low dihydrogen binding energies, which directly affect storage temperature. This adversely impacts system costs, volumetric capacity, and available gravimetric capacity. Thus, the main focus of future applied development efforts must be enhancing and/or optimizing hydrogen binding energies. This focus will require balancing improved hydrogen storage system costs and capacities with perhaps adversely affected material contamination sensitivity, durability, refill rates, and material costs issues.

Table ES-1. Summary of Sorbent Material Classes Recommendations for Further Applied Research and Development for On-Vehicle Refuelable Hydrogen Storage Systems. All material results (unless specifically stated) are measured reversible excess surface capacities and based on either a measured or reasonably assumed bulk density.

Material Class/ Mechanism	Example Materials	Material Results to Date (volumetric and wt%)	Recommended Development Path
Physisorbents	Greater than 3000 m^2/g with pore sizes between 0.7 and 1.2 nm	>50 g/L, >7 wt% excess capacity at 77K and ~50 bar	Only materials that have the potential to exceed those already demonstrated should be investigated further.
Substituted/ Heterogeneous materials	Predominately BC_x materials; exposed metals in metal organic frameworks (MOFs) and covalent organic frameworks (COFs)	~30 g/L, ~4 wt% excess capacity at 77 K and 50 bar. >40 g/L, >6 wt% at 195K possible	Only efforts that focus on viable routes to incorporating properly coordinated elements in high surface area structures should be pursued.
Multiple Dihydrogen Sorption sites	Coordinated but unsaturated metal centers like Ca-graphene, Ca-COF, Metallocarbohedrenes, Sc or Ti, B-doped fullerenes	Theoretical potential to have >100 g/L, >10 wt% at ~298K, ~10 bar	Substantial synthetic development is required to catch up with theoretical predictions. Only the most synthetically viable and stable materials should be developed initially.
Spillover	Catalyst (Pt, Ru, Ni) integrated with porous carbon structures and/or MOFs	>30 g/L, >4 wt% excess capacity at 298K, 100 bar	Efforts should focus on improving reproducibility, hydrogen uptake rates (e.g. hydrogen diffusion on the receptor materials), and catalyst integration.

INTRODUCTION

Significant improvements over currently available hydrogen storage technologies are required if hydrogen-fueled vehicles are to be broadly competitive across the full light-duty vehicle fleet. The hydrogen storage targets and technology barriers presented in DOE's Multi-Year Research, Development and Demonstration (RD&D) Plan[1] (the FCT Program Plan) for the Fuel Cell Technologies (FCT) Program state the critical application needs and goals. At this time, no known storage system can simultaneously meet all the capacity, operability, transient performance, cost, safety, and efficiency requirements for on-board, light-duty vehicular hydrogen storage systems. Similarly, improvements in hydrogen storage systems are needed for stationary power, portable power, and early market applications.

Nanostructured high-surface-area sorbent materials containing carbon, boron, lightweight metals, oxygen, and other elements show promise for breakthrough performance in hydrogen storage. However, the limits of performance remain unclear based on a lack of understanding of both the factors governing their performance and the design principles for synthesizing the materials and constructing the required systems.

The DOE-funded Hydrogen Sorption Center of Excellence (HSCoE) is developing on-board reversible sorbent materials.[2] A guiding principle in developing the required materials is that a continuum of energies exists for hydrogen bound to substrates and molecules (see Figure 1).

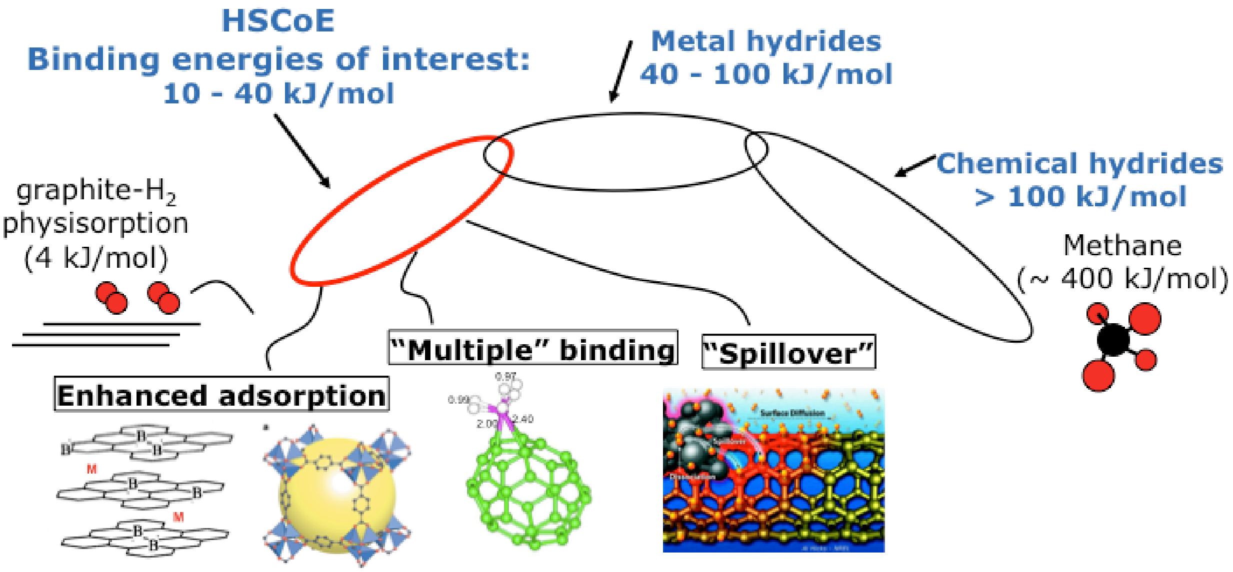

Figure 1. Depiction of the range of binding energies and several of the nanostructured materials of interest to the HSCoE.

On the weak side of the continuum is non-dissociative physisorption, which is due purely to van der Waals (vdW) forces (~4 kJ/mol). On the opposite end is the full C-H chemical bond in methane with an energy of ~400 kJ/mol. Between these two limits, with nominal binding energies between 10 and 40 kJ/mol, are:

- Physisorption (related to key parameters affecting vdW forces)
- Enhanced dihydrogen binding via the formation of complexes that exhibit electron transfer interactions from both the hydrogen and adsorbate
- Weak, reversible, chemical bonding of mono-atomic hydrogen to lightweight receptor materials (via a "spillover" mechanism). (See Figure 2 and Figure 3)

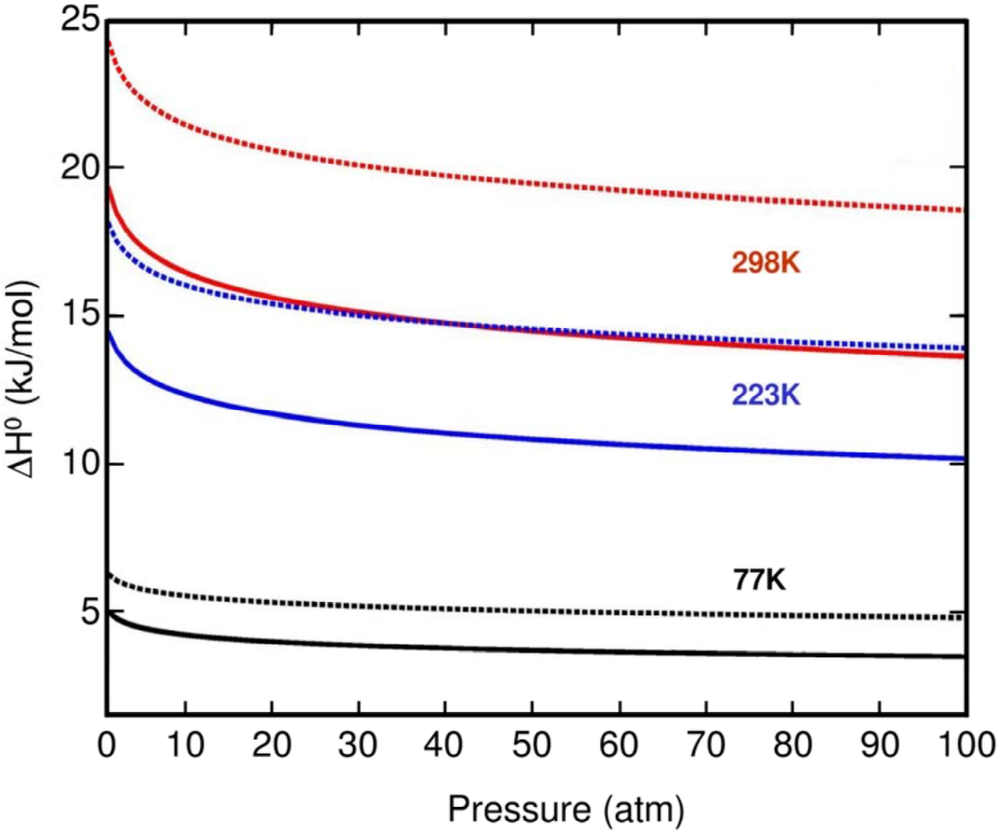

Figure 2. The optimal enthalpy for hydrogen storage depends on the pressure, temperature, and sorption interaction (i.e., entropy: e.g. dotted lines $\Delta S=-10R$, and solid lines $\Delta S=-8R$). For example, as shown in this plot (recreated from S.K. Bhatia, & A.L. Myers, Langmuir, 2006, 22, 1688) if materials with enthalpies between ~13 and 25 kJ/mol can be made, then ambient temperature hydrogen storage is possible with pressures between ambient and 100 bar. For lower binding energies, lower storage temperatures will be required.

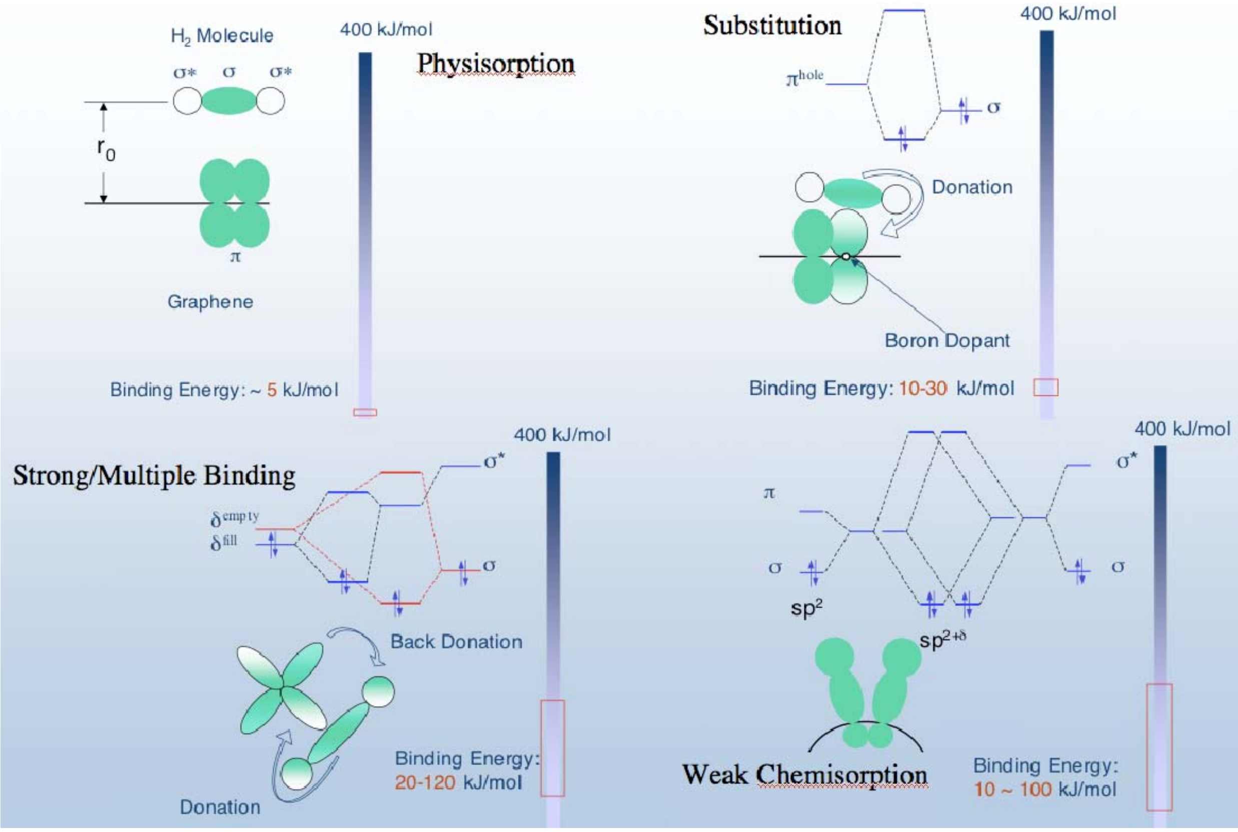

Figure 3. Illustrations of the four types of sorbent binding mechanisms investigated by the HSCoE.

The DOE goals may be met with sorbent materials if: (i) the energy for hydrogen adsorption can be designed to be in an nominal optimal range (~10–40 kJ/mol: depending upon the entropy, desired operating pressure, and temperature; e.g., see Figure 2)[3]; and (ii) efficient volumetric arrangement (see Figure 4) of a sufficient number of suitable binding sites can be achieved with a low-weight material.

These goals are difficult to reach in conventional high-surface-area adsorbents like most activated carbon and metal-organic frameworks (MOFs) that are limited by low-physisorption binding energies, heterogeneity of the adsorbent surfaces and adsorption sites, and excessive macroporosity and poor volumetric packing.

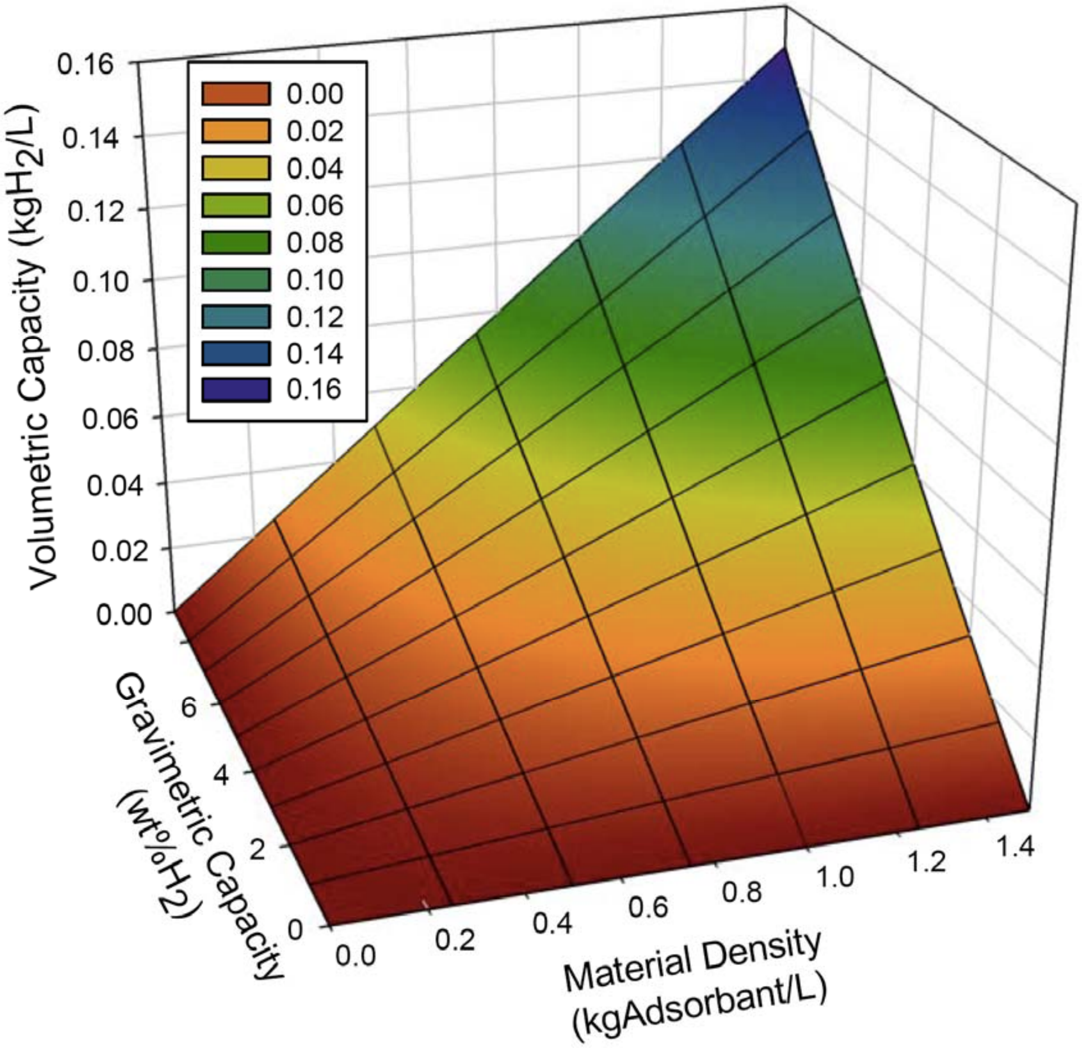

Figure 4. Graph from Argonne National Laboratory showing the dependence of volumetric density on gravimetric and bulk density for sorption materials. The plot indicates that to have the potential to meet DOE 2015 volumetric target (0.04 kgH_2/L, yellow band on chart), bulk material densities between 0.7 and 1 g/L will be required for sorbent materials with 6 to 7 wt% gravimetric capacities.

The HSCoE addresses the following technical barriers as defined by the FCT Program Plan.

General:
- A. Weight and Volume
- B. Cost
- C. Efficiency
- D. Durability/Operability
- E. Charging/Discharging Rates
- J. Thermal Management
- M. Reproducibility of Performance.

Reversible Materials-Based Storage System:
- P. Lack of Understanding of Hydrogen Physi- and Chemisorption.

As a general rule, sorbent materials have relatively low (e.g., less than 25 kJ/mol) dihydrogen enthalpies of adsorption (i.e., binding energies) where cryogenic temperatures and moderate pressures (i.e., 30 to 50 bar) are required. Therefore, thermal management (e.g., heat dissipation and rates during filling), delivered pressure, delivery rates, and refueling rates are not controlling issues. Thus, sorbent materials have the potential to be used to meet the vast majority of DOE hydrogen storage targets (see Appendix I), if cost and volumetric and gravimetric net available capacity issues can be adequately addressed.

The Center was charged with developing materials that would meet the former DOE FY2010 hydrogen storage system targets. In addition, the Center is investigating viable routes that may be used to meet DOE's Ultimate storage targets (including net available capacity of 70 g H/L system and 7.5 percent by weight system) and is also identifying potential early market applications that will benefit from sorbent materials. As discussed later in this document, sorbents may be used to enhance hydrogen storage capacities and other properties, with the caveat that the hydrogen storage system be designed to take full advantage of the material's capabilities as well as the specific performance needs for the application.

APPROACH AND RESEARCH ACTIVITIES

From the outset, in order for the Center to select among a relatively large number of potential sorbent materials, researchers placed more emphasis on identifying and developing mechanisms that lead to higher volumetric capacity and more favorable operating conditions rather than on specific, individual materials. This enabled efficient and rapid progress by focusing resources on identifying and optimizing specific properties and critically evaluating hydrogen storage material classes. This is why the Center was organized into four focused efforts, each of which is designed to efficiently address a specific set of issues associated with a specific hydrogen sorption mechanism (see Figure 3).

These focused research efforts are complementary, with lessons learned and materials developed in one effort often being applicable to another. For example, for physisorption the main issues are optimized pore sizes and very high specific-surface areas. Similar issues arise for other sorbent material classes, and thus lessons learned for physisorption materials are directly applied to other Center development activities. The key advantage of the mechanism-focused approach is that selection criteria can be identified for each material class based on a limited amount of experimental and calculation work. This enables identification of the most promising materials and thus elimination of the vast majority that will not be able to meet DOE goals. This approach substantially reduced the Center's overall work while prioritizing development efforts.

Engineered Nanospaces

In almost all hydrogen sorption materials with the potential to meet DOE targets, almost every atom will need to be accessible and lightweight. Thus, materials with high specific-surface area will be required. In addition, to meet volumetric targets, the sorption sites will need to be arranged to minimize the amount of open space (see Figure 4). This suggests that porous structures should be optimized to allow hydrogen egress in and out, but the hydrogen should be in contact with some kind of sorption site. Thus, the materials should have minimal macroporosity (pores greater than ~50 nm diameter) or mesoporosity (pores between 2 and 50 nm diameter), and, depending on the specific sorption mechanism, the materials should have pore sizes between 0.7 and ~1.2 nm.[4]

In general, to allow sorption on all surfaces of a pore, the distance between the surfaces should be at least twice that of the kinetic diameter of dihydrogen (2.89 Å). In addition, multilayer adsorption effects, H-H repulsion, and other space-optimization considerations suggest that the pore sizes may need to be ~1.2 nm. Calculations[5] suggest that some enhanced binding may occur if the pore structure is on the order of 0.7 to 1.2 nm.

The "engineering nanospaces" effort designs and synthesizes lightweight, high-surface-area, optimal-pore-size materials. Results from this effort are applicable to almost all sorption materials. The effort focuses on how to stabilize large quantities of hydrogen directly by physisorption. Researchers investigated methods to optimize sorption properties and increase dipole-dipole interaction (i.e., van der Waals) binding energies via appropriate geometrical pore structures by arraying high-surface-area structures (e.g., scaffolds). This was done by forming high-surface areas directly during synthesis, or by creating porosity in dense structures. The key to these efforts included optimizing sorption sites and optimizing space to enhance binding without loss of volumetric capacity.

Specific activities for the engineered nanospace effort involved performing theoretical modeling[6] and experiments to determine potential mechanisms for higher storage capacities and to provide guidance for materials development. In addition, these efforts developed and/or improved scalable and reproducible synthesis methods of nanoporous materials. Several different synthetic pathways were investigated, including templated carbon/boron,[7] polymers,[8] metal-organic frameworks (MOFs),[9] aerogels,[10] single-wall nanohorns (SWNHs),[11] and scaffolded single-wall nanotubes (SWNTs).[12] Synthesized materials were characterized to determine their hydrogen storage properties and, when appropriate, to identify unique sorption mechanisms. In some cases, this involved optimizing materials for other sorption processes beyond physisorption.

Substitution

The Center formed the “substitution” development effort to focus on increasing the intrinsic binding energy of storage materials, and thus their storage capacity at higher temperatures. In general, increasing the intrinsic heats of dihydrogen adsorption is difficult, and the Center identified only a few potential pathways.

For most pure materials, or materials with electronic configurations that induce no significant adsorption, the primary adsorption mechanism is physisorption, which typically has enthalpies below 5 kJ/mol for interaction with a single surface. Enhanced physisorption binding energies (i.e., 5 to 10 kJ/mol) are often observed with high specific-surface-area materials. This is primarily a result of interaction with multiple adsorption sites that then limits the total volumetric capacity. In general, physisorbed dihydrogen on single surfaces has relatively low binding energies, and capacity requires operation at lower cryogenic temperatures and higher intermediate pressures. Typically, increased binding energies, lower temperature, and higher pressure are required to overcome the intrinsic repelling force between dihydrogens to yield higher storage capacities on the sorbent surface at a specific temperature and/or pressure.

To go beyond pure physisorption requires enhanced electron interactions between the sorption material and dihydrogen. In general, heterogeneous elemental structures or surface functionalization can induce enhanced electron interactions. However, after relatively comprehensive investigations, very few material systems were identified with the potential to enhance dihydrogen binding.[13,14]

In general, the exchange of a different atom species in an elementally homogeneous lattice induces an electronic perturbation that may enhance dihydrogen binding. For example, the empty p orbitals on boron (B)-substituted [for] carbon induces electron donation from H_2 to provide a reasonable enhancement in binding (i.e., 10 to 15 kJ/mol) and capacities. However, it was determined that only boron substituted with a sp2 or similar coordination produced the enhanced dihydrogen binding. Other B-C or C-C coordination,[13] the presence of other elements such as nitrogen (N) in the lattice, or other (except for Be) substituted lightweight elements (e.g., Li, N, O, F, Na) in carbon lattices do not enhance dihydrogen binding. Furthermore, in addition to needing to be in the correct coordination state, calculations predict that enhanced binding may occur only if the B remains both electronically and structurally “frustrated” such that the B atoms are out of the plane of the carbon matrix, thus potentially expanding the lattice.

In addition to direct substitution, initial efforts identified that materials with intercalated and/or absorbed ions may enhance dihydrogen binding. For example, anions with high charge/volume ratio (e.g., fluoride)[15] can donate electron density to s*-orbitals of dihydrogen. Similarly, other intercalated species (e.g., alkali and alkaline metals, anions) may induce charge interactions to improve hydrogen adsorption enthalpies.[16] In some cases, it is theorized that molecular dopants complexed with nanostructures can generate sufficient electric fields to enhance H_2 storage. Finally, some of these substituted or functionalized materials may improve sorption of other elements/molecules for different hydrogen mechanisms associated with back-donation[17,18] and/or spillover.

Based on initial predictions and experimental results, the Center partners developed scalable synthesis methods to form substituted and intercalated materials that demonstrate enhanced dihydrogen storage properties. Boron substitution was achieved by either starting with chemical compounds with high concentrations of B and forming high specific-surface-area materials, forming boron-substituted activated and graphitic carbons (e.g., BC_3), or substituting boron for carbon atoms in preformed materials. In addition, the Center partners developed anion-intercalated graphitic and other intercalated/functionalized materials with enhanced hydrogen storage properties.

Strong/Multiple Dihydrogen Binding

The final set of methods to improve dihydrogen binding is characterized by forward- and back-electron donation from the sorption material that induces a significant molecular bond stretching between the hydrogen atoms. Typically, this is achieved when the sorption sites are electronically and coordinately unsaturated. These types of sorption sites can bind a dihydrogen molecule more strongly (10 to 200 kJ/mol), but more importantly, can also bind multiple dihydrogen molecules to a single sorption site.[17,18] This method enables a substantial increase in volumetric densities if these sites can be densely arrayed. As stated previously, the Center focused on materials with an optimal range between ~10 and 40 kJ/mol to enable reversible near-ambient temperature and pressure hydrogen storage.

In general, the specific partially coordinated atom sites needed for strong and multiple dihydrogen binding can be attained in a number of ways. These include stabilizing single metal atoms on high-surface materials (e.g.,[19] Li/THF co-intercalation compounds or Ca on graphene lattices[18,13]) or in crystalline structures such as MOFs or metallocarbohedrenes (Met-Cars). Thus, two of the Center's tasks focused on methods to develop hydrogen interactions with coordinated but unsaturated metal centers and to design and synthesize these types of sorbents. This involved using calculations to identify and guide tractable reactions that balance reactivity with stability and capacity.

The Center investigated integrating appropriate metal centers with binding energies to 40 kJ/mol, with materials such as aerogels, carbon nanohorns, carbon nanotube scaffolds, polycyclic aromatic hydrocarbons, graphene, and MOFs. These efforts included utilizing the higher Coulomb repulsion between alkaline metals to facilitate metal/substrate binding and/or enhancing charge transfer to stabilize the metal/substrate interaction with substitutional integration of different atoms in the support materials. One key issue with the use of open metal centers is the fact that their higher reactivity makes them susceptible to an array of issues. Such issues include agglomeration of the metals and reaction with contaminants, both of which eliminate the hydrogen storage enhancement, which makes durability and synthetic processing more challenging.

Weak Chemisorption/Spillover

The Center also actively investigated methods to efficiently store dissociated hydrogen. In general, dissociated or atomic hydrogen forms strong bonds with other materials (e.g., metal hydrides or chemical hydrides) that require high temperatures (e.g., more than 500K) or catalysts to break bonds. However, it is possible for hydrogen atoms to be adsorbed to surfaces in such a way that the bonding is weaker[20] and conducive to nominal reversible storage capacities at near-ambient temperature and under moderate pressure.[21] From a practical standpoint, a catalyst is typically needed to dissociate the dihydrogen gas; this is a known technology in the chemical process industry. However, because most common industrial catalysts (e.g., Pt, Pd, Ni) are relatively heavy and expensive (e.g., platinum group metals), reaching the DOE targets will require catalysts that are appropriately integrated with a lightweight and compact material such as carbon or boron so that the dissociated hydrogen can "spillover" and be stably and reversibly stored, primarily on the lightweight receptor material.

Maximizing performance and costs via spillover involves focused development efforts to optimize catalyst performance and dispersion and to integrate with receptor material properties and hydrogen surface transport/diffusion mechanisms. This involves performing systematic experiments to quantify spillover processes, determining the causes for material degradation and irreproducibility, and developing scalable and reproducible synthesis methods of spillover materials. For example, due to the mechanisms associated with hydrogen diffusion on the receptor material surfaces, low refueling rates and small materials surface properties are major challenges that must be resolved. To address these issues, the Center leveraged modeling[22] to identify and to construct new spillover materials with improved properties and to chemically modify known spillover materials to improve spillover performance.

SELECTION CRITERIA

The Center is working on material classes that could be used to meet DOE hydrogen storage system targets for light-duty vehicles. The primary classes include:

- Cryogenic Sorbents (nominally 77K storage)
- Substituted Materials
- Strong Binding/Multiple H_2 Metal Centers
- Weak Chemisorption/Spillover.

As stated in the Introduction, the adsorption binding energy significantly affects the hydrogen storage system cost, net available volumetric and gravimetric capacities, and operating conditions. Thus, as the binding energies increase, the gravimetric capacity increases at higher temperatures and lower pressures.

This critical point means that the selection criteria used for each material class must be adjusted, because, on balance, meeting the DOE targets becomes easier with higher dihydrogen binding energies. Thus, within each material class, the Center developed a set of selection criteria for the most critical issues, and recommended down-selected materials based on these selection criteria or other issues identified by the Center (see Appendix II). The selection criteria allow materials to be developed that do not yet meet some of DOE's hydrogen storage targets. In addition, the selection criteria do not replace the DOE hydrogen storage targets. In most cases, the materials being developed must have a clear potential to either meet the DOE hydrogen storage targets or provide useful insights into specific properties of interest to help make materials that can meet the DOE targets.

Cryogenic Sorbents (nominally 77K storage)

1. The material's volumetric storage capacity should be approximately 0.03 kg H_2/L, with a material excess gravimetric storage capacity of approximately 0.03 kg H_2/kg, in a temperature range of 77–200K, and a nominal pressure range of 30–100 bar—with a *clear potential* for further improvement.
2. The high-pressure adsorption isotherm should be >80% reversible, i.e., at least 80% of the stored hydrogen is desorbed or discharged between 77 and 200K, at nominal fuel cell operating pressures (i.e., ~100 to 4 bar).
3. The desorption or discharge rate at 77–200K should be more than 0.4 g/s for a material reservoir containing 5 kg H_2.
4. The charge rate should have 90% of the H_2 adsorbed by the material at 77–200K within 3.3 minutes for storage of a total of 5 kg H_2.
5. Full-scale commercial manufacturing material cost projections should be less than half the system cost targets.

Substituted Materials

1. The initial binding energy should be in the range of 10–25 kJ/mol, and the material should operate within a temperature range of 77–353K and pressure range of 30–100 bar. There should be a *clear potential* for volumetric and gravimetric capacity optimization in excess of the DOE 2015 targets for the given operating range.
2. The high-pressure adsorption isotherm should be >80% reversible, i.e., at least 80% of the stored hydrogen is desorbed or discharged between 77 and 353K, for nominal fuel cell operating pressures.
3. The desorption or discharge rate at 77–200K should be more than 0.4 g/s for a material reservoir containing 5 kg H_2.
4. The charge rate at 77–353 K should meet or be within 90% of the DOE target of 3.3 minutes for storage of a total of 5 kg H_2.
5. Full-scale commercial manufacturing material cost projections should be less than half the system cost targets.

Strong Binding/Multiple H_2 Metal Centers

1. The initial binding energy should be in the range of 10–40 kJ/mol, and the material should operate within a temperature range of 77–353K and pressure range of 30–100 bar. There should be a *clear potential* for gravimetric and volumetric capacity optimization in excess of the DOE 2015 targets for the given operating range.
2. The high-pressure adsorption isotherm should be >80% reversible, i.e., at least 80% of the stored hydrogen is desorbed or discharged between 77 and 353K, for nominal fuel cell operating pressures.
3. The desorption or discharge rate at 77–353K should be more than 0.4 g/s for a material reservoir containing 5 kg H_2.
4. The charge rate at 77–353K should meet or be within 90% of the DOE target of 3.3 minutes for storage of a total of 5 kg H_2.
5. Full-scale commercial manufacturing material cost projections should be less than 75% of the system cost targets.

Weak Chemisorption/Spillover

1. The material's volumetric storage capacity should be approximately 0.01 kg H_2/L with a gravimetric storage capacity of approximately 0.01 kg H_2/kg, a possible temperature range of 298–353K at 100 bar, and with a *clear potential* for further improvement.
2. The high-pressure adsorption isotherm should be >80% reversible, i.e., at least 80% of the stored hydrogen is desorbed or discharged with a temperature that does not exceed 353K, for a nominal fuel cell operating pressure.
3. The desorption or discharge rate at 298–353 K should be more than 0.4 g/s for a material reservoir containing 5 kg H_2.
4. The charge rate at 298–353K should not exceed 10 hours for a full charge of 5 kg H_2. In this case, since hydrogen loading is still a substantial development effort for spillover materials, charge rates have been adjusted to enable work to be performed on materials that have the potential to meet DOE targets.
5. Full-scale commercial manufacturing material cost projections should be less than 75% of the system cost targets.

RESULTS AND DISCUSSION

Substantial work in developing and characterizing nanostructured materials has demonstrated their potential to have more than ~30 g/L and ~7 wt% hydrogen storage excess material capacities at 80 to 100K and 30 to 100 bar conditions.[7,9] Based on this body of work, it is clear that increasing a material's specific-surface area is necessary, but it is not by itself sufficient for achieving high volumetric hydrogen storage capacities. Optimized pore sizes in the range of approximately 0.7 to 1.2 nm are also required to provide some potential adsorption enthalpy enhancements that may enable multilayer adsorption and minimize open volumes where hydrogen is not being bound to a surface.

Optimized pore sizes also enhance the material's ability to be packed at higher densities without loss of storage capacity to improve volumetric capacity further. Finally, electronic and surface functionalization may also enhance the adsorption properties for both hydrogen and other atoms and molecules that can be integrated with the high-surface-area materials to enhance hydrogen storage capacity. Results are summarized below for:

- Optimizing structures
- Increasing dihydrogen binding energy
- Optimizing weak chemisorption.

Optimizing Structures

In general, numerous synthetic methods have been used to create high specific-surface-area materials with the appropriate properties for good hydrogen storage. Typically, the synthetic methods used involve formation of porous structures from gas or solution phases and/or creation of pores from solids. Some of the more specific techniques include those described below.

Superactivated Carbon

By far, the most common way to synthesize porous structures is to start with relatively solid materials and process them to create high surface-area materials. The history of activated and superactivated carbons[23] spans hundreds of years and will not be discussed here. Suffice it to say that the state-of-the-art for hydrogen storage is embodied in materials such as AX-21,[24] which typically has specific surface areas in excess of 3,000 g/m^2 and material excess hydrogen storage capacities at 77K of between 5 and 6 wt% (15 to 20 g/L; based on measured bulk densities of ~0.3 g/ml).

The main issue with commercially available superactivated carbon is the relatively broad pore size distribution that includes substantial amounts of mesoporosity and some macroporosity. In general, materials with uniform pore sizes in the range of 0.7 to 1.2 nm are optimal for hydrogen storage, and thus all Center efforts involving similar pyrolysis processes have focused on making materials with optimum uniform pore sizes. For example, pyrolyzation techniques of chemicals such as polyetheretherketone (PEEK)[25] and inexpensive carbon sources such as corncobs[26] have been optimized to form materials with the pore size distributions closer to optimal. Although the main issue (that materials with higher specific-surface areas typically have large pore sizes) still remains, the Center has demonstrated that materials with improved pore sizes enhance hydrogen storage capacities.

Aerogels

The use of aerogel synthesis techniques[10] offers inexpensive and scalable processing that has the ability to tune pore sizes. These materials, which are also being used as scaffolds for metal hydrides, demonstrate reasonable hydrogen storage capacities at 77K. However, achieving suitable material thermal conductivity, uniform small pore sizes, and integration of boron into the carbon structure are remaining challenges.

The introduction of materials such as carbon nanotubes has been demonstrated to improve electrical/thermal conductivity. Although carbon aerogels have been optimized to provide ~20 g/L (with measured bulk densities of ~0.3 g/ml) and ~5.5 wt% material excess capacity at 77K and ~50 bar, the use of single-element carbon or silica aerogels has been down-selected. In this case, the Center decided that further optimization with pure carbon aerogels would not provide significant capacity improvements, and that efforts should be focused on increasing hydrogen binding energies via substitution of elements such as boron and integration of coordinated metal centers.

Graphene and Ordered Carbon

The use of graphene (via exfoliation or intercalation), nanotubes, nanohorns, and/or fullerenes has been demonstrated to be a way to form relatively durable and thermally conductive hydrogen storage materials. Cost and the ability to attain the appropriate pore sizes remain substantial issues that have yet to be resolved. In sheet form, intercalated materials have demonstrated very favorable binding energy results. For example, Cs-intercalated graphite demonstrated ~12 kJ/mol dihydrogen binding for the entire range of storage capacity.[27] However, in this case, because the graphene layers are separated by less than 0.6 nm, there is insufficient room for two dihydrogen layers between the graphene layers, and thus the potential capacity is less than 40 g/L and 4 wt% at ~77K and moderate pressures. Thus, if suitable layer-to-layer spacing (i.e., 0.7 to 1.2 nm) can be achieved, intercalated graphite offers an intriguing storage solution.

In a similar way, carbon nanotubes and fullerenes may be good hydrogen storage materials if they can be arranged with optimum spacing. Scaffolds with nanotubes,[6] fullerenes, and/or graphene have been designed that have the potential to be used to meet the DOE 2015 targets. Even so, appropriate synthetic methods must be developed to actually form the requisite structures.

Finally, in the case of nanotubes and fullerenes, the predicted higher availability of the π-electron due to the strained sp^2 coordination of the curved surfaces provides enhanced dihydrogen binding.[28] However, due to the sensitivity of this type of enhancement to functional groups and surface passivation, the exact amount of enhancement has been difficult to quantify. Estimates of a few percent to ~100% enhancements have been predicted.

Metal Organic Frameworks

Chemical synthesis of high specific-surface-area materials has progressed tremendously since the Center's inception. For example, metal organic frameworks (MOFs) and similar materials[9] have been developed with more than twice the specific-surface-area of superactivated carbons. These materials have demonstrated more than 7 wt% excess hydrogen storage capacities, but typically their low crystal density, and thus bulk density (e.g., ~0.3 g/ml), limits their volumetric densities to less than 30 g/L. In addition, porous polymers have been developed with more than twice (i.e., ~1.4 g/ml)[8] the densities of superactivated carbons.

These results demonstrate that inherent improvements can be made with pseudo-ordered structures and substantially raise the bar for what hydrogen storage capacities can be achieved with high specific-surface-area materials with optimum pore structures.[4] For example, once materials are made with optimum pore structures and specific-surface-areas in excess of 3,500 m^2/g, the Center expects capacities will be approximately 7 wt% (excess) and 70 g/L at 77K. The latter will be higher than that of liquid hydrogen, but at much higher temperature. As exemplified here, it may be that sorbents may ultimately have a greater impact on volumetric density than on gravimetric density compared to other gas compression or liquefaction physical approaches.

Thin Films on Templates

Several other synthetic methods are used to form the requisite porous materials. Perhaps one of the more intriguing methods involves synthetic processes that deposit thin films of lightweight materials on "templates" that have optimal pore structures. In this way, the optimal pore structures are obtained via the template. Typically, the heavier materials of the template are then removed, leaving behind the lighter-weight deposited material. Although relatively new, these techniques have been used to demonstrate materials with excellent hydrogen storage properties.[7]

Additional improvements in engineering design and/or material gravimetric capacities will be required for high surface-area sorption materials to meet DOE's 2015 gravimetric system targets (5.5 wt%). From a practical standpoint, material availability and low atomic mass will be needed to create inexpensive sorbents with high specific-surface-areas.

In general, carbon is an inexpensive material, and high-specific-surface-area materials are commercially produced at ~$1/Kg today. Thus, for carbon, the raw materials are not a significant factor in hydrogen storage system costs, leaving the system hardware as the main cost issue.

Initial work performed by TIAX LLC as part of the EERE Hydrogen Storage System Analysis Working Group (SSAWG)[29] indicates that sorption-based tank system costs (~$15/kWh) need to be significantly reduced to meet DOE cost targets. However, the analysis to date has not been optimized to the material. If optimized high specific-surface-area materials with sufficient capacity are used, the system costs can be substantially reduced by decreasing the operational system pressure to ~50 bar and increasing tank capacity to ~10Kg H_2. In this scenario, using an initial analysis performed by TIAX LLC in 2007,[30] increasing the tank capacity to ~10Kg H_2 should reduce overall costs by ~25% to ~$11/kWh.

Furthermore, carbon fibers used to strengthen the tank may be reduced and thus reduce tank cost fiber reductions by perhaps a factor of five to ~$1.5/kWh. In addition, the lower pressure may reduce the balance-of-plant (BOP) component costs from ~$2/kWh to perhaps <$1.5/kWh. If processing costs were to decrease more than twofold (with improved designs and materials) to <$1/kWh, and the media costs were more in line with present commercial activated carbon costs of <$1/kWh it may be possible with these assumption to make an ~10 Kg H_2 tank for the DOE 2015 target of ~$4/kWh. The latter two assumptions are within the sensitivity range of TIAX's analysis, while the first two are projections of the decreased costs associated with reducing the system operating pressure from 250 bar to 50 bar.

A detailed analysis must be performed to validate these assumptions, but this initial set of assumptions demonstrates a potential path for meeting the DOE 2015 cost targets with physisorption based materials. Furthermore, as seen from this analysis, as storage temperatures and pressures approach ambient, the overall system costs should decrease, even if more thermal management components are needed. Thus, the Center has focused on developing materials with higher binding energies that enable ambient-temperature and pressure storage; such materials should have a better chance of meeting the DOE targets.

Increasing Dihydrogen Binding Energy

To increase dihydrogen binding beyond what is typically achieved with physisorption, more "chemical" type bonding must occur. In the case of dihydrogen, this means enhanced electron sharing between the gas molecule and the sorption material. This can only be achieved by creating structures in the material that are electronically out of equilibrium (i.e., reactive or frustrated). Unfortunately, this is relatively difficult and thus only a few approaches work.

Even though the Center performed relatively exhaustive searches, when considering all the other hydrogen storage targets, sp^2-coordinated boron in carbon and coordinated (but electronically unsaturated) single-metal 1st row transition atoms are the only ways to significantly enhance dihydrogen binding with lightweight elements. The main challenges with these approaches include being able to uniformly disperse these higher binding sites in such a way that they are accessible to the dihydrogen, are stable and do not degrade with time/refueling cycles, and provide relatively uniform dihydrogen binding throughout as much of the material storage capacity range as possible. This latter point is important from an engineering perspective so that the net available capacity can be maximized over as small a temperature and pressure range as possible, which reduces the overall system costs.

In general, sorbent materials typically have a broad binding energy range (e.g., high specific-surface-area sorbents typically have a few sites with ~8-10 kJ/mol and then the binding quickly decreases to ~4 kJ/mol at higher coverage). Typically, as the binding energy range increases, the storage temperature and/or pressure range will also need to increase. Promising approaches to increasing dihydrogen binding are described below.

B-Substituted for Carbon
Calculations and experimental measurements both show that stronger dihydrogen binding between 10 and 15 kJ/mol[13] occurs when B is substituted with sp^2 coordination with carbons. This is sufficient to substantially increase the storage temperature compared to typical cryo-compressed materials, and it may be possible to meet DOE hydrogen storage capacity targets with BC_3-like materials at 150 to 250K temperatures. Any significant storage temperature increase towards ambient temperature significantly reduces weight and costs, thus making it easier to meet DOE system targets.

In general, if the binding energy increases occur with relatively small changes in low entropy and is in the range of 10 to ~30 kJ/mol, there will be limited impact on heat transport issues even at ambient temperatures. Therefore, the main challenge is being able to create materials with high substitution concentrations (>20 atom%) and high specific-surface areas (>1,000 m^2/g) with the substituted element in the correct electronic state. Because the specific concentration and specific-surface-area requirements depend on many factors, including the binding energy, it is difficult to quantify the exact properties needed. As a general rule, as the binding energy increases, the more tightly the hydrogen can be packed on the surfaces., and thus the less specific-surface area is required for a given temperature and pressure.

For dihydrogen, besides beryllium (Be), other compositions like nitrogen-substituted carbons do not significantly increase binding. To form the requisite B-C materials, approaches similar to those discussed for creating high-specific-surface-area materials with optimized pore sizes have been investigated. In general, pyrolyzation and templating of B-C precursors have produced ~500 m^2/g materials with ~15% B. However, materials with higher specific-surface areas have lower boron concentrations. Attempts to sublime boron into carbon materials have not proven to be reproducible. Furthermore, most materials made to date demonstrate multiple binding states. This is probably because B goes into amorphous and other carbon coordinations more easily than sp^2. However, it is the higher energy sp^2 coordination that has the greater electronic affinity and perhaps the structural stress needed for enhanced dihydrogen binding.

Heterogeneous Compositions That Enhance Other Binding
Although other lightweight atomic substitutions in carbon do not enhance dihydrogen binding, they can increase binding of other elements and molecules. For example, as with B-C compounds, nitrogen-substituted [for] carbons and some structures in crystalline materials such as MOFs can have a higher affinity for single-metal atoms or molecules. This method can be

used to coordinate elements and molecules that in turn enhance dihydrogen binding. For example, calculations indicate that F^-/BF_4^- have dihydrogen isosteric heats of adsorption of ~12 kJ/mol.[15] This is sufficient to substantially increase hydrogen storage capacities at higher temperatures than liquid nitrogen temperature. Unfortunately, after a focused effort to engineer such materials, the limited storage capacities achieved suggested that, at this time, this material should be down-selected and the Center should perform no further work on it. Along these lines, it is believed that charge-compensated structures can be synthesized that affect the dihydrogen electronic structure sufficiently to enhance storage. However, no experimental validation of these effects has been demonstrated to date.

Coordinated Metal Centers

The final class of materials that enhance dihydrogen binding was first experimentally identified by Kubas et al.[31] and involves creating materials in which individual metal atoms are coordinated to, or in, structures to keep them from agglomerating, but with electrons that are not fully compensated. Although initial experimental work demonstrated enhanced dihydrogen adsorption, the key experimental and theoretical findings are that this approach can be used to enhance binding of multiple (more than two) dihydrogen molecules with a single metal atom.[17,19]

This enhanced binding can occur at the metal atom site itself, or potentially, be charge transferred to the matrix material, which may enhance adsorption over the entire exposed surface.[16] The structurally coordinated but electronically unsaturated metal centers can be stabilized at higher energy binding sites on or within a material (e.g., boron- or nitrogen-substituted sites in carbon, or “exposed” sites in materials such as MOFs,[32] Metallocarbohedrenes, or macromolecules). These types of metal centers enable even ambient-temperature dihydrogen storage. Metal clustering and reaction with other elements reduce or eliminate the enhanced capacities, and thus materials must be designed to stabilize the metal centers.

The calculations used to make these initial predictions[17] are in good agreement with experimental results that have observed adsorption of two or more dihydrogen molecules.[19] Furthermore, similar calculations have predicted that Ca has unique hydrogen storage properties; specific materials incorporating Ca are predicted to have more than 10 wt% and 100 g/L hydrogen storage capacities.[18] Although the observed storage capacity has yet to be experimentally determined for these materials, the implication from the theoretical work indicates that the dihydrogen binding energy is sufficiently high to enable reversible storage at ambient temperatures and relatively low pressures (e.g., 10 to 50 bar), whereas the entropy and other factors should be appropriate so that heat generation during refueling should not be a significant issue.

In general, a few other first-row transition metals are also good candidates for hydrogen storage materials. However, based on work to date, it is imperative that approaches be used to stabilize the coordination of the metal centers. Calculations and synthetic experience are used to predict new energetically stable materials and to identify viable synthetic routes.

Optimizing Weak Chemisorption

Reversible storage at near-ambient temperature and nominal pressure can also be accomplished by weak chemisorption of atomic hydrogen with sorbent materials.[21] This chemisorption could possibly be achieved via a hydrogenation process. However, when gas-phase hydrogen (H_2) is used, catalysts or autocatalytic materials are typically required to dissociate the dihydrogen molecules, and then the atomic hydrogen "spills over" and is stored on receptor materials.

This process has been observed in part in the catalytic processes used in the petroleum and petrochemical process industries. Only recently has this process been demonstrated to create moderate storage capacities at ambient temperature and ~100 bar pressure. Hydrogen discharge rates via spillover storage are predicted to be able to meet DOE system targets.[21] However, hydrogen charge or refill rates and total storage capacity must be improved.

Furthermore, because the binding energies for spillover are relatively moderate (i.e., 10 to 25 kJ/mol), heat generation during refueling should not be a significant issue. A detailed mechanistic understanding of all the spillover reaction steps is being developed to provide the insights necessary to improve the storage-uptake rates and total available capacity. A thermodynamic framework for the spillover process is well developed for atomic hydrogen stored on receptor materials,[22] catalyst-assisted hydrogen dissociation, and hydrogen transport to the receptor materials from the catalysts.[33] These components have been validated using known results with spillover on the MoO_3.[20]

Computationally, MoO_3 is an analogous model system for carbon and MOF receptor materials. The main issue that needs to be understood (even though a couple of potential mechanisms have been identified) is how the hydrogen travels along the receptor material's surfaces.[34] Current experimental investigations involve methods to improve reproducible catalyst integration with the receptor materials, receptor-surface functionalization effects, and hydrogen transport on the receptor. Incorporation with specific functional groups has been shown computationally and experimentally to enhance or reduce spillover effects.

For example, the use of carbon "bridges" between the catalysts and the receptor substrate more than doubled the capacity of the spillover material to more than 4 wt% at ambient temperature and ~100 bar for an MOF-based material.[21] In addition, experimental results indicate that improved catalysts, integration processes, and/or surface-functional groups improved spillover rates and capacities.

The Center will continue performing systematic experiments to investigate structural, surface functionalization and physisorption effects for spillover. In addition, the Center will continue developing specific characterization procedures to ensure that side chemical reactions and measurement baseline-drift issues are not skewing the results. With some processing conditions, an irreversible set of chemical reactions can account for some, or all, of the initial hydrogen uptake observed during initial exposure to hydrogen. These chemical reactions typically produce by-products such as water or methane, which can be easily detected in the effluent during discharging.

In addition, due to the relatively long times associated with hydrogen loading on some spillover materials, it is critical to have extremely good thermal control of the measurement system to ensure that pressure changes observed are not related to changes in temperature. Based on the experimental results obtained so far, spillover has the potential to be used to meet DOE targets using a potentially near ambient temperature material.

RECOMMENDATIONS FOR FUTURE RESEARCH DIRECTION

The Center recommends that development efforts for specific material classes be continued where viable routes exist for synthesizing sorbents that can be used to meet the appropriate set of targets. The specific selection criteria for future efforts should focus on the DOE 2015 and the Ultimate Full-Fleet hydrogen storage targets. As noted previously, the focus has been, and should remain, on capacity, transient performance (including thermal management) and costs. We recommend this because the majority of the other DOE 2015 and Ultimate targets for sorbents will be more of a system-engineering issue than an intrinsic material property issue.

For example, even when dihydrogen binding energies are substantially increased to enable near-ambient-temperature storage, these binding energies (typically 10 to 25 kJ/mol) and the associated entropies of dihydrogen are low enough that the relatively small amount of heat generated during refueling should be easily removed with the typical sorption material's intrinsic thermal conductivity properties and/or appropriately designed integration of thermal conductivity materials in condensed "pelletize" materials. In addition, because most sorbent materials will likely operate at moderate pressures (i.e., 10 to 100 bar), delivery rates and system pressures should not be significant issues.

In general, a range of temperature and pressure can be used as long as the materials and systems can be constructed to meet the DOE targets. However, typically, the closer to ambient the system operating conditions, the less expensive the system costs. This must be traded against overall system performance, which includes the potential need for added heat removal.

This need for balance leads to five specific recommendations.

Recommendation 1 – Develop only a select set of materials in which the primary storage mechanism is physisorption.

The Center recommends that present and future development should be performed only on a select set of materials in which the primary storage mechanism is physisorption. To meet the DOE 2015 targets, the only physisorption materials that should be considered for development are those that can have specific-surface areas greater than 3,000 m^2/g, optimized uniform pore sizes in the range of ~0.7 to ~1.2 nm, and excess material hydrogen storage capacities greater than 50 g/L and 7 wt% at cryogenic temperatures (~80–200 K) and moderate pressures (less than 100 bar).

Although it may be possible to meet the DOE 2015 system targets with high-specific-surface-area materials, isosteric heats of adsorption between 10 and 25 kJ/mol will be required to increase storage temperatures above ~100K to significantly improve system capacity and/or costs. Near ambient temperatures will be required to meet DOE Ultimate full-fleet storage targets. Such targets can be met in a number of ways, including developing specific heterogeneous materials, coordinated but unsaturated metal centers, and weak hydrogenation processes such as spillover.

Recommendation 2 – Develop substituted/heterogeneous materials that have demonstrated hydrogen binding energies in the range 10 – 25 kJ/mol.

As stated earlier, for pure carbon systems, only a few elements (e.g., boron substituted in sp^2 coordination) substantially enhance dihydrogen binding. However, other heterogeneous systems (e.g., certain MOFs) have demonstrated enhanced dihydrogen binding.[14] In general, the principle is well established; the main issues include access and creating enough high-binding energy sites to substantially increase capacities.

In addition, these heterogeneous materials also demonstrate substantial stabilization of single-metal centers and other absorbed species that improve hydrogen storage. Thus, the Center recommends that researchers should develop substituted/heterogeneous materials that can be used to enhance dihydrogen isosteric heats of adsorption in the range of 10–25 kJ/mol. These materials will enable near-ambient-temperature (150–250K) hydrogen storage. Development efforts should focus on creating materials with the appropriate chemical and electronic structures, sufficient composition, and high specific-surface areas. These materials will potentially decrease system hardware costs and constraints and may be used to meet DOE's 2015 hydrogen storage system targets (40 g H_2/L; 5.5 wt%).

Recommendation 3 – Develop materials for hydrogen storage by spillover.

Ambient-temperature storage via catalytic hydrogen dissociation and transfer to high-specific-surface-area receptor materials (i.e., spillover) demonstrate 10 to 30 kJ/mol reversible hydrogen binding energies, which enable ambient-temperature storage. Furthermore, because the binding energies for spillover are much lower than for typical metal or chemical hydrides, thermal management issues for heat removal during refueling and delivery rate issues should be moderate, and thus should not significantly impact the overall storage system.

Although some of the processes involved have been demonstrated experimentally and by thermodynamic principles, additional development is needed to further understand and improve atomic hydrogen transport on the receptor material (for uptake/refill and discharge kinetics) and to improve the performance reproducibility and effectiveness of the synthetic processes. Once these issues are addressed, initial analyses indicate that because spillover enables ambient-temperature storage, systems with more than 75%[35] of the material capacities can be achieved using basic pressurized (~100 bar) tanks.

Initial analysis indicates that excess material storage capacities of more than 7 wt% should be possible with spillover. In addition, because spillover should be applicable to materials with more than 1 g/ml bulk density, storage systems with more than 50 g/L and more than 5.5 wt% capacities should be achievable at ambient temperature and ~100 bar. Thus, with inexpensive carbon-based materials and the development of inexpensive highly dispersed catalysts (e.g., nanoparticle Ni), spillover materials should be usable in systems that meet DOE's 2015 targets. Thus, the Center recommends that spillover or equivalent materials continue to be developed for hydrogen storage.

Recommendation 4 – Develop materials for multiple dihydrogen storage on designated sites.

Multiple-dihydrogen adsorption on designed sites provides a reasonable path toward meeting DOE's Ultimate full-fleet targets, with the proviso that this may require substantial development efforts. Several inexpensive material systems have been predicted that may be used to meet these targets at near-ambient temperature. One prediction includes the use of inexpensive Ca with inexpensive carbon supports to form materials that may be able to store hydrogen at ambient temperature with twice the gravimetric and volumetric densities compared to liquid hydrogen. Such a structure, if it is possible to synthesize and stabilize, promises to be a tremendous breakthrough. Thus, while substantial efforts will be needed to form the novel structures, development of multiple-dihydrogen adsorption on designed sites should be continued because the resulting structures could meet DOE Ultimate targets. Meeting those targets will enable hydrogen to become a viable energy carrier for transportation and other important renewable energy applications.

Recommendation 5 - Develop materials in concert with designs for hydrogen storage systems.

Compared to compressed (350 to 700 bar) or cryo-compressed hydrogen storage technologies, with demonstrated material packing densities and storage properties, the main benefits of sorption materials include substantial (twofold) reductions in volume (see Figure 4), reductions in pressure (~20-fold), and a fourfold or more increase in storage temperature. All this substantially improves system costs, resonance times for boil-off, and resolution of engineering-design issues.

Thus, development efforts should continue to optimize the materials for specific storage systems. Based on the successes achieved since the Center's inception, researchers have created sorption materials that have the potential to meet DOE's new 2010 targets, assuming that storage systems are optimized for the sorbent material being used. If sorbent materials are to be used to meet the DOE 2015 and Ultimate targets, it will be even more imperative that storage systems be optimized for the new sorbent materials with higher binding energies and other substantially different but critical performance characteristics.

Conclusion

At the time of the Center's inception, the required hydrogen storage performance criteria used to identify potential development materials were strict. Based on this and a number of other factors, a substantial amount of materials have been down-selected that should not be developed further. However, a limited number of viable routes exist to synthesize sorbent materials that can likely be used to meet DOE's 2015 and even DOE's Ultimate full-fleet on-board system targets.

Sorbent materials, which will be refilled on-vehicle, enables the potential for substantially higher refueling efficiencies (and thus lower costs) since storage material transport and regeneration will not be needed; as may be the case for off-vehicle regeneration. Thus, the Center believes that the on-vehicle refueling capability of sorbent materials is a tremendous advantage that should be exploited for hydrogen storage. However, to fully exploit this advantage, it is imperative that development efforts focus on reducing material and system costs. This cost reduction can be achieved by improving material storage capacities at near ambient temperatures. Furthermore, any future efforts must also investigate the material properties related to hydrogen storage systems, so that thermal conductivity, heat dissipation, refill and discharge rates, durability, and other engineering issues can be fully quantified.

Table 1: List of materials investigated that should be considered (Go Decision) for future materials development and hydrogen storage system analysis and design. The maximum reversible hydrogen capacity achieved for each system as well as the reason for the selection is provided.

System	Partner(s) Involved	Predicted Capacity[a]	Predicted ΔH (kJ/mol-H_2) [a]	Observed ΔH (kJ/mol-H_2)	Maximum Reported Hydrogen Capacity[c]	Status
Nanoporous (<1.2 nm pore size) materials (e.g., pyrolyzed, templated, polymer, etc.)	Duke, UMC, ANL, Rice, ORNL, NREL	5–8 wt%, 50 to 80 g/L	4–8	4–8	1 wt% (293 K, 100 bar)[n] >7 wt%, >50 g/L (77 K, ~50 bar)[m] >3000m^2/g	SSAWG indicates that it could meet 2015 system targets.
B-C materials with high SSA and B>20 atom% in correct coordination	PSU, NREL, APCI, ANL, Duke, LLNL, UMC	6–9 wt% 50 to 80 g/L	4–12	4–12	0.6 wt% (293 K, 100 bar)[n] ~3.8 wt% (77 K, ~50 bar),[m] only had ~500 m^2/g	Could meet DOE 2015 system targets at near-ambient T if SSA and B increased.
Coordinated metal centers; metal atoms on B-Cs, Ca-Graphene, Met-Cars, opened MOFs, etc.	NREL, TAMU	5 to 11 wt% 50 to 120 g/L	10 - 40	10 - 35	4.5 wt%, 37 g/L (77 K, 45 bar)[m] ~0.2 wt% (300K, 2 bar & 5 g/m^2) [n, b] ~10 times higher than AC	Could meet DOE ultimate targets at ambient T if stable materials can be made.
Spillover on catalyst-integrated materials	UM, NREL, ORNL, LLNL	8 wt% 80 g/L	10–25	10-25	4 wt% (298 K, 100 bar)[n] ~2 times increase at 200 bar measured[d] ~550m^2/g	Could meet DOE 2015 targets at ambient T with better catalysts/ materials.

a. Predicted storage capacities and ΔH are based on first principle models with an accurate accounting of probable reversible hydrogen storage capacity for idealized conditions. The idealized conditions (e.g., pressure and temperature) will depend upon several factors, including the ΔH and entropy of the storage materials/system.

b. The specific material formed had virtually no porosity, but showed that ambient-temperature storage by even a limited number of higher energy binding sites has a substantial impact on capacity. Superactivated carbon with more than 3,000 m^2/g has 10 times less hydrogen storage at the same conditions. Other materials have been formed with much higher specific-surface areas.
c. In general, other properties (e.g., thermal conductivity, rates, bulk densities) of the sorbent materials were not quantified because no specific issues were observed during the measurements. Thus, volumetric capacities can be assumed from the gravimetric results by assuming 0.5 to 1 g/L bulk densities for the materials. This level of bulk density has been achieved in a number of sorbent materials and should be achievable for most other materials made.
d. In general, spillover tends to be somewhat linear with pressure. Recent unpublished measurements at NREL demonstrated that a Ru/AC material that had ~1.1 wt% at ~100 bar had ~2 wt% at 200 bar pressures at ambient temperature. This suggests that for spillover, capacity will need to be traded with pressure to construct an optimized system.
m. Maximum excess adsorption quantities
n. Not a maximum excess adsorption quantity, just a directly measured value at the temperature and pressure provided.

REFERENCES AND SELECTED PUBLICATIONS ON MATERIALS INVESTIGATED BY THE HSCoE

Note that this report and thus the references provided in this report were not meant to be comprehensive in review, and so represent only examples of the vast amount of literature available for the topics discussed.

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[1] Multi-Year Research, Development and Demonstration Plan: Planned Program Activities for FY2005–2015. http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/index.html (accessed September 23, 2009).

[2] "GRAND CHALLENGE" FOR BASIC AND APPLIED RESEARCH IN HYDROGEN STORAGE", Funding Opportunity Announcement DE-PS36-03GO93013, September 2003.

[3] S.K. Bhatia, A.L. Myers, *Langmuir* [online] **2006**, *22*, pp.1688–1700.

[4] High-Pressure Hydrogen Storage in Zeolite-Templated Carbon Hirotomo Nishihara, Peng-Xiang Hou, Li-Xiang Li, Masashi Ito, Makoto Uchiyama, Tomohiro Kaburagi, Ami Ikura, Junji Katamura, Takayuki Kawarada, Kazuhiko Mizuuchi, and Takashi Kyotani. *J. Phys. Chem. C*, **2009**, *113 (8)*, pp.3189–3196.

[5] e.g., (i) Serguei Patchkovskii, John S. Tse, Sergei N. Yurchenko, Lyuben Zhechkov, Thomas Heine, Gotthard Seifert. Graphene Nanostructures as Tunable Storage Media for Molecular Hydrogen. *PNAS* [online] **2005**, *102*, pp.10439–10444.

[6] e.g., (i) B. Yakobson, IV. C Hydrogen Storage, *DOE Annual Hydrogen Storage Report 2009*. (ii) A.K. Singh, J. Lu, R. Aga, B.I. Yakobson. Comparative Evaluation of Carbon-Foams Hydrogen Storage Capacity through Monte-Carlo Simulations. In preparation. (iii) O.V. Pupysheva, A.A. Farajian, B.I. Yakobson. Fullerene Nanocage Capacity for Hydrogen Storage (cover article). *Nano Letters* [online] **2008**, *8*, pp.767–774.

[7] e.g., (i) Zhuxian Yang, Yongde Xia, Robert Mokaya. Enhanced Hydrogen Storage Capacity of High Surface Area Zeolite-like Carbon Materials. *J. AM. CHEM. SOC.* **2007**, *129*, pp. 1673–1679. (ii) L.J. Simpson, IV.C Hydrogen Storage, *DOE Annual Hydrogen Storage Report 2009*.

[8] e.g., (i) Polyanaline. (ii) S. Yuan, S. Kirklin, B. Dorney, D.-J. Liu, L. Yu. Nanoporous Polymers Containing Stereo-contorted Cores for Hydrogen Storage. *Macromolecules* **2009**, *42(5)*, pp.1554–1559. (iii) Y. Yuan, I. Cabasso, H. Liu. Surface Morphology of Nanostructured Polymer-based Activated Carbons. *J. Physical Chem. B* **2008**, pp.14364–14372.

[9] e.g., (i) Antek G. Wong-Foy, Adam J. Matzger, Omar M. Yaghi. Exceptional H_2 Saturation Uptake in Microporous Metal-Organic Frameworks. *J. Am. Chem. Soc.* [Online] **2006**, *128*, pp.3494–3495. (ii) D.J. Collins, H.-C. Zhou. Hydrogen Storage in Metal-organic Frameworks. *J. Mater. Chem.* **2007**, *17*, pp.3154–3160.

[10] e.g., (i) T.F. Baumann, M.A. Worsley, T.Y. Han, J.H. Satcher, Jr. High Surface Area Carbon Aerogel Monoliths with Hierarchical Porosity. *J. Non-Cryst. Solids* [Online] **2008**, *354*, pp.3513–3515. (ii) M.A. Worsley, J.H. Satcher, Jr., T.F. Baumann. Synthesis and Characterization of Monolithic Carbon Aerogel Nanocomposites Containing Double-walled Carbon Nanotubes. *Langmuir*[Online] **2008**, *24*, pp.9763–9766. (iii) Houria Kabbour, Theodore F. Baumann, Joe H. Satcher, Jr., Angelique Saulnier, Channing C. Ahn. Toward New Candidates for Hydrogen Storage: High-Surface-Area Carbon Aerogels. *Chem. Mater*. [Online] **2006**, *18 (26)*, p 6085.

[11] e.g., (i) A.A. Puretzky, D.B. Geohegan, D. Styers-Barnett, C.M. Rouleau, B. Zhao, H. Hu, M.D. Cheng, D.W. Lee, I.N. Ivanov. High Power Laser Vaporization Synthesis of Single Wall Carbon Nanotubes and Nanohorns. *Appl. Phys. A* [Online] **2008**, *93(4)*, pp.849– 855. (ii) D.B. Geohegan, A.A. Puretzky, D. Styers-Barnett, H. Hu, B. Zhao, H. Cui, C.M. Rouleau, G. Eres, J.J. Jackson, R.F. Wood, S. Pannala, J. Wells. In Situ Time-Resolved Measurements of Carbon Nanotube and Nanohorn Growth. *Phys. Stat. Sol. (b)* [Online] **2007**, *244 (11)*, pp.3944–3949.

[12] e.g,. (i) P.F. Weck, E. Kim, N. Balakrishnan, H. Cheng, B.I. Yakobson. Designing Carbon Nanoframeworks Tailored for Hydrogen Storage. *Chem. Phys. Lett.* [Online] **2007**, *439*, pp.354–359. (ii) F. Ding, Y. Lin, P. Krasnov, B.I. Yakobson. Nanotube Derived Carbon Foam for Hydrogen Storage. *J. Chem. Phys.* [Online] **2007**, 127, pp.164703. (iii) Ashley D. Leonard, Jared L. Hudson, Hua Fan, Richard Booker, L.J. Simpson, K.J. O'Neill, P.A. Parilla, Michael J. Heben, Carter Kittrell, Matteo Pasquali, James M. Tour. Nanoengineered Carbon Scaffolds for Hydrogen Storage. *J. Am. Chem. Soc.* [Online] **2008**, *131(2)*, pp.723–728. (iv) Dmitry V. Kosynkin, Amanda L. Higginbotham, Alexander Sinitskii, Jay R. Lomeda, Ayrat Dimiev, B. Katherine Price, James M. Tour**.** Longitudinal Unzipping of Carbon Nanotubes to Form Graphene Nanoribbons. *Nature* [Online] **2009**, *458*, pp.872–876.

---

[13] e.g., (i) Yong-Hyun Kim, Yufeng Zhao, Andrew Williamson, Michael J. Heben, S. B. Zhang. Nondissociative Adsorption of H_2 Molecules in Light-Element-Doped Fullerenes. *Phys. Rev. Lttr*. [Online] **2006**, *96*, pp.016102. (ii) T.C. Mike Chung, Youmi Jeong, Qiang Chen, Alfred Kleinhammes, Yue Wu. Synthesis of Microporous Boron-Substituted Carbon (B/C) Materials Using Polymeric Precursors for Hydrogen Physisorption. *J. Am. Chem. Soc*. [Online] **2008**, *130*, pp.6668. (iii) A. Cooper, IV.C Hydrogen Storage, *DOE Annual Hydrogen Storage Report 2008*.

[14] e.g., (i) Y. Liu, J.-H. Her, A. Dailly, A.J. Ramirez-Cuesta, D.A. Neumann, C.M. Brown. A Reversible Structural Transition of MIL-53 with Temperature Hysteresis, *J. Am. Chem. Soc.* [Online] **2008**, *130*, p 11813. (ii) N.J. Hess, M.R. Hartman, C.M. Brown, E. Mamontov, A. Karkamkar, D.J. Heldebrant, L.L. Daemen, T. Autrey. Quasielastic Neutron Scattering Experiments of Orthorhombic Ammonia Borane. *Chem. Phys. Letts.* [Online] **2008**, *459*, pp.85–88.

[15] A. Cooper, IV.C Hydrogen Storage, *DOE Annual Hydrogen Storage Report 2008*.

[16] Sun Q, Wang Q, Jena P. Functionalized Heterofullerenes for Hydrogen Storage. *App. Phys. Lett.* [Online] **2009**, *94*, p. 013111.

[17] e.g., (i) Yufeng Zhao, Yong-Hyun Kim, A.C. Dillon, M.J. Heben, S.B Zhang. Hydrogen Storage in Novel Organometallic Buckyballs. *Phys. Rev. Letts*. [Online] **2005**, *94*, p 155504. (ii) Cheng-Gen Zhang, Renwu Zhang, Zhi-Xiang Wang, Zhen Zhou, Shengbai B. Zhang, Zhongfang Chen. Ti-Substituted Boranes as Hydrogen Storage Materials: A Computational Quest for the Ideal Combination of Stable Electronic Structure and Optimal Hydrogen Uptake. *Chem. Eur. J.* **2009**, *15*, pp.5910–5919. (iii) Yufeng Zhao, Y.-H. Kim, L.J. Simpson, A.C. Dillon, S.-H. Wei, M.J. Heben. Opening Space for H_2 Storage: Cointercalation of Graphite with Metal and Small Organic Molecules. *Phys. Rev. B* [Online] **2008**, *78*, pp.144102. (iv) Y. Liu, H. Kabbour, C.M. Brown, D.A. Neumann, C.C. Ahn. Increasing the Density of Adsorbed Hydrogen with Coordinatively Unsaturated Metal Centers in Metal-Organic Frameworks. *Langmuir* [Online] **2008**, *24*, p 4772. (v) Y. Zhao, M.T. Lusk, A.C. Dillon, M.J. Heben, S.B. Zhang. Boron-Based Organometallic Nanostructure: Hydrogen-Storage Properties and Structure Stability. *Nano Lett.* [Online] **2008**, 9, pp.157–161. (vi) Yufeng Zhao, Y.-H. Kim, L.J. Simpson, A.C. Dillon, S.-H. Wei, M.J. Heben. Opening Space for H_2 Storage: Cointercalation of Graphite with Metal and Small Organic Molecules. *Phys. Rev. B* [Online] **2008**, *78*, p 144102.

[18] (i) Y.-H. Kim, Y.Y. Sun, S.B. Zhang. Ab initio Calculations Predicting the Existence of an Oxidized Calcium Dihydrogen Complex to Store Molecular Hydrogen in Densities up to 100 g/L. *Phys. Rev. B* [Online] **2009**, *79*, p 115424. (ii) Y.Y. Sun, Kyuho Lee, Yong-Hyun Kim, S.B. Zhang. Ab initio Design of Ca-Decorated Organic Frameworks for High Capacity Molecular Hydrogen Storage with Enhanced Binding. *Appl. Phys. Lett.* [Online] **2009**, *79*, p 115424. (iii) M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, Z. Zhang. Calcium as a Superior Coating Metal in Functionalization of Carbon Fullerenes for High-Capacity Hydrogen Storage. *Phys. Rev. Lett.* [Online] **2008**, *100*, p 206806.

[19] (i) Ahmad Hamaed, Michel Trudeau, David M. Antonelli. H_2 Storage Materials (22KJ/mol) Using Organometallic Ti Fragments as σ-H_2 Binding Sites. *J. Am. Chem. Soc.* [Online] **2008**, *130*, pp.6992–6999. (ii) Lee, K.; Lucking, M.; Sun, Y.Y.; Chen, Z.; Zhang, S. Structural Stability and Hydrogen Storage Properties of Ti Anchored on Silica. *Nano Lett.* **2009**.

[20] (i) Chen, L.; Cooper, A.C.; Pez, G.P.; Cheng, H. J. On the Mechanisms of Hydrogen Spillover in MoO_3. *Phys. Chem. C.* [Online] **2008**, *112*, p. 1755. (ii) Chen, L.; Pez, G.P.; Cooper, A.C.; Cheng, H. A Mechanistic Study of Hydrogen Spillover in MoO_3 and Carbon-based Graphitic Materials. *J. Phys.: Condens. Matter* [Online] **2008**, *20*, p 064223.

[21] e.g., (i) A.J. Lachawiec, Jr., R.T. Yang. Isotope Tracer Study of Hydrogen Spillover on Carbon-Based Adsorbents for Hydrogen Storage. *Langmuir* [Online] **2008**, *24*, p. 6159. (ii) Y.W. Li, R.T. Yang. Hydrogen Storage in Metal-Organic Frameworks and a Covalent-Organic Framework. *AIChE Journal* **2008**, *54*, p 269. (iii) Y.W. Li, R.T. Yang. Hydrogen Storage on Platinum Nanoparticles Doped on Super-Activated Carbon. *J. Phys. Chem. C.* [Online] **2007**, *111*, p. 11086. (iv) L.F. Wang, R.T. Yang. New Sorbents for Hydrogen Storage by Hydrogen Spillover – A Review. *Energy & Environmental Science, Roy. Soc. Chem. Cambridge* **2008**, *1*, p 268. (v) Y.H. Wang, R.T. Yang. Increased Hydrogen Spillover by Gaseous Impurity -Benson-Boudart Method for Dispersion Revisited. *J. Catalysis* **2008**, *260*, p 198. (vi) R.T. Yang, Y.H. Wang. Catalyzed Hydrogen Spillover for Hydrogen Storage. *J. Am. Chem. Soc.* [Online] **2009**, *131*, p 4224.

[22] e.g., (i) C.K. Lin, Z.Z. Yang, T. Xu, Y.Z. Zhao. An in Situ Electrical Study on Primary Hydrogen Spillover from Nanocatalysts to Amorphous Carbon Support. *Appl. Phys. Lett.* [Online] **2008**, *93*, p 233110. (ii) Y. Lin, F. Ding, B.I. Yakobson. Hydrogen Storage by Spillover on Graphene as a Phase Nucleation Process. *Phys. Rev. B* **2008**,

---

78, p 041402-R. (iii) Chen, L.; Cooper, A.C.; Pez, G.P.; Cheng, H.J. Mechanistic Study on Hydrogen Spillover onto Graphitic Carbon Materials. *Phys. Chem. C.* [Online] **2007**, 111, p 18995 (2007).

[23] e.g., see Schwarz, J.A. *Final Report for the Tasks XC-1-1108-1 and XAE-3-13346-01* (National Renewable Energy Laboratory, Golden, Colorado) 1994.

[24] (i) P. Bénard, R. Chahine. *Scr. Mater.* 2007, 56, p 803. (ii) P. Bénard, R. Chahine. *Int. J. Hydrogen Energy* **2001**, *26*, p 849.

[25] (i) J. Liu, IV.C Hydrogen Storage, *DOE Annual Hydrogen Storage Report 2009*. (ii) Thomas P. McNicholas, Simiao Zhang, Yanqin Wang, Lin Simpson, Alfred Kleinhammes,Yue Wu, Jie Liu. Effect of Surface Area and Microporosity of Miroporous Carbon Materials Prepared from Decomposition of PEEK Polymer on the Hydrogen Storage Capacity and Binding Energy. In Preparation, **2009**.

[26] Pfeifer, P.; Burress, J.W.; Wood, M.B.; et al. High-surface-area Biocarbon for Reversible On-board Storage of Natural Gas and Hydrogen. *Life-Cycle Analysis for New Energy Conversion and Storage Systems Conference Proceedings, Boston, MA* **2007**, pp.63–74.

[27] C. Ahn, IV.C Hydrogen Storage, *DOE Annual Hydrogen Storage Report 2009*.

[28] Y. Zhao, Y.-H. Kim, S.B. Zhang. Theory of Hydrogen Storage in Nanoscale Materials. In *Frontiers in Nanoscience and Nanotechnology*, Vol. 3.

[29] See for example the *DOE Annual Hydrogen Reports* for years 2005–2009.

[30] See S. Lasher, K. McKenney, Y. Yong, B. Rancatore, S. Unnasch, M. Hooks, TIAX LLC, *DOE Hydrogen Program Annual Merit Review 2007*.

[31] Kubas, G. J. Metal–dihydrogen and σ-bond coordination: the consummate extension of the Dewar–Chatt–Duncanson model for metal–olefin π bonding. *Journal of Organometallic Chemistry* ***2001*** *635, pp.37–68.*

[32] e.g., (i) M. Dinca, A. Dailly, Y. Liu, C.M. Brown, D.A. Neumann, J.R. Long. Observation of Cu^{2+}-H_2 Interactions in a Fully Desolvated, Sodalite-type Metal-organic Framework. *Angewandte Chemie* [Online] **2007**, *46*, p 1419.

[33] A.K. Singh, M.A. Ribas, B.I. Yakobson. H-spillover through the Catalyst Saturation: An ab initio thermodynamics study. *Nano Lett.* [Online] **2009**, *3*, p 1657.

[34] e.g., (i) L.J. Simpson, IV.C Hydrogen Storage, *DOE Annual Hydrogen Storage Report 2009*. (ii) D. West, K. Lee, S.B. Zhang. Hole Mediated Diffusion of H on SP^2 Carbon Networks. *Phys. Rev. Lett.* [Online] **2009**.

[35] Internal DOE Storage System Analysis Working Group Report, 2009.

APPENDICES

Appendix I: Updated Table (June 2009) of DOE On-Board Hydrogen Storage System Targets for Light-Duty Vehicles

Technical System Targets: On-Board Hydrogen Storage for Light-Duty Vehicles

Storage Parameter	Units	2010	2015	Ultimate
System net Gravimetric [a]	kWh/kg (kg H_2/kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage system cost [b] (& fuel cost)[c]	\$/kWh net (\$/kg H_2) \$/gge at pump	4* (133) 2-3	2* (67) 2-3	TBD 2-3
Durability/Operability				
- Operating ambient temperature [d]	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
- Min/max delivery temperature	°C	-40/85	-40/85	-40/85
- Cycle life (1/4 tank to full) [e]	Cycles	1000	1500	1500
- Cycle life variation [f]	% of mean (min) at % confidence	90/90	99/90	99/90
- Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine	Atm (abs)	4FC/35 ICE	3FC/35 ICE	3FC/35 ICE
- Max delivery pressure from storage system[g]	Atm (abs)	100	100	100
Charging/discharging Rates				
- System fill time (for 5-kg H_2)	min (Kg H_2/min)	4.2 min (1.2 kg/min)	3.3 min (1.5 kg/min)	2.5 min (2.0 kg/min)
- Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
- Start time to full flow (-20°C)[h]	s	5	5	5
- Start time to full flow (20°C)[h]	S	15	15	15
- Transient response 10%-90% and 90% -0%[i]	s	0.75	0.75	0.75
Fuel Purity (H_2 from storage)[j]	% H_2	99.99 (dry basis)		
Environmental Health & Safety				
- Permeation & leakage [k]	Scc/h	Meets or exceeds applicable standards		
- Toxicity	-			
- Safety	-			
- Loss of useable H_2 [l]	(g/h)/kg H_2 stored	**0.1**	**0.05**	**0.05**

*The storage system costs are currently under review and will be changed at a future date.

Note: Targets are based on the lower heating value of hydrogen; targets are for a complete system, including tank, material, valves, regulators, piping, mounting brackets, insulation, added cooling capacity, and/or other balance-of-plant components. Unless otherwise indicated, all targets are for both internal combustion engine and fuel cell use, based on the low likelihood of power-plant-specific fuel being commercially viable. Also note that while efficiency is not a specified target, systems must be energy efficient. For reversible systems, greater than 90% energy efficiency for the energy delivered to the power plant from the on-board storage system is required. For systems regenerated off-board, the energy content of the hydrogen delivered to the automotive power plant should be greater than 60% of the total energy input to the process, including the input energy of hydrogen and any other fuel streams for generating process heat and electrical energy.

Footnotes to Table

Useful constants: 0.2778kWh/MJ, ~33.3kWh/gal gasoline equivalent.

[a] Generally the 'full' mass (including hydrogen) is used; for systems that gain weight, the highest mass during discharge is used.

[b] 2003 US$; total cost includes any component replacement if needed over 15 years or 150,000-mile life.

[c] 2005 US$; includes off-board costs such as liquefaction, compression, regeneration, etc.; 2015 target based on H_2 production cost of \$2 to \$3/gasoline gallon equivalent untaxed, independent of production pathway.

[d] Stated ambient temperature plus full solar load. No allowable performance degradation from –20C to 40C. Allowable degradation outside these limits is TBD.

[e] Equivalent to 200,000; 300,000; and 300,000 miles respectively (current gasoline tank spec).

[f] All targets must be achieved at end of life.

[g] For delivery *to* the storage system, in the near term, the forecourt should be capable of delivering 10,000 psi (700 bar) compressed hydrogen, liquid hydrogen, or chilled hydrogen (35 to 77K) and up to 5,000 psi (350 bar). In the long term, it is anticipated that delivery pressures will be reduced to between 50 and 150 atm for solid state storage systems, based on today's knowledge of sodium alanates.

[h] Flow must initiate within 25% of target time.

[i] At operating temperature.

[j] The storage system will not provide any purification, but will receive incoming hydrogen at the purity levels required for the fuel cell. For fuel cell systems, purity meets SAE J2719, Information Report on the Development of a Hydrogen Quality Guideline in Fuel Cell Vehicles. Examples include: total non-particulates, 100 ppm; H_2O, 5 ppm; total hydrocarbons (C_1 basis), 2 ppm; O_2, 5 ppm; He, N_2, Ar combined, 100 ppm; CO_2, 1 ppm; CO, 0.2 ppm; total S, 0.004 ppm; formaldehyde (HCHO), 0.01 ppm; formic acid (HCOOH), 0.2 ppm; NH_3, 0.1 ppm; total halogenates, 0.05 ppm; maximum particle size, <10 µm, particulate concentration, <1µg/L H_2. These are subject to change. See Appendix on Hydrogen Quality in the DOE EERE Hydrogen Fuel Cells and Infrastructure Technologies Program Multiyear Research, Development and Demonstration Plan (www.eere.energy.gov/hydrogenandfuelcells/mypp/) to be updated as fuel purity analyses progress. Note that some storage technologies may produce contaminants for which effects are unknown; these will be addressed as more information becomes available.

[k] Total hydrogen lost into the environment as H_2; relates to hydrogen accumulation in enclosed spaces. Storage system must comply with CSA/HGV2 standards for vehicular tanks. This includes any coating or enclosure that incorporates the envelope of the storage system.

[l] Total hydrogen lost from the storage system, including leaked or vented hydrogen; relates to loss of range.

Appendix II: Recommended Down-Selected Materials by Class

Table 1: List of physisorption-based high-specific-surface area materials that were considered and discontinued (No-Go Decision). The maximum reversible hydrogen capacity achieved for each, as well as the reason for the down-select is provided.

System	Partner(s) Involved	Predicted Capacity[a]	Predicted ΔH (kJ/mol-H_2)[a]	Observed ΔH (kJ/mol-H_2)	Maximum Reported Hydrogen Capacity	Status
Pure carbon single-wall nanotubes (SWNTs)	NREL, Rice, Duke, APCI, NIST, UNC	5–10 wt%	16–46	19.6	0.01 wt% (223 K, 0 bar)[n] 3 wt% (77 K, 20 bar)	Discontinued; predicted reversible capacity not observed.
Fe-decorated carbon multi-wall nanotubes (MWNTs)	NREL	Not Predicted	Not Predicted	50	0.04 wt% (273 K, 0 bar)[n]	No longer considered; high reversible capacity not achieved.
Co-decorated SWNTs	NREL	Not Predicted	Not Predicted	27.9	0.01 wt% (223 K, 0 bar)[n]	No longer considered; high reversible capacity not achieved.
Small-diameter, cut single-wall nanotubes	APCI	7 wt. %	8–18	8–11	1.5 wt. % (77 K, 1 atm)[n] 0.5 wt. % (298 K, 115 bar)[n]	Discontinued; high adsorption enthalpy not achieved.
Undoped activated carbon aerogels	LLNL, CalTech	6+ wt%	Not Predicted	~6 kJ/mol	5.3 wt% (77 K and 30 bar)[m] 0.8 wt% at RT and 100 bar	Reached maximum capacity that was below DOE target.
Double-wall carbon nanotubes	Duke	Not Predicted	Not Predicted	Not Predicted	0.11 wt% (77K ,2 bar)[n]	Reported improvement in DWNTs not observed in measurements.

a. Predicted storage capacities and ΔH are based on first principle models with an accurate accounting of probable reversible hydrogen storage capacity for idealized conditions. The idealized conditions (e.g. pressure and temperature) will depend upon several factors including the ΔH and entropy of the storage materials/system.

m. Maximum excess adsorption quantities

n. Not a maximum excess adsorption quantity, just a directly measured value at the temperature and pressure provided.

Table 2: List of substituted materials that were considered and discontinued (No-Go Decision). The maximum reversible hydrogen capacity achieved for each system as well as the reason for the down-select is provided.

System	Partner(s) Involved	Predicted Capacity[a]	Predicted ΔH (kJ/mol-H_2) [a]	Observed ΔH (kJ/mol-H_2)	Maximum Reported Hydrogen Capacity	Status
Multiple wall enhanced binding	Caltech	~ 4 wt%	4 to 15	4 to 13	1.5 wt% (77 K and 3 bar)[n]	Model systems, provide good data, cannot meet capacity targets
B-doped SWNTs produced from B-containing graphite target	NREL, NIST	4 wt% (capacity for 10 kJ/mol - H_2)	10	4	2 wt% (77 K, 20 bar)[n]	Discontinued; at 1.8 at%, maximum boron loading was too low.
Li, N, O, Na, etc. substituted carbon	NREL	~7 wt%	4	Not Measured	Not Measured	These substituted elements do not increase binding compared to just pure C
Lithium-doped SWNTs	APCI	Not Predicted	Not Predicted	6.5 – 10.5	0.7 wt.% (77 K, 1 bar) [n]	Discontinued; small observed capacity.
F-intercalated carbons	APCI	1 – 8 wt%	4 – 24 (for range of 1 – 8 wt%)	8 – 14	0.24 wt% at 298 K, 100 bar)	Discontinued; small observed capacity.

a. Predicted storage capacities and ΔH are based on first principle models with an accurate accounting of probable reversible hydrogen storage capacity for idealized conditions. The idealized conditions (e.g., pressure and temperature) will depend upon several factors including the ΔH and entropy of the storage materials/system.

m. Maximum excess adsorption quantities

n. Not a maximum excess adsorption quantity, just a directly measured value at the temperature and pressure provided.

Table 3: List of strong/multiple H_2 binding metal center materials that were considered and discontinued (No-Go Decision). The maximum reversible hydrogen capacity achieved for each system as well as the reason for the down-select is provided.

System	Partner(s) Involved	Predicted Capacity[a]	Predicted ΔH (kJ/mol-H_2)[a]	Observed ΔH (kJ/mol-H_2)	Maximum Reported Hydrogen Capacity [n]	Status
Fe(C_{60})	NREL	3.5 wt%	60	4	1 wt% (77 K, 85 bar)	Discontinued; theoretical capacity/ structure not observed.
Li(C_{60})	NREL	9 wt%	6	6	0.2 wt% (77 K, 2 bar) 0.8 wt% (300 K, no overpressure)	Discontinued; high reversible capacity not observed due to LiH formation.
Na(C_{60})	NREL	Not Predicted	Not Predicted	Not Measured	1 wt% (300 K, no overpressure)	No longer considered; high desorption temperature.
Ca(C_{60})	ORNL, NREL	8.4 wt%	20	6	0.25 wt% (77 K, 2 bar) 1 wt% (300 K, no overpressure)	Discontinued: high reversible capacity not observed due to CaH formation.
K(C_{60})	NREL	Not Predicted	Not Predicted	Not Measured	0.004 wt% (RT, 2 bar) 0.06 wt% (77 K, 2 bar)	No longer considered; high desorption temperature and low capacity.
Sc(C_{60})	NREL	Not Predicted	Not Predicted	Not Measured	0.02 wt% (RT, 2 bar) 0.04 wt% (77 K, 2 bar)	No longer considered; high desorption temperature and low capacity.
Cr(C_{60})	NREL	Not Predicted	Not Predicted	Not Measured	0.02 wt% (RT, 2 bar) 0.31 wt% (77 K, 2 bar)	No longer considered; high desorp. temp. and low capacity.
Co(C_{60})	NREL	Not Predicted	Not Predicted	Not Measured	0.01 wt% (RT, 2 bar) 0.12 wt% (77 K, 2 bar)	No longer considered; high desorption temperature and low capacity.

System	Partner(s) Involved	Predicted Capacity[a]	Predicted ΔH (kJ/mol-H_2)[a]	Observed ΔH (kJ/mol-H_2)	Maximum Reported Hydrogen Capacity [n]	Status
HKUST-1	NIST, U Sydney, A.U.	~4 wt %		6.6	3.26 wt % (77 K, 30 bar)	Binding strength too low.
Co-TCTHF	NIST, U Sydney, A.U.	Not Predicted	Not Predicted	9.6	1.2 wt % (77 K, 1 bar)	Low surface area
Nickel metal complexes on functionalized inorganic aerogel supports	NREL, LLNL	Not Predicted	Not Predicted	20.5 (@ low H_2 coverage)	0.29 wt% (77 K, 2 bar)	Upon scaling up of the synthesis of the Ni-supported aerogel materials, the new H_2 binding sites were not reliably reproduced and metal agglomeration was not avoided.
Organometallic scandium (Sc) complex with multiple dihydrogen ligands via solution chemisty	NREL	~9 wt %	~29	Not Measured	Not Measured	Sc sites were not coordinatively and electronically unsaturated in materials synthesized.

a. Predicted storage capacities and ΔH are based on first principle models with an accurate accounting of probable reversible hydrogen storage capacity for idealized conditions. The idealized conditions (e.g. pressure and temperature) will depend upon several factors including the ΔH and entropy of the storage materials/system.

n. Unless specifically stated, the material capacities listed are not a maximum excess adsorption quantity, just a directly measured value at the temperature and pressure provided.

Table 4: List of spillover materials that were considered and discontinued (No-Go Decision). The maximum reversible hydrogen capacity achieved for each system as well as the reason for the down-select is provided.

System	Partner(s) Involved	Predicted Capacity	Predicted ΔH (kJ/mol-H_2)	Observed ΔH (kJ/mol-H_2)	Maximum Reported Hydrogen Capacity^n	Status
Ti-6Al-4V-decorated SWNTs	NREL	Not Predicted	Not Predicted	Not Measured	3.76 wt% (77 K, 85 bar)	No longer considered; high desorption temperature.
Pd-doped nanofibers	NIST, ORNL (not center)	Not Predicted	Not Predicted	Not Measured	Not Measured	Did not observe much spillover H using neutrons.
NaAlH4-doped AX-21	UM	Not Predicted	Not Predicted	Not Measured	<1% (298 K, 100 atm)	No longer considered; H_2 amount too low.
Pt-NaAlH4-doped AX-21	UM	Not Predicted	Not Predicted	Not Measured	1% (298 K, 100 atm)	No longer considered; H_2 amount too low.
LiCl-doped MOF-177	UM	Not Predicted	Not Predicted	Not Measured	-	Lower than undoped MOF
Pt-bridged MCM-41 (mesoporous silica, BET~1200)	UM	Not Predicted	Not Predicted	Not Measured	0.65% (298 K, 100 atm)	No longer considered; H_2 amount too low.
Pt-bridged COF-1	UM	Not Predicted	Not Predicted	Not Measured	0.7% (298 K, 100 atm)	No longer considered; H_2 amount too low.
Hg-Pd codoped AX-21	UM	Not Predicted	Not Predicted	Not Measured	Not Measured	Adding Hg decreased spillover compared to Pd alone
Pt-doped Activated Carbon Fibers (Osaka Gas)	UM	Not Predicted	Not Predicted	Not Measured	Not Measured	No longer considered; H_2 amount too low.
Pd-doped on MOF-177	UM	Not Predicted	Not Predicted	Not Measured	Not Measured	Succeeded in reducing Pd <200 C, but H_2 amt. too low.
Pt-bridged ZIF-8	UM	Not Predicted	Not Predicted	Not Measured	0.95% (298K,100 atm)	Although ZIF-8 is the only H2O-stable MOF, but capacity is too

System	Partner(s) Involved	Predicted Capacity	Predicted ΔH (kJ/mol-H_2)	Observed ΔH (kJ/mol-H_2)	Maximum Reported Hydrogen Capacity[n]	Status
						low to continue
Pt-bridged MIL-53	UM	Not Predicted	Not Predicted	Not Measured	0.92% (298K, 100 atm)	No longer considered; H_2 amount too low.
Pt-doped on N-doped carbon	UM	Not Predicted	Not Predicted	Not Measured	Not Measured	No longer considered; H_2 amount too low.

n. Unless specifically stated, the material capacities listed are not a maximum excess adsorption quantity, just a directly measured value at the temperature and pressure provided.