

**Executive Summaries
for the
Hydrogen Storage Materials Centers of Excellence**

**Chemical Hydrogen Storage CoE,
Hydrogen Sorption CoE,
and
Metal Hydride CoE**

Period of Performance: 2005-2010

**Fuel Cell Technologies Program
Office of Energy Efficiency and Renewable Energy
U. S. Department of Energy**



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Introduction and Background

The use of hydrogen and fuel cells to power light-duty vehicles offers an effective pathway as part of a portfolio of technologies to reduce greenhouse gas emissions and petroleum usage.¹ In addition to the challenges associated with improving the power density and durability of polymer electrolyte membrane fuel cells while reducing their costs, there are challenges in developing hydrogen storage technologies that offer high specific energy and energy density at acceptable costs for use onboard vehicles.² Working with the U.S. automotive manufacturers through the FreedomCAR and Fuel Partnership (now U.S. DRIVE), the U.S. Department of Energy (DOE) established in 2003 a comprehensive set of performance metrics for onboard hydrogen storage systems based on comparison with gasoline fueled vehicles. The metrics included 2015 system-level targets for specific energy and energy density of 3.0 kWh/kg (9 wt.%) and 2.7 kWh/L (81 g H₂/L) respectively.³ In 2009, after re-evaluating the performance metrics with comparisons to available fuel cell, hybrid, and electric vehicle performance data, the DOE issued a revised set of performance targets that included “Ultimate Full Fleet” system-level targets for specific energy and energy density of 2.5 kWh/kg (7.5 wt.%) and 2.3 kWh/L (70 g H₂/L) respectively.⁴ Considering the energy density target alone as an example, compressed hydrogen at ambient temperature has a density of about 40 g H₂/L; liquid hydrogen at its normal boiling point of 20 K has a density of 71 g H₂/L. Since the energy density targets are for the complete system, neither normal compressed hydrogen nor liquid hydrogen is theoretically able to meet the system-level targets. Therefore it was recognized that advanced hydrogen storage technologies would need to be developed if all the performance metrics were to be achieved.

When hydrogen interacts with other materials or elements, either as the dihydrogen molecule or as monoatomic hydrogen, hydrogen densities greater than that of compressed hydrogen gas or liquid hydrogen, can be obtained. For instance, dihydrogen can be adsorbed onto high-surface area, porous materials, where even at low pressures of a few bar, the hydrogen density of the adsorbed layer can approach the density of liquid hydrogen. When atomic hydrogen bonds to other elements, either through metallic-type bonding as in interstitial metal hydrides, covalent bonding as in complex hydrides, compounds such as ammonia borane and even water, or ionic bonding as in binary alkali metal hydrides such as sodium hydride, hydrogen densities up to twice that of liquid hydrogen can be obtained.⁵ It was therefore recognized that materials-based hydrogen storage might provide a pathway to high energy density storage of hydrogen at low pressure and near ambient temperature with the potential to meet the DOE performance targets. The materials-based storage technologies can be roughly categorized into three groups: sorbents, reversible metal hydrides, and off-board regenerable chemical hydrogen storage. Prior to the 2003 timeframe, most materials-based hydrogen storage technology development had focused on reversible interstitial metal hydrides, hydrolysis of chemical hydrogen storage materials, specifically sodium borohydride (NaBH₄), and investigation of carbon nanotubes and nanofibers as hydrogen adsorbents.

In an effort to accelerate the development of materials-based hydrogen storage technologies, in 2004 the DOE announced the formation of three “Materials Centers of Excellence” to develop reversible metal hydrides, chemical hydrogen storage materials, and high-surface area hydrogen sorbents.⁶ Each of the three centers consisted of multiple partner institutions which worked in a concerted, synergistic way to carry out hydrogen storage materials discovery, characterization, and development for the three categories of hydrogen storage materials. Each center included computational analysis, materials synthesis, and materials characterization capabilities. The centers continued their efforts for approximately five years and were concluded in 2010. The following three sections include the executive summary of the final report for each center. They provide summaries of the work performed and accomplishment achieved within each center and their recommendations for continued work in their specific material category. For those interested in more detailed descriptions of the center activities, the complete center final reports can be accessed through the DOE Hydrogen and Fuel Cells Program’s website at:

http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage.

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- ¹ Tien Nguyen, Jake Ward, **Program Record 10001**, Oct. 5, 2010, http://hydrogen.energy.gov/pdfs/10001_well_to_wheels_gge_petroleum_use.pdf
 - ² Sunita Satyapal, John Petrovic, George Thomas, *Gassing up with Hydrogen*, **Scientific American**, April 2007, 80-87
 - ³ Specific energy and energy density are based on a lower heating value of hydrogen of 33.3 kWh/kg H₂.
 - ⁴ DOE Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles, http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf
 - ⁵ N.T. Stetson, L. S. Blair, *Hydrogen Storage Technologies – A Tutorial with Perspectives from the US National Program*, **Ceramic Transactions**, Ed.: G. Wicks, J. Simon, et. al., Vol. 224, (2011), pg 3-16
 - ⁶ JoAnn Milliken, **Proceedings of the 2004 DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting**, http://www.hydrogen.energy.gov/pdfs/review04/st_1_miliken.pdf.

FINAL REPORT FOR THE DOE CHEMICAL HYDROGEN STORAGE CENTER OF EXCELLENCE

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Summarizing Contributions from Center Partners:

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Pacific Northwest National Laboratory (PNNL)
Millennium Cell, Inc.
Northern Arizona University
Rohm and Haas/Dow Chemical Company
University of Alabama
University of California, Davis
University of California, Los Angeles/University of Missouri
University of Oregon
Pennsylvania State University
University of Pennsylvania
University of Washington
U.S. Borax Corporation
Intematix Corporation

This final report was prepared with the assistance of Tom Autrey (PNNL), and Fran Stephens (LANL) who prepared the drafts of Chapter 1 and Chapter 2 respectively.

Executive Summary. Chemical Hydrogen Storage Center of Excellence

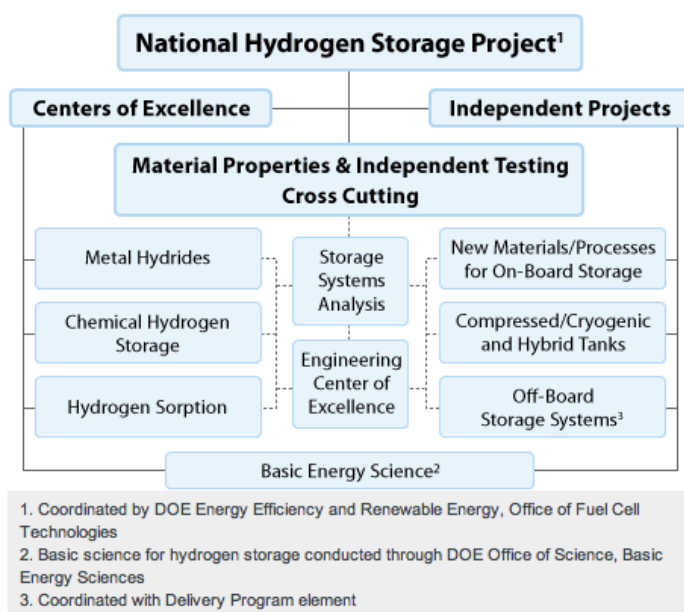
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1.0 Overview of the Chemical Hydrogen Storage Center of Excellence and High Level Recommendations[§]

This final report documents the successes, lessons learned, recommendations, and overall outcomes of the research and development of the Chemical Hydrogen Storage Center of Excellence. The report is in three sections and is comprised of an Executive Summary and two Chapters, one on hydrogen release from chemical hydrogen storage materials, and the second chapter is on the off board regeneration of spent chemical hydrogen storage fuels.

The Chemical Hydrogen Storage Center of Excellence (henceforth referred to as CHSCoE, or the Center) arose from a competitive solicitation in 2004 through the U.S. Department of Energy's (DOE) Energy Efficiency and Renewable Energy (EERE) Hydrogen Program. It was one of three Hydrogen Storage Materials Centers of Excellence, and joined the Metal Hydride Center and the Sorption Center as integral contributors to the National Hydrogen Storage Project. This national project represented the first time that such large-scale concerted effort was undertaken



in the area of materials-based on board vehicular hydrogen storage R&D. These Centers explored a wide variety of materials compositions and configurations with a goal to discover and develop viable hydrogen storage materials with potential to meet DOE technical targets for on board vehicular applications.

Chemical hydrogen storage is defined as the release of hydrogen from covalent chemical compounds, and their subsequent regeneration. Regeneration of many of these materials must be

[§] Detailed information that supports the conclusions and high level recommendations given here is presented in the subsequent chapters on hydrogen release and spent fuel regeneration and also in the various Final Reports from the Partners of the CHSCoE.

performed off board for reasons related to the thermodynamics of the chemical processes that interconvert spent fuel and fuel.

As the Center was in its formative stages, little was known about the potential for storing hydrogen in covalent chemical bonds. Some work had been done on ‘activated’ hydrocarbons systems by researchers at Air Products; and the release of hydrogen from ammonia borane was known largely through its utility as a precursor to the ceramic, boron nitride. Much of the literature of chemical hydrogen storage was from the area of hydrolysis of sodium borohydride (SBH), performed by researchers at Millennium Cell, who at the time was developing an on board hydrogen storage system demonstration with Daimler-Chrysler. A plot of the materials weight fraction of hydrogen versus temperature for all of the materials known to store hydrogen in covalent molecular bonds is shown in Figure 1, and discussed in a little more detail below in section 1.2.1. The DOE system target lines are estimates of the temperature regime where the storage system must perform, being -20 to 100 °C.

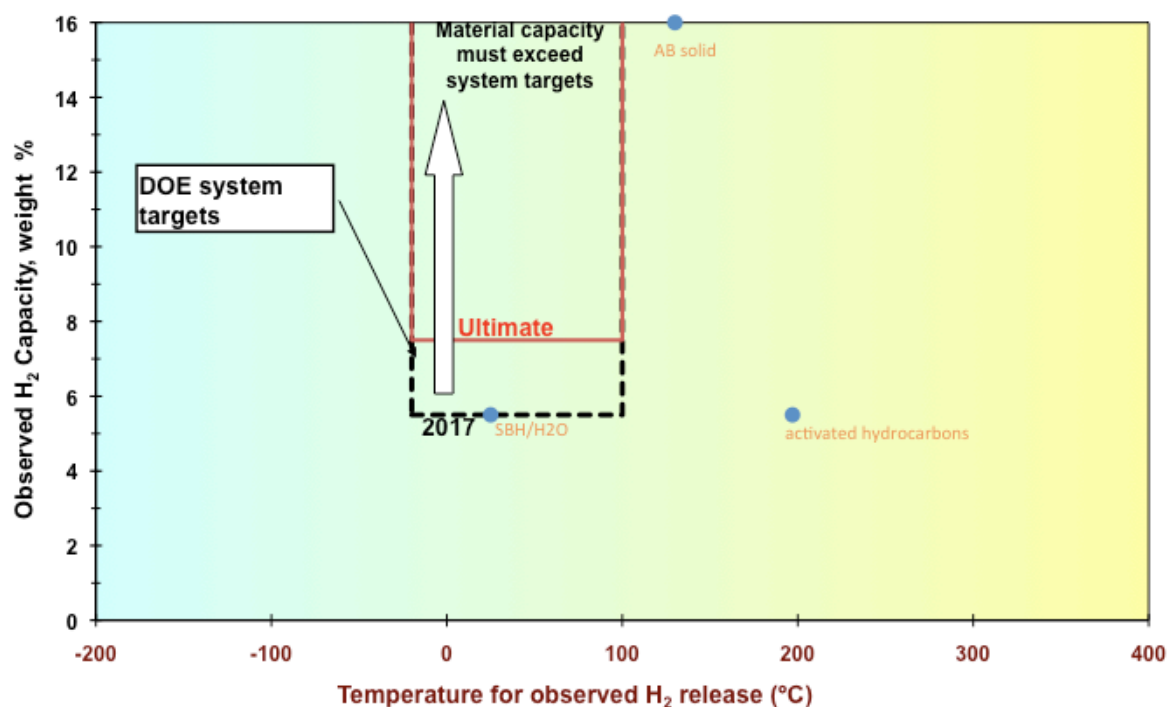


Figure 1. State of chemical hydrogen storage in 2005, before the Center started its work.

The Chemical Hydrogen Storage Center of Excellence began its work in spring of 2005, and completed its research in the fall of 2010. The Center was comprised of two national laboratory partners, originally four companies, and originally seven academic institutions. The Center’s work focused primarily around the chemistry of boranes, and thus many of the partners in the Center were experts in boron chemistry and catalysis, or processing of boron compounds.

During the tenure of the Center, its partners discovered or explored 12 major classes of compounds having over 130 materials or materials combinations. Many of the materials classes examined were chosen because of their potentially very high hydrogen storage capacity coupled with their typically high rates of hydrogen evolution related to their exothermic release of hydrogen. Material gravimetric capacities up to 16% were demonstrated, and many other candidate materials demonstrated capacities in excess of 9 wt. %; these materials capacities are consistent with what will be needed to meet the stringent DOE system capacity requirements for an engineered storage system. Two plots are shown below that illustrate the progress made during the Center's tenure; the plot made after the Center's R&D was completed does not contain all of the data points, as it would be too crowded, but rather shows representative data from several of the various families of chemical hydrogen storage materials explored by the Center.

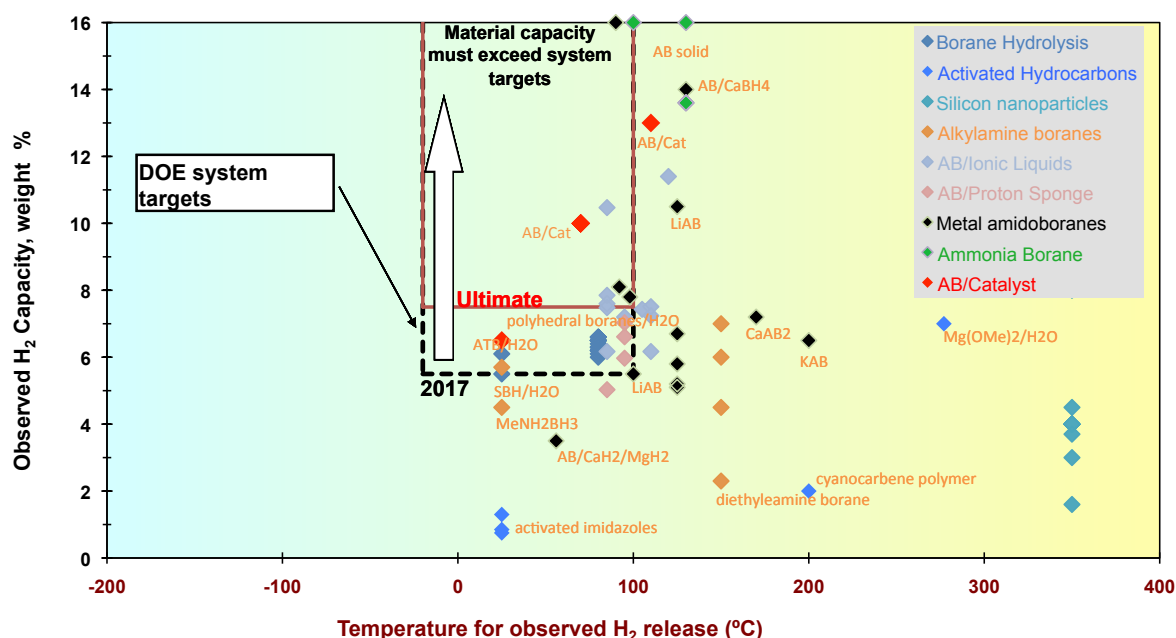
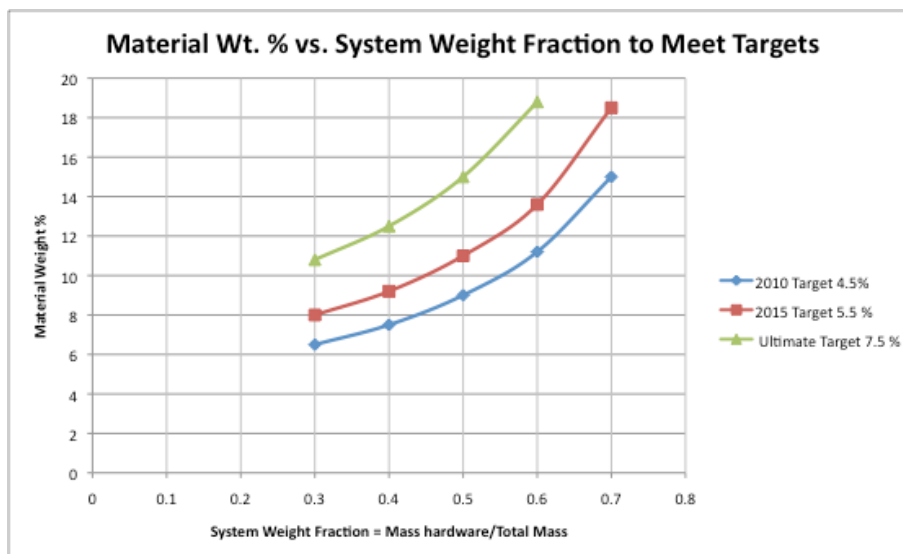


Figure 2. State of chemical hydrogen storage in 2010 after completion of the CHSCoE activities. The plot indicates the general types of families of hydrogen storage materials the Center contributed, and the temperature span over which the various materials release the indicated quantity of hydrogen.

In Figure 2, data for release from some materials are shown at multiple temperatures to indicate the temperature range over which hydrogen can be released. For example, catalysed release of hydrogen from AB is shown as three distinct points (red diamonds) ranging in temperature from 25 °C to 110 °C, a range over which hydrogen can be released with high rates with the potential to meet DOE targets. Similarly, AB in ionic liquids (gray diamonds) also indicate a broad temperature range for fast hydrogen release in the temperature regime of practical application for vehicular applications. From this plot, it can be seen that a number of materials fall close to the gravimetric and temperature ranges considered necessary for vehicular applications. Others, such as silicon nanoparticles release hydrogen at too high a temperature, and do not release hydrogen with adequate gravimetric capacity.

In 2007, the Center developed a robust decision tree process for logical down selection of the broad range of storage materials that were being discovered or developed by the Center. The Center's primary down select criterion was the materials gravimetric capacity. This criterion was based upon a simple plot (below) of the algebraic relationship between system wt. % and



materials wt. % with varying system hardware mass contributions. The Center assumed, based upon Millennium Cell's aggressive system design for on board hydrolysis of sodium borohydride, and our additional experience, that the system hardware mass is likely to represent about 50% of the total system. The plot below shows graphically ***that to be able to meet the 2010 and 2017 system targets, that any storage material must contain greater than 7 or 9 wt. % hydrogen respectively.*** This analysis is described in more detail in Chapter 1, Section 1.5.1. Many scientifically interesting, but technologically inferior materials were set aside as a result of the Center's continuous decision tree driven down select process. Of the materials examined, 95% were not down selected for further development as they were considered unable to meet all of the DOE technical targets simultaneously. The remaining 5% of these materials or classes of materials that had the potential to meet all the targets simultaneously are considered as candidates for continued research. These include members of the family of solid ammonia borane with additives, potentially liquid fuels consisting of ammonia borane dissolved in ionic liquids or liquid cyclic carbon-boron-nitrogen heterocyclic materials, and certain metal amidoboranes, a class of materials wherein potentially reversible hydrogen storage materials may be discovered. A preliminary system capacity analysis by Argonne National Laboratory (ANL) showed a system gravimetric capacity of 4.9 wt. % and a system volumetric capacity of 49.5 g H₂/l for an ammonia borane/ionic liquid mixture. While preliminary, this analysis indicated that such a chemical hydrogen storage system was able to achieve the 2010 hydrogen capacity targetsⁱ.

The candidate materials down selected have been demonstrated to have the potential to meet all of the DOE 2010 technical targets (the complete listing of technical targets and a description of DOE's hydrogen storage multiyear program plan may be found online¹) for on board vehicular

storage and they also have been demonstrated to have the potential (with the exception of the metal amidoboranes) for efficient off board regeneration. The metal amidoboranes, while not off board regenerable by energy efficient chemical processes, have shown that they have significant potential to yield new discoveries of near-thermoneutral release materials that in principle can be rechargeable on board a vehicle.

Recommendations: Hydrogen release. Our analysis indicates that to achieve system capacity targets, *any* hydrogen storage material must be able to achieve > 9 wt. % while also achieving the target rate of hydrogen release. Even with aggressive hardware budgets, a material < 9 wt. % H₂ will be challenged to fulfill a 4.5 wt. % system target. Discovery of high capacity materials that release hydrogen less exothermically (nearly thermoneutral) is required to simplify on board heat rejection, and to enable the material to be potentially on board rechargeable. High capacity materials that produce negligible gas-phase impurities under hydrogen release conditions are still required.

In the area of off board regeneration of spent fuel, the Center has made remarkable progress. Five years ago, no concepts existed for the regeneration of a spent borane-based fuel. In a relatively short period, the Chemical Hydrogen Storage Center of Excellence conceived of 10 distinct schemes for the chemical regeneration of spent fuel arising from dehydrogenation of ammonia borane. Of these 10 schemes, the Center demonstrated eight complete cycles in the laboratory. Two of these demonstrated processes were assessed for both cost and energy efficiency by Dow Chemical Co. (Dow) and ANL, respectively. TIAX, LLC provided independent validation of the Dow and ANL assessments. In one of the eight completely demonstrated regeneration process, Center partner Dow developed a cost estimate for spent fuel regeneration of between \$7 and \$8 per kilogram of hydrogen. This was for a process that is far from optimal, but provided the proof-of-principle that spent fuel could be regenerated, and at a cost that was not beyond reasonable. A second more chemically simple process was also assessed, and in this instance, the process and capital costs not including raw materials were found to be significantly lower (\$2/kg H₂) relative to the first process estimate (\$6.5/kg H₂), again providing proof-of principle that simpler regeneration schemes may provide a cost effective route to off board regeneration.

Recommendations: Regeneration. The Center has demonstrated that given a spent fuel from a chemical hydrogen system, that efficient process chemistries can be devised and implemented for off board regeneration. The chemistries that should be considered must have the minimal number of separations steps, and any separations should be of low energy intensity (e.g. crystallization). The reagent that transfers the hydrogen to the spent fuel should be inexpensive to recycle. Ideally, the incorporation of hydrogen into the spent fuel cycle should involve an efficient catalytic approach that can be directly coupled into a spent fuel regeneration scheme. Raw materials costs must be minimal, or there must be processes to make currently expensive reagents less expensive when practiced on a world scale.

While regeneration costs represent a critical contribution to the overall fuel costs, also important are the costs of the ‘first fill’ of storage material. Center partner Dow expended significant effort in analyzing first fill costs, and along with partner PNNL, they developed improved ‘first fill’ chemistries and processes for the preparation of ammonia borane. Dow’s analysis indicates that the cost of sodium borohydride (SBH) is the major contributor to the first fill cost. Dow estimates that to achieve the DOE target of \$2-4/kg H₂, the a SBH cost of \$5/kg is required to achieve an ammonia borane first fill cost of around \$9.1/kg; at \$5/kg, SBH represents roughly 2/3 of the first fill cost.

Recommendations: First Fill of Storage Material. For any storage material, the cost of the material is central to the overall cost of the fuel. Many storage materials, whether they are a chemical hydrogen storage material, a sorbent, or a complex metal hydride, are derived from currently expensive starting materials. Our Center’s work on sodium borohydride has shown that reducing raw materials costs is required to reduce the overall fuel cost. The Center’s work on first fill also has implications for the Metal Hydride Center of Excellence, as many of the storage materials they have examined are borohydride based, and the cost of these fuels will also rely upon cost effective synthesis of borohydride intermediates.

More emphasis on process analysis and process research is needed to determine whether there is a path forward for a given material type to achieve cost targets. If so, more emphasis is required on research to develop energy and chemically efficient syntheses of first fill hydrogen storage materials of all types.

The Center has made remarkable progress in the last five years in addressing materials needs for viable chemical hydrogen storage. Many challenges remain. Further reductions in cost of borohydride production are necessary to minimize overall fuel cost for any borane or borohydride fuels. While the Center has demonstrated a quite simple ‘one pot’ regeneration of ammonia borane using hydrazine, substantially reducing the costs of hydrazine and other raw materials used in the off board chemical regeneration of spent fuel are also necessary to reduce the cost of fuel. Dramatic improvements in the efficiency of raw materials production is also required to improve the overall spent fuel regeneration process efficiency.

Another important contribution of the Center was in the evaluation of US and global reserves of borate minerals. Center partner US Borax analyzed non-proprietary borate mining data, and concludedⁱⁱⁱ that the proven US borate reserves are sufficient to sustain the US light duty fleet operating on boron-based fuels without displacing existing borate markets. The world reserves of borates are substantially greater than the US reserves, with a significant reserve in Turkey. This reserve evaluation is also important to the Metal Hydride Center, as their main research focus also involved boron-based storage materials.

Recommendations: Resource Availability. When large-scale hydrogen storage materials needs are considered, resource availability studies should be performed at an early stage to ensure that

there is enough U.S. and/or global resource available at a reasonable cost to accomplish the scale at which the implementation of the storage material is intended.

After five years, the Chemical Hydrogen Storage Center of Excellence demonstrated that chemical hydrogen storage is a viable materials-based approach. The Center made significant advancements in the understanding the chemistry and materials properties of boron-based chemical hydrogen storage materials, and developed the relationship between what is required of an engineered chemical hydrogen storage system and the materials properties required to achieve the system targets. The root cause of this Center's achievements may be traced to the Center concept that brought together the best boron chemists, boron process chemists, modelers, and chemical engineers into a focused team. The Center concept enabled efficient, quality communication and collaboration among all of the scientists and engineers, and allowed a Center culture to develop that inspired the Center participants to maintain scientific and technical momentum and drive towards progress on many fronts of chemical hydrogen storage. The Center concept encouraged being accepting and responsive to the substantial peer review input and external engineering assessments the Center received, catalyzing rapid progress along the critical path to demonstrating that chemical hydrogen storage in covalent chemical compounds is a viable materials-based hydrogen storage approach.

1.1 Introduction

The Chemical Hydrogen Storage Center of Excellence (hereafter referred to as the CHSCoE or as the 'Center') was one of three 'materials' Centers of Excellence initiated by DOE's Office of Fuel Cell Technologies in early 2005. The Center's missions were to conduct exploratory R&D and demonstrate feasibility of what were considered the three most promising areas of hydrogen storage materials research for on board vehicular applications. These three Centers were to provide focused efforts either on sorption of hydrogen on materials (the Hydrogen Sorption Center), storage of hydrogen in metal hydrides (The Metal Hydrides Center), or 'chemical hydrides' (the Chemical Hydrogen Storage Center). All three Center's technical targets were directed at achieving high hydrogen storage capacity that will allow a hydrogen powered vehicle a >300 mile of range while preserving all of the positive attributes of vehicle electrification and without compromising passenger or cargo space. A government – industry partnership of U.S. automotive and fuel companies known at the time as the FreedomCAR and Fuel Partnership (now referred to as U.S. DRIVE) had developed a set of technical targets for hydrogen storage *systems*. A storage *system* includes the storage material, and also all of the associated containers, valves, and associated on board hardware required to generate the hydrogen and deliver the hydrogen to the propulsion system at a rate to achieve a specified power. These systems targets encompass challenging volumetric and gravimetric targets to hydrogen purity specifications to shelf-life stability among many others that will be discussed in the body of this report. All of the targets need to be met *simultaneously*, in other words, a high capacity material that does not release hydrogen rapidly enough, or that does not have adequate stability is of marginal technical interest. Only those materials that have the chemical and physical properties that allow them to

meet, or have the potential to meet system targets are of interest for further development into viable storage systems.

High pressure hydrogen tanks, systems that store hydrogen in a cryocompressed state, or liquid hydrogen storage systems that are more technologically mature may not be able to meet the long-term storage system targets were not topics of study for these three materials Centers. Rather, the materials Centers were tasked to explore materials that had the potential to exceed the capacities available by strictly physical methods of hydrogen storage.

These three Centers thus set out to seek out and develop hydrogen storage materials that have the potential to meet the specified DOE technical targets for an engineered system. The Sorption Center set out to explore the utility of sorption of molecular hydrogen onto novel carbons at cryogenic temperatures, an approach significantly different than the Metal Hydride or the Chemical Hydrogen Centers. These latter two Centers focused on storing hydrogen by compound formation either as ‘complex metal hydrides’ or as ‘chemical hydrides’, respectively.

Some introduction to hydride materials is needed at this point. A common approach to describing the spectrum of ‘hydride’ materials is to organize them into the bins based on chemical properties. A convenient classification system is to classify hydrides into the three groups: 1). Ionic hydrides, 2). Covalent hydrides, and 3). Interstitial metal hydrides.

Ionic hydrides are the true salts like sodium hydride, etc. where there is little covalent bonding between hydrogen and the metal, and thus a high degree of ionic character in the M-H bonding. These tend to be quite thermally stable toward releasing hydrogen.

Covalent hydrides encompass compounds such as MgH_2 , AlH_3 , the boranes and borohydrides and related derivatives, hydrocarbons, amines and ammonia complexes, etc. where the bonding is highly localized between the hydrogen and the central element (Al, B, C, N, etc). Many of these materials are known to release hydrogen at temperatures above room temperature and up to several hundred degrees Celsius, and can release > 9 and up to 20 wt. % hydrogen such that when placed into a system these compounds have the potential to meet DOE’s 2010 and 2017 gravimetric system targets of 4.5 and 5.5 wt %, respectively.

The interstitial hydrides are distinct from these two classes of ‘hydrides’, in that there is usually not discrete compound formation, in other words, interstitial hydrides may form where H atoms reside in tetrahedral or octahedral interstices within the metal or alloy framework over a wide range of M/H ratios; solid solution formation is common. The bonding between the metal(s) and the hydrogen atom is highly delocalized, with multi-center, multi-electron bonding similar to that in metals occurring. These hydrides can release hydrogen and re-hydride at temperatures that range from sub-ambient to several hundred degrees Celsius depending on the specific composition. Interstitial hydrides by their nature are composed of high atomic number transition metals, and therefore contain a low mass fraction of hydrogen of only a few percent and are not capable of meeting the strict gravimetric system targets set forth by DOE for on board vehicular applications.

In the class of covalent ‘hydrides’, many of these materials do not contain only hydridic hydrogen atoms, but in many instances also protonic hydrogen atoms, and so we prefer not to use the terminology of ‘chemical hydride storage’, but rather we use the term ‘chemical hydrogen storage’ to delineate the storage of hydrogen in covalent molecular solids.

1.2 Mission and scope of the Chemical Hydrogen Storage Center of Excellence

In the topical area of hydrogen storage, a goal of the DOE Office of Fuel Cell Technologies is to develop viable hydrogen storage materials and engineered sub-scale prototypes for a variety of applications ranging from personal power, storage for ‘niche’ vehicles such as forklifts, to onboard hydrogen storage for light duty vehicles. In the latter area, a key goal is to discover and develop materials for onboard hydrogen storage and propulsion systems that enable hydrogen powered vehicles a range of 300+ miles between refueling without compromising performance or space. The mission of the Chemical Hydrogen Storage Center of Excellence was to discover potential hydrogen storage materials and explore the feasibility of using chemical hydrogen storage materials for on board vehicular storage to enable DOE’s goals for hydrogen-fueled vehicles. A major expectation of the Center was to down select and/or rank from the multitude of candidate materials the most promising material(s), release process(es), and regeneration process(es) for more detailed study, with an overarching goal of moving the most promising material(s) from all of the ‘materials Centers’ that meet all of DOE’s technical targets for hydrogen storage toward sub-scale prototype demonstration.

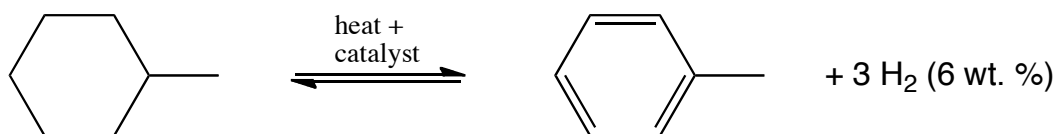
The scope of the Center included all aspects of materials development and assessment activities, ranging from first principles theory and modeling of materials, modeling of the thermodynamics of chemical reactions and reaction sequences, to chemical synthesis and characterization of storage materials, characterization of hydrogen release kinetics and mechanisms and thermodynamics, to catalysis of hydrogen release, to engineering assessments and process modeling studies of regeneration of spent fuels. The scope did not include the problems of hydrogen production and distribution, or of fuel distribution or fueling infrastructure. With the formation of the Hydrogen Storage Engineering Center of Excellence, the Center’s initial task of demonstrating a sub-scale prototype was transferred to the Engineering Center. Thus, the CHSCoE’s focus was strictly on the discovery and development of high capacity hydrogen storage materials having rapid release, adequate storage stability, and acceptable levels of impurities, among other properties that were defined by DOE technical targets that will be described in more detail below. First, we describe the ‘state of the art’ for chemical hydrogen storage prior to the Center’s formation.

1.2.1 Storage of hydrogen in covalent chemical bonds

At the time DOE requested proposals for a ‘chemical hydrides’ Center in the period of 2004 - 2005, the science of removing hydrogen ‘stored’ in covalent bonds of molecular species was relatively undeveloped. The few examples were the reversible dehydrogenation-rehydrogenation

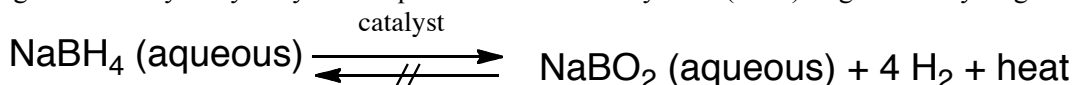
of hydrocarbons, e.g. methylcyclohexane ‘releases’ 3 moles of hydrogen to yield toluene as shown schematically in Figure 1. This is an endothermic process that occurs at very low rates in the absence of a catalyst and/or at low temperatures. More recently, in support of DOE’s Hydrogen Storage Program, scientists from Air Products Inc. explored a wide series of heterocyclic molecules that are activated toward hydrogen release and re-uptake.

Figure 1. Catalytic, reversible dehydrogenation of a hydrocarbon storage material. Here, the example is the dehydrogenation of methylcyclohexane to toluene to generate 6 wt. % hydrogen.



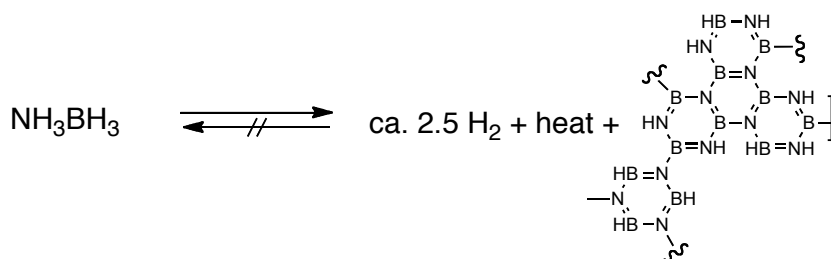
There was also some prior work from Millennium Cell in the highly exothermic, irreversible hydrolysis of sodium borohydride to release hydrogen and sodium borates in aqueous solution. Here, a significant fraction of the hydrogen derives from the water, and the product contains very strong B-O bonds that would require a chemical process to chemically reduce the B-O bonds to B-H bonds and regenerate the borohydride. Millennium Cell’s work was incorporated into the CHSCoE, and is discussed at length in Chapter 1 of this report.

Figure 2. Catalytic hydrolysis of aqueous sodium borohydride (SBH) to generate hydrogen.



It had also been reported that the molecule ammonia borane released hydrogen when heated to form BNH_x polymers. This process was known to be moderately exothermic, and could not be reversed simply with the application of hydrogen pressure. There was no chemical process that had been conceived of to regenerate the spent fuel, completing the cycle.

Figure 3. Thermal decomposition of ammonia borane to release hydrogen and form polymeric polyborazylene.



polyborazylene.

1.3 The partners of the Chemical Hydrogen Storage Center of Excellence

During the period of 2004 to early 2005, LANL and PNNL partnered together to assemble a technical team to respond to the Request for Proposals for the ‘chemical hydride’ Center. The original proposed concept of the Center was to explore the feasibility of a few well-specified

classes of chemical hydrogen storage materials with a near- or medium term prospects for success. Many of the materials that were of interest to us at that time were boron-based compounds, e.g. boranes and borohydrides for reasons that will be explained in more detail below in Section 1.5. A number of innovative concepts ‘beyond boron’ were also developed and tended to be potentially more risky, but with high benefit if the chemistry could be worked out. Materials in this class included activated hydrocarbons, nano-scale main group compounds, metal alkoxides, and polymeric carbenes, among others. With these focus areas, LANL and PNNL engaged additional partners that brought together all of the necessary scientific capabilities to address the key scientific and engineering questions surrounding storage of hydrogen in covalent bonds. As the focus of the proposed Center’s work had a large focus on boron chemistry, partners that could bring boron chemistry and materials expertise were sought. Indeed, in the final analysis, the Center assembled a ‘who’s who’ of boron chemistry in the US as a portion of the proposal team. This included prominent boron chemists from academia and companies that had business interests and technical experience in boron chemistry and boron process chemistry, as well as experts in boron chemistry at the two national laboratories.

The proposal and eventual Center partners (and principals) and the capabilities they brought were:

1. Los Alamos National Laboratory: Molecular synthesis, inorganic and organometallic chemistry, kinetics and mechanism, boron chemistry, chemical characterization, gas-solid reaction characterization, homogeneous and heterogeneous catalysis.
2. Pacific Northwest National Laboratory: Chemical engineering, theory and modeling, nuclear magnetic resonance characterization, materials synthesis and characterization, catalysis, kinetics and mechanism.
3. Millennium Cell, Inc.: Sodium borohydride hydrolysis systems and experience, chemical and mechanical engineering (discontinued in FY2008).
4. Northern Arizona University (Prof. C. Lane, deceased May 2007): Chemical synthesis, chemical safety, chemical process experience.
5. Rohm and Haas (now Dow): Chemical process engineering and assessment, chemical synthesis, borohydride process chemistry.
6. University of Alabama (Prof.s D.A. Dixon, A. J. Arduengo): Theory and modeling, organic synthesis and characterization
7. University of California, Davis (Prof.s S. M. Kauzlarich and P.P. Power): Main group organometallic and solid state chemistry and characterization, nano-phase chemistry and characterization
8. University of California, Los Angeles (now University of Missouri) (Prof. F. Hawthorne): Boron chemistry, organometallic chemistry.

9. University of Oregon (Prof. Liu): Organic synthesis and characterization of cyclo-CBN compounds (added as partner in September, 2008)
10. Pennsylvania State University (Prof. D. McDonald): Electrochemistry and electrochemical synthesis.
11. University of Pennsylvania (Prof. L. Sneddon): Boron chemistry, kinetics and mechanism of organometallic and inorganic reactions.
12. University of Washington (Prof.s K. Goldberg, M. Heinekey): Organometallic chemistry and catalysis, molecular synthesis.
13. US Borax Corporation: Boron chemistry, boron process chemistry, borate mining and resource assessment (informal participant of Center, added as a funded partner in October, 2009).
14. Intematix Corporation: Rapid throughput screening of chemical processes, catalyst library design and synthesis (discontinued in FY2008).

After successfully competing for the CHSCoE and the final negotiation of work scope with DOE, the Center began its work in March 2005.

1.4 Overview of the principles to the Center's research

The CHSCoE formally kicked off its activities in March 2005. The Center's work initially focused on chemical hydrogen storage in a three-tiered approach to storage materials development that is described in Section 1.6. How we developed this strategy is described in the following paragraphs and Sections.

To determine the promise of a hydrogen storage material, the Center's approach was to synthesize storage materials, characterize the materials both chemically and physically, and determine parameters relevant to their use as hydrogen storage media. A partial list of materials parameters that are required of a potentially interesting storage material include high hydrogen capacity, adequate kinetics and thermodynamics of hydrogen release, impurities (i.e. characterization of the products of release in the gas phase and the solid state), shelf life and thermal stability of the storage material, and regenerability of the 'spent fuel' resulting from the dehydrogenation of the storage material. A subset of the DOE technical targets for hydrogen storage that were in place in 2005 is shown below in Table 1.4.1. In addition to the many materials-related parameters, system related parameters such as cost of the production of the fuel (i.e., the 'first fill'), the cost of regeneration of the fuel, and the overall energy efficiency of the storage cycle from fuel to spent fuel and regeneration back to fuel were also crucial to consider when determining if a particular storage concept was of potential interest to down select for further study. As the research in the three materials Centers evolved, a few of the DOE technical targets for hydrogen storage also evolved, particularly in the volumetric and gravimetric capacity targets. These updated targets are indicated in Table 1.4.1.

1.4.1 Guiding principles and technical targets of the CHSCoE

A key goal of the DOE Office of Fuel Cell Technologies has been to develop a viable onboard hydrogen storage system that enables hydrogen powered vehicles a range of 300+ miles between refueling without compromising performance or space. There are a number of considerations that need to be addressed to achieve DOE's goal. The overall system weight and volume are of particular importance. Since gravimetric and volumetric hydrogen capacities are key contributors to the overall system mass and volume, they have been the primary drivers of our research. Our Center also considered kinetics of H₂ release *not a target, but a requirement fundamental to viable system operation*. Therefore we have focused considerable attention on the measurement of the rates of hydrogen release within temperature ranges of likely vehicle operation; our Center did not work on any material that did not have the potential to release hydrogen with rates approaching the H₂ flow rate target at temperatures below 150 °C, preferably not above 120 °C (caveat – an exception would be given for a material discovered that could be on board rechargeable with H₂). At the same time, it is imperative that the material not release hydrogen under normal ambient conditions (<50 °C) the vehicle will experience during normal operation or while parked; therefore, fuel stability is another challenge we addressed by experimental measurements of stability from hours to days at 50 °C. The next major consideration is how to recharge or regenerate the spent fuel once hydrogen has been released. There must be a chemically and energetically efficient method for regeneration of the spent fuel (a topic that is so important that we address it in a separate section of this report). Since off boarding spent fuel and fuel loading are impacted by the fuel form, the physical form of the fuel (fresh and spent) is a parameter of note. The fuel must be durable enough to the refueling and off boarding as well as normal automotive operations. Finally, the fuel cost is very important. Should the fuel be too expensive, no matter how good it is, it will not be acceptable to consumers. Thus, our Center expended significant effort at developing both efficient 'first fill' syntheses of chemical hydrogen storage fuels, regeneration schemes for spent fuels, proving these processes in the laboratory, and working with our industrial partner to develop preliminary regeneration and first fill cost estimates.

What our Center considered to be the key technological barriers and DOE targets for On-Board Hydrogen Storage are described below and are tabulated in

Table 1.4.1. In addition the regeneration of spent fuel or refueling efficiency must be taken into account. DOE set efficiency goals for on board reversible storage systems and off board regenerable systems. For systems generated 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 during regeneration. This efficiency is defined as the onboard efficiency of 90 percent multiplied by the "well-to-tank" efficiency of regenerating the chemical hydrogen storage material. The target total efficiency to the power plant for off-board regenerable systems is 60 percent.¹ Thus, for systems regenerated *off-board*, the energy efficiency target includes an allowance of only 40% of the total energy in the fuel for the energetic 'expense' of regeneration.

All of the technical targets including those discussed above are found in the DOE's Multiyear Program Plan (MYPP) for hydrogen storage. The MYPP also includes a list of technical barriers that must be overcome to provide viable on board hydrogen storage systems. This Center's work addressed the following barriers for hydrogen storage (the letters refer to barriers described in the MYPP):

- | | |
|---------------------------------------|----------------------------|
| (A) System Weight & Volume | (B) System Cost |
| (C) Efficiency | (D) Durability/Operability |
| (E) Charging & Discharging Rates | (J) Thermal Management |
| (K) System Life-Cycle Assessments | (R) Regeneration Processes |
| (S) By-Product/Spent Material Removal | |

Table 1.4.1 Summary of Selected Material Related Targets from 2007 with Feb. 2009 Updates

Storage Parameter	Units	2007	2010	2017	Ultimate
System Gravimetric Capacity	Wt.% H ₂ (updated)	4.5 (--)	6 (4.5)	9 (5.5)	(7.5)
System Volumetric Capacity	g H ₂ /cc (updated)	0.036 (--)	0.045 (0.028)	0.081 (.040)	(.070)
Operability (Operating ambient T)	°C	-20/50	-30/50	-40/60	-40/60
Operability (Min/max delivery T)	°C	-30/85	-40/85	-40/85	-40/85
Discharge Rate (min full flow rate)	g H ₂ /sec/kW	0.02	0.02	0.02	0.02
Hydrogen Purity	% H ₂	99.99	99.99	99.99	99.99
Storage System Cost (& fuel cost)	\$/kWh net	6	4	2	TBD
	(\$/kg H ₂) \$/gge @ pump	(200) ----	(133) 2-3	(67) 2-3	2-3

1.5 Motivation of the Center's choice of classes of compounds for study

In the lifetime of the Center from 2005 – 2010, the CHSCoE explored, discovered or developed a rather vast expanse of chemical hydrogen storage landscape where the proper choice of molecular properties or processes was shown to lead to facile release of hydrogen from covalent bonds in molecules. Nearly all of the compounds we eventually focused on were borane amines, and all contained B-H bonds. Why is this? This is a result of several boundary conditions driven by the gravimetric and volumetric targets that require that much of the molecular mass of a storage material must be hydrogen, restricting the search for high gravimetric capacities to elements of low atomic number such as B, N, C, etc.. Boron hydrides, and *especially boron amine compounds are quite unique compared to any other class of compounds, as more than 2 atoms of hydrogen per B atom may be readily released*, and in principle, hydrogen weight

fractions of up to 20% could be realized. In the series of analogous, isoelectronic carbon-carbon bonded systems (hydrocarbons), only one hydrogen can be released per carbon atom (without going to extremes of temperature). This limits hydrocarbons to releasing at most 1H/CH₂ unit, or a weight fraction of at most 1/14 or 7% wt. % hydrogen. Ammonia borane, on the other hand, can release up to 3 moles of hydrogen, or a weight fraction of about 6/31 or around 20 wt. % hydrogen (in practice, this would generate the rather stable ceramic BN, and it is doubtful this material could be readily regenerated). It is well demonstrated now, however, that ammonia borane can readily release 2.0 – 2.5 moles of hydrogen, or 13-16 wt. % hydrogen depending on the conditions chosen for release, and generate regenerable BNH_x polymeric spent fuel. In another remarkable achievement, researchers at PNNL found that the ‘unstable’ compound ammonium borohydride can be stabilized and handled. This compound releases an additional mole of hydrogen compared to ammonia borane, and so ammonium borohydride is able to release up to 3.5 moles of hydrogen, or a weight fraction of about 7/33 = 21 wt %! As we will discuss in this report, if ammonium borohydride could be stabilized further, it would represent a potentially very high capacity hydrogen storage material. These are just a few examples of why the Center initially focused on and continued to work on these B-N-H compounds and why the B-N-H compounds are superior as a storage media to many other analogous chemical hydrogen storage systems such as the hydrocarbons.

While the release properties of the B-N-H compounds were known to be of interest, the regeneration of spent fuel was an open question. For vehicular applications on a world scale, it is required that a storage material be efficiently and cost-effectively regenerated to minimize total energy expended, and to recycle *all* of the spent fuel back to active fuel. Certain metal hydrides have been demonstrated to be on board rechargeable with hydrogen, and some covalent chemical hydrogen storage materials may be regenerated directly with hydrogen (which can in principle be done on board the vehicle but has not been demonstrated). However, many chemical hydrogen storage materials, particularly those that release hydrogen very exothermically, are not able to be recharged directly with hydrogen, and must be chemically reprocessed off board. As this report will detail in subsequent chapters, as it became apparent that ammonia borane had interesting release properties, it also became necessary to demonstrate that regeneration is chemically possible in an energetically acceptable process. If the feasibility of chemical regeneration of spent fuel was not proven, it was obvious that the amine boranes would not survive any down select decision, and the Center would move on to other more promising materials. This report outlines the significant expenditure of resources on exploring and then demonstrating the regeneration of spent fuel from ammonia borane.

In the formative stage of the Center, Center researchers recognized that the nature of any regeneration route would depend strongly on the thermodynamics of the release process. For example, in the case of the endothermic dehydrogenation of hydrocarbons, such as the conversion of methylcyclohexane to toluene and hydrogen, the regeneration is performed by reversing the reaction by the well-known and industrially practiced exothermic catalytic rehydrogenation of cyclic aromatic hydrocarbons to yield hydrogen saturated cyclic compounds. For exothermic release systems, particularly strongly exothermic systems like ammonia borane,

the simple reverse rehydrogenation is far too endothermic, and not even extreme hydrogen pressure can force the direct regeneration of spent fuel in a practical sense. Instead, it was understood that regeneration of spent fuel from ammonia borane would require a potentially chemically complex regeneration scheme to replace the B-H bonds while maintaining the B-N bond, avoiding loss of ammonia from the system, and avoiding the formation of diborane and subsequent loss of B from the system. Thus the Center was motivated to develop wholly new chemistries and for the first time attempt to demonstrate the resynthesis of a storage material such as ammonia borane from its dehydrogenation product. Without such concepts in place, it was felt that there was no path forward for the general class of off board regenerable hydrogen storage materials.

1.6 Organization of the Center's research and its evolution

As discussed above, the Center began with three tiers of materials research ranging from an assessment of current technology, to a mid-term assessment of a variety of non-hydrolytic borane chemistry, to higher risk approaches that were 'beyond boron'. These three tiers are described in the following subsections. As the Center matured, and successfully passed through several down selection or go/no go processes, the organization of the Center evolved from the three-tiered materials-centric organization to an organization focused on the Center's chosen down selected materials. The Center organization then focused on two major tasks, those being 1). hydrogen release properties (capacity, kinetics of release, impurities, thermochemistry), and 2). the regeneration of spent fuel from ammonia borane.

1.6.1 Tier 1. SBH hydrolysis and regeneration of B-O to B-H

We began investigating the hydrolysis of sodium borohydride and the regeneration of the product borates back to borohydride in Tier 1. This work involved Millennium Cell. Their work was to engineer the SBH and build a prototype hydrogen storage system based upon SBH hydrolysis. In addition, processes for the energy and cost efficient regeneration for the spent sodium borate back to SBH were assessed. This research area was focused on achieving progress in advance of a DOE Go/No Go decision process in Fall 2007. As will be discussed in greater detail in Chapter 1, the SBH Go/No Go process resulted in terminating hydrolysis of SBH as well as polyhedral boranes and amine boranes as a viable storage mechanism, and Tier 1 research was ended, and resulted in the discontinuation of Millennium Cell's research as part of the Center. As the work on conversion of sodium borate to SBH was needed as part of the Center's 'first fill' strategy for synthesis of key boron hydride intermediates, this aspect of the Center's research was continued.

1.6.2 Tier 2. Alternative Boron Chemistry for Hydrogen Storage

In Tier 2, research was performed that was focused mainly on non-hydrolytic pathways to hydrogen release. The Center recognized early on that regeneration of the very stable B-O bonds

of borates from hydrolysis of borohydrides was going to be energy intensive and difficult, and so we explored non-hydrolytic approaches to release hydrogen from amine boranes and polyhedral boranes and other similar B-N compounds. Some hydrolysis work on polyhedral boranes was carried out in the task and this was ended with the SBH No Go. The primary focus of this Tier was the class of compounds that can release hydrogen to form BNH_x polymeric spent fuels that are less thermodynamically stable than the borates that result from hydrolysis. Thus it was felt that these BNH_x polymers had a more likely chance of being able to meet the energy efficiency and chemical efficiency targets set forth for spent fuel regeneration. This area evolved into the major focus area of the Center's research.

1.6.3 Tier 3. Advanced concepts for hydrogen storage in covalent compounds

In Tier 3, we explored higher risk approaches such as the coupling of exothermic and endothermic processes to hydrogen release in compounds such as the metal alkoxides, the dehydrogenation of activated hydrocarbons, as well as the release of hydrogen from hydrogenated nanoparticles of main group elements such as Si. This Tier was also informally referred to as 'beyond boron', where we planned to explore hydrogen release from C-H and Si-H bonded covalent materials, among others. As the Center matured, most of these advanced concepts did not show enough promise, and were not down selected for additional study. At the conclusion of the Center, two classes of materials remained, one being the metal amidoboranes (the focus of an International Partnership for Hydrogen in the Economy (IPHE) collaboration and a few Center partners), and the other being the so-called cyclo CBNs. These are both discussed in detail in Chapter 1, and both materials classes continue to show promise.

As the Center's work evolved and as a result of a major Center down select process and milestone in late 2007, it became apparent that the Center's research had coalesced into two major areas of 1). Hydrogen release from B-N-H compounds and 2). Chemical regeneration of spent fuel from ammonia borane. Each of these major areas continued to be informed by theory and modeling and guidance from internal and external engineering assessments of materials and processes. These two large organizational units remained with the Center to its conclusion in 2010.

1.7 The general approach of the Center to performing hydrogen storage research

The general approach of the CHSCoE was to combine experimental, computational chemistry, and engineering expertise from all of the Center partners to develop viable storage materials and processes. Even before the Center was operating, the nascent Center had in place a robust intellectual property (IP) agreement ready to promote free and open discussions among the Center partners. This enabled communication to brainstorm on new ideas, solve problems, share samples and data, and to provide for a path to generating a 'patent estate' for Chemical Hydrogen Storage materials. The Center maintained an excellent chemical synthesis capability, particularly in the area of boron chemistry that enabled the ready manipulation of a variety of

boron compounds and derivatives, but also in solid state and solution chemistry of other main group elements. The Center often utilized mechanistic understanding of hydrogen release from chemical hydrogen storage materials to guide our efforts in developing improved materials, additives, and catalysts. The Center also maintained a distributed engineering capability to provide assessments of materials in a systems context, and engaged the industrial partners early and often to provide engineering assessments of chemical processes, particularly for estimating regeneration and ‘first fill’ materials costs. These assessments provided crucial guidance to the chemists and materials experts in our search for improved regeneration pathways and processes.

The Center also capitalized on the broad spectrum of additional expertise that the partners brought to the Center in theory and modeling, manufacturing, borate minerals processing and boron chemical speciation, chemical characterization, gas speciation and quantification, catalyst design and discovery, electrochemistry, structure and bonding, chemical kinetics and mechanisms, and safety analysis. Certainly all of these contributions were important. Of particular importance was the theory and modeling capability that helped to guide much of the experimental research the Center accomplished. The Center used computational chemistry approaches to predict the thermodynamic properties of a wide range of compounds containing boron, nitrogen, hydrogen, and other elements as appropriate including carbon. These calculations were done in most cases with high-level molecular orbital theory methods that have small error bars on the order of ± 1 to 2 kcal/mol. The results were used to benchmark more approximate methods such as density functional theory for larger systems and for database development. We predicted reliable thermodynamics for thousands of compounds for release and regeneration schemes to aid/guide materials design and process design and simulation. In many cases the values predicted for several critical classes of materials are the first reliable computed values for these compounds and for many represent the only available values as experimental data for many compounds we worked with was simply unavailable.

Even with this tremendous capabilities within the Center, if the capabilities couldn’t communicate among themselves, they were valueless. The communication plan for the Center, which had as it’s hub the robust multilateral intellectual property agreement that encompassed all partners, was critical in ensuring that the geographically dispersed partners all knew what the research goals of the Center were, and what each partner’s tasks were. This was communicated in a variety of face-to-face meetings, brain storming meetings, topical conference calls among sub-team members coordinated through single points of contact that informed the Center Director, and peer-to-peer phone calls and emails. Students at the academic institutions were able to spend time at PNNL performing research and accessing unique characterization tools and facilities that accelerated information exchange and experimental progress.

As the Center matured beyond it’s formative period, a “fail fast” culture was developed to down select to the most promising materials quickly, leaving behind materials where we felt there was no viable path forward to a storage system, and refocusing the Center’s resources on the most promising materials. The Center’s computational capability provided substantial guidance in rapidly responding to experimentalists needs to quickly make informed experimental choices.

The theory and modeling capability was largely provided by the University of Alabama, and to a lesser extent PNNL. The computational chemists used highly accurate and validated first principles computational chemistry approaches on advanced computer architectures to predict the electronic structure of molecules to obtain thermodynamics and reaction pathway information as well as to predict materials physical properties in support of the design of hydrogen storage materials and regeneration processes. Trends in reactivity or in complex equilibria were often rapidly assessed by computation, which informed the experimentalists choice of chemistries to probe first, or to help explain complex experimental results. Computational approaches were benchmarked when necessary against known chemical and physical properties. In the end, the Center's successful partnerships between experimentalists and theorists demonstrated time and again the value of theory in helping to make rapid experimental progress.

1.8 Major technical accomplishments of the Center

In this section are listed high-level outcomes of the Center that allowed the Center to move ahead efficiently throughout its lifetime. Positive outcomes that led to down selections for continued study, as well as no go decisions and major findings that de-selected systems for further study and that also taught significant lessons are captured here. More detailed accomplishments are found in the following Chapters, and in the individual partner's final reports.

A most significant accomplishment of the Center was to demonstrate, multiple times over, that chemical reprocessing of spent fuel is feasible. At the start of the Center in 2005, the storage community at large felt that the completely undeveloped notion of spent fuel regeneration represented a daunting and significant technical barrier to the acceptance of the concept of off board regenerable storage materials. Lacking a demonstration of feasibility, it is unlikely that such off board regenerable systems would ever find acceptance. Five years ago, Center researchers had only the very vaguest of notions as to how to proceed to regenerate BNHx spent fuel. Because of this, the Center dedicated a significant amount of research effort, transferring significant effort from the materials discovery tasks to the regeneration effort during years 2-5. This decision accelerated the Center forward in filling in our knowledge gaps in regeneration chemistry, and led to our eventually successfully demonstrating the regeneration of spent fuel from ammonia borane. The early concepts of 'bootstrapping' the reformation of B-H and B-N bonds using chemical methods to add H^+ and H^- in stepwise fashion to BNHx were proven, and subsequently improved upon multiple times over. Five years hence, after the input of a great deal of creativity from both experimentalists and theorists, the Center demonstrated multiple pathways to ammonia borane regeneration, and have provided preliminary cost and efficiency estimates for two of these pathways. These accomplishments are described in detail in Chapter 2. Along the way, we have learned a great deal about what the key features of a successful off board chemical regeneration scheme must be. We believe that after 5 years of research into off board regeneration processes, the Center has demonstrated that if presented with a spent fuel, it is feasible to conceptualize and demonstrate in the laboratory efficient regeneration schemes, and

off board regeneration is in principle no longer the major technical barrier for acceptance of the concept of off board regeneration.

In the area of hydrogen release, a major accomplishment of the Center has been to show that the exothermic nature of amine borane compounds and derivatives can release hydrogen at high rates at temperatures as low as room temperature. The Center developed catalysts and additives that further increase the rate of release and decrease the release temperatures. These accomplishments enable a variety of possible approaches to engineered release systems that the Hydrogen Storage Engineering Center is currently studying and analyzing to determine which has the greatest potential for further system development.

In addition to these major areas of accomplishment, the Center made significant advances to the field of hydrogen storage by either discovering and developing new storage materials and processes, or in defining materials and processes that are unlikely to achieve the technical targets for hydrogen storage systems. These accomplishments are listed below:

1. An early no go decision on SBH hydrolysis system and the termination of all related hydrolysis routes and set the Center on the path to focus on amine boranes, which in the long term was fruitful.
2. Early on, the Center developed an engineering-guided approach to materials development and down selection. This enabled the Center to move quickly to successes, and discard scientifically interesting but technically flawed storage materials in an efficient and rational manner. This approach is evident in each of the following accomplishments.
3. The Center demonstrated time and again that progress in hydrogen storage materials research was accelerated by the deliberate and judicious use of theory to make predictions of chemical reaction outcomes, or to aid in the interpretation of experiments. The utilization of high-level computational chemistry is evident in each of the following accomplishments.
4. Demonstration that ammonia borane releases 2-2.5 moles of hydrogen, equivalent to 13-16 wt. % hydrogen at temperatures below 200 °C. This was, and still is the lowest temperature, highest capacity release material that has adequate shelf life stability (ammonium borohydride has a higher capacity, but as a solid, is quite thermally unstable).
5. Understanding of influence of additives on nucleation and growth kinetics of ammonia borane (AB) dehydrogenation that led to discovery of additives that mitigated the foaming of neat solid AB, a critical observation for any future solid ammonia borane fuel composite.

6. Impregnation of mesoporous scaffolds with ammonia borane were observed to alter the temperature of hydrogen release onset of the composite underscoring importance of surfaces and length scales on reaction chemistry of AB
7. Homogeneous acids, and subsequently metal complexes were demonstrated to catalyze the release of hydrogen from AB. Certain catalysts were found to release one mole of hydrogen (6 wt. %) rapidly at room temperature. This work inspired our Center's research into gaining additional understanding of the mechanism of the catalysis of hydrogen release from AB that informs present and future catalyst design efforts.
8. Preliminary observations of 'digestion' of spent fuel in acids (HX) to produce processable BX_3 and subsequent reduction of BX_3 with aluminum and silicon hydrides to yield amine boranes provided early proof-of-principle for the digestion – reduction regeneration scheme for BNH_x spent fuel derived from dehydrogenation of AB.
9. Addition of lithium amide or –hydride to AB decreased the temperature of hydrogen release from AB mixtures, and altered the overall release-temperature profile and nature of the spent fuel. This was an early 'hint' to the existence of metal amidoboranes that eventually became a significant research interest of the Center.
10. Ionic liquids, and addition of hindered bases to AB substantially altered the rates and extent of AB dehydrogenation. Two moles of hydrogen are lost below 110 °C when AB is heated in an ionic liquid. Subsequently, metal catalysis was observed to be effective in ionic liquids at lower temperatures. These observations led to the Center's interest in developing liquid fuels from ionic liquid/AB mixtures. This was a key observation for the Center, as enabling liquid fuel formulations may contribute significantly to achieving an engineered hydrogen storage system based on AB.
11. Development of a systematic decision tree process for down selection of materials within the Center. This focused subsequent materials discovery and development efforts, and focused the Center's attention on only the most promising materials having materials having >7 wt. % hydrogen, preferably > 9 wt. % hydrogen. This framework for decision-making enabled the Center to move rapidly towards the most promising materials, and thus deserves mention as a significant accomplishment of the Center.
12. The demonstration of a complete regeneration cycle using thiocatechol as the digesting agent and a tin hydride as the reducing agent was a key accomplishment of the Center. This led to the eventual optimization of this regeneration chemistry that was the subject of the first preliminary off board chemical regeneration cost assessment. This resulted in an estimate cost of \$7-8/kg H_2 , a significantly promising result. Lessons learned from this analysis drove further improvements and discoveries of regeneration chemistries. One crucial lesson learned from this exercise was that the most thermodynamically efficient process might not be the least costly. Thermodynamic efficiencies that come at the cost

of equilibrium-controlled processes can result in significant separations costs, and significant capital equipment expenditures.

13. The Center demonstrated higher yielding syntheses of SBH and AB with higher purities, and performed preliminary cost analyses indicating that potentially lower costs could be achieved for these two crucial intermediates. This was significant for both our Center and the MHCoe, as the cost of boron starting materials currently dominates the ‘first fill’ cost.
14. Center researchers discovered and characterized a wide variety of metal amidoboranes; these were synthesized for a variety of metals using both solid state and solution state techniques. Trends in hydrogen release as a function of metal cation lead to a search for thermoneutral release compounds. Metal amidoboranes were subsequently observed to emit substantially lower quantities of borazine into the product gas, although ammonia is still detected in most cases as a gas phase impurity that must be mitigated.
15. The Center completed a preliminary assessment of the world borax reserves indicating that DOE commercialization targets for U.S. hydrogen vehicles can be accommodated using U.S. supplies of borax for boron-based fuels without displacing existing boron markets.
16. The Center demonstrated that AB in liquids could be dehydrogenated with a base metal heterogeneous catalyst. This observation enables a flow reactor configuration for future AB liquid fuels. Heterogeneously catalyzed AB dehydrogenation was subsequently observed to result in reduced quantities of gas-phase impurities relative to the uncatalyzed reaction.
17. Based on earlier experience and lessons learned, the Center developed a chemically simple, one-pot regeneration of spent fuel for AB. A cost assessment of this process suggests that significant savings can be gained in process and capital costs when reducing the number of unit operations, and provided an additional significant lessons-learned for future regeneration efforts.
18. The University of Northern Arizona compiled an early report on the safety of borane compounds as fuels. This helped guide Center’s partners safety planning for the safe handling of borane materials.

1.9 Lessons learned from the ‘Center concept’

During the 5-year tenure, the Center and its research and development work was the subject of DOE annual merit reviews, and annual technical team reviews by FreedomCAR and Fuel Partnership representatives (the ‘storage tech team’). Consensus of these reviews either in written or in verbal comments was that our Center moved science and technology of chemical

hydrogen storage forward at a rate far faster and an extent farther than what was anticipated at the beginning of the Center of Excellence ‘experiment’. Clearly, the Center made greater advances than what could have been possible if all the partners had worked, but worked apart. There are a multitude of plausible reasons as to why the Center succeeded. A few of the most important are discussed in the following sections.

1.9.1 The Center success was derived from quality communication and intellectual property management plans

The ease, frequency, and quality of communication among the partners at all stages of the project are the main root causes of the progress that was made. In an area where it was clear that inventions were going to occur, it was also necessary to put into place an intellectual property (IP) management plan that enabled all of the partner’s background and developing IP to be protected, and to be shared with other partners in a timely fashion. Indeed, the Center generated a substantial amount of IP, and the patents and patent applications are described in Table 1.9 at the end of this section.

The high quality of communication among the partners was made possible by having an effective intellectual property management plan in place at the very onset of the Center’s activities which removed the usual barriers encountered among collaborating scientists, engineers, and technologists, where ownership of ideas problems arise that discourage open discussion of ideas and results in a timely manner. This formal structure allowed for trust to develop among the partners, and once trust established, open communication was enjoyed across the Center. Up to the minute results could be discussed, problems brainstormed, and potential solutions plotted within this framework of open and trusted communication among peers.

An important component of our effective communication was with DOE program management. Frequent and detailed communication between the Center’s Director and DOE allowed for consistent communication of program goals to flow to and from partners in an efficient manner. The Center concept allowed DOE to typically have but one conversation, and that was with the Center Director and occasionally members of the Center’s coordinating council.

1.9.2 The Center built the right team having the right capabilities

While the quality of communication was key to our success, clearly building the ‘right’ team was crucial. All the best communication tools in the world won’t make up for deficiencies in team capabilities and experience. The Center’s success also hinged upon putting the right team together of the nation’s best boron chemists coupled with expert experience in the experimental study, engineering, and theory and modeling of reacting chemical systems. The Center concept allowed any major technical gaps to be filled by recruitment of the partners having the best capabilities match for the R&D to be performed. This is most apparent when our Center was compared against single principal investigator (PI) projects. The ability for any Center member to access any of the equipment at any of the Center institutional partners, or to access the

intellectual capability or experience of any of the Center researchers, enabled every partner to progress in ways that are not possible in individual PI-based projects.

An important feature of our Center was that we coupled excellent academic scientists and industrial researchers with experienced national laboratory researchers accustomed to working in a milestone and deliverables-driven R&D environment that encompasses most if not all of DOE EERE-funded research. Where many academicians are unaccustomed to working in this type of program environment, the national lab partners worked well with positioning the scientific and technical capabilities of the academic partners within the proper context to take maximal advantage of the teams overall scientific capability, and to ensure that milestones were addressed, deliverable met, and program direction was consistent with program needs, and that the program momentum remained high and program focus remained sharp.

1.9.3 The Center concept promotes collaboration and a drive to accomplish

An aspect of the Center concept that is somewhat harder to capture and define is that when a talented set of R&D scientists and engineers gather to work on a problem, camaraderie develops, and the team's desire to solve the problem at hand grows. Perhaps it is also because of some friendly competition as well, but the Center concept clearly galvanized this team to accomplish much more than what it could have had the Center's PI's worked apart.

1.9.4 The Center concept enables near real-time informal peer review

Related to quality of communication is the aspect of informal peer review that goes on in any gathering of scientists and engineers. It is only natural that results are debated, hypotheses are questioned, and problems are brainstormed. All of these occurred during our frequent Center meetings and phone calls. In the process, an informal peer review occurs. Questions are asked, ideas are sharpened, hypotheses changed, conclusions may be abandoned and subsequently reformulated. Without the Center concept in place, independent projects even if working toward a common goal, are unable to achieve this level of trust in communication and concomitant idea flow that the Center concept promotes.

1.9.5 The Center had strong technical leadership with a vision

From its inception, the Center profited by having strong collective technical leadership, and a vision for making scientific and technical progress in the relatively new field of chemical hydrogen storage. The leadership had the technical background necessary to make any changes in technical direction, and the backing of DOE and the Center researchers to make the hard down select decisions that enabled the Center to move forward. As a result, the Center moved ahead rapidly in most areas that were critical to achieving the Center's goals.

The remainder of this report provides a detailed description of the CHSCoE's research and progress in the two main areas: Hydrogen Release (Chapter 1) and Regeneration of Spent Fuel (Chapter 2).

1.9.6 The Center's R&D resulted in new science

When the Center began, there were but few examples of chemical hydrogen storage materials, and fewer examples of regeneration of spent fuels. The Center's researchers often had to uncover fundamental chemistries of the materials that were focused upon. In exploring how to increase the rates and decrease the temperature of hydrogen release from ammonia borane, much mechanistic work had to be done to understand a few of the details in the molecular pathways involved in hydrogen evolution, and how those details influenced the eventual products (e.g. spent fuel) of dehydrogenation. As examples, Professor Sneddon's group at the University of Pennsylvania explored the use of ionic liquids and non-nucleophilic bases to accelerate the rate of release of hydrogen from ammonia borane, AB. They found new pathways that lead to more facile extrusion of hydrogen from in this class of boron-nitrogen compounds. In exploring the catalysis of hydrogen release from AB and other amine borane compounds, researchers at Los Alamos and the University of Washington discovered new catalytic chemistry as they explored the underlying differences among catalysts that led to substantially different rates and product specificity. Using microporous environments or nanoscale particles, researchers at Pacific Northwest and the University of California-Davis found that the chemistry of hydrogen release is controlled by phenomena occurring at small length scales. In the regeneration chemistry of spent fuels from AB, researchers at Los Alamos, Pacific Northwest, Alabama, and Dow Chemical found new, previously unexplored chemical reactivity between chemical reductants and spent fuels on the pathway to complete regeneration. These are but a few examples of new science that resulted from the Center's R&D; additional examples can be found in the subsequent chapters in this final report, and within the references cited at the end of each chapter. Additionally, as some of this new science also represented new intellectual property, the Center partners applied for and received patents on a number of these observations that resulted from their Center-related R&D. Many of these patents are tabulated below, others that are in process may appear in the future.

1.10 Listing of U.S. Patents and Patent Applications Resulting from CHSCoE R&D

1). United States Patent 7,963,116

Autrey, et al. June 21, 2011

Bulk-scaffolded hydrogen storage and releasing materials and methods for preparing and using same

Abstract

Compositions are disclosed for storing and releasing hydrogen and methods for preparing and using same. These hydrogen storage and releasing materials exhibit fast release rates at low release temperatures without unwanted side reactions, thus preserving desired levels of purity and enabling applications in combustion and fuel cell applications.

Executive Summary

2). United States Patent 7,897,129

Autrey, et al. March 1, 2011

Process for synthesis of ammonia borane for bulk hydrogen storage

Abstract

The present invention discloses new methods for synthesizing ammonia borane (NH₃BH₃, or AB). Ammonium borohydride (NH₄BH₄) is formed from the reaction of borohydride salts and ammonium salts in liquid ammonia. Ammonium borohydride is decomposed in an ether-based solvent that yields AB at a near quantitative yield. The AB product shows promise as a chemical hydrogen storage material for fuel cell powered applications.

3). United States Patent 7,316,788

Autrey, et al. January 8, 2008

Materials for storage and release of hydrogen and methods for preparing and using same

Abstract

The invention relates to materials for storing and releasing hydrogen and methods for preparing and using same. The materials exhibit fast release rates at low release temperatures and are suitable as fuel and/or hydrogen sources for a variety of applications such as automobile engines.

4). United States Patent 7,439,369

Thorn, et al. October 21, 2008

Method and system for hydrogen evolution and storage

Abstract

A method and system for storing and evolving hydrogen employ chemical compounds that can be hydrogenated to store hydrogen and dehydrogenated to evolve hydrogen. A catalyst lowers the energy required for storing and evolving hydrogen. The method and system can provide hydrogen for devices that consume hydrogen as fuel.

5). United States Patent 7,544,837

Blacquiere, et al. June 9, 2009

Base metal dehydrogenation of amine-boranes

Abstract

A method of dehydrogenating an amine-borane having the formula R₁H₂N--BH₂R₂ using base metal catalyst. The method generates hydrogen and produces at least one of a [R₁HN--BHR₂]_m oligomer and a [R₁N--BR₂]_n oligomer. The method of dehydrogenating amine-boranes may be used to generate H₂ for portable power sources, such as, but not limited to, fuel cells.

6). United States Patent 7,645,902

Stephens, et al. January 12, 2010

Acid-catalyzed dehydrogenation of amine-boranes

Abstract

A method of dehydrogenating an amine-borane using an acid-catalyzed reaction. The method generates hydrogen and produces a solid polymeric [R₁R₂B--NR₃R₄]_n product. The method of dehydrogenating amine-boranes may be used to generate H₂ for portable power sources.

7). United States Patent 7,713,506

Burrell et al. May 11, 2010

Metal aminoboranes

Abstract

Metal aminoboranes of the formula M(NH₂BH₃)_n have been synthesized. Metal aminoboranes are hydrogen storage materials. Metal aminoboranes are also precursors for synthesizing other metal aminoboranes. Metal aminoboranes can be dehydrogenated to form hydrogen and a reaction product. The reaction product can react with hydrogen to form a hydrogen storage material. Metal aminoboranes can be included in a kit.

8). United States Patent 7,736,531

Thorn, et al. June 15, 2010

Composition and method for storing and releasing hydrogen

Abstract

Executive Summary

A chemical system for storing and releasing hydrogen utilizes an endothermic reaction that releases hydrogen coupled to an exothermic reaction to drive the process thermodynamically, or an exothermic reaction that releases hydrogen coupled to an endothermic reaction.

9). United States Patent 7,837,852

Thorn, et al. November 23, 2010

Energy efficient synthesis of boranes

Abstract

The reaction of halo-boron compounds (B--X compounds, compounds having one or more boron-halogen bonds) with silanes provides boranes (B--H compounds, compounds having one or more B--H bonds) and halosilanes. Inorganic hydrides, such as surface-bound silane hydrides (Si--H) react with B--X compounds to form B--H compounds and surface-bound halosilanes. The surface bound halosilanes are converted back to surface-bound silanes electrochemically. Halo-boron compounds react with stannanes (tin compounds having a Sn--H bond) to form boranes and halostannanes (tin compounds having a Sn--X bond). The halostannanes are converted back to stannanes electrochemically or by the thermolysis of Sn-formate compounds. When the halo-boron compound is BCl₃, the B--H compound is B₂H₆, and where the reducing potential is provided electrochemically or by the thermolysis of formate.

10). United States Patent 7,846,410

Davis, et al. December 7, 2010

Regeneration of polyborazylene

Abstract

Method of producing ammonia borane, comprising providing polyborazylene; digesting the polyborazylene with a dithiol-containing agent to produce a boro-sulfide compound and a byproduct; converting the byproduct to the boro-sulfide product of step (b) by reaction with a first alkyl-tin hydride; and, converting the boro-sulfide compound produced in steps (b) and (c) to ammonia borane by reaction with a second alkyl-tin hydride.

11). United States Patent Application 20090274613

Hamilton; Charles W. ; et al. November 5, 2009

Hydrogen Production Using Ammonia Borane

Abstract

Hydrogen is produced when ammonia borane reacts with a catalyst complex of the formula L_nM-X wherein M is a base metal such as iron, X is an anionic nitrogen- or phosphorus-based ligand or hydride, and L is a neutral ancillary ligand that is a neutral monodentate or polydentate ligand.

12). United States Patent Application 20080175781

Thorn; David L.; et al. July 24, 2008

Bootstrap synthesis of boranes

Abstract

Metal hydride materials react with BZ₃ compounds in the presence of ligand to form BH₃-L compounds. A compound of the formula HBZ₂ is prepared from a compound of the formula BZ₃ by reacting a first amount of a compound of the formula HBZ₂ with a metal hydride material "MH" and a compound "L" to form a material of the formula BH₃-L, and then reacting the BH₃-L thus formed with a compound of the formula BZ₃ to form HBZ₂ in a second amount greater than the first amount of HBZ₂. Z is selected from alkoxy, aryloxy, amido, arylamido, doubly substituted alkoxy, doubly substituted aryloxy, doubly substituted amido, doubly substituted arylamido, alkoxy-amido, and aryloxy-arylamido. When Z is bidentate, then HBZ₂ has a ring structure. "L" is selected from ethers, aromatic ethers, amines, aromatic amines, heterocyclic nitrogen compounds, sulfides, aromatic sulfides, and heterocyclic sulfur compounds. "L" becomes a ligand in the BH₃-L material.

13). United States Patent Application 20100272622

Sutton; Andrew ; et al. October 28, 2010

REGENERATION OF AMMONIA BORANE FROM POLYBORAZYLENE

Abstract

Method of producing ammonia borane, comprising providing a reagent comprising a dehydrogenated material in a suitable solvent; and combining the reagent with a reducing agent comprising hydrazine, a hydrazine derivative, or combinations thereof, in a reaction which produces a mixture comprising ammonia borane.

14). United States Patent Application 20090302269

Choi; Daiwon ; et al. December 10, 2009

Executive Summary

Process and Composition for Controlling Foaming in Bulk Hydrogen Storage and Releasing Materials

Abstract

New methods and compositions are disclosed that minimize foaming in hydrogen-releasing materials. Foaming can be minimized during release of hydrogen in composites that include structured forms such as wafers and discs. Change tolerances of from 0% to 25% in solid products described show promise for next-generation fuel elements and devices.

15). United States Patent Application 20110021818

Liu; Shih-Yuan ; et al. January 27, 2011

AZABORINE COMPOUNDS AS HYDROGEN STORAGE SUBSTRATES

Abstract

Selected 1,2-azaborine compounds exhibit utility as hydrogen storage substrates, and are useful as components of hydrogen storage devices.

16). United States Patent Application 20110021735

Liu; Shih-Yuan ; et al. January 27, 2011

SUBSTITUTED 1,2-AZABORINE HETEROCYCLES

Abstract

Aromatic heterocycles incorporating boron and nitrogen atoms, in particular, 1,2-azaborine compounds and their use as synthetic intermediates.

1.11 References

¹http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage_explanation.pdf

² U.S. Borax, Final Report, Chemical Hydrogen Storage Center of Excellence, 2010.



**U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy
Fuel Cell Technologies Program**

Hydrogen Sorption Center of Excellence

Executive Report

August 12, 2011

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Introduction and Background

The U.S. Department of Energy (DOE) Hydrogen Sorption Center of Excellence (HSCoE) was formed in 2005 as a 5-year project to develop hydrogen (H₂) storage materials primarily for light-duty vehicle applications. The HSCoE was competitively selectedⁱ and led by the National Renewable Energy Laboratory (NREL), and comprised partners from U.S. national laboratories, universities, and industry.ⁱⁱ The HSCoE concluded operations in September 2010 as per its planned schedule.

Because H₂ has relatively low volumetric energy density compared to typical liquid transportation fuels, the primary focus of the HSCoE was to develop sorbent materials that could be used to meet DOE 2010 and 2015 on-board hydrogen storage system targets. These targets included on-board fuel storage in which the system contains more than ~5.5 percent by weight (wt %) and ~40 grams of hydrogen per liter (g/L). State-of-the-art compressed-gas H₂ systems operate at pressures between 350 and 700 bar at ambient temperature and store 3–4 wt % and less than 25 g/L. In addition, current liquid-hydrogen systems use more than 30% of the energy in the hydrogen for liquefaction and cannot meet the DOE long-term targets for volumetric capacity. Thus, the HSCoE's goal was to develop sorbents that enable systems to operate at temperatures closer to ambient and at nominal pressure (less than 350 bar), to help meet all DOE performance targets simultaneously.

Hydride species often have high binding energies (typically 40–60 kilojoules per mole [kJ/mol]) with the hydrogen, which can result in poor energy efficiencies for reversible storage and may require off-vehicle regeneration of the spent material. By comparison, the hydrogen sorbents investigated by the HSCoE typically rely on non-covalent interactions (for example, typically 5 kJ/mol to ~30 kJ/mol), thus providing a range of advantages compared to hydride and high-pressure physical storage systems for transportation applications. The optimal hydrogen interactions with sorbents could enable fast hydrogen on-vehicle fill and discharge rates, nominal thermal management requirements during fueling, lower pressure requirements for on-board storage and fueling, ease of engineering on the vehicle, and favorable “well-to-fuel cell” energy efficiencies that decrease vehicle and station costs.

In general, sorbents increase hydrogen-storage capacities compared to high-pressure compressed-gas systems at a given pressure and temperature, thus enabling lower pressure to be used to achieve a capacity that's comparable or higher. At sufficiently high pressures where compressed H₂ becomes very dense (typically 250 to 300 bar at ambient temperature), sorbents no longer improve hydrogen-storage capacities. When the HSCoE was established, the main challenge for sorbents revolved around the low binding energies of H₂ with interfaces, and thus the need to use cryogenic temperatures to achieve high capacity. Thus, from the outset, the HSCoE focused on adjusting the binding energies to achieve higher capacity at temperatures closer to ambient. Overall, the main issues for hydrogen storage with sorbents involve achieving required volumetric and gravimetric capacities as well as system cost. These issues are related, because system costs are directly addressed by increased capacities and storage at temperatures closer to ambient and at lower pressures.

Because detailed system analysis, which was outside the scope of the HSCoE, is needed to project actual H₂ storage system capacities, the HSCoE typically reported what is termed “excess” H₂ storage material values. Excess values represent the H₂ actually stored on the sorbent surfaces and thus what the material is contributing to storage in the system/tank. Because sorbents tend to have additional pore and intraparticle volume where H₂ gas also resides, a given material will typically “contain” more (i.e., material “total”) H₂ than the reported material excess value. However, DOE-directed detailed analyses indicate that systems using sorbents will have usable system capacities close to the excess values, and thus these excess values can be used to gauge differences between materials and what an actual system may store.ⁱⁱⁱ Specifically, while the exact details will vary based on the storage pressure, temperature, and storage mechanism, the HSCoE focused on developing sorbents with excess capacities greater than ~6 wt % and 40 g/L, and in reducing system and station costs by limiting storage pressures to less than 200 bar and temperatures to higher than ~77 degrees Kelvin (K) (–200 degrees Celsius, °C), with the ultimate goal of higher than 200 K (–80 °C). Note that material “total” capacities are only normalized to the sorbent weight and are often misleading because they typically translate to far lower system capacities when the weight of the entire system is used.^a

Results

During its 5-year tenure, the HSCoE made substantial progress in developing sorbents that can be used for light-duty vehicle and other applications (see Highlight I). The HSCoE developed high specific surface area sorbents that could be used to construct systems that meet DOE's 2010 system targets (i.e., 4.5 wt % and 28 g/L). Furthermore, the HSCoE identified development paths for designing and synthesizing sorbents with the potential to meet DOE's 2015 and DOE's ultimate full-fleet system targets for light-duty vehicles.^{iv} The HSCoE systematically developed or investigated hundreds of different materials and/or processes, resulting in over 200 peer-reviewed publications, with more than 25% of them involving multiple U.S. and international institutions as co-authors. Based on the huge number of framework (e.g., metal organic frameworks) materials alone, as well as the huge number of potential new materials identified, the exact number of materials developed/studied is impossible to quantify. However, the efforts led by DOE and the HSCoE helped accelerate sorbent development worldwide, as demonstrated by the thousands of papers that have been published in hydrogen sorption during the last few years. In addition to hundreds of conference presentations, proceedings, and published reports, the HSCoE partners submitted and/or received more than 40 patents.

The HSCoE also determined more than a hundred pathways (e.g., synthesis routes) and/or materials that were down-selected as not being applicable to meeting current light-duty vehicle targets. However, some of the down-selected materials and the materials developed for light-duty vehicles may have many other transportation applications and portable or stationary power applications. Many may be useful in today's major high technology applications including carbon capture/CO₂ sequestration, energy storage, batteries, semiconductor electronics, composites, drilling fluids, inks, drug delivery, transparent conductors, photovoltaics, purification, biomass catalysts, fuel cell catalysts, and energy generation.

HSCoE principals identified four main mechanisms for adsorbent hydrogen storage and created specific development plans to solve the associated technical issues. Specific results include:

1. Cryogenic Storage via Physisorption on High Specific Surface Area Materials

For most chemically stable materials or materials with electronic configurations that induce no significant adsorption, the primary adsorption mechanism is physisorption, with typical adsorption enthalpies (i.e., binding energies) of ~5 kJ/mol for H₂/material surface interactions. Regardless of the chemical composition, a physisorption material needs to have a specific surface area (SSA) of more than ~3,000 square meters per gram (m²/g) to meet DOE hydrogen-storage targets^v at temperatures greater than ~77 K. This requirement alone eliminates hundreds of elements and materials that are too heavy (See Highlight I).

In general, storage capacities increase with higher SSAs and bulk densities.² Although these are necessary requirements for high capacity, other factors, including optimized pore sizes (i.e., 0.7 to 1.5 nm) and enhanced binding energies (i.e., >5 kJ/mol) for the entire capacity range, are also important. The HSCoE focused its efforts on improving all of these material properties independently and simultaneously. As summarized in Highlights II and III, this team effort successfully created materials with extremely high SSAs (>5,100 m²/g)³ and excess gravimetric capacities (near 7 wt %) at 77 K and ~50 bar,^{vi} high bulk densities in the range of 0.7 to 1.4 grams per milliliter (g/ml), and in a few cases, materials with both high SSAs and bulk densities. For example, Duke made pyrolyzed polyether ether ketone (PEEK) materials and worked with NREL, Caltech, NIST, and UNC to optimize its pore structures to produce carbon based sorbents with tunable pore sizes that provide excellent gravimetric and volumetric hydrogen storage capacities (See Highlight II).^{vii} This and other synthesis techniques were employed by the HSCoE to develop a number of different high SSA materials.

In addition, TAMU, Michigan, Caltech, NREL, UNC, and NIST developed (via molecular modeling and design) crystalline nanoporous materials based on coordination of multifunctional and multiple binding

^a More details on excess versus total capacities are available in a white paper by request (lin.simpson@nrel.gov).

² The bulk density is calculated based on the actual volume of the lightweight highly porous sorbent powder or pellets.

³ Specific surface areas provided in this report are measured using the Brunauer, Emmett, and Teller (BET) method; S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, 1938, 60, 309.

ligands to well-defined metal centers (See Highlight III). With a vast library of ligand “building blocks” and different coordination chemistries, the HSCoE literally made hundreds of frameworks that were characterized by X-ray diffraction, SSA analysis, and H₂ capacities. The HSCoE was at the forefront of formulating and synthesizing frameworks for hydrogen storage^{viii} and the first to make materials with greater than 3,800 m²/g SSA and 7 wt % excess H₂ storage capacities. Subsequently, frameworks with ~6,500 m²/g and ~8.5 wt % excess H₂ storage have been reported.^{ix} The main issues with these framework materials are the need of cryogenic temperature and the trade-off between very high SSAs that achieve good gravimetric capacities and lower bulk densities (i.e., 0.1 to 0.5 g/ml) that have relatively low volumetric storage capacities (at best, less than ~30 g/L).

Finally, the HSCoE, through detailed investigations of numerous published results to the contrary, concluded that standard physisorption-based dihydrogen adsorption scales with specific surface area, and thus no substantial increase in capacity can be achieved with geometric structures alone. The main issue here is that increases in H₂ binding can be achieved with very small (less than 0.4 nanometer, nm) pores due to multiple wall interactions, but less space is available for hydrogen and thus the capacities actually decrease.

2. Toward Ambient Temperature Storage with Increased and Multiple H₂ Binding

To have higher capacities at temperatures closer to ambient, compared to pure physisorption, enhanced electronic interactions between the sorption material surface and H₂ are required. For example, the empty p-orbitals created by substituting boron (B) for carbon (C) in a C-matrix induces electron donation from the hydrogen molecule to enhance binding energies by a factor of three (i.e., from ~5 to 10–15 kJ/mol)^x and thus increase capacities, especially at operating temperatures above 200 K. Thus, the HSCoE partners developed scalable synthesis methods to form substituted and intercalated materials that demonstrated enhanced H₂-storage properties at higher operating temperatures than 77 K. The predicted enhanced binding achieved by appropriately substituting B in C was measured with a number of different techniques and agreed with the theoretical predictions of 10–15 kJ/mol. However, challenges remain, including optimization of B loading levels with the required bonding coordination (i.e., sp² electronic coordination) and simultaneously obtaining high SSA (See Highlight IV). Several other low molecular weight (i.e., materials with lithium, beryllium, nitrogen, oxygen, fluoride, sodium, magnesium, potassium, and/or sulfur) heterogeneous materials were investigated.^x Boron-substituted carbon was found to be the most promising substituted material.

The HSCoE also championed the use of unsaturated coordinated metal centers to increase H₂ binding energies (predicted values of greater than 20 kJ/mol) and to enable the potential of multiple H₂-molecule binding at a single adsorption metal site. In these materials, the metal atoms interact with a lattice, but are sufficiently configured to have enhanced interactions with H₂ via both forward and back donation of electrons. Zhao et al.’s^{xi} seminal paper in this area was the first to predict unique structures that may have the potential to hold multiple (i.e., 2 or more) H₂ molecules at a specific metal site. This paper, which has been referenced more than 220 times, has opened up an entirely new area of investigation for hydrogen storage. The key findings on this topic since the inception of the HSCoE are that lightweight alkali, alkaline earth, and 3d-transition metals may be configured to enhance binding and have the potential to bind multiple H₂ molecules to a single metal atom. More fundamental experimental work is needed to fully prove these concepts and provide experimental validation for the model predictions. However, the potential is promising: the HSCoE identified materials with improved synthesis pathways with the potential to store 10 wt % and 100 g/L at ambient temperature.^{xii}

3. Ambient Temperature Storage via Weak Chemisorption/Spillover

In general, chemical covalent bonding between hydrogen and carbon is relatively strong (i.e., 50 to 400 kJ/mol) and requires high temperature to dissociate the bond. However, hydrogen atoms can interact with materials such as graphene in a way in which the graphene structures are not substantially (irreversibly) changed, and the hydrogen interaction is more like adsorption.^{xiii} Spillover is a metal catalyzed process in which the hydrogen molecule dissociates to H-atoms on the metal catalyst, followed by the migration of hydrogen atoms onto the surface of a receptor material and subsequent diffusion away from the catalyst site. For this process to occur, the diffusion and storage of atomic hydrogen on the receptor surfaces must have substantially weaker bonding/barriers to migration than typically observed with chemical covalent bonding (i.e., weak chemisorption). Although the phenomenon of spillover has been known for decades for

petrochemical and refining catalysis applications with ~0.01 wt % hydrogen adsorption,^{xiv} the HSCoE partners demonstrated that this process could be used to reversibly store substantially more (>30 g/L and >4 wt %)^{xv} hydrogen at ambient temperatures and nominal pressures (less than 200 bar). This is over 300% greater than H₂ storage on a sorbent or as gas in a compressed tank at the same pressure and temperature. The HSCoE demonstrated spillover both experimentally and by confirming agreement with thermodynamic principles as a revolutionary new process for ambient-temperature, reversible hydrogen storage (see Highlight V). However, the materials tend to be very sensitive to processing conditions, the material synthesis procedures lacked reproducibility, and the accuracy of the measurement techniques varied, all of which can lead to substantial variations in sorption capacities. For example, although the work performed by the HSCoE at Michigan on “bridged” framework materials has been reproduced by international groups,^{xvi} and the hydrogen uptake was measured by DOE’s validation laboratory at the Southwest Research Institute, the base materials for this particular sample are very air sensitive and thus full evaluations of these materials were difficult. Ultimately, theoretical predictions and non-reversible hydrogenation experiments demonstrate that capacities of close to one hydrogen atom per receptor atom (e.g., carbon) should be achievable via spillover. This translates to a potential for excess capacities greater than 7 wt % and 50 g/L at ambient temperatures and less than 200 bar. At the end of the HSCoE, DOE formed an international team led by NREL to validate the measurement and synthesis methods of spillover materials to improve reproducibility. In addition, the team is determining the specific hydrogen-receptor interactions using spectroscopic techniques to fully understand the mechanisms involved. This is important to understanding the significant difference between fill and discharge rates, as well as issues that limit capacities. Ultimately, the issues with slow fill rates and lower than expected capacities may be related, and once the mechanisms are fully understood, these issues should be addressable.

Conclusions and Recommendations

The major findings of the HSCoE include:

1. **Cryogenic Storage:** New materials increase gravimetric (>60%, i.e., from ~5 to >8.5 wt % at ~80 K) and volumetric (~150%, i.e., from ~15 to >35 g/L at ~80 K) hydrogen storage on high-SSA sorbents by optimizing pore size distributions (0.7 to 1.5 nm) to increase SSA and packing density. Standard physisorption-based H₂ gravimetric capacity scales with SSA. Thus, no substantial increase in capacity can be achieved with geometric structures alone. Although binding energies can be effectively doubled with very small pores that enable multiple wall interactions with the H₂ molecules, effectively, the space for adsorption is decreased, thus decreasing the overall capacity.
2. **Toward Ambient Temperature Storage:** Substitutional materials such as boron in carbon or metal-organic frameworks (MOFs) exhibit enhanced dihydrogen binding energy (i.e., 8 to 12 kJ/mol) that increases capacities (e.g., doubles or triples) on a per SSA basis at near-ambient temperatures.
3. **Ambient Temperature Storage:** Reversible high-capacity sorbents that were designed and made via ambient-temperature hydrogenation techniques such as spillover store 1 to 4 wt % at ambient temperatures, with the potential of 7 wt % and 50 g/L at ambient temperatures and less than 200 bar. In addition, *coordinated unsaturated metal centers* are a new class of H₂ storage materials with the potential to store at ambient temperature >10 wt % and >100 g/L. More fundamental experimental work is needed to fully prove these concepts and provide validation for the model predictions.
4. **Improved Measurements:** Unique measurement capabilities developed by the HSCoE accurately and reproducibly characterize H₂ storage properties of small laboratory-scale samples (1–200 mg). These measurement capabilities enhanced high-throughput, rapid-screening analyses. In addition to capacity measurements, a high-pressure nuclear magnetic resonance spectroscopy system was developed to help identify hydrogen interactions in micropores versus those in macropores. The HSCoE also used several different techniques including neutron scattering, Raman and Fourier transform infrared spectroscopies, as well as differential volumetric measurements to provide unique hydrogen-storage materials’ characterization. In addition, the HSCoE led the publication of DOE’s “Best Practices” guide for hydrogen-storage measurements—a reference guide for kinetics, capacity, thermodynamics, and cycling measurements.^{xvii}

5. **Predictive Theory:** Research approaches used by the HSCoE that combined iterative and coupled theory and experimental efforts, accelerated materials design and development. First-principles theorists designed synthesis pathways and accompanying materials with optimal hydrogen-storage properties. These predictive approaches sped identification of materials with the potential to meet DOE hydrogen-storage targets, including novel heterogeneous materials, paths to creating high-capacity, fast-filling spillover materials, and new classes of sorbents with the potential of greater than 100 g/L and 10 wt % at ambient temperature. If these materials are reproducibly synthesized, they would have the potential of enabling systems that exceed DOE's 2015 system targets.

The HSCoE demonstrated that the on-vehicle fueling capability of sorbent materials offers tremendous advantages that should be exploited for light-duty vehicle applications. Thus, the HSCoE recommends that future development efforts be performed that focus on reducing material and associated balance-of-plant system costs by improving material storage capacities and transient performance at near-ambient temperatures (i.e., between -80° and 80°C). Overall, the HSCoE recommends that development efforts for specific material classes be continued where viable reproducible routes exist for synthesizing sorbents that can be used to meet the appropriate set of application targets. In general, the closer to ambient conditions the system operates, the less expensive the system. This must be traded against overall system performance, which includes the potential need for added heat removal during fueling at the station. This need for balance leads to four specific recommendations related to materials for associated hydrogen storage systems and classes:

1. Develop materials for hydrogen storage by weak chemisorption, emphasizing reproducible syntheses and performance, with improved hydrogen fill kinetics and overall net available capacity.
2. Limit development of materials in which the storage mechanism is purely physisorption to only those with optimized pore structures and surface areas greater than $3,000\text{ m}^2/\text{g}$.
3. Develop substituted/heterogeneous materials with demonstrated hydrogen binding energies of 10–25 kJ/mol over most of the capacity range.
4. Conduct fundamental experimental work to fully prove concepts of multiple-dihydrogen adsorption on designed metal complexes and provide experimental validation for the model predictions. Develop materials for multiple-dihydrogen storage on designed sites.

The recommended sorbent classes as a whole have common issues remaining that must be adequately addressed. These include the need to:

1. Use fundamental and applied research to develop robust, reproducible, scalable, and cost-effective syntheses that manufacture materials in which all adsorption sites are accessible to the hydrogen.
2. Improve fundamental computational methods to more accurately predict the ability to synthesize designed materials and hydrogen-storage capacity as a function of temperature and pressure.
3. Develop a better fundamental and applied understanding of atomic hydrogen transport energetics and kinetics on receptor materials.
4. Develop a better fundamental understanding of metal center coordination and how the processes can be directly applied to create high-capacity, low-cost hydrogen sorbents.
5. Develop materials in concert with designs for hydrogen-storage systems.
6. Develop sorbent-material measurements standards and certifications.

Based on systematic development efforts, the HSCoE also recommended that no additional R&D be performed on numerous materials and processes. In general, future sorbent development should follow the recommendations outlined in the full report and minimize repeating work that has already been done. Only a select few elements and materials used in sorbents will be able to meet DOE light-duty vehicle system targets. The key is arranging those elements and materials optimally for hydrogen storage. Thus, future development should eliminate any materials that cannot be used to meet the DOE 2015 targets.

For more details, please see the Executive Summary and full Final Report for the HSCoE. The Executive Summary provides a basic overview of the entire project in a self-contained document. The full Final Report provides a complete accounting including all the different HSCoE participants, the background, the different approaches used, major results, and recommendations for future efforts, with references. The Final Report also provides the most up-to-date bibliography of all the publications and patents from HSCoE partners.

Appendices: Highlights of the HSCoE

- HSCoE Impact of Investment
- Cryogenic Hydrogen Storage with High Specific Surface Area Sorbent
- Molecularly Designed Frameworks for Hydrogen Sorbents
- Toward Ambient-Temperature Storage by Increasing Molecular Hydrogen Binding to the Sorbent
- Ambient-Temperature Storage with Weak Chemisorption/Spillover

References

- ⁱ “Grand Challenge” for Basic and Applied Research in Hydrogen Storage; Solicitation Number DE–PS36–03GO93013.
- ⁱⁱ See partner list on cover page. The HSCoE also worked with many more institutions around the world.
- ⁱⁱⁱ Argonne National Laboratory contribution to the DOE Fuel Cell Technologies Annual Progress Report, 2010; http://www.hydrogen.energy.gov/annual_progress10.html.
- ^{iv} U.S. DOE Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Program, *Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles*. http://www.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage_explanation.pdf
- ^v *Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan: Planned Program Activities for FY 2005–2015*. <http://www.eere.energy.gov/hydrogenandfuelcells/mypp/index.html>.
- ^{vi} Zhou et al., Tuning Topology and Functionality of MOFs by Ligand Design *Acc. of Chem. Res.* 2010, 44, 123.
- ^{vii} McNicholas et al., H₂ Storage in Microporous Carbons from PEEK Precursors, *JPCC* 2010, 114, 13902.
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- ^{ix} e.g., Farha et al., De Novo Syn. of MOF Mat. Feat. Ultrahigh SA and Gas Stor. Cap., *Nature Chem.* 2010, 2, 944.
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- ^{xiv} e.g., Conner, W. C.; Falconer, J. L., *Chem. Rev.* 1995, 95, 759.
- ^{xv} Yang et al., Hyd. Storage in MOFs by Bridged Hyd. Spillover, *JACS.*, 2006, 128, 8136.
- ^{xvi} Lifeng Wang and Ralph T. Yang, *Catalysis Reviews: Science and Engineering*, 52:411–461, 2010.
- ^{xvii} *Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials*. http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/bestpractices_h2_storage_materials.pdf.

HIGHLIGHT I: HSCoE Impact of Investment (Lin Simpson, National Renewable Energy Laboratory)

Team: Air Products and Chemicals, Argonne National Laboratory, California Institute of Technology (Caltech), Duke University (Duke), Lawrence Livermore National Laboratory, National Institute of Standards and Technology, National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory, Pennsylvania State University, Rice University, Texas A&M University, University of California, Los Angeles, University of Miami, Ohio, University of Michigan (Michigan), University of Missouri, University of North Carolina (UNC), and University of Pennsylvania. Subtier partners included Ford Motor Company, Jet Propulsion Laboratory, Los Alamos National Laboratory, Rensselaer Polytechnic Institute, Rochester Institute of Technology, University of Chicago, and Virginia Polytechnic Institute and State University.

The Hydrogen Sorption Center of Excellence (HSCoE) seamlessly integrated diverse multidisciplinary expertise and sorbent development efforts. Prior to the HSCoE, state-of-the-art hydrogen (H₂) sorbents were exemplified by commercial activated high-specific-surface-area (SSA) carbon (AX-21, now sold as MSC-30). These H₂ sorbents had ~5 percent by weight (wt %) and 15 grams of hydrogen per liter (g/L) storage capacities at 77 degrees Kelvin (K) and ~30 bar. In addition, there was substantial uncertainty and controversy about the measurement and capacity reproducibility of many sorbents. Specific HSCoE accomplishments include:

1. **Developed and demonstrated hundreds of sorbents with up to 300% improvement in hydrogen-storage capacities, some of which may be used to meet DOE hydrogen storage targets.**
 - a. **Cryogenic Storage:** Developed new materials that increased the gravimetric (~60%, from ~5 to >8.5 wt % at 77 K) and volumetric (~150%, from ~15 to >35 g/L at 77 K) hydrogen-storage capacities by physisorption onto high-SSA sorbents by optimizing pore sizes (0.7 to 1.5 nanometers [nm]) to increase SSA and packing density.
 - i. Duke, NREL, UNC, and Caltech worked together to synthesize and characterize pyrolyzed PEEK materials with controlled pore sizes of 0.7 to 1.5 nm.⁴
 - ii. Michigan's MOF-177 publication has been cited ~750 times.⁵
 - iii. Texas A&M University's porous coordination network (PCN) material was shown to store >8.5 wt % excess H₂ storage at 77 K.⁶
 - b. **Toward Ambient Temperature Storage:** Through close collaboration between theorists and experimentalists, systematically searched through potential lightweight materials and determined that, without using metals, appropriately coordinated boron substituted in carbon is one of the very few viable methods to increase H₂ binding in a heterogeneous high-SSA material. The HSCoE championed this new approach, developing BC_x substitutional materials that achieved the theoretically predicted ~11 kJ/mol H₂ binding, and on a per SSA basis, had >2 times the H₂ storage capacities compared to typical activated carbons, even at near-ambient temperatures. The HSCoE partners collaborated closely to synthesize and characterize these BC_x materials.⁷ The HSCoE also developed a new class of materials that is predicted to have high capacities (i.e., potentially >10 wt % and 100 g/L at ambient temperature) by creating sorption sites that store multiple (i.e., 2 to 8) H₂ molecules with binding energies between 10 and 30 kJ/mol. If the predictions can be demonstrated with fundamental experimental investigations, then the materials could have more than twice the H₂ storage densities of liquid H₂, but at ambient temperature.
 - i. The seminal paper in this area was published by HSCoE partners, has been cited more than 200 times,⁸ and spurred R&D resulting in hundreds of new publications.
 - ii. Substantial fundamental discovery and systematic development efforts are needed.

⁴ e.g., McNicholas et al., *JPCC* 2010, 114, 13902.

⁵ Antek G. Wong-Foy, Adam J. Matzger, and Omar M. Yaghi, *J. Am. Chem. Soc.* 2006, 128, 3494-3495.

⁶ Daqiang Yuan, Dan Zhao, Daofeng Sun, and Hong-Cai Zhou, *Angew. Chem. Int. Ed.* 2010, 49, 5357–5361.

⁷ Chung, T.C.M.; et al. (2008). *J. Am. Chem. Soc.* (130:21); pp. 6668–6669 and NIST contribution to DOE Annual Hydrogen Program Report 2008.

⁸ e.g., Zhao, Y.; et al. (2005) *Phys. Rev. Lett.* 94, 155504-1. Kim, Y.-Y.; et al. (2009) *Phys. Rev. B* 79, 115424-1.

- c. **Ambient Temperature Storage:** The center pioneered the design and development of reversible sorbents via ambient-temperature spillover (e.g., weak chemisorption) that demonstrated 1 to 4 wt % storage capacities (over two orders of magnitude gain compared to previous materials, i.e., ~0.01 wt %) with isosteric heats of adsorption between 10 and 30 kilojoules per mole (kJ/mol).⁹
2. **Six Nature and Science publications with over 3000 citations, and 17 scientific journal cover articles.**
 3. **Over 200 publications in peer-reviewed journals. Over 50 co-authored by multiple U.S. and international institutions. These publications include three book chapters and a reference book.**
 4. **Over 40 hydrogen-storage material patents (12 issued) or applications submitted by HSCoE partners.**
 5. **Two small businesses start-ups associated with HSCoE partners involving nanomaterials (i.e., CNT, Inc., and Unidym) and the scaled production of frameworks (e.g., BASF) that can be used as hydrogen-storage materials.**
 6. **Worked with world-class investigators around the world, including three Nobel Laureates.**
 7. Major awards including a President's Young Investigator Award (PECASE), American Physics Society Fellow Appointment, Academy of Engineers Appointment, Neutron Scattering Society of America Science Prize, Neutron Scattering Society of America Fellow Appointment, Endowed Academic Chairs, Discover Magazine R&D 100, Materials Research Society Medal, Department of Commerce Silver Medal, AAAS Newcomb Cleveland Prize, Top 10 Green-Tech Breakthroughs of 2008, and multiple DOE awards for scientific excellence.
 8. Mentored over 50 postdocs, approximately 40 Ph.D. and 5 M.S. candidates. **Over 10 accepted tenure-track academic appointments** and 10 accepted scientist positions at national laboratories.
 9. Over 800 conference presentations, proceedings, and published reports.
 10. Accelerated hydrogen-storage material development around the world by organizing more than a dozen technical conference sessions on hydrogen storage, an entire Materials Research Society Conference, and over 20 national and international workshops on hydrogen sorption.
 11. Performed hundreds of systematic investigations, after which the ultimate conclusion for most of the specific materials and/or processes was that they should not be investigated further for vehicular hydrogen-storage applications. For example, elements with molecular weights over ~16 grams per mole (g/mol) probably cannot be used to meet DOE 2015 storage targets at temperatures above ~80 K with physisorption. Furthermore, if stronger H₂ bonding is produced, then elements with molecular weights higher than ~32 g/mol will require multiple H₂ adsorption per sorbent atom to be able to meet DOE targets. In addition, nearly all the atoms must be accessible to the hydrogen to have sufficient capacities. These simple criteria virtually eliminate many typical sorbents such as zeolites.
 12. **Developed unique measurement capabilities** to accurately and reliably characterize hydrogen-storage properties of laboratory-scale (1–100 mg) samples to enhance high throughput and rapid screening analysis (isotherms, SSA, pore size distribution, isosteric heats of adsorption, temperature-programmed desorption, Raman and Fourier transform infrared spectroscopies, neutron scattering, and nuclear magnetic resonance).

The HSCoE's close interactions enabled substantially more development to occur more quickly than could have ever been done as independent projects. The synthesis, predictive theory, and materials directly address the issues of on-vehicle hydrogen storage and have uses in most of today's major high technology applications including carbon capture, CO₂ sequestration, batteries, energy storage, semiconductor electronics, composites, drilling fluids, inks, drug delivery, transparent conductors, photovoltaics, purification, biomass catalysts, fuel cell catalysts, and energy generation.

⁹ Li, Y.W.; et al. (2006). *J. Am. Chem. Soc.* (128:25); 8136 and Lifeng W.; et al., *Catalysis Reviews*, 52:411–461, 2010.

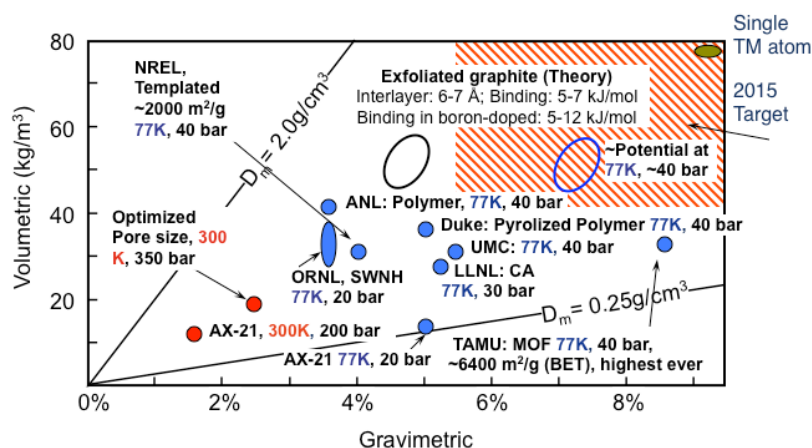
HIGHLIGHT II: Cryogenic Hydrogen Storage with High Specific Surface Area Sorbents¹⁰

Team: Air Products and Chemicals, Argonne National Laboratory (ANL), California Institute of Technology, Duke University (Duke), Lawrence Livermore National Laboratory (LLNL), National Institute of Standards and Technology, National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory (ORNL), Rice University, Texas A&M University (TAMU), University of Chicago, University of Missouri (UMC), University of North Carolina, and University of Pennsylvania.

Accomplishment: The Hydrogen Storage Center of Excellence (HSCoE) developed new water- and air-stable materials that increased bulk volumetric material capacity ~150% (i.e., from ~15 to >35 grams of hydrogen per liter [g/L] at ~80 degrees Kelvin [K] and 30 bar) by physisorption onto high-specific-surface-area (SSA) sorbents by optimizing pore sizes (i.e., 0.7 to 1.5 nanometers [nm]) to increase packing density (see Summary Plot). After systematic investigations, the HSCoE concluded that standard physisorption-based H₂ gravimetric capacity scales with SSA. As the center concluded operation, no validated experimental evidence existed that any substantial capacity enhancement occurs as a result of geometric configurations alone, contrary to reported values prior to the HSCoE's establishment. The main issue here is that increases in H₂ binding can be achieved with very small (less than 0.4 nanometer, nm) pores due to multiple wall interactions, but less space is available for hydrogen and thus the capacities actually decrease. Some of the issues with previous results were due to the irreproducibility and inaccuracies in the measurements. The HSCoE developed high-accuracy characterization systems for the small sorbent samples often produced to obtain accurate capacity measurements. In addition, the HSCoE led the publication of DOE's "Best Practices" guide for hydrogen-storage measurements, a reference guide for kinetics, capacity, thermodynamics, and cycling measurements.

Context: In most hydrogen-sorption materials with the potential to meet DOE targets, almost every atom must be accessible and lightweight. Therefore, materials with high SSA are required. In addition, to meet volumetric targets, the sorption sites need to be arranged to minimize the amount of open space so that the bulk density can be as high as possible, approaching the skeletal density of the material. This suggests that porous structures should be optimized to allow hydrogen egress in and out, to reduce diffusion resistances, but the hydrogen should be in contact with some kind of sorption site. Logically, the materials should have no mesoporosity or macroporosity (pores greater than ~2 nm diameter) and should have nominal pore sizes between 0.7 and ~1.5 nm.

The HSCoE interactively used theory¹¹ and experiment to design and synthesize different high-SSA sorbents to tune pore size distributions and understand their relationship to H₂ storage capacity. Syntheses developed included precursor pyrolysis, polymer chemistry, aerogel chemistry, templating, chemical vapor nanotube and nanohorn processing, and scaffolding. Typically, materials made by these processes followed the general



Summary Plot of Excess Volumetric and Gravimetric Capacities Achieved for Different Sorbents. Note that the “AX-21” data are representative of sorbent materials before the HSCoE started.

¹⁰ For more information, contact Lin Simpson (lin.simpson@nrel.gov) at the National Renewable Energy Laboratory or Channing Ahn (cca@caltech.edu) at the California Institute of Technology

¹¹ e.g., Ding, F., et al., *J. Chem. Phys.*; Vol. 127, **2007**; p. 164703. Sun, Y. Y., et al., *J. Chem. Phys.* 129, 2008, 154102.

empirical rule of ~1 percent by weight (wt %) maximum excess H₂ storage capacity for every 500 meter square area per gram (m²/g) SSA at 77 K and ~30 to 60 bar. Several materials were made with SSAs >2,500 m²/g that had ~5 wt % excess H₂ storage capacities at 77 K. However, unlike commercially available activated carbons that typically have bulk densities of 0.1 to 0.3 g/ml, several of these materials have pore sizes in the range of 0.7 to 1.5 nm,¹² which enable bulk densities between 0.7 and 1.4 grams per milliliter (g/ml). With ~5 wt % excess capacity, these materials have volumetric capacities over 35 g/L. In general, activated-carbon-based materials with SSAs substantially greater than 3,000 m²/g were not achieved, and therefore, while optimization of pore sizes may still improve the volumetric capacities slightly, no significant additional improvement is anticipated with these materials. However, material optimization may still be needed if high-SSA sorbents are used for applications where substantially cooler storage temperatures are used. As shown in Table 1, H₂ excess storage capacities vary substantially with temperature, and ~14 wt % and 90 g/L can be achieved at ~30 K.

At the outset of the HSCoE's activities, numerous publications had reported extraordinary results for high-SSA materials in which the enhanced capacities were potentially a result of novel geometries or structures within the material.¹³ In general, heats of adsorption can be increased with multiple wall interactions, but this ultimately reduces capacities due to the decrease in space for the hydrogen molecules.¹⁴ The HSCoE did not validate any single-element material or any materials with unexceptional electronic states that have substantially higher capacities beyond that expected based on SSA and specific storage conditions. For example, at one time carbon nanotubes were thought to possibly have unique H₂-storage properties, but after a dedicated focused effort, the HSCoE made a No-Go decision on using carbon nanotubes as an ambient-temperature hydrogen-storage material. Ultimately, carbon nanotubes may still provide excellent hydrogen storage at cryogenic temperatures.

Significance of Accomplishment and Recommendations:

The HSCoE found that sorbents have the potential to meet DOE hydrogen-storage targets with physisorption alone, but cryogenic temperatures (see Table 1) are required, which impacts fueling station, system, and H₂ costs. The relatively low binding energies associated with physisorption means that only ~50 kilowatts of heat will need to be removed during refueling. This will have minimal impact on the fueling station costs compared to materials with higher binding energies such as metal hydrides, which could require 800 kilowatts of cooling. To meet the DOE 2015 targets, the HSCoE recommends that the only physisorption materials that should be considered for development are those with SSAs greater than ~3,000 m²/g, optimized uniform pore sizes in the range of ~0.7 to ~1.5 nm, excess material H₂-storage capacities >50 g/L and 7 wt % at temperatures between ~80 and 200 K, and moderate pressures (less than 200 bar). The HSCoE recommends that planning and implementation of useful standards and certifications be performed to help the research community accelerate materials development and to minimize wasting limited resources on efforts that ultimately resolve poor measurements. The HSCoE also recommends that additional fundamental work is needed to predict more accurately H₂ storage capacity as a function of temperature and pressure, which will accelerate sorbent development by estimating capacities before the materials are ever synthesized.

Table 1. Capacities of High SSA (~ 3000 m²/g) Sorbents at Different Temperatures

Temperature (K)	Excess Gravimetric Capacity (wt %)	Excess Volumetric Capacity (g/L)	Nominal Pressure (Bar)
30	~14	~90	3
50	~8	~55	8
80	~5	~35	20
300	~1	~7	350

¹² e.g., McNicholas et al., JPCC 2010, 114, 13902 and Yuan, S., et al., Vol. 42 (5), 2009; pp. 1554-1559.

¹³ e.g., see references and data in Zlotea, C. et al., *Int. J. of Hyd.* 34, 2009, 3044.

¹⁴ Purewal, J. et al., *Phys. Rev. B*; Vol. 79, 2009; p. 054305.

HIGHLIGHT III: Molecularly Designed Frameworks for Hydrogen Sorbents¹⁵

Team: California Institute of Technology, National Institute of Standards and Technology (NIST), National Renewable Energy Laboratory (NREL), Texas A&M University, University of Michigan (moved to University of California, Los Angeles), University of North Carolina

Accomplishment: The HSCoE designed new framework materials with increased gravimetric (~60%, i.e., from ~5 to >8.5 percent by weight [wt %] at ~80 degrees Kelvin [K]) hydrogen storage (via physisorption) by increasing the specific surface area (SSA) from ~3,000 square meters area per gram (m²/g) to ~6,000 m²/g. This new approach for H₂ storage is highly scalable for future manufacture of materials. Ligand libraries and coordination chemistries enabled HSCoE partners to make literally hundreds of frameworks.¹⁶ Also, through highly coordinated work by HSCoE partners with groups around the world, the specific binding sites in framework structures were determined, which will help develop accurate predictive models of the hydrogen/surface interactions.

Context: To meet DOE targets, in most hydrogen-sorption materials almost every atom must be accessible and lightweight. Molecularly designed adsorbents such as metal organic frameworks (MOF) enable crystalline materials to be formed with high SSA and controlled pore sizes by coordinating multifunctional (multiple binding) ligands to well-defined metal centers. As with all porous physisorption-based materials, the goal is to design pores with sizes between 0.7 and ~1.5 nanometers (nm), which are ideal for high volumetric molecular hydrogen storage. This has been a challenge for framework materials that tend to have a substantial amount of their pores larger than 2 nm. Furthermore, the heavier molecular weight of the metal centers can be offset to some degree by the potential for high binding energies. Thus, the HSCoE focused on developing framework materials with optimal pores sizes and metal centers that were not sterically hindered for molecular hydrogen storage. In addition, due to the nature of the chemical interactions in the structure, framework materials can be sensitive to contaminants such as water and oxygen. The specific methods investigated to improve hydrogen-storage capacities and binding energies included:

- Reducing pores size with nanoscopic cages or catenation (interconnected frameworks).
- Synthesizing stable frameworks with mesocavities (>2 nm) but microwindows (<2 nm).
- Synthesizing anthracene-derivative frameworks to provide additional binding sites.
- Using different coordinated metal centers to improve their affinities to hydrogen.
- Constructing frameworks with “close-packing” alignment of open metal sites.

Early in the HSCoE, Dr. Yaghi's group¹⁷ began the explosion in framework development for hydrogen-storage materials with a *Nature* paper on MOF-177. At the time, MOF-177 had the highest reported SSA (i.e., ~3,800 m²/g) and excess hydrogen uptake (i.e., ~7 wt %) of any material at ~80 K. Subsequent work within the HSCoE by Zhou's group¹⁸ produced framework materials with ~5,100 m²/g and ~7 wt % excess H₂ storage at ~80 K. Zhou's materials have been the basis used recently to form MOFs with 8.5 to 9 wt % excess H₂ storage at ~80 K. Also, within the HSCoE, NIST worked with many groups from around the world to determine the isosteric heat of adsorption at specific adsorption sites. NIST found that isosteric heats of H₂ adsorption to the metal sites were the highest in the frameworks (i.e., in a manganese framework, ~10 kilojoules per mole [kJ/mol]).¹⁹ NIST worked with theorists at NREL²⁰ to understand the four key factors that affect the orbital interactions between the metal centers and H₂, finding that the binding could range between 10 and 50 kJ/mol depending on the specific metal used. NIST subsequently worked with Dr. Long's group at the University of California, Berkeley to experimentally demonstrate the relationship between the

¹⁵ For more information, contact Lin Simpson (lin.simpson@nrel.gov) at the National Renewable Energy Laboratory or Hongcai Zhou (zhou@mail.chem.tamu.edu) at Texas A&M University.

¹⁶ Dan Zhao, Daren J. Timmons, Daqiang Yuan, and Hong-Cai Zhou, *Acc. of Chem. Res.* 44, 2011, 123.

¹⁷ Antek G. Wong-Foy, Adam J. Matzger, and Omar M. Yaghi, *J. Am. Chem. Soc.* 2006, 128, 3494-3495.

¹⁸ Daqiang Yuan, Dan Zhao, Daofeng Sun, and Hong-Cai Zhou, *Angew. Chem. Int. Ed.* 2010, 49, 5357–5361.

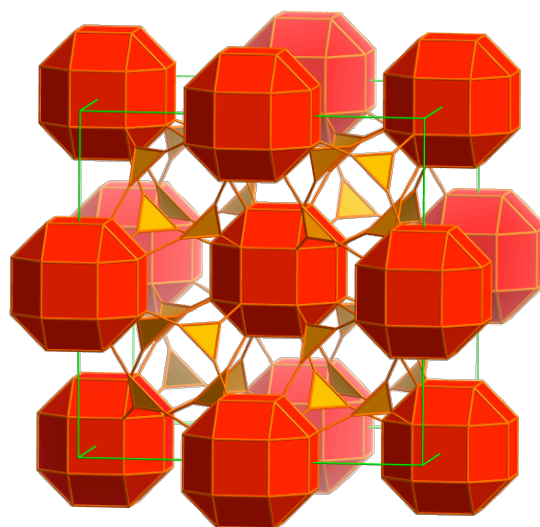
¹⁹ M. Dinca, W.S. Han, Y. Liu, A. Dailly, C. M. Brown, and J. R. Long, *J. Am. Chem. Soc.*, **128**, 16876-16883 (2006).

²⁰ Y.Y. Sun, Y. H. Kim, S. B. Zhang, *J. Am. Chem. Soc.* **2007**, 129, 12606.

specific metal used and the binding of H₂. Unlike previous predictions,²¹ these results demonstrated that the relationship was not specifically related to the metal ion size.

Significance of Accomplishment and

Recommendations: Frameworks offer a huge potential to continue increasing the SSA and gravimetric capacities of H₂ storage materials past 9 wt %. Furthermore, their ability to have higher binding energies and sub-nanometer-sized pores offers additional opportunities. For example, cantenation or developing frameworks with smaller pore sizes has tended to result in decreased SSA and thus lower H₂ capacities. Furthermore, the relatively small number of metal atoms and their limited access by H₂ means that only one to two H₂ could interact and have enhanced binding. Because metals make up only a small percentage of the frameworks, and due to the relatively high molecular weight of many metals typically used (i.e., copper, iron, manganese, zinc), H₂ storage by the metal centers may decrease the overall H₂ storage capacity of the material. Thus, the enhanced binding from the metal centers must be carefully integrated to enhance storage capacities. The main focus for future framework-development efforts needs to be on optimizing the pore sizes for H₂ adsorption with air- and water-stable materials, while still retaining very high SSAs. In addition, future framework development should also investigate methods for improving binding energies of the high-SSA ligand components.



Schematic of Porous Coordinated Network

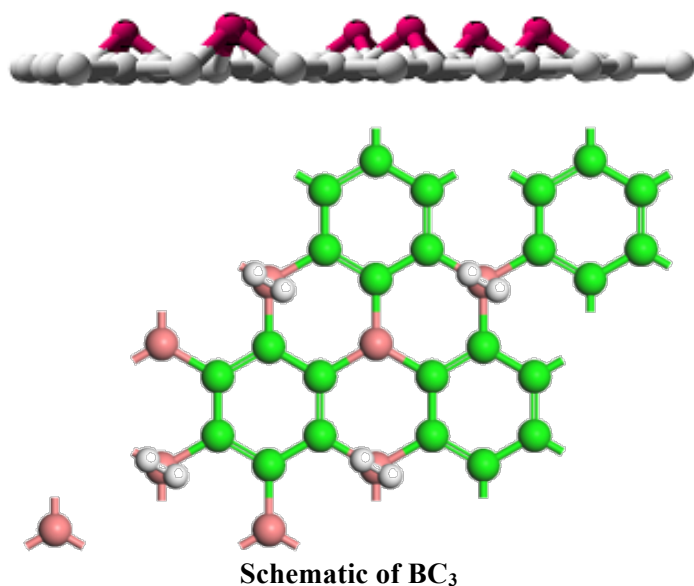
²¹ W. Zhou, H. Wu and T. Yildirim, *J. Am. Chem. Soc.*, 130, 15268-15269, 2008.

HIGHLIGHT IV: Toward Ambient-Temperature Storage by Increasing Molecular Hydrogen Binding to the Sorbent²²

Team: Air Products and Chemicals, Inc., National Institute of Standards and Technology, National Renewable Energy Laboratory, Pennsylvania State University, Rice University, University of North Carolina

Accomplishment: The HSCoE developed dozens of different sorbents involving substitutional materials using a few different approaches with measured isosteric heats of H₂ adsorption close to the predicted ~11 kilojoules per mole (kJ/mol) and demonstrating twice the H₂ capacity on a per specific surface area (SSA) basis. Prior to the HSCoE, little systematic work had succeeded in identifying ways of increasing H₂ binding to well-coordinated chemically stable sorbents, especially for the majority of the material capacity. Typically, the isosteric heat of adsorption for hydrogen physisorption to most single surfaces is ~4 kilojoules per mole (kJ/mol). Higher isosteric heats of adsorption (i.e., 10 to 25 kJ/mol) are needed to enable substantial hydrogen storage at 200 to 300 K (i.e., near-ambient temperature). For these efforts, experimentalists worked closely with theorists to guide specific material and process development.

Context: For materials to be stable, all bonds must be chemically satisfied. For pure elemental and/or stable high-SSA materials, H₂ can adsorb on the surfaces, but with no chemical bonds significantly altered, only physisorption can occur. To increase the binding, materials must be formed in which components of the surfaces are chemically frustrated and able to induce enhanced interactions with H₂. The HSCoE investigated several methods to do this, with perhaps the most conceptually simple approach being the substitution of specific elements in otherwise chemically homogeneous structures. For example, boron (B) substituted into carbon (C) graphene lattices (See schematic of BC₃) was predicted²³ and then experimentally validated²⁴ to enhance H₂ isosteric heats of adsorption to ~11 kJ/mol. Enhancement occurs because the empty p-orbitals on boron substituted for carbon induce electron donation from H₂. Substitution of lithium, nitrogen (N), oxygen, or other lightweight elements into graphene does not enhance H₂ binding.²³ Similarly, C-substituted B structures, BN, BCN, and other lightweight materials either do not enhance or have decreased H₂ binding. Thus, after an initial short set of collaborative efforts to identify potential materials, the HSCoE focused its experimental development on forming high-SSA BC_x with several different scalable and inexpensive synthesis methods. BC₃ represents the ultimate material composition goal. This level of B concentration allows the maximum concentration where the H₂ binding energy will be increased throughout the lattice. Higher or lower B concentrations will have lower overall binding energy.



²² For more information, contact Lin Simpson (lin.simpson@nrel.gov) or Jeff Blackburn (jeffrey.blackburn@nrel.gov) at the National Renewable Energy Laboratory, or Alan Cooper (cooperac@airproducts.com) at Air Products and Chemicals Inc.

²³ Kim, Y.-H., et al. (2006). *Phys. Rev. Lett.* (96:1); pp. 016102-1.

Boron substitution was achieved by either starting with chemical compounds with high concentrations of B²⁴ and forming high-SSA materials, forming B-substituted activated and graphitic carbons (e.g., BC₃),²⁵ or substituting boron for carbon atoms in preformed materials.²⁶ These multiple institution efforts culminated with neutron spectroscopy data showing, for the first time, a large rotational splitting, indicative of enhanced H₂ interactions in a B-substituted carbon.²⁷ Similarly, for the first time, HSCoE measurements from diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) showed reversible hydrogen interaction with the B:C material. Although different approaches were used, the ultimate boron concentration and SSA achieved were approximately the same: SSAs of ~800 m²/g with 10% to 15% B substitution. This is well short of the ~3000 square meters area per gram (m²/g) and ~25% B concentrations expected to be achievable. In addition, based on X-ray photoelectron spectroscopy (XPS), approximately 25% of the B in these materials is in the correct coordination for enhanced binding, indicating that only small fractions of the B in the materials were providing enhanced hydrogen binding. However, the BC_x materials typically have approximately twice the hydrogen-storage adsorption on a per SSA basis compared to activated carbon. In general, maximum excess gravimetric hydrogen adsorption capacities of ~3 wt % are observed at 77 degrees Kelvin (K) for materials with 600 to 800 m²/g SSAs. This compares to ~1.5 wt % for activated carbons with similar surface areas at 77 K. In addition, ~65% of the 77 K capacity has been retained with some porous BC_x materials at ~200 K. This compares to 25% to 30% with pure carbon materials at 200 K.

Significance of Accomplishment and Recommendations: Theoretical predictions and accompanying experimental measurements show that stronger dihydrogen binding of between 10 and 15 kJ/mol can be achieved when B is substituted with sp² coordination with carbon. This is sufficient to substantially increase the storage temperature compared to typical cryo-materials and to potentially enable BC₃-like materials to be used to meet DOE hydrogen storage capacity targets at 150–250 K temperatures if sufficient SSAs can be obtained. Any significant storage-temperature increase toward ambient significantly reduces weight and costs of the storage system, thus making it easier to meet DOE system targets. Future efforts must focus on increasing simultaneously both the boron concentration (in BC₃ coordination) and SSAs of these substituted materials. Paths forward to do both include solution-phase synthesis and lower energy chemical vapor synthesis in which the BC_x surfaces with the stronger binding are not allowed to interact and collapse. If a BC₃ material can be made, then more than half of the hydrogen-storage capacity would be at the higher isosteric heats of adsorption needed to have substantially higher hydrogen storage at temperatures greater than ~200 K. Other routes to enhance dihydrogen binding were identified by the HSCoE, but a substantial amount of both fundamental theoretical and experimental work needs to be done before these materials can be demonstrated for light-duty vehicle hydrogen storage.²⁸

²⁴ Chung, T.C.M.; et al. (2008). *J. Am. Chem. Soc.* (130:21); pp. 6668–6669.

²⁵ Bult, J.; et al. In Preparation. NREL and PSU contributions to DOE Annual Fuel Cell Technologies Report 2010.

²⁶ DOE Fuel Cell Technologies Annual Merit Review Presentation ST076, 2010.

²⁷ NIST contribution to DOE Annual Hydrogen Program Report 2008.

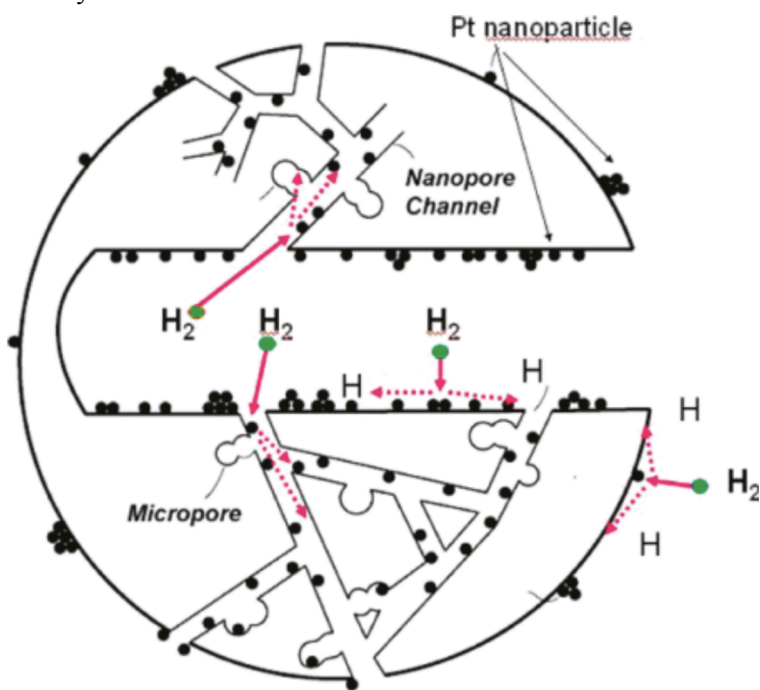
²⁸ e.g., Zhao, Y.; et al. (2005) *Phys. Rev. Lett.* 94, 155504-1. Kim, Y.-Y.; et al. (2009) *Phys. Rev. B* 79, 115424-1.

HIGHLIGHT V: Ambient-Temperature Storage with Weak Chemisorption/Spillover²⁹

Team: Air Products and Chemicals, Inc. (APCI), California Institute of Technology, Lawrence Livermore National Laboratory, National Institute of Standards and Technology, National Renewable Energy Laboratory (NREL), Oak Ridge National, Rice University (Rice), University of Michigan (Michigan), University of North Carolina

Accomplishment: The Hydrogen Sorption Center of Excellence (HSCoE) partners demonstrated both experimentally and by thermodynamic principles that certain materials can be used to reversibly store substantial amounts (i.e., >30 grams hydrogen per liter [g/L] and 1³² to 4³⁰ percent by weight [wt %]) of hydrogen at near-ambient temperatures and nominal pressures (i.e., 100–200 bar) by a process termed spillover or weak chemisorption. In general, at ambient temperatures, weak chemisorption on activated carbons has demonstrated ~2 wt% hydrogen storage and ~4 wt% with bridged frameworks. However, irreproducible measurements, material performance sensitivity to synthetic processing conditions, and material instability all resulted in substantial lack of reproducibility of experimental data across laboratories. Furthermore, the intrinsic nature of the spillover storage mechanism makes hydrogen refill rates, material stability/durability, and material costs challenging issues that must be resolved. Because the potential storage limits are ~80 g/L and ~8 wt %, and fill rates, materials costs, and durability are tractable issues, this mechanism may provide a means to meet DOE's 2015 targets (e.g., 5.5 wt % and 40 g/L) at operating conditions of near-ambient temperature and moderate pressure. At the end of the HSCoE's life, DOE formed an international team lead by the NREL to validate the measurement and synthesis methods of spillover materials to improve reproducibility. In addition, the team is determining the specific hydrogen/receptor interactions using spectroscopic techniques to fully understand the mechanisms involved.

Context: The HSCoE actively investigated methods to efficiently store dissociated hydrogen molecules (e.g., hydrogen atoms). Dissociated or atomic hydrogen forms strong bonds with other materials (e.g., metal or chemical hydrides) that require high temperatures (e.g., >500 degrees Kelvin [K]) to break the bonds. However, it is possible for hydrogen atoms to adsorb on surfaces in such a way that the bonding is weaker (i.e., 10 to 25 kilojoules per mole [kJ/mol]) and conducive to reversible storage capacities at near-ambient temperature and moderate pressure (see conceptual diagram for spillover). From a practical standpoint, a metal catalyst is typically needed to dissociate the H₂ gas. The concept of hydrogen spillover has its genesis in heterogeneous metal catalysis, particularly with the type of systems used for chemical hydrogenation reactions.³¹ Because most common industrial catalysts (e.g., platinum, palladium, nickel) are relatively heavy and



Conceptual diagram of hydrogen spillover processes. Reversible room-temperature spillover hydrogen storage involves a series of steps: (a) molecular H₂ dissociates on metal catalyst particles; (b) atomic H migrates to the receptor; (c) diffusion of atomic H across the receptor surfaces.

²⁹ For more information contact, Lin Simpson (lin.simpson@nrel.gov) or Thomas Gennett (thomas.gennett@nrel.gov) at the National Renewable Energy Laboratory, or Ralph Yang (yang@umich.edu) at the University of Michigan.

³⁰ Li, Y.W.; Yang, R.T. (2006). *J. Am. Chem. Soc.* (128:25); pp. 8136–8137.

³¹ e.g., Conner, W. C.; Falconer, J. L. *Chem. Rev.* 1995, 95, 759.

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 inexpensive receptor material. The HSCoE group at Michigan³² provides a good review of more than a hundred different spillover publications, including several result summary tables. These tables show that spillover can increase hydrogen-storage capacities by more than nine times compared to H₂ adsorption on the same base materials. The HSCoE also identified several other potential spillover materials including endohedral fullerenes, boron-substituted materials, and Met-Cars.

Computations by Rice, APCI, and NREL identified that it is thermodynamically possible for hydrogen atoms to be stably stored in groups or clusters. The main step that is not well understood is that of hydrogen atom diffusion on the receptor. The team was the first to identify that barriers to migration are lowered sufficiently via structural (e.g., hopping between closely spaced surfaces) and electronic features.³³ Collaborative work using inelastic neutron scattering spectroscopy observed spillover hydrogen on carbon supports.³⁴ Deuterium tracer investigations demonstrated that, effectively, the spillover process is sequential with the first hydrogen adsorbed being the last desorbed. The results are direct evidence that (1) atomic species are formed during the spillover processes, as shown by hydrogen-deuterium formation, and (2) the desorption follows a reverse spillover process in which atoms migrate back onto the metal particle to recombine and desorb as molecules. In general, the size, dispersion, and type of catalyst affect the efficiency and thus the capacity of spillover.

Significance of Accomplishment and Recommendations: Overall, the HSCoE demonstrated that substantial increases in hydrogen-storage capacity are achieved at ambient temperatures with weak chemisorption processes such as spillover. Future work must improve adsorption rates (e.g., refill kinetics) via improved catalyst dispersion and integration, and improved receptor properties. Care must be taken to ensure that irreversible chemical reactions with the receptor materials do not occur and that the measured uptake is truly representative of the amount of hydrogen that can be delivered to the fuel cell. Although a significant amount of work is still required (including fundamental surface science studies) to develop highly reproducible and robust materials that have high adsorption rates, kinetics, and capacities, the clear indication is that weak chemisorption is a viable path for on-vehicle hydrogen storage.

³² Lifeng Wang; Ralph T. Yang, *Catalysis Reviews: Science and Engineering*, 52:411–461, 2010.

³³ Lee, K.; et al. *Physical Review Letters* 104 (23), 236101.

³⁴ Mitchell, P.C.H.; et al. (2003). *J. Phys. Chem. B* (107:28); pp. 6838–6845.

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Final Report for the DOE Metal Hydride Center of Excellence

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Abstract

This report summarizes the R&D activities within the U.S. Department of Energy Metal Hydride Center of Excellence (MHCoe) from March 2005 to June 2010. The purpose of the MHCoe has been to conduct highly collaborative and multi-disciplinary applied R&D to develop new reversible hydrogen storage materials that meet or exceed DOE 2010 and 2015 system goals for hydrogen storage materials. The MHCoe combines three broad areas: mechanisms and modeling (which provide a theoretically driven basis for pursuing new materials), materials development (in which new materials are synthesized and characterized) and system design and engineering (which allow these new materials to be realized as practical automotive hydrogen storage systems). This Final Report summarizes the organization and execution of the 5-year research program to develop practical hydrogen storage materials for light duty vehicles. Major results from the MHCoe are summarized, along with suggestions for future research areas.

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-- Lennie Klebanoff and Jay Keller, January 2012

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Executive Summary

The purpose of the Metal Hydride Center of Excellence (MHCoe), funded by DOE's Fuel Cell Technology Program within the Office of Energy Efficiency and Renewable Energy (EERE), has been to conduct highly collaborative and multi-disciplinary applied R&D to develop new reversible hydrogen storage materials that meet or exceed DOE 2010 and 2015 system goals for hydrogen storage materials. Although the MHCoe was originally tasked with system design and engineering, this latter responsibility shifted to the Hydrogen Storage Engineering Center of Excellence (HSECoE), which was established in 2009. This Final Report summarizes the organization and execution of a 5-year research program to develop practical hydrogen storage materials for light duty vehicles.

During the 5-year life of the MHCoe, the following organizations and institutions have been partners, providing technical leadership and making important technical contributions to the MHCoe R&D program:

- Brookhaven National Laboratory (BNL)
- California Institute of Technology (Caltech)
- Carnegie Mellon University (CMU)
- General Electric (GE)
- Georgia Institute of Technology (GT)
- HRL Laboratories, LLC
- Intematix
- Jet Propulsion Laboratory (JPL)
- National Institute of Standards and Technology (NIST)
- Oak Ridge National Laboratory (ORNL)
- Ohio State University (OSU)
- Sandia National Laboratories (SNL)
- Savannah River National Laboratory (SRNL)
- Stanford University
- United Technologies Research Center (UTRC)
- University of Hawaii at Manoa (UH)
- University of Illinois at Urbana-Champaign (UIUC)
- University of Nevada, Reno (UNR)
- University of New Brunswick (UNB)
- University of Pittsburgh (PITT)
- University of Utah

Sandia National Laboratories has served as the “lead partner” for the MHCoe. The technical work was originally divided into five “project groups,” A–E. The purpose of the project areas was to organize the MHCoe technical work along appropriate and flexible technical lines and to foster collaboration. These projects included the following:

Project A (Destabilized Hydrides), whose objective has been to develop strategies for reducing hydrogen storage thermal requirements and improve kinetics by destabilizing metal hydrides systems. Project A also aimed to enhance kinetics by evaluating nanoengineering. In this Final Report, research highlights are given on destabilization studies of the $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ system, which has shown the potential for destabilization to alter reaction pathways. Work is also described on the dramatic increase (50 times) in kinetics observed when metal hydride materials are confined to nanoscaffolds such as carbon aerogel.

Project B (Complex Anionic Materials), whose objective has been to predict and synthesize highly promising new anionic hydride materials, with a particular focus on borohydride materials. This report highlights the extensive work on the synthesis and reaction characterization of $\text{Mg}(\text{BH}_4)_2$. This material was shown to be reversible in MHCoe work, making it the highest weight capacity (12 wt. % hydrogen) reversible material in existence. Work is also presented here on the $\text{Ca}(\text{BH}_4)_2$ system and the reactivity of $[\text{B}_{12}\text{H}_{12}]^{2-}$ salts, which were found to be very important intermediates in borohydride hydrogen release reactions.

Project C (Amide/Imide Storage Materials), whose objective has been to assess the viability of amides and imides (materials containing $-\text{NH}_2$ and $-\text{NH}$ moieties, respectively) for onboard hydrogen storage. This Final Report gives highlights for the synthesis and characterization of LiMgN , with an 8 wt. % capacity to store hydrogen. An account is also given of work on the related material $2\text{LiNH}_2/\text{MgH}_2$, which has proven to be a fully reversible 5 wt. % system with attractive thermodynamics.

Project D (Alane, AlH_3), whose objective has been to understand the sorption and regeneration properties of alane (AlH_3) for hydrogen storage. AlH_3 is a nearly ideal hydrogen releasing material, but to regenerate AlH_3 directly from the end-product Al with gaseous H_2 requires unreasonably high pressures. This report summarizes the MHCoe successes in rehydrogenating Al by organometallic approaches, as well as by a novel electrochemical approach. Both of these are “off-board” rehydrogenation processes. A particularly novel way of regenerating LiAlH_4 is also described, which makes this a potential off-board reversible material with nearly 7 wt. % hydrogen.

Project E (Engineering Analysis and Design), whose objective was to understand the materials engineering properties of metal hydrides as they were undergoing cycling. The responsibilities of Project E ended with the commissioning of the Hydrogen Storage Engineering Center of Excellence (HSECoE) at SRNL in 2009. Nonetheless, a review of selected Project E highlights is given here, including the characterization of the thermal conductivity of $2\text{LiNH}_2 + \text{MgH}_2$, and a description of a detailed numerical model that was constructed for a general metal hydride bed that couples reaction kinetics with heat and mass transfer, for both hydrogen release and hydrogen charging of the metal hydride.

In addition to these formal projects, the MHCoe established a Theory Group (TG). The MHCoe TG made use of first-principles methods to predict new materials and their thermodynamic properties, provide new directions for experimentalists, and assist in the interpretation of experimental results. In many ways, the MHCoe Theory Group set a new standard for how collaboration amongst theorists can be achieved, and how that theoretical activity can guide experimental work. Highlights from the TG are given here, starting with a description of a reaction screening protocol that allowed over 20 million possible reactions to be screened for theoretically favorable hydrogen release properties. Favorable reactions so identified were followed up by the MHCoe experimentalists.

A powerful new theoretical method was developed in the MHCoe. This new Prototype Electrostatic Ground State (PEGS) method allows the prediction of crystal structures of unknown compounds. Knowing the crystal structure of a material is required to examine its thermodynamics, and examples of this are described here. Finally, given the importance of thermodynamics, it is very important to understand in ever finer detail the physical processes that affect reaction thermodynamics. A remarkably accurate theoretical account of the thermodynamics for the LiBH_4 material and for the $\text{LiBH}_4 + \text{MgH}_2$ reaction are described herein.

The MHCoe has been engaged in applied research with the goal of finding a practical material that satisfies the DOE hydrogen storage targets. It has been very important to quickly assess a material's real potential for practically satisfying the targets. This Final Report summarizes the criteria that were used for downselecting materials, namely discontinuing work on materials due to lack of promise, and continuing work on downselected materials that do show promise. Examples are given for discontinued materials. A comprehensive table is given in Appendix I for those materials that were discontinued, including the reasons for abandoning their study.

New materials continued to be investigated in the final months of the MHCoe, and a number of them showed promise, but there was insufficient data to warrant a downselect decision. These "Materials Examined Near Program End" included $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$, $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ and $\text{AlB}_4\text{H}_{11}$ amongst others, and are described along with the high-priority materials that are discussed in the various project highlights.

A detailed comparison is made of the most promising materials coming from the MHCoe and the DOE hydrogen storage targets. This comparison is accomplished with a series of "spider charts" that are built from a number of material properties such as gravimetric density and volumetric density. These spider charts are presented for both the "off-board regenerated" materials AlH_3 and LiAlH_4 , as well as for the "on-board regenerated" materials $\text{Mg}(\text{BH}_4)_2$, $2\text{LiNH}_2/\text{MgH}_2$, $\text{LiNH}_2/\text{MgH}_2$, $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$ and $\text{LiBH}_4/\text{MgH}_2$.

Given the progress made in the MHCoe, it is important to come away with recommendations on future high-priority fundamental R&D directions. These different directions are discussed, including more work on destabilized systems, nanoconfinement of metal hydrides in nanoporous materials, and the need to gain a better understanding of solid-state reaction kinetics and catalysis. The borohydrides are identified as a particularly important class of materials from which a truly remarkable hydrogen storage material may emerge.

Also given is a listing of the DOE awards garnered by the MHCoe and its participants.

Three appendices close out the report. Appendix I gives a full accounting of the materials that were discontinued, removing them from further study. Appendix II lists all publications coming from the MHCoe activity, organized according to Project. Appendix II also lists the publications coming from the TG, as well as patents coming from the MHCoe work. Finally, Appendix III reproduces the contents of a “lessons learned” facilitated review of the MHCoe that was conducted at the last face-to-face meeting of the MHCoe held at the University of Utah on November 4, 2009.

Benefits of the Center Construct

The MHCoe R&D effort over the 5-year duration of the project can be numerically summarized as follows. Ninety-four new material systems were explored, leading to 279 publications describing the MHCoe R&D activity. These papers were published in the best chemistry and physics journals in existence (e.g., *Physical Review Letters*, *Physical Review B*, *Journal of the American Chemical Society*, etc.). Approximately one-third of the publications were collaborative in nature, involving at least two different institutional partners in the MHCoe. Thirteen patents were submitted in the course of the MHCoe work.

The MHCoe was formed to allow collaborations amongst the scientific community to work on hard problems in hydrogen storage that require interdisciplinary effort and collaboration. At the same time, that collaboration cannot be at the expense of individual inspiration and the creative research ideas that arise from independent work. The level of collaboration achieved in the MHCoe was near optimal. Strong collaborations, often involving as many as six institutional partners, were brought to bear on challenging problems of hydrogen storage. At the same time, this collaboration was not the only way for the center to operate, and we maintained strong independent programs that made progress in different areas, but whose work was, as needed, enabled by the strong collaborations that came to exist within the MHCoe. This Final Report also documents the domestic collaborations between MHCoe investigators and the U.S. hydrogen storage community, as well as international collaborations throughout the world.

It was the consensus of the MHCoe Principal Investigators that the Center construct was an excellent way to achieve rapid progress in this field. Towards the end of the MHCoe, we held a facilitated “Lessons Learned” session. The report from that activity is provided in Appendix III. Regarding the usefulness of the center concept, the Lessons Learned Report was quite clear:

“The response that received the most consensus from the participants was that the center concept provided an efficient way for technical collaboration that otherwise would not have occurred. The statement that more technical progress was made in the Center than would have in independent projects was the overarching theme of the Center Successes Session.”

The purpose of a Center is to solve hard technical problems requiring collaborations that cannot be established otherwise. Collaboration between two individuals is easy without a Center. Although a collaboration amongst three individuals or institutions is harder, this can also be established without a Center. However, collaborations amongst four or more institutions is best created within a Center construct. Was collaboration unique to a Center achieved in the MHCoe? It will be clear from this MHCoe Final Report that the answer to this question is “yes.” In the MHCoe, sometimes five or six partners worked together on these materials. This was true for the MHCoe studies of $\text{Mg}(\text{BH}_4)_2$, AlH_3 , and 1:1 $\text{LiNH}_2/\text{MgH}_2$, just to name a few examples. The collaboration between five or six partners at different institutions is highly unlikely without the funding and structure of a Center. Overall, the center concept was very successful for making rapid progress in this field.

Were hard technical problems solved? The reader will see that hard technical problems were indeed solved, although it will be evident that the hydrogen storage materials still need to be improved. The program did not find one material that simultaneously supports all of the DOE targets. However, as described in the Project Summaries, critical understanding was gained on many topics and important “sub problems” in the areas of theory, synthesis, characterization, and regeneration that lay the foundation for developing a truly remarkable solid-state H₂ storage material.

Major Accomplishments of the MHCoe

1. Dramatically expanded the scientific knowledge base of metal hydride hydrogen storage materials. Examined 94 material systems, published 279 papers, with approximately one-third of the publications being collaborative in nature, involving at least two different institutional partners in the MHCoe.
2. Developed 13 patents related to metal hydride hydrogen storage materials.
3. Solidified technical collaboration in hydrogen storage materials science. The MHCoe established technical collaborations with 17 domestic U.S. research institutions and 9 international research organizations.
4. Investigated 94 hydrogen storage materials systems in the MHCoe, providing a wide-ranging survey of the materials space, and giving clear directions and guidance for future work.
5. Investigated over 50 borohydride material systems for hydrogen storage, developing high-yield syntheses and characterizing their structural and hydrogen release properties. The work provides clear indication that a truly remarkable hydrogen storage material may reside amongst the borohydrides. Prior to the MHCoe only a few borohydrides had been studied for their hydrogen storage potential (OSU, SNL, UH, PITT, GT, SRNL, ORNL, Caltech, NIST, Utah, UTRC).
6. Discovered an approach allowing $\text{Mg}(\text{BH}_4)_2$ to reversibly store approximately 12 wt. % hydrogen, a record gravimetric capacity for a reversible hydrogen storage material. $\text{Mg}(\text{BH}_4)_2$ remains one of the most interesting compounds for H_2 storage due to the high theoretical wt. % H (14.8 %) and good hydrogen desorption enthalpy ($\Delta H = 40$ kJ/mole H_2). If the kinetic limitations can be overcome, then the thermodynamics of the system would allow facile hydrogen release and reversibility (OSU, UH, SNL, Caltech, NIST).
7. Developed and demonstrated a method to increase 50-fold the dehydrogenation rate from LiBH_4 by its incorporation in 13-nm carbon aerogel. Incorporation into the aerogel also improves the cycling stability three-fold. The MHCoe established nanoconfinement as a general method for enhancing kinetics and cycling stability in metal hydride materials (HRL).
8. Developed a flexible low-temperature homogenous organometallic approach to incorporate Al- and Mg-based hydrides into carbon aerogels, leading to high loadings without degradation of the nano-porous scaffold (UH).
9. Developed two independent low-energy “off board regeneration” routes to rehydrogenate Al back to AlH_3 with energy efficiency approaching the DOE target. BNL developed an organometallic approach in which AlH_3 could be generated from H_2 in the presence of a stabilizing agent, with that stabilizing agent eventually removed to yield pure AlH_3 . SRNL developed an electrochemical route in which spent aluminum could be converted to AlH_3 with high purity and good yield.
10. Created a remarkably facile method to regenerate LiAlH_4 with WTT efficiency approaching 60%. The method utilizes dimethyl ether, low (100 bar) hydrogen pressures

and room-temperature conditions to quantitatively convert spent Li-Al to LiAlH₄ (UNB and UH).

11. Developed theoretical methods to screen over 20 million different reaction conditions (composition, T, P) to search for promising hydrogen storage systems, and the influence of multistep reactions on the reactive pathways. These methods revolutionized the way materials can be searched for desired reaction properties using computational techniques (PITT, GT).
12. Conceived the Prototype Electrostatic Ground State (PEGS) method for predicting crystal structures beyond the use of the ICSD database, thereby increasing accuracy and enabling thermodynamic predictions for new structural phases of materials. This is a breakthrough theoretical development with a wide applicability to diverse hydrogen storage compositions (SNL).
13. Investigated 20 new “destabilized” hydrogen storage systems, expanding by a factor of 10 the number of known destabilized storage systems. Established “destabilization” as a general method for reducing the enthalpy barriers to hydrogen release (HRL, Caltech, PITT, GT, SNL).
14. Discovered a hydrogen storage system (LiBH₄/Mg₂NiH₄) that exhibited full reversibility, reaction through a direct low-temperature kinetic pathway, formation of a ternary boride phase, and low reaction enthalpy coupled with low entropy. This interesting system reveals in many ways the full power of the destabilization approach, and points the way to possible future hydrogen storage R&D involving ternary borides (HRL).
15. Elucidated the role of [B₁₂H₁₂]²⁻ salts in the hydrogen storage reactions of borohydrides.. The MHCoe developed NMR methods of detecting the [B₁₂H₁₂]²⁻ intermediates, and formulating straightforward synthesis methods to directly make MB₁₂H₁₂ materials to permit their further study (SNL, OSU, UH, Caltech, PITT, GT, NIST).
16. Discovered and developed the (2LiNH₂ + MgH₂) material system, which reversibly stores 5 wt. % hydrogen, has demonstrated 264 reversible cycles, and can be catalyzed with KH to readily release hydrogen at 180 °C, providing a 20-bar equilibrium pressure. This material has been recommended to the HSECoE as an important “near-term” material for subsystem engineering development (SNL).
17. Discovered that LiMgN forms the basis for a reversible ~ 8 wt. % hydrogen storage material that releases H₂ at approximately 200 °C, with a ΔH = 32 kJ/moleH₂. These experimental findings dramatically confirmed the earlier theoretical predictions made for this material by MHCoe theorists. This material has also been recommended to the HSECoE as an important “near-term” material for subsystem engineering development (Utah, GT, Caltech, SNL).
18. Developed quantitative first-principles theoretical methods for predicting enthalpies of selected reactions by taking into account contributions to the free energy arising from harmonic and non-harmonic vibrations. The techniques revealed the origin and importance of such vibrational effects in determining the structural transformations of LiBH₄ with temperature. For the first time, a quantitative explanation was given for the enthalpy of the reaction $2\text{LiBH}_4 + \text{MgH}_2 \leftrightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2$. This work

establishes a reliable means to include all vibrational effects, and yields quantitative predictions for the reaction enthalpies in all molecular-solid, H-storage materials (UIUC).

19. Conducted the first theoretical studies of the chemical interactions between nanoscaffolds and metal hydrides incorporated therein. Studies revealed the reactive stability of $\text{Ca}(\text{BH}_4)_2$ when incorporated into inorganic aerogels materials ZrO_2 , Y_2O_3 and C (UTRC).
20. Conceived and developed the method of incorporating 20% N_2 into the hydrogen gas stream to increase the reversible storage capacity of the $\text{LiN}_3\text{-H}$ system to 10.5 wt. % at the relatively low temperature of approximately 250 °C. The increased capacity is explained by CALPHAD modeling that shows that small amounts of pure liquid lithium metal form during cycling, which the added N_2 converts to Li_3N and then eventually to Li_2NH . In this way, elemental Li, which is formed in the absence of N_2 and represents a loss in H_2 storage capacity, is recovered by the added N_2 , preserving the full hydrogen storage capacity (UNR, NIST).