

IV.B.1c Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

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Start Date: March 1, 2005
 End Date: September 30, 2010

phase impurities, and demonstrate adequate purity of hydrogen stream.

- Lead most and coordinate all Chemical Hydrogen Storage Center of Excellence efforts and collaborative projects, and communicate recommendations to the Hydrogen Storage Engineering Center of Excellence.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (K) System Life-Cycle Assessments
- (R) Regeneration Processes

Objectives

- Provide demonstrated spent fuel regeneration chemistries and physical properties to enable preliminary cost analyses by Dow.
- Develop and demonstrate heterogeneous catalysts and continuous flow reactor operation.
- Develop liquid ammonia-borane (AB) fuels and increase rate and extent of hydrogen release.
- Identify and demonstrate new materials and strategies for near-thermoneutral hydrogen release (ΔG° ideally no less negative than ca. -0.8 kcal/mol).
- Develop analytical methods to quantify gas-phase impurities that may accompany hydrogen release, develop materials and processes to minimize gas-

Technical Targets

While all of the relevant targets detailed in the DOE MYRDDP will be addressed, our main emphasis focuses on the material requirements. The Center has developed interim technical guidelines to facilitate down selection of promising materials for further development. The Center's key criteria for down-selection of storage materials include gravimetric and volumetric hydrogen capacities, as well as hydrogen release rate and temperature. The Center's criteria for materials down-selection, which are mapped to the DOE technical targets for storage systems, are tabulated in Table 1. Gravimetric capacity of materials must exceed 7 wt%, with the potential to exceed 9 wt%. The latter value was determined via an analysis of Millennium Cell's very aggressive process design for hydrogen release from

TABLE 1.

Criterion	Description	Metric
Material Wt. %	Maximum calculated hydrogen weight fraction, potential to exceed 9 wt %	> 7 wt. % H ₂
Potential to Regenerate On-Board	Potential to rehydrogenate spent fuel directly	yes/no/potential
Regenerable	Ability to chemically reprocess fuel offboard	yes/no/potential
Acceptable Phase Change	Problematic liquid to solid phase change	yes/no/potential
Acceptable H ₂ Release Rate	Maximum rate of hydrogen release	> .02g H ₂ /s/kW material
Stable Material < 50 °C	Stable in fuel tank < 50 °C to H ₂ release, or decomposition	yes/no/potential
Temperature of Release	Demonstrated, or potential for release at T < 100 °C	< 200 °C

aqueous sodium borohydride. The goal for temperature is for hydrogen release to occur with high rate below 100°C, with an interim goal of release occurring at high rates below 120°C. The Center's criterion for the rate of hydrogen release, 0.02 g H₂/s/kW, is the DOE 2010 target. A tabulation of all of the Center's interim targets are published as "2008 Overview - DOE Chemical Hydrogen Storage Center of Excellence", http://www.hydrogen.energy.gov/annual_progress08_storage.html#b.

The targets for regeneration of spent fuel include an interim target of 40% energy efficiency, with an ultimate goal of 60% energy efficiency, with chemical efficiencies approaching 100%, e.g. minimum losses to byproducts.

Accomplishments

- Completed chemistry and demonstration of a one-pot simplified spent fuel regeneration scheme utilizing hydrazine and liquid ammonia.
- Demonstrated regeneration of spent fuel from ionic liquid AB mixtures indicating that properly designed ionic liquids will not interfere with regeneration chemistries.
- Prepared new storage materials that have lower exothermicity, higher rates to higher extents of release at lower temperatures compared to AB, with many compounds exceeding 2010 targets.
- Heterogeneous base metal catalysts for hydrogen release have been prepared and demonstrated to have high rates of release to >9 wt% H₂.
- Worked with University of Pennsylvania (Penn) partners to further develop promising ionic liquid AB fuels that remain liquid throughout the dehydrogenation cycle.
- Worked with Argonne National Laboratory (ANL) and Penn to provide data ANL required to develop preliminary onboard release system analysis of an ionic liquid AB fuel.
- De-selected liquid fuel systems comprised of alkylamineborane-AB because of catalyst lifetime issues.
- Using previously developed hydrogen purity test stand, examined numerous hydrogen release systems, quantifying evolution of impurities vs. time and temperature where impurities were observed.
- Worked with Hydrogen Storage Engineering Center of Excellence to define acceptable impurity mitigation strategies for onboard gas cleanup



Introduction

Chemical hydrogen storage involves storing hydrogen in molecular chemical bonds where an on-board chemical reaction is used to release hydrogen. Currently, the resulting spent fuel may be regenerated off-board using chemical processing. In addition to the importance of on-board storage capacity and hydrogen release rates, the energy efficiency of the off-board regeneration of spent fuel is a key contributor to the overall energy efficiency of the fuel cycle. Chemical hydrogen storage provides a diversity of options to enable hydrogen for transportation as well as other niche and stationary applications, and could also be used for hydrogen delivery where it offers the opportunity for a liquid or solid fuel infrastructure with the potential for no direct hydrogen handling by the consumer.

Researchers at LANL are advancing a number of integrated projects involving the development of materials, catalysts, catalytic processes, and new concepts for hydrogen release and regeneration of spent fuels, as well as the development of engineering feasibility of the processes. In addition, Los Alamos hydrogen storage research benefits from productive interactions with theory collaborators across the Center at the University of Alabama, the University of California, Davis, the University of Missouri, the University of Pennsylvania, Pennsylvania State University, the University of Washington, Dow, U. S. Borax, and the Pacific Northwest National Laboratory (PNNL). These partners collectively work with LANL on four major areas of research and development (R&D) in chemical hydrogen storage: 1) hydrogen release from AB, 2) regeneration of spent fuel, 3) new materials discovery, and 4) engineering supporting R&D. Additionally, the Center is also working on 'first-fill' R&D to assess processes to provide the first load of a boron-containing fuel derived from mineral borates, and with U. S. Borax in assessing domestic and foreign borate resources and reserves. LANL participates in all of these activities either by contributions to laboratory research, or in coordinating the R&D efforts among the partners, and in providing Center-wide communications among the various areas of R&D to keep all partners apprised of progress and issues.

Approach

LANL contributes to collaborative experimental projects in all areas of the Center's efforts, primarily through investigations of storage materials chemistry and reactivity, experimental evaluation of the limits of capacity, release rates, and regeneration efficiencies, as well as development of new chemistry and catalytic processes and optimization of promising systems. In work on hydrogen release from AB, LANL's approach is to develop liquid compositions containing AB,

and to develop mechanistic information to guide heterogeneous catalyst discovery for hydrogen release from AB and AB-like liquid systems. In the area of spent fuel regeneration, LANL's approach is to optimize the routes to the digestion, reduction, and recycle of reagents to complete a spent fuel regeneration process, and work closely with Dow process engineers to develop preliminary baseline cost and efficiency analyses of spent fuel regeneration. This also involves collaborating closely with Penn and PNNL, who are working on separate approaches to spent fuel regeneration, and also with the University of Alabama that provides theory and modeling, and thermodynamics calculations of spent fuel regeneration chemistries. In the area of new materials discovery, LANL's role is to work with International Partnership for the Hydrogen Economy (IPHE) partners in synthesizing, characterizing, and testing metal amidoborane compounds for hydrogen release, as well as in assessing other potential new hydrogen storage materials concepts. In the area of engineering supporting R&D, LANL contributes to the Center's activities by performing experimental work that allows for engineering assessments of chemical hydrogen storage processes to be analyzed. LANL's engineering effort designs, fabricates, and operates chemical reactor systems for assessing continuous hydrogen release processes, as well as systems that analyze for potential gas impurities that may impact the operation downstream devices such as fuel cells. LANL's engineering effort also assists the development of criteria for hydrogen storage materials, an activity that informs the materials development and spent fuel regeneration efforts. LANL is a member of the Hydrogen Storage Engineering Center of Excellence lead by Savannah River National Laboratory, and has the task of helping to coordinate input into the design and development of subscale prototypes of chemical hydrogen storage systems.

Results

1. Hydrogen Release from Ionic-Liquid Ammonia Borane Liquid Fuel Mixtures

To enable low-temperature catalytic release of hydrogen over a heterogeneous catalyst, the fuel must be a liquid. Liquid systems are also more readily engineered into a system. Research has continued in working with Penn and ANL to work toward a preliminary onboard hydrogen release system analysis of the liquid fuel system of AB in ionic liquids. Work has continued to develop a complete set of kinetics from which ANL bases their onboard release analysis, and to optimize the liquid properties of the fuel and spent fuel. In addition, LANL has made progress in understanding some of the systematics of impurity formation in hydrogen release materials, and has worked closely with

the Engineering Center to develop mitigation strategies to deal with any residual gas-phase impurities.

LANL has discontinued working on what was an initially promising liquid fuel formulation comprised of certain alkylamineboranes mixed with AB. While many of these compositions had useful liquid ranges, an additional requirement is that they must be compatible with catalytic release strategies to obtain the highest rates of hydrogen release possible at the lowest temperatures possible. Our work during this past year indicates that the alkylamineborane mixtures lead to rapid deactivation of the catalyst. The accompanying figure indicates that the rate of hydrogen release from mixtures of sec-butylamineborane/AB are low, and are similar with and without catalyst, indicating that the catalyst is deactivated (Figure 1). In a separate experiment, we observe that sec-butylamineborane by itself is unstable above 50°C, and also decomposes to yield free sec-butylamine, which is a potential catalyst poison (Figure 2). While there may be a solution to these two problems, LANL did not feel it was warranted to expend the effort to continue this line of research in the last year of the project.

2. Regeneration of Spent Fuel

LANL's prior work in regeneration of spent fuel focused on optimizing the thiocatechol route described previously, and working with Dow (formerly Rohm and Haas) to perform the process modeling necessary to develop a preliminary baseline cost analysis of spent fuel regeneration for AB (see our partner's annual report from Dow). Upon completion of the cost analysis by Dow, several key features to reduce cost and improve efficiency were apparent. Major improvements were potentially available from reducing the overall mass flow of reagents that was responsible for significant

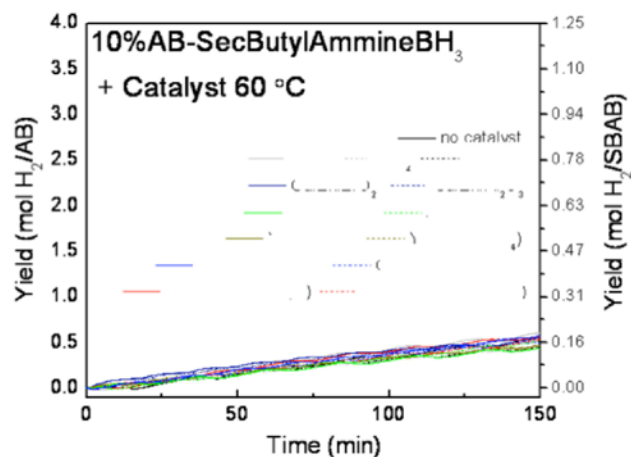


FIGURE 1. Dehydrogenation of a mixture of sec-butylamineborane and AB at 60°C is invariant in rate with or without a catalyst, indicating that the catalyst is deactivated.

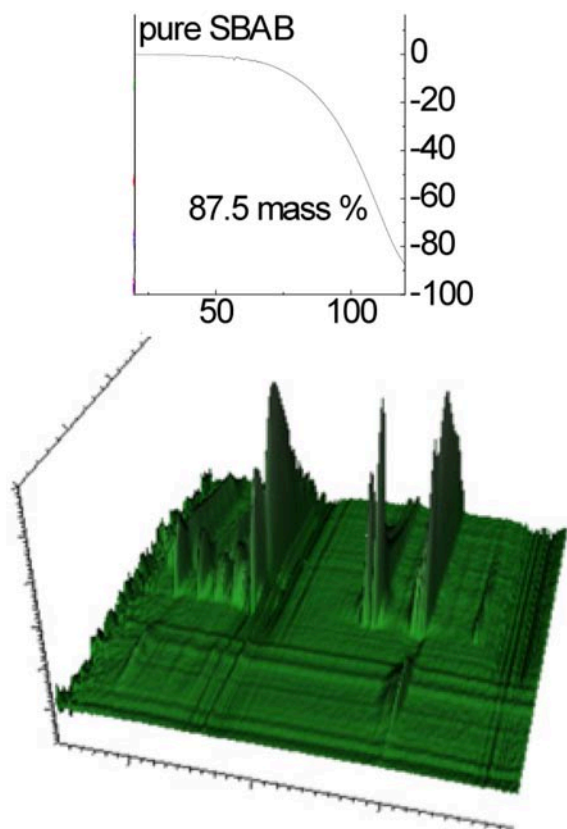


FIGURE 2. Thermogravimetric analysis-infrared (TGA-IR) analysis of pure sec-butylamineborane (SBAB). The TGA trace (upper) shows that SBAB begins to decompose and volatilize at 50°C. IR spectroscopy of the gas phase taken during decomposition indicates numerous impurities, including sec-butylamine, a potential catalyst poison.

cost and energy inputs. The reducing agent is one key contributor to overall mass, as is the digesting agent. Another potential improvement was to combine steps whenever possible. LANL successfully addressed these opportunities, and discovered and developed a new, simplified spent fuel regeneration scheme that is shown in Figure 3. This scheme involves the use of hydrazine, N_2H_4 , a lightweight reducing agent as digestion and reduction agent. During the past year, LANL has demonstrated that by optimizing the conditions, the generation of byproducts can be avoided, and by using liquid ammonia solvent, pure AB may be obtained directly from spent fuel in a single operation of dissolving spent fuel in a hydrazine/ammonia mixture that results in reduction of spent fuel directly to AB. Removing the volatile excess ammonia completes the cycle. Dow has begun a preliminary analysis of this process, and it appears that the process energy is substantially less than the thiocatechol route, and because of the significant reduction in unit operations and separations that the capital costs for the hydrazine route are very favorable. The largest cost appears to be in hydrazine, which is not a surprise to us, as hydrazine

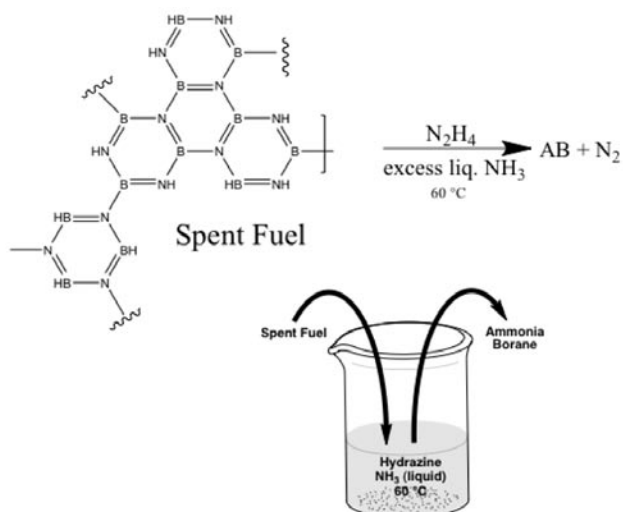


FIGURE 3. New, single process for regeneration of AB from spent fuel using hydrazine as the digestion and reduction agent.

is not produced in an efficient process nor on a large scale that makes hydrazine expensive. Future research could be directed at significantly reducing the cost of hydrazine.

3. New Materials Discovery

Our previous effort in the discovery of new materials has focused on preparing metal amidoboranes. The driving force behind our research in this area was to explore whether replacing a hydrogen atom of AB with a metal atom would sufficiently alter the reaction pathways and thermodynamics of hydrogen release such that potentially reversible systems would result. We feel that to be practical that these compounds must be reversible, because we have no ideas that will result in an energy efficient regeneration of the resulting spent fuel. It appears to us that any regeneration will require the re-synthesis of the corresponding metal hydride (M-H), and react that with AB to prepare metal amidoborane (M-AB). Of course, if the regeneration requires synthesis of M-H, one might as well use M-H as the storage material, and consider hydrolysis. However, this approach has been determined by DOE to not have a path forward because of the too numerous issues with hydrolysis systems and the regeneration efficiencies involved.

Among the metal amidoborane compounds that LANL has examined to date (M = Na, Li, K, Ca, Mg, Al, Ti, Sc, Zn, Sr), the thermochemical properties and the hydrogen release temperatures show a good deal of diversity. However, the thermodynamics of hydrogen release for all of the mono metal amidoboranes are still too exothermic to enable direct rehydrogenation using H_2 gas pressure, and so to date, no materials have

been discovered that can be directly regenerated on board. LANL has discontinued work on mono metal amidoboranes, but we suggest that bimetallic M, M'-amidoboranes still should be surveyed to determine if there are any members of that series that offers the potential of direct rehydrogenation with hydrogen pressure.

4. Engineering Supporting R&D

Engineering supports all of the decision making within the Center to drive R&D towards the most promising near-term solutions. This year our efforts in engineering support have been focused on working with Penn on their ionic liquid (IL)-AB system that is a potential liquid fuel. Two issues that influence engineering design decisions for these potentially liquid systems are 1) impurities that may arise during release, and 2) stability of the materials at 50-60°C. Impurities and stability are monitored using similar approaches. LANL monitored the stability of IL-AB mixtures as a function of time at three temperatures of 50 and 60°C for periods of 5 days. Fourier transform IR spectroscopy of the gas above the IL-AB mixture was monitored to detect potential impurities while the mass of the sample was simultaneously and continuously monitored to detect any weight loss due to decomposition resulting in gas phase products. To monitor impurities at higher temperatures during release, we use both gas-phase IR, TGA, and mass spectroscopy of the evolved gas stream to detect and quantify impurities. Among the impurities that may be detected this way are diborane, ammonia, borazine, and any impurities arising from potential decomposition of the ionic liquid. Figure 4 indicates that at 50°C, there is no detectable mass change, and we find no impurities in the gas phase over a period of 5 days. At 60°C, we detect no mass change after 5 days, but we do observe water in the gas phase. As the particular IL used is known to be hygroscopic, we assume for now that the water arises from water adsorbed on the IL starting material used to prepare the mixture. At 70°C (data not shown) where the onset of hydrogen evolution begins, we observe small quantities of ammonia being evolved initially. A small amount of borazine is also observed, but in quantities much less than from neat AB dehydrogenation.

Conclusions and Future Directions

Research at LANL in collaboration with Penn has demonstrated that the use of heterogeneous catalysts for the release of hydrogen from AB-IL fuels may begin to release hydrogen at high rates at low temperatures, and that these mixtures are quite stable up to at least 60°C. Impurities are released as well, and they include ammonia (an initial small pulse at low temperatures) and a small quantity of borazine at higher temperatures. The quantity of borazine released

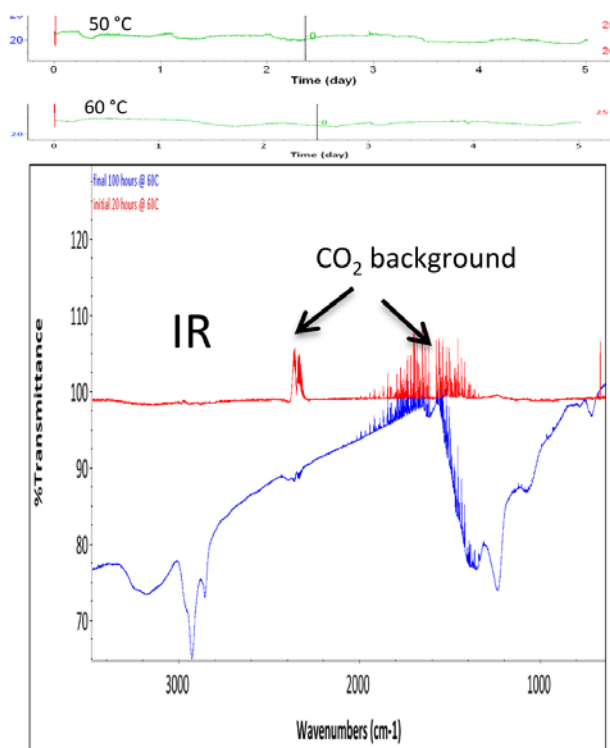


FIGURE 4. Stability of AB in ionic liquid. The top two traces are TGA data taken at 50 and 60°C. The plot at the bottom is the gas-phase IR taken at 20 hrs into the run (red), and at the end of 5 days (blue) that indicates that water is being desorbed from the AB-ionic liquid because of traces of water sorbed onto the starting materials. No other impurities are identified.

is relatively smaller than from pure AB. In the area of regeneration, we have discovered and demonstrated an entirely new regeneration scheme that involves digestion and reducing spent fuel to AB in a single process using hydrazine. This hydrazine process successfully regenerates a variety of spent fuel types, including the spent fuel from dehydrogenation of AB-IL mixtures. With our partners at Dow, we have provided laboratory-scale demonstration of spent fuel regeneration and the information necessary to finish a preliminary baseline cost analysis of spent fuel regeneration of ammonia borane using hydrazine.

FY 2010 Publications/Presentations and Patents

Peer-Reviewed Publications

1. "B-N compounds for chemical hydrogen storage", Hamilton, C.W. and Baker, R.T., *Chem. Soc. Reviews* **38**, 279-293 (2009).
2. "Efficient Regeneration of Partially Spent Ammonia Borane Fuel", Davis, BL, Dixon, DA, Garner, EB, Gordon, JC, Matus, MH, Scott, BL, Stephens, FH, *Angew. Chemie Int. Ed.* **48** 6812-6816, (2009).

3. “Recycle of tin thiolate compounds relevant to ammonia-borane regeneration”, Sutton, AD, Davis, BL, Bhattacharyya, KX, Ellis, BD, Gordon, JC, Power, PP, Chem. Comm. **46** 148-149, (2010).
4. “Catalytic dehydrogenation of ammonia borane in non-aqueous medium”, Shrestha, RP, Diyabalanage, HVK, Semelsberger, TA, Ott, KC, Burrell, AK, Int. J. Hydrogen Energy **34** 2616-2621 (2009).
5. “Ammonia Borane as a Hydrogen Carrier: Dehydrogenation and Regeneration”, Smythe, NC, Gordon, JC, European J. of Inorg. Chem. **2010/4**, 509-521.

Invited Presentations

Invited presentations by K. Ott

1. “Hydrogen Storage in Covalent Chemical Compounds: Current State and Future Challenges”, April 1, 2010, University of Tennessee.
2. “Recent results from DOE’s Chemical Hydrogen Storage Center of Excellence”, American Ceramic Society Meeting, Cocoa Beach, FL February 22-25, 2010.
3. “Hydrogen Storage at Los Alamos National Laboratory”, 4th International Workshop on Sustainable Materials Science Hiroshima, Japan, November 2009.
4. “Recent results from DOE’s Chemical Hydrogen Storage Center of Excellence”, 2nd LANL-HU Workshop, Hiroshima, Japan, November 2009.
5. “Chemical Hydrogen Storage at LANL – Update”, LANL - NEDO/AIST Hydrogen Storage Workshop, Boston, MA December 2009
6. “Recent results from DOE’s Chemical Hydrogen Storage Center of Excellence”, PIRA Intertech PIRA Workshop “Hydrogen Production and Storage 2009” Washington, D.C., Sept. 30 – Oct. 2, 2009.

Invited presentations on chemical hydrogen storage by A.K. Burrell

1. Florida State University, May 2010.
2. IEA HHA Meeting Death Valley, CA April 2010.

3. IPHE Meeting, PNNL April 2010.
4. LANL - NEDO/AIST Hydrogen Storage Workshop, Boston, MA December 2009.
5. Fall Meeting Materials Research Society, Hydrogen Storage Symposia, December 2009.
6. 2nd LANL-HU Workshop, Hiroshima, Japan, November 2009.
7. AIST Osaka, Japan, November 2009.
8. 4th International Workshop on Sustainable Materials Science Hiroshima, Japan, November 2009.
9. Fall American Chemical Society National Meeting, Hydrogen Storage, August 2009.
10. Plenary, Hydrogen-Metal Systems Gordon Conference, Lucca, Italy, July 2009.

Patents

Patents Issued:

1. 7,736,531 June 15, 2010, “Composition and method for storing and releasing hydrogen” Thorn, Tumas, Ott, Burrell.
2. 7,713,506 May 11, 2010, “Metal aminoboranes”, Burrell, Davis, Thorn, Gordon, Baker, Semelsberger, Tumas, Diyabalanage, Shrestha.
3. 7,645,902 Jan. 12, 2010, “Acid-catalyzed dehydrogenation of amine-boranes” Stephens, Baker
4. 7,544,837 June 9, 2009, “Base metal dehydrogenation of amine-boranes”, Blacquiere, Keaton, Baker

Patent Applications Published:

1. 20090297423 Dec. 3, 2009, “Energy efficient synthesis of boranes” Thorn, Tumas, Schwarz
2. 20090274613 Nov. 5, 2009, Hydrogen Production Using Ammonia Borane” Hamilton, Baker, Semelsberger, Shrestha