

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

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Start Date: February 1, 2005

Projected End Date: September 30, 2010

Objectives

- Provide preliminary cost analysis of LANL regen process.
- 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 materials and processes to minimize gas-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 Hydrogen, Fuel Cells and Infrastructure 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

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 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 in the Center's 2008 annual report, available at http://www.hydrogen.energy.gov/annual_progress08_storage.html#b.

TABLE 1. Technical Targets for Storage Systems

Criterion	Description	Metric
Material wt%	Max	> 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 Release H ₂ Rate	Maximum rate of hydrogen release	> 0.2 g H ₂ /s/kW
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

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

- Prepared new storage materials that have lower exothermicity, higher rates to higher extents of release at lower temperatures compared to ammonia borane, with many compounds exceeding 2010 targets.
- In collaboration with Ottawa University, discovered additional liquid fuel compositions with liquid range to -30°C .
- Discovered heterogeneous base metal catalysts for hydrogen release from ammonia borane. These catalysts have been prepared and demonstrated to have high rates of release to >9 wt% H_2 at 70°C , potentially exceeding DOE technical targets.
- Demonstrated all individual steps in an AB spent fuel regeneration cycle having an overall thermodynamic efficiency of 80%, and with overall ‘once through’ chemical yield exceeding 70% conversion of spent fuel to AB in an integrated process.
- Designed, fabricated, and demonstrated flow reactor for catalyst screening and process development
- Assembled and made operational a hydrogen stream purity analysis system to identify and quantify impurities in H_2 streams.
- Polymer electrolyte membrane fuel cell apparatus for hydrogen stream purity testing has been assembled and is operating for testing of effects of impurities from chemical hydrogen release compounds.
- Provided ultra-pure ionic liquids and modified electrodes to support the Penn State University effort on electrochemical regeneration of borate to borohydride to complete Phase 1 research and development (R&D) on sodium borohydride regeneration.



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 (Penn), Pennsylvania State University, the University of Washington, Rohm and Haas, U.S. Borax, and the Pacific Northwest National Laboratory (PNNL). These partners collectively work on four major areas of 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. Los Alamos 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 (1) *hydrogen release from AB*, LANL’s approach is to develop liquid compositions containing ammonia borane, and to develop mechanistic information to guide heterogeneous catalyst discovery for hydrogen release from AB and AB-like liquid systems. In the area of (2) *spent fuel regeneration*, LANL’s approach is to optimize the thiocatechol route to the digestion, reduction, and recycle of reagents to complete a spent fuel regeneration process, and work closely with Dow (formerly Rohm and Haas) process modelers to develop preliminary baseline cost and efficiency analyses. This involves closely working

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 (3) *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 (4) *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 AB

Research has continued on heterogeneous catalytic release of hydrogen from ammonia borane, AB. The focus has been on finding additional non-precious metal catalysts, and achieving higher rates to higher capacities at lower temperatures.

Figure 1 shows the recent results on hydrogen release from AB at 70°C catalyzed by several different types of heterogeneous catalysts derived from first row transition metal cations on a support. The best non-precious group metal catalyst has activity approaching the Pt catalysts described last year. Catalyzed dehydrogenation at higher temperatures increases the rate and capacity substantially, as shown in Figure 2.

To enable catalytic release, one must have a liquid fuel. LANL began work on liquid amine borane/AB mixtures last year. This year, working with Prof. Tom Baker at the University of Ottawa, we have found that sec-butyl amine borane/AB mixtures remain liquid at room temperature before and after catalytic dehydrogenation. Further work as a function of ratio of reagents and temperatures is ongoing.

2. Regeneration of Spent Fuel

LANL's 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). Several process improvements were demonstrated in the lab, and incorporated into the cost analysis. Major improvements were demonstrated in the use of a 'lean' digestion that minimizes losses of reducing agent, optimization of the ligand exchange/reduction steps, and final separation of AB from the reaction mixture. 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 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.

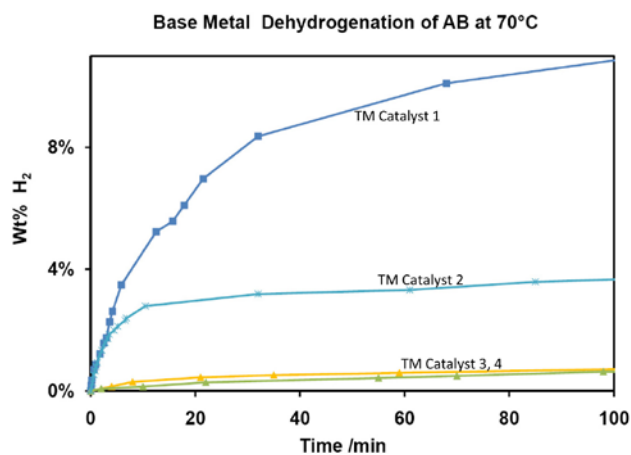


FIGURE 1. Base Metal Catalyzed Dehydrogenation of AB at 70°C

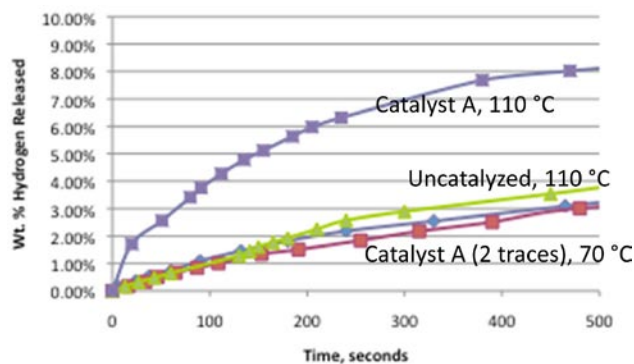


FIGURE 2. Catalyzed and Uncatalyzed Hydrogen Release from AB at 70°C and 110°C

Subsequent laboratory research led to the discovery of two new, simplified spent fuel regeneration schemes that are shown in Figure 3. These schemes involve hydrazine, N_2H_4 , a light weight reducing agent. One option is direct digestion/reduction using hydrazine in a single step, that produces AB, hydrazine borane complex, and a small quantity of a material that may be $B(N_2H_3)_3$, but this has not been positively determined yet. The hydrazine borane complex may be converted to AB with the addition of ammonia, the topic of current investigations. An alternative pathway is also shown in Figure 3, and that is by way of digesting the spent fuel with thiocatechol as previously known, followed by reduction of the thiocatechol borane ammonia complex with hydrazine to yield once again AB, hydrazine borane, and the unidentified byproduct thought to be $B(N_2H_3)_3$.

Either of these hydrazine pathways results in simplified processing, reduced mass, and more straight forward separations. It is thought at this point that this should result in reduced cost and improved energy efficiency relative to the thiocatechol/tin hydride route previously described.

3. New Materials Discovery

LANL's efforts in new materials discovery have focused on discovering compounds that release hydrogen with near thermoneutrality. AB releases hydrogen exothermically at around 6-8 kcal/mole AB. Because of these energetics, dehydrogenated AB cannot be directly rehydrogenated using hydrogen pressure. In order to regenerate with reasonable pressures of hydrogen, hydrogen release from a storage material should not be more exothermic than approximately 1 kcal/mole.

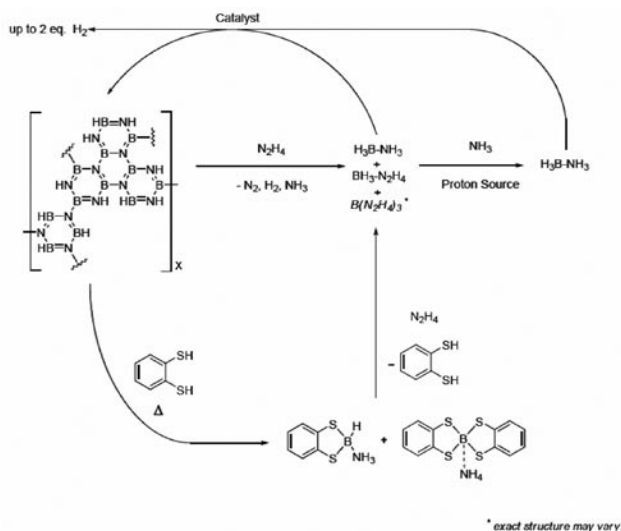


FIGURE 3. New Schemes for Regeneration of AB from Spent Fuel Using Hydrazine

Los Alamos researchers are collaborating with partners at PNNL, and IPHE partners in the UK and New Zealand to explore and develop metal derivatives of AB. The resulting metal amidoboranes have been shown to release hydrogen at lower temperatures, but at higher rates and with the release of fewer volatile contaminants. As an example, the thermal release profile for potassium amidoborane, KAB, is shown in Figure 4, top panel. The top panel shows the weight loss curve, and the mass spectrum of the gas evolved. The concentration of gas impurities is much lower than found for the thermolysis of pure ammonia borohydride, AB. The bottom panel of Figure 4 indicates the thermochemistry of hydrogen release indicating that there is an endothermic event coupled with an overall exothermic event at the release temperature of around 100°C. LANL has recently characterized the thermochemical properties of the series of M-AB compounds for M= Li, Mg, Ca, K, and Al (prepared by our partners at the University of Missouri). These results are summarized in Table 2. While the thermochemical

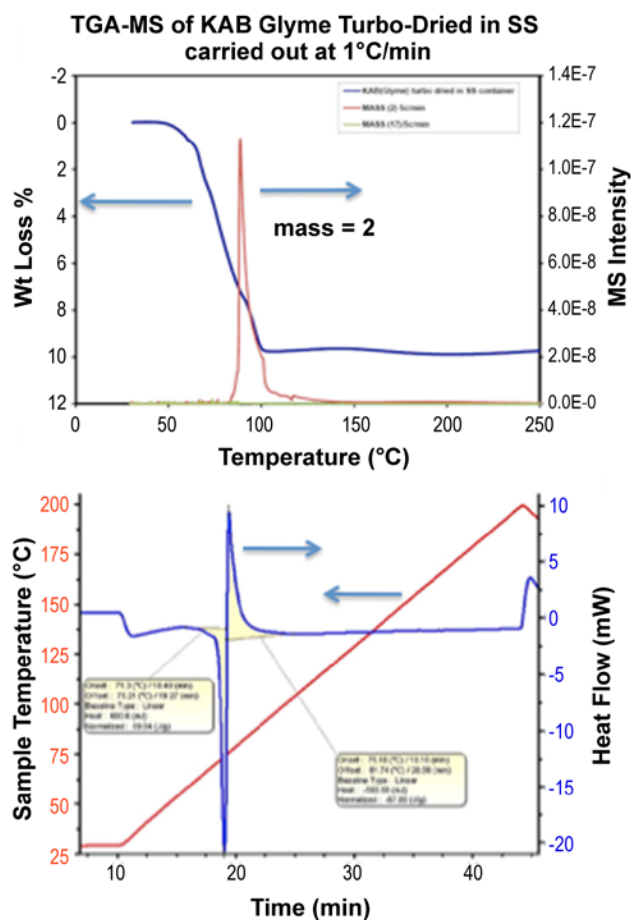


FIGURE 4. Top panel – Thermal gravimetric analysis-mass spectrometry (TGA-MS) of release of hydrogen from potassium amidoborane. Bottom panel – thermochemistry of a series of metal amidoborane storage materials.

TABLE 2. Thermochemical Properties of the Series of M-AB Compounds for M= Li, Mg, Ca, K, and Al

Compound	Normalized 1 st exotherm J/g (onset/°C)	Normalized 2 nd exotherm J/g (onset/°C)	Normalized 3 rd exotherm J/g (onset/°C)	On Board Regeneration
Li AB	-621.9 (77)*			No
KAB	+70 (71)	-48.6 (75)		No
Mg (AB) ₂	-6.7 (78)	-188 (108)		No
Ca(AB) ₂	-102 (101)	-56 (120)		No
Al(AB) ₃	-38.5 (66)	-5.1 (106)	-5.9 (154)	No

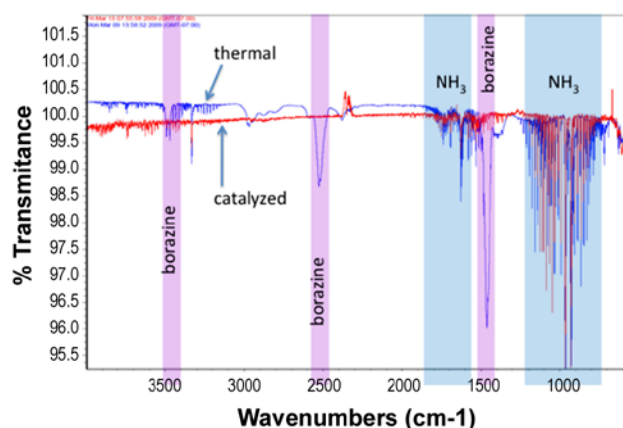
properties, and the hydrogen release temperatures show a good deal of diversity, the thermodynamics of hydrogen release are still too exothermic to enable direct rehydrogenation using H₂ gas pressure, and so to date, no materials have been discovered that can be directly regenerated on board.

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. In addition to many of engineering activities described above, LANL is currently working on bringing a previously designed an fabricated flow reactor system into operation to begin to measure steady state kinetics of catalytic dehydrogenation of liquid AB systems. This system will also be used to address the measurement of any catalyst deactivation or poisoning effects during reaction under a variety of conditions.

A major activity of this task during the past year was to interact with both Dow and with Argonne National Laboratory researchers on providing data and experimental support for the process analysis efforts both on regeneration baseline cost estimates and our upcoming work on an estimate of an on-board hydrogen release energy efficiency estimate.

Another portion of the engineering support task was to begin to gather the data on detection of any gas-phase impurities from chemical hydrogen storage materials and processes. Systems using gas-phase infrared spectroscopy and mass spectroscopy detection of potential impurities such as diborane, ammonia, borazine, among others, in the evolved hydrogen have been developed. Numerous release materials and processes have been qualitatively characterized for gas-phase impurities. Significant differences have been observed. By way of example, LANL has worked with our partners at Penn to begin to characterize any impurities that arise from hydrogen release from ionic liquid-AB mixtures that Penn has been exploring. In this instance, no diborane is detected, however ammonia and borazine are both detected by infrared and mass

**FIGURE 5.** Effect of catalytic vs. thermal hydrogen release for an AB-ionic liquid mixture as determined by gas-phase infrared spectroscopy. Catalysis mitigates borazine impurities. No diborane is detected.

spectroscopy. This result is shown in Figure 5. When hydrogen release from the ionic liquid-AB mixture is performed in the presence of a catalyst, no diborane is detected, ammonia is still present, but no borazine is detected indicating that the catalyst mitigates the release of volatile borazine. Quantification of these impurities is in progress.

Conclusions and Future Directions

Research at LANL has demonstrated the use of heterogeneous catalysts for the release of hydrogen from AB and potential liquid fuels including AB-alkylamine borane mixtures and AB-ionic liquid 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 AB. The baseline cost for regeneration of AB from spent fuel using LANL's thiocatechol process is \$7-8/kg. This cost analysis indicated opportunities for substantial process improvements. This led to further regeneration research at LANL, and the discovery of a simplified, potentially less costly and more energy efficient process using hydrazine as both digesting agent and reducing agent. In collaboration with Center and IPHE partners, LANL has carried out the synthesis, chemical characterization, hydrogen release studies, and thermochemical characterization of additional new metal amidoborane storage materials bringing the total of such new compounds to greater than a dozen.

In Fiscal Year 2010 we will:

- Prepare fuels that meet DOE targets for operability, including storage stability.
- Identify, test metal AB derivatives (mixed metal systems) with potential for on-board regeneration.

- Identify, demonstrate additional non-precious metal heterogeneous catalyst with yet higher rates and with high durability using a continuous flow reactor that will also begin to help us address cold-start issues (supports the Hydrogen Storage Engineering Center of Excellence).
- Quantify purity of hydrogen – identification, quantification, and mitigation.
- Improve regeneration process efficiency and reduce cost.
- Confirm regeneration capability of liquid fuel mixtures with regeneration processes.
- Prepare final report.

FY 2009 Publications, Presentations, and Patents

Peer-reviewed Publications

- 1. Efficient Regeneration of Partially Spent Ammonia Borane Fuel**, Benjamin L. Davis, David A. Dixon, Edward B. Garner, John C. Gordon, Myrna H. Matus, Brian Scott, and Frances H. Stephens, *Angewandte Chemie*, Published Online, June 9, 2009.
- 2. Coordination of aminoborane, NH₂BH₂, dictates selectivity and extent of H-2 release in metal-catalysed ammonia borane dehydrogenation**, Pons, V.; Baker, RT; Szymczak, NK; Heldebrant, DJ; Linehan, JC; Matus, MH; Grant, DJ; Dixon, DA, *Chemical Communications* (2008) iss.48, p.6597-6599.
- 3. B-N compounds for chemical hydrogen storage**, Hamilton, CW; Baker, RT; Staubitz, A; Manners, I, *Chemical Society Reviews* (2009) Vol.38, iss.1, p.279-293.
- 4. Catalytic dehydrogenation of ammonia borane in non-aqueous medium**, Shrestha, RP; Diyabalanage, HVK; Semelsberger, TA; Ott, KC ; Burrell, AK; et al., *International Journal of Hydrogen Energy*, (MAR 2009) Vol.34, iss.6, p.2616-2621.
- 5. Formation of Benzodiazaborolanes From Borazine**, Benjamin L. Davis, Andrew D. Sutton, John C. Gordon, Daniel E. Schwarz, Brian L. Scott, David L. Thorn, Main Group Chemistry, *submitted for publication*.
- 6. Recycle of Tin Thiolate Compounds Relevant to Ammonia-Borane Regeneration**, Benjamin L. Davis, Andrew D. Sutton, Koyel X. Bhattacharyya, Bobby D. Ellis, Philip P. Power, John C. Gordon, *Chemical Communications*, in preparation.
- 7. Two-Step Regeneration of Dehydrogenated Ammonia-Borane Fuel**, Andrew D. Sutton, John C. Gordon, David D. Dixon, Manuscript in preparation

Symposia Proceedings

- 1. Transition metal initiated catalytic dehydrogenation of ammonia borane in non-aqueous medium**, Shrestha, Roshan P.; Diyabalanage, Himashinie V.K.; Semelsberger, Troy A.; Burrell, Anthony K. From Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2008), 53(2), 691-692.
- 2. Metal derivatives of ammonia-borane: potential hydrogen storage materials**, Diyabalanage, Himashinie V.K.; Shrestha, Roshan P.; Semelsberger, Troy A.; Scott, Brian L.; Burrell, Anthony K. From Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2008), 53(2), 672-673.

Presentations

- 1. Chemical hydrogen storage at Los Alamos**, Gordon, John C.; Davis, Benjamin L.; Dixon, David A.; Matus, Myrna H.; Stephens, Frances H. From Abstracts of Papers, 237th ACS National Meeting, Salt Lake City, UT, United States, March 22-26, 2009 (2009), INOR-404.
- 2. Transition metal initiated catalytic dehydrogenation of ammonia borane in nonaqueous medium**, Shrestha, Roshan L.; Diyabalanage, Himashinie V.K.; Burrell, Anthony K. From Abstracts of Papers, 236th ACS National Meeting, Philadelphia, PA, United States, August 17-21, 2008 (2008), FUEL-065.
- 3. Metal derivatives of ammonia-borane: Potential hydrogen storage materials**, Diyabalanage, Himashinie V.K.; Shrestha, Roshan L.; Semelsberger, Troy A.; Scott, Brian L.; Burrell, Anthony K. From Abstracts of Papers, 236th ACS National Meeting, Philadelphia, PA, United States, August 17-21, 2008 (2008), FUEL-056.
- 4. Cheap, easy, fast and selective: Optimizing catalysts for ammonia-borane dehydrogenation**, Hamilton, Charles W.; Baker, R. Tom; Shrestha, Roshan; Semelsberger, Troy A. From Abstracts of Papers, 235th ACS National Meeting, New Orleans, LA, United States, April 6-10, 2008 (2008), INOR-147.

Patents

- 1. Process for stepwise preparation of boranes and borane complexes by reaction of boron compounds with metal hydrides**, Thorn, David L.; Tumas, William. From PCT Int. Appl. (2008), WO 2008039312 A2 20080403.
- 2. Regeneration of Ammonia Borane From Polyborazylene**, Andrew D. Sutton, John C. Gordon, Provisional patent applications: S-116,299.
- 3. Regeneration of Ammonia Borane From Polyborazylene**, Andrew D. Sutton, John C. Gordon, Provisional patent application S -116,318.