IV.B.4 Development of Regenerable High Capacity Boron Nitrogen Hydrides as Hydrogen Storage Materials

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Objectives

Phase I

- Evaluate approaches for complete and fast release of hydrogen from ammonia-borane at moderate temperatures and partial hydrogen release at low temperatures.
- Demonstrate hydrogen release greater than 6% by wt of ammonia borane material.
- Develop an efficient on-board hydrogen extraction process.
- Demonstrate lab-scale synthesis of pure ammonia borane starting from ammonia borane decomposition byproducts.

Phase II

- Preliminary design of an on-board ammonia borane-based hydrogen storage system with >9 wt% H_2 and >45 gH_2/L system capacity.
- Complete technical and economic feasibility assessment.

Phase III

- Scale-up the ammonia-borane regeneration process.
- Design, develop, and demonstrate prototype (1 kg hydrogen capacity) hydrogen extraction system with >9 wt% hydrogen capacity.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Storage System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(F) Codes and Standards
(G) Materials of Construction
(H) Balance of Plant (BOP) Components
(I) Dispensing Technology
(J) Thermal Management
(K) System Life-Cycle Assessment
(R) Regeneration Processes
(S) By-Product/Spent Material Removal

Technical Targets

This project is evaluating the feasibility of using ammonia-borane (NH_3BH_3) as an on-board hydrogen storage medium. With 19.6% by weight of hydrogen in its molecular formula, ammonia-borane has potential to meet DOE's year 2015 targets of gravimetric (0.09 kg H_2/kg of system weight) as well as volumetric (0.081 kg H_2/L of system volume) energy densities. Evaluation of approaches to regenerate ammonia-borane decomposition products will determine the feasibility of approaching DOE's fuel cost ($2 to $3/gge ~kg H_2) target. Development of an efficient hydrogen release system will allow approaching the storage system cost ($67/kg H_2) target.

Accomplishments:

- Studies involving slow non-catalytic heating of ammonia-borane indicated three distinct stages of hydrogen release occurring at 85-100°C, 105-

150°C, and beyond 200°C. About 2/3 or 67% of the available hydrogen was released during the first two stages with a material-based hydrogen density of 13 wt%.

- Studies involving rapid heating of ammonia-borane indicated release of ~85% of the available hydrogen in ammonia-borane at 500°C in less than 30 seconds with a material-based hydrogen storage density of 16.5 wt%.
- Full cycle energy balance estimations for the chemical regeneration of ammonia borane decomposition products identified decomposition of hydrochloric acid as a single most energy-intensive step in the regeneration sequence involving chlorination of decomposition products, hydrogenation of boron chloride to diborane, and ammoniation of diborane to ammonia-borane.
- Due to several individual steps involved in chemical regeneration and difficulties in realizing efficient heat exchange between endothermic and exothermic reactions, the chemical regeneration of the ammonia borane based on chlorination of decomposition products was deemed not likely to meet the 60% energy efficiency target.
- Procedures were established for high-throughput synthesis and screening of a library of catalysts for dehydrogenation of ammonia borane at low temperatures including: loading a library of ammonia-borane and catalyst on a suitable substrate, development of a hydrogen sensor for direct measurement of hydrogen release and decomposition residue characterization.
- Preliminary evaluation of a number of catalyst compositions was conducted for their effectiveness in dehydrogenation of ammonia-borane at <120°C.

Introduction

The objective of this three-phase project is to develop synthesis and hydrogen extraction processes for nitrogen/boron hydride compounds that will permit exploitation of the high hydrogen content of these materials. The primary compound of interest in this project is ammonia-borane (NH_3BH_3), a white solid, stable at ambient conditions, containing 19.6% of its weight as hydrogen. With low-pressure on-board storage and an efficient heating system to release hydrogen, ammonia-borane has potential to meet DOE's 2015 specific energy and energy density targets. If the ammonia-borane synthesis process could use the ammonia-borane decomposition products as the starting raw material, an efficient recycle loop could be set up for converting the decomposition products back into the starting boron-nitrogen hydride. With production at a large scale typical of a commodity chemical (as may be expected from a potential gasoline substitute), the cost of ammonia-borane regeneration has potential to meet DOE's fuel cost targets based on the cost of hydrogen and raw materials used for regeneration. By designing an efficient heating system for aminoborane decomposition, a net high energy density will be realized and the system cost will be minimized approaching DOE's goals.

Approach

This project is addressing two key challenges facing the exploitation of the boron/nitrogen hydrides (ammonia-borane), as hydrogen storage material:

- Development of a simple, efficient, and controllable system for extracting most of the available hydrogen, realizing the high hydrogen density on a system weight/volume basis, and
- Development of a large-capacity, inexpensive, ammonia-borane regeneration process starting from its decomposition products (BNH_x) for recycle.

During Phase I of the project both catalytic and non-catalytic decomposition of ammonia borane will be investigated to determine optimum decomposition conditions in terms of temperature for decomposition, rate of hydrogen release, purity of hydrogen produced, thermal efficiency of decomposition, and regenerability of the decomposition products. The non-catalytic studies will provide baseline performance to evaluate catalytic decomposition. Utilization of solid phase catalysts mixed with ammonia-borane will be explored for their potential to lower the decomposition temperature, to increase the rate of hydrogen release at a given temperature, and to lead to decomposition products that may easily be regenerated by direct hydrogenation of the decomposition products in the presence of catalysts. The most promising catalysts will then be explored for direct catalytic hydrogenation of the decomposition residue.

Two different approaches of heating ammonia-borane are being investigated: a) "heat to material approach" in which a fixed compartmentalized ammonia-borane cartridge will be heated by directing the heating medium to progressive zones with a carefully controlled heating pattern, and b) "material to heat approach" in which a small amount of ammonia-borane will be dispensed at a time in a fixed hot zone. In the first approach the ammonia-borane heating rate as well as the rate of hydrogen release from the storage system will be regulated by a controlled heating pattern, whereas, in the second approach the hydrogen release rate will be controlled by the rate of ammonia-borane dispensing in the hot zone. The complete decomposition of the ammonia-borane is overall exothermic which

would allow the small "hot zone" used in the second approach for heating to be self-sustaining. Careful heat management both to supply the heat during the initial heating and removal of heat, if necessary to maintain a desired temperature, will be needed in the first approach.

Contingent upon demonstration of hydrogen release greater than 6% by wt of ammonia borane material and lab-scale synthesis of ammonia borane starting from its decomposition products, a conceptual design will be prepared in Phase II for an on-board hydrogen storage system using the most promising approach for maximum and high purity hydrogen yield. Techno-economic feasibility analysis will then be conducted to estimate the storage system as well as regeneration (fuel) costs to provide a go/no go decision for the Phase III project.

Upon successful completion of the Phase I and Phase II, the ammonia-borane regeneration process steps will be scaled-up in the Phase III project to be able to synthesize sufficient quantities of ammonia-borane for testing, demonstration, and delivery to DOE. A prototype on-board hydrogen storage system with 1 kg hydrogen capacity will be designed and fabricated for demonstration of this concept. An integrated process design will be developed for large-scale regeneration of ammonia-borane and an economic analysis will be conducted to determine the minimum production volume necessary to be able to meet DOE's fuel cost targets.

Results

- Thermal decomposition of ammonia-borane was studied using two different approaches for heating ammonia-borane material: a) slow heating with controlled heating program to identify stages of ammonia-borane decomposition, and b) fast heating of ammonia-borane in a high temperature reactor to determine hydrogen release as a function of temperature and exposure time.
- Slow heating studies were conducted using a thermogravimetric analyzer (TGA) as well as temperature programmed desorption (TPD) techniques in an inert atmosphere. Gas species released during heating were monitored by an on-line mass spectrometer and the total amount of hydrogen released was quantified by an on-line thermal conductivity detector analysis. Three distinct stages of hydrogen release were observed occurring at 85-100°C, 105-150°C, and beyond 200°C, respectively. About 2/3 or 67% of the available hydrogen was released during the first two stages with a material-based hydrogen density of 13 wt%.
- Fast heating studies were conducted using a high temperature tubing reactor for quantitative determination of the amount of hydrogen released as a function of the reactor temperature and the sample hold time. Gas species released during the fast heating were determined by the gas chromatographic and mass spectrometer analysis of the gas generated. About 85% of the available hydrogen in ammonia-borane was observed to be released at 500°C in less than 30 seconds with a material-based hydrogen storage density of 16.5 wt%. The elemental analysis of the decomposition product indicated a composition of an empirical formula $BN_{0.9}H$ consistent with the observed release of 85% of the available hydrogen in ammonia borane. Mass spectrometer analysis of the gas produced indicated borazine to be the only minor impurity in the gas produced.
- Full cycle energy balance estimates for the chemical regeneration of ammonia borane decomposition products were made starting with chlorination of decomposition products, hydrogenation of boron chloride to diborane, and ammoniation of diborane to ammonia-borane as well as the decomposition of hydrochloric acid to produce chlorine gas used in chlorination and formation of ammonia used in ammoniation to close the regeneration loop. The analysis identified decomposition of hydrochloric acid as the single most energy-intensive step in this specific ammonia borane chemical regeneration sequence.
- Although ideal thermodynamic calculations indicated the chlorination-based chemical regeneration to be an energy efficient regeneration process; due to the presence of several individual steps involved in this route of chemical regeneration, large energy consumption in the hydrochloric acid electrolysis, and difficulties in realizing efficient heat exchange between individual endothermic and exothermic reactions, this route for chemical regeneration of the ammonia borane decomposition products was deemed not likely to meet the 60% energy efficiency target. The approach of chemical regeneration of the ammonia borane based on chlorination of decomposition products was therefore suspended. An alternative route of catalytic hydrogenation of the ammonia borane decomposition products will however be pursued.
- Procedures were established for high-throughput synthesis and screening of a library of catalysts for dehydrogenation of ammonia borane at low temperatures including: loading a library of ammonia-borane and catalyst on a suitable substrate, development of a hydrogen sensor for direct measurement of hydrogen release and decomposition residue characterization. Methanol was selected as a solvent for ammonia borane for deposition on the substrate. A suitable substrate non-reactive to ammonia-borane was identified.

A hydrogen sensor was developed for directly detecting hydrogen as it is evolved during ammonia borane. The hydrogen sensor is placed on the catalyst library using a porous spacer to prevent direct contact with ammonia borane/catalyst surface.

- Baseline non-catalytic hydrogen release and X-ray diffraction pattern of the decomposition residue was established at 50°C, 90°C, and 110°C temperatures.
- Preliminary qualitative evaluation of a number of catalyst compositions was conducted for their effectiveness in dehydrogenation of ammonia-borane at <120°C temperature. The effectiveness of the catalyst for hydrogen release is determined by optical mapping of the hydrogen sensor placed directly above the library of catalysts. An example of mapping of catalyst activity is shown in Figure 1. Detailed quantification of hydrogen release will be conducted next.

Conclusions and Future Directions

The hydrogen release studies have confirmed the potential of ammonia-borane for meeting DOE's 2015 hydrogen storage density targets. The ammonia-borane decomposition studies will be continued to evaluate non-catalytic as well as catalytic decomposition approaches and to optimize process conditions for maximizing hydrogen yield. Suitable catalysts will be identified using combinatorial synthesis technology to efficiently generate hundreds of different catalyst compositions. Direct catalytic hydrogenation of ammonia-borane decomposition products will first be evaluated to determine its feasibility using the catalysts discovered for hydrogen release. Alternative catalysts will also be explored if necessary. The nature and concentration of impurities in the hydrogen gas produced will be determined and approaches will be evaluated to produce high purity hydrogen suitable for PEM fuel cells.

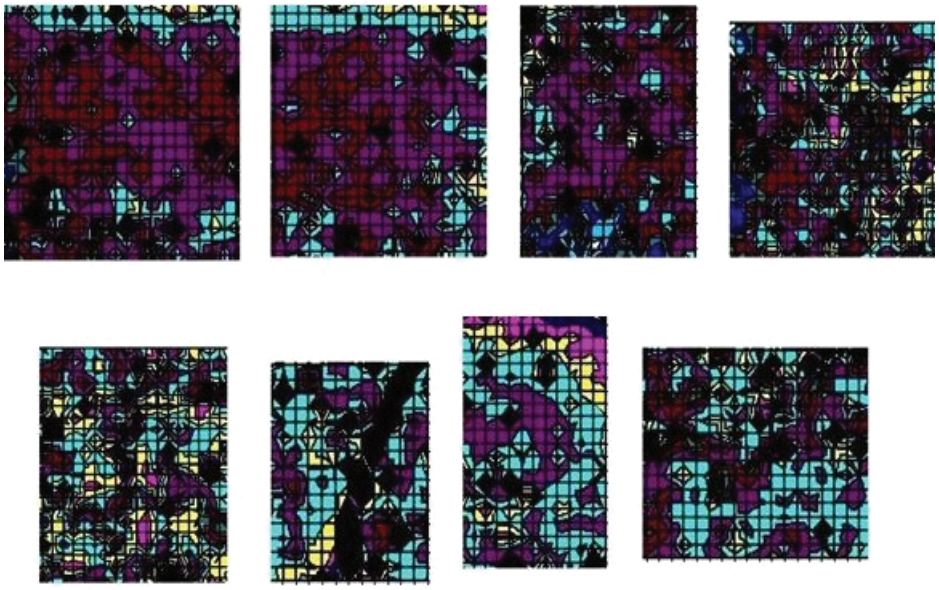

FIGURE 1. Mapping of Activity of Catalyst Samples (Areas of higher reflectivity correspond to a more metallic state, and thus more hydrogen. Areas of higher reflectivity are shown by the red and purple. Yellow and aqua are areas of lower reflectivity.)