IV.B.5 DOE Chemical Hydrogen Storage Center of Excellence

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Objectives

- Implement a coordinated approach to identify, research, develop, and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet DOE Hydrogen Storage 2010 system goals with the potential to meet the 2015 system goals.
- Develop materials, catalysts, catalytic processes, and new concepts for hydrogen release and spent fuel regeneration for the complete fuel cycle.
- Design, synthesize, and test materials and compositions to control the thermochemistry and kinetics of hydrogen release and spent fuel regeneration.
- Assess concepts and systems for hydrogen release and spent fuel regeneration using supporting engineering analysis and validation to rank viable candidates.
- Perform lab-scale engineering studies to evaluate performance of hydrogen storage systems.
- Develop lifecycle inventory to assess regeneration energy requirements.
- Demonstrate a 1 kg prototype storage system.

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) 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

Technical Targets

The Chemical Hydrogen Storage Center of Excellence (CHSCoE) is taking a multi-pronged approach to identifying and developing chemical hydrogen storage materials and systems capable of meeting the 2010 DOE goals for on-board hydrogen storage with the potential to meet the 2015 DOE targets. The CHSCoE has developed a set of quantitative metrics to track progress towards the DOE targets:

- Gravimetric capacity for the reaction system (i.e. the material and any solvent/catalyst), in wt% hydrogen.
- Volumetric capacity for the reaction system (i.e. the material and any solvent/catalyst), in kg hydrogen/liter.
- Hydrogen release rates (reported as amount of material/catalyst needed to meet DOE target rate of 0.02 g H_2/sec/kg) for the maximum rate, rate to one, two and maximum equivalents released.
- Theoretical thermodynamic efficiency of the regeneration process (i.e. the ratio, in percent, of the amount of energy in hydrogen released to the sum of the energy in the hydrogen released and the amount of energy needed to regenerate spent storage material).

The reporting metrics for these targets include the material, any solvents and catalysts, but do not include tanks, piping, reactors, and ancillary equipment that would make up an operable storage system. CHSCoE partners have made substantial progress toward these targets during FY 2007. Research and development has been primarily directed at obtaining greater capacities and higher rates from viable candidate materials. This year, the CHSCoE put additional effort on providing a demonstration of proof-of-principle chemistries for the energy efficient regeneration of spent fuels having a thermodynamic efficiency of greater than 60%. This additional effort resulted in significant progress on regeneration of spent fuel. Progress toward DOE's 2010 and 2015 technical targets is being tracked quarterly, CHSCoE-wide. Partner progress toward these goals is documented in the appended reports from CHSCoE partners that follow this CHSCoE overview report.

Selected FY 2007 Accomplishments

- Demonstrated proof-of-principle chemistries that avoid the generation of B-O bonds for the regeneration of ammonia borane from spent ammonia borane (AB) fuels using two different chemical approaches having thermodynamic efficiencies approaching or exceeding 60% (Penn, LANL).
- Demonstrated 16 wt% hydrogen release from solid AB at 155°C, and determined factors that increase fuel stability at 60°C (PNNL, and PNNL with ROH).
- Achieved liquid fuel compositions with theoretical storage quantities with potential to achieve 2015 targets (NAU).
- Developed mechanistic understanding of hydrogen release from AB which has led to increased rates and/or quantities of hydrogen released at 85°C from AB or AB/MeAB (ammonia borane/methylamine borane mixtures) in the solid state (5.5%), solution state (5.5%), and from ionic liquids (6.5%) (PNNL, LANL, Penn).
- Guided and accelerated experimental work with theoretical and computational modeling support (Alabama).
- Developed catalysts for the rapid release of one equivalent of hydrogen in less than 100 seconds at room temperature from AB and from MeAB/AB mixtures (UW).
- Assessed the landscape of B-O-to-B-H regeneration schemes in support of hydrogen release from sodium borohydride hydrolysis has generated a prioritized list of reaction chemistries (ROH).
- Extended experimental B-O to B-H regeneration research on electrochemical reduction of borate solutions under a variety of conditions with numerous electrode configurations (PSU and ROH).
- Demonstrated pathway to preserve B-H bonds and reform AB from spent fuels using t-butanol (PNNL) or thiolates (LANL) in the presence of ammonia.
- Discovered a new H_2-release system, based on the chemical promotion of AB dehydropolymerization in ionic liquids that results in faster and greater extent of hydrogen release (Penn).
- Identified an active Rh catalyst for the hydrogen release from AB under hydrolytic conditions (UMC).
- Assessed engineering aspects of hydrogen release from AB. Defined boundary conditions for solids characteristics, solvents, thermal stability of AB (PNNL).
- Identified base metal catalysts for hydrogen release from AB or AB/MeAB mixtures (UW, LANL).
- Drafted preliminary design reports and borate regeneration pathways analysis for the $NaBH_4$ go/no go decision anticipated in September, 2007 (MCEL, ROH).
- Initiated 'medium throughput' capability for hydrogen release catalyst discovery and optimization (LANL).
- Completed work on Bronsted acid catalyzed hydrogen release work (LANL).
- Completed hydrolysis of ammonia triborane (AT) research (Penn).
- Demonstrated hydrogen elimination pathways of heterocyclic hydrocarbons to form carbenes (Alabama).
- Demonstrated release of hydrogen from new metal amine borane compounds (LANL and PNNL with International Partnership for the Hydrogen Economy [IPHE] partners).
- Coordinated overall CHSCoE R&D efforts through implementation of monthly conference calls, project level meetings, semi-annual meetings, site visits, and Coordinating Council meetings.

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Introduction

Chemical hydrogen storage involves storing hydrogen in chemical bonds in molecules where an on-board reaction is used to release hydrogen. The resulting spent fuel is regenerated off-board. 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 provide a diversity of options 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 in the CHSCoE are advancing a number of integrated projects involving the development of storage compounds, catalysts, catalytic processes, and new concepts for hydrogen release and regeneration of spent fuels, as well as the assessment of the feasibility of engineered processes. The objectives of the CHSCoE are to develop and assess new methods for on-demand release of hydrogen from chemical systems that can achieve DOE targets and to develop high yield, energy efficient off-board methods for regeneration of spent storage material. The key elements in the CHSCoE's collaborative activities are computation and modeling; the design, synthesis, and testing of structures and compositions to control the thermochemistry and kinetics of hydrogen release and spent fuel regeneration; development of chemical processes and catalysts for hydrogen release and regeneration; and iterative engineering assessment including evaluation, modeling and testing ranging from process identification through optimization of hydrogen release and regeneration reaction conditions.

Approach

The overall CHSCoE approach capitalizes on its broad spectrum of expertise to carry out collectively a number of focused projects listed below that are divided into three tiers with distinct goals:

Tier 1. "Borohydride": Develop new borate-to-borohydride (B-O to B-H) regeneration alternatives and assess economics and lifecycle analysis of borohydride/water hydrolysis to release hydrogen.

Tier 2. "Novel Boron Chemistry": Alternative boron chemistry that avoids thermodynamic sinks using catalytic hydrogen release from polyhedral boranes (BxHy) or amine-boranes. Develop alternative boron chemistry approaches including polyhedral boranes and amine-boranes. This tier also addresses the energy and chemically efficient regeneration of the spent fuel compositions generated from the release of hydrogen from amine borane compositions.

Tier 3. "Innovation Beyond Boron": Develop new compounds and concepts beyond boron for chemical hydrogen storage using coupled endo/exothermic reactions, nano-scale materials, and heteroatom-substituted organic systems for thermodynamic control.

Pursuing three tiers of material discovery and development in parallel will maximize our ability to achieve the DOE targets for hydrogen storage. The goal is to provide DOE with several working options for chemical hydrogen storage, as well as an evolving knowledge and critical evaluation to assist future R&D, technology demonstration, and policy decision-making. The overall approach of the CHSCoE is to screen and assess concepts and ideas against a set of hierarchical criteria that are derived from the DOE technical targets for hydrogen storage and shown schematically in Figure 1.

The specific CHSCoE projects are listed in Table 1 along with the CHSCoE partners who are involved in the research. Our collaborative project structure enables the close coupling of experimental and computational R&D with engineering assessment to facilitate the transition from discovery of new concepts through development to implementation. The CHSCoE is addressing storage capacity by developing, synthesizing, and testing molecular compounds with high hydrogen density, appropriate energetics, and potential pathways for hydrogen release. Theory and modeling as well as engineering assessment are being used to provide insight and down-select the diversity of options. We are developing and optimizing catalysts and chemical processes for hydrogen release and studying their rates and mechanisms. Work on regeneration is focused on developing pathways closer to the thermodynamic limits by avoiding intermediates with high energy content, i.e. reducing agents that can be regenerated by low energy routes.

The CHSCoE is organized as shown in Figure 2, with the key people that help to coordinate the tier

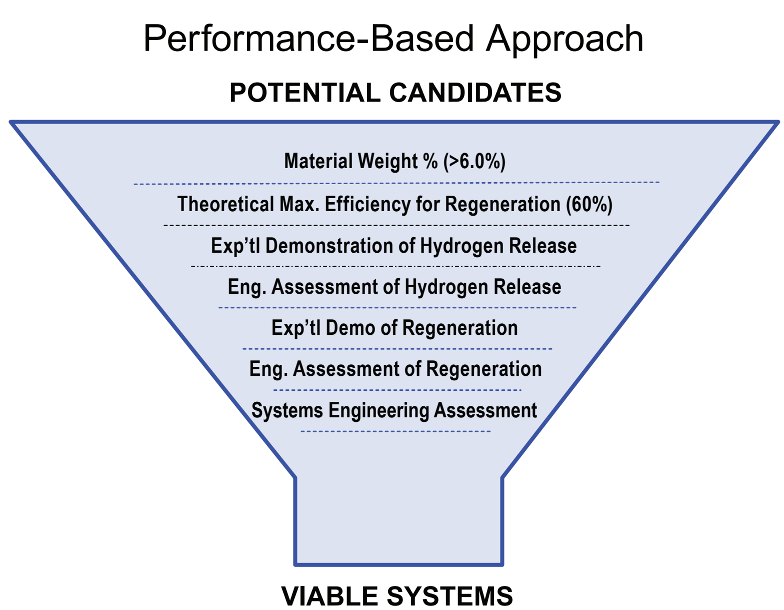

FIGURE 1. Performance-Based Criteria for Assessment of CHSCoE Activities

TABLE 1. CHSCoE Projects and Partners

Tier	Task	Partners
1.1	BO to BH Engineering Guided Research	ROH, MCEL, PSU, PNNL, LANL
1.2	Engineering Assessment of Hydrogen Gneration Systems	MCEL, ROH, PNNL, LANL
2.1	Polyhedral Borane Chemistry	UMC, Penn, IMX, PNNL, LANL
2.2	Amine Borane Chemistry for Release and Regeneration	Penn, UW, NAU, IMX, PNNL, LANL
2.3	Amine Borane Systems Engineering, Safety	NAU, PNNL, ROH, LANL
3.1	Organics and Coupled Reactions	Alabama, PNNL, UW, LANL
3.2	Nanoparticles, Main Group Hydrides, Innovation for Reducing Agent Recycle	UCD, Alabama, LANL, PNNL

research activities. CHSCoE communication challenges across such a diverse, and technically broad spectrum of partners are met by tier and sub-tier conference calls, face-to-face meetings, one-on-one phone conversations, and three annual CHSCoE-wide meetings at the annual Hydrogen Program merit review, a mid-year meeting in Denver, and the annual Tech Team Review. In addition, co-workers from PNNL and LANL collaborate with a group of international scientists that are participating in an IPHE project that also allows for additional opportunities to meet and discuss the science and technology of chemical hydrogen storage.

In addition, we communicate with the Metal Hydride and Sorption Storage Centers through our participation in the Storage Systems Analysis Working Group, a sub-group that examines engineering and integrations aspects that are common to all of the hydrogen storage concepts being developed within the individual CoE. We have also initiated a dialog with the Metal Hydride Center of Excellence to attempt to see if there is some synergy that can be gained through the CHSCoE's experience and expertise in chemical regeneration processes that may be useful for the metal hydride activities in alane-based storage/regeneration systems.

Results

The selected CHSCoE accomplishments listed above are further detailed and extended in the partner reports, IV.B.5a through 5l.

Conclusions and Future Directions

Even with the significant progress the CHSCoE has made this year, on-board chemical hydrogen storage remains a significant scientific and technical challenge. Adding to this challenge is the requirement to achieve a highly chemically and thermally efficient regeneration of spent fuel off-board. As the project proceeds next year, the CHSCoE will increase the emphasis on using engineering tools and expertise to provide more guidance and focus to the research activities and use engineering feasibility studies to down-select to the most promising materials and processes to meet the 2010 goals, and identify materials that with more R&D can meet 2015 targets. In early FY 2008, the CHSCoE will be performing a materials down-selection process. In addition to the materials-based properties of the storage problem, engineering aspects of hydrogen release and spent fuel regeneration will be among the criteria considered in the down-selection process.

In the area of sodium borohydride hydrolysis, progress has been made in the design of a hydrogen release system and in the assessment and down-selection to a set of regeneration schemes that are the most thermally and chemically efficient. This effort will be assessed in a DOE-organized go/no go decision to determine the path forward for sodium borohydride on-board hydrolysis and BO-to-BH off-board regeneration in September, 2007.

In the area of polyhedral borane hydrolysis, work at Penn on polyhedral borane has been completed, whereas

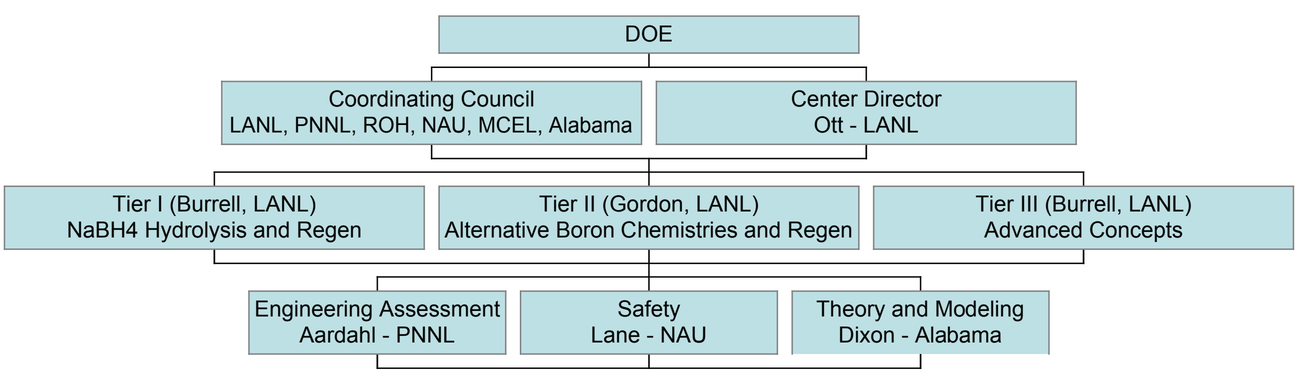

FIGURE 2. CHSCoE Organization

work on polyhedral boranes at UMC is ongoing. Because the hydrolysis pathways rely on BO-to-BH regeneration, the path forward for this research has been tied to the sodium borohydride go/no go decision.

The regeneration of spent fuel from AB saw a great deal of activity and progress this fiscal year, with two chemical routes to spent fuel regeneration providing experimental proof-of-principal that thermodynamic efficiencies could attain or exceed the DOE target of 60% thermodynamic efficiency for off-board regeneration. Collaborative research and excellent coordination among researchers at Penn, LANL, and PNNL and with substantial and key input from the theoretical effort at Alabama led to this substantial and important progress this past year. Future work on regeneration will focus on additional innovative pathways to spent fuel digestion coupled with B-H regeneration and recovery and the recycle of reducing agent. Innovative new approaches will be sought to further improve the thermal efficiencies of the individual steps. Improvements in chemical efficiency and rates must be made as well, and catalytic approaches to improve the rates of key regeneration steps require innovation. Theory will continue to play a key role in our ability to make rapid progress in this area. Additionally, because each hydrogen release system for AB (catalytically, thermally, chemically activated) appears to generate subtly to significantly different spent fuel chemistries, studies of the influence of the origin of the spent fuel versus regeneration chemistries will be explored. Next year, more emphasis will be placed on defining metrics for AB spent fuel regeneration processes from an engineering approach. Thermal efficiency, chemical efficiency, kinetics and process integration aspects will be fed back into the research chemistry tasks.

The dehydrogenation of AB or amine boranes also saw significant progress toward meeting DOE targets, mostly because of the CHSCoE's investment in the effort to understand the chemical mechanisms of hydrogen release from these unusual chemical systems. Work at Penn, PNNL, UW, and LANL, again with support from theory at Alabama led to new mechanisms, and new understanding of thermally, chemically, and catalytically activated hydrogen release from AB systems. This knowledge resulted in the experimental demonstration of higher capacities and improvements in the kinetics of hydrogen release. Future work in this area is required to improve the kinetics and capacities while reducing the temperature of release. For catalytic hydrogen release systems, our current understanding of catalyst design must be transferred to heterogeneous catalysts to enable more easily engineered release and control systems. Design, fabrication, and operation of a small flow system will occur next year to begin to scope the engineering aspects of catalyzed release in liquid systems. In the area of chemically activated release from amine borane systems, with the new mechanistic insights achieved last year, improvements in the kinetics of release to higher capacities will be sought. For hydrogen release from solid-state AB, understanding the mechanism and enhancing the kinetics of the 2^{nd} and greater equivalents of hydrogen will be a focus of research. Also, understanding and controlling the volume expansion that AB undergoes upon hydrogen release will be addressed in the upcoming year as part of the solid AB engineering support and assessment task.

Another key development was the very intriguing observation made by the late Professor Clint Lane at NAU. Clint searched for and found low melting, liquid compositions of methylamine borane – AB mixtures having liquid ranges that extended down to 30°C and that could achieve the 2010 and possibly the 2015 targets for gravimetric and volumetric capacity. He was searching for additional additives that could further extend the liquid range. Also, Clint was performing studies of the stability and safety of these mixtures at the time of his death. The CHSCoE will be developing a plan with DOE to attempt to continue Clint's line of inquiry, as his work is integral to the success of the CHSCoE. Engineering assessments of the MeAB/AB liquid system to map out process options and regeneration options will begin during the next year.

In the Tier III activities we will seek continuing innovation in the discovery of new chemical hydrogen storage systems. The carbene pathway to hydrogen release from heterocyclic organic compounds being explored at Alabama must demonstrate experimental progress toward achieving capacities to meet 2010 goals. In coupled endothermic/exothermic release systems such as the magnesium methoxide (fuel) – magnesium hydroxycarbonate (spent fuel) system which we have previously shown to meet 2010 capacity targets, the ability to store hydrogen by direct hydrogenation of the magnesium carbonate/hydroxide will be the focus of our experimental work. Other thermodynamically coupled systems, such as the metal amine borane systems that can exceed 2010 and potentially meet 2015 capacity targets, will be designed and examined for evidence of hydrogen dissociation on the metal sites and subsequent spillover to the spent fuel framework as a pathway to directly rehydrogenate and regenerate "MBNHx" spent fuel.

Pursuing these three tiers of material discovery, characterization of hydrogen release, regeneration chemistry, and engineering assessment will maximize our ability to achieve the DOE targets for hydrogen storage. The goal is to provide DOE with several working options for chemical hydrogen storage, as well as an evolving knowledge and critical evaluation to assist future R&D, technology demonstration, and policy decision-making.

Acknowledgement

This report is dedicated to the memory of Clint Lane of Northern Arizona University and former President of Aldrich Chemical Company. Clint was a valued and key contributor to the Chemical Hydrogen Storage Center of Excellence. Clint was a well-respected expert boron and synthetic chemist. His chemical wisdom and easy going good nature is missed by all.

Special Recognitions & Awards/ Patents Issued and FY 2007 Publications/Presentations

All Awards, Patents, Publications and Presentations resulting from work within the CHSCoE are given in the accompanying partner reports that follow in IV.B.5a-l.