IV.B.4 Chemical Hydride Rate Modeling, Validation, and System Demonstration

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Project Start Date: February 2009
Project End Date: February 2015

Overall Objectives

- Develop an automotive chemical hydrogen storage system capable of meeting all of the 2017 DOE targets simultaneously
- Develop and validate chemical hydrogen storage system models
- Quantify viable chemical hydrogen storage material properties that will meet DOE 2017 technical targets with our current system
- Develop and demonstrate "advanced"(non-prototypical) engineering concepts

Fiscal Year (FY) 2014 Objectives

- Quantify chemical hydrogen storage material properties meeting the DOE 2017 technical targets
- Design, build, and demonstrate advanced dehydrogenation reactors

Technical Barriers

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

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(D) Durability/Operability

(E) Charging/Discharging Rate

(F) Codes and Standards

(G) Materials of Construction

(H) Balance-of-Plant (BOP) Components

(J) Thermal Management

(K) System Life-Cycle Assessment

(R) By-Product/Spent Material Removal

Technical Targets

The summary of our progress in relation to the DOE 2017 technical targets for both ammonia borane and alane can be seen in Figure 1. The cost target was assumed to be seven dollars per kilogram of hydrogen. The projections are based on the Hydrogen Storage Engineering Center of Excellence's chemical hydrogen storage system design. Both systems assume 50 wt% slurry loadings for ammonia borane and alane.

FY 2014 Accomplishments

- Developed chemical hydrogen storage material property guidelines
- Demonstrated 50 and 60 wt% alane slurries in flow through reactor

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INTRODUCTION

Hydrogen storage systems based on chemical hydrides require a chemical reactor to release the hydrogen from the storage media, which is a fundamental difference from the other modes of hydrogen storage, adsorbents, and metal hydrides. This hydrogen-release reactor is crucial to the performance of the overall storage system, especially in meeting the DOE targets for hydrogen generation rate, transient operation, and startup times. The reactor must be designed to achieve these targets while meeting the constraints of the overall system volume and weight targets.

LANL will also address the unique requirements of onboard automotive hydrogen storage systems. For example, these systems require fast startup, operation over a wide dynamic range (10:1 turndown or greater), and fast transient

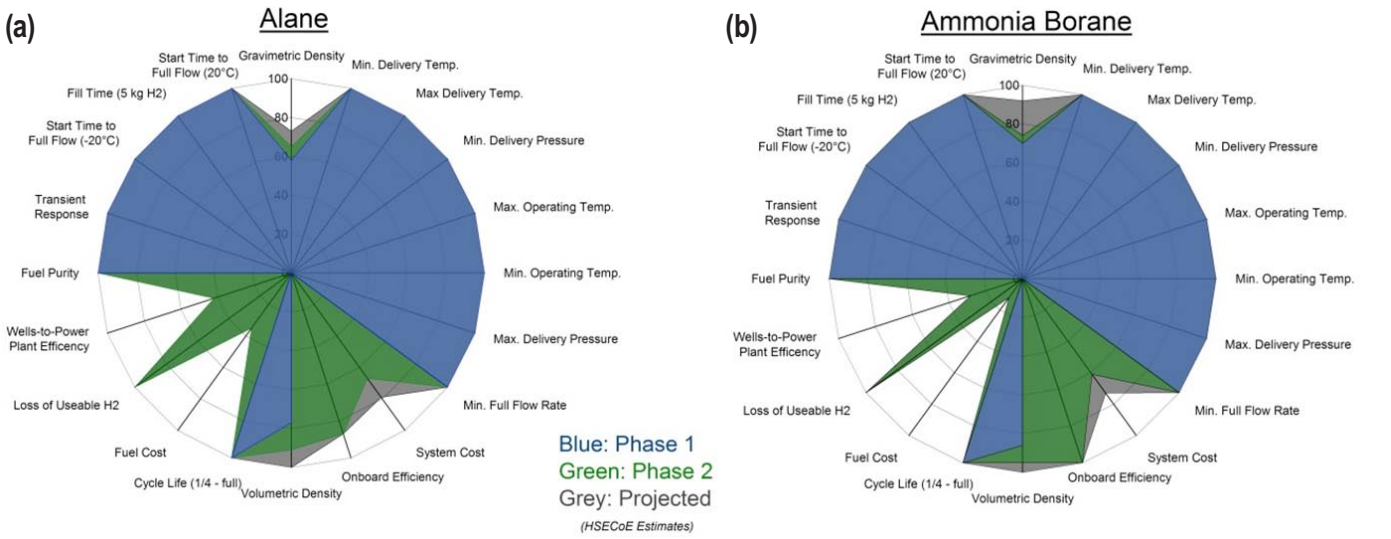

FIGURE 1. Spider chart summarizing our progress in meeting the DOE 2017 technical targets for (a) 50 wt% alane slurry and (b) 50 wt% ammonia borane slurry (note: values are Hydrogen Storage Engineering Center of Excellence estimates).

response to meet the demands of a drive cycle. The LANL team will develop novel reactor designs and operation strategies to meet these transient demands. In addition, the shelf life and stability of the hydrogen storage media is crucial for an automotive system, especially pertaining to safety and cost. Starting with the kinetics models, the LANL team will develop mathematical models for the aging characteristics of candidate hydrogen storage media (for example, complex metal hydrides or chemical hydrogen storage materials) subjected to a range of environmental factors. These models can be incorporated into system-level models of performance and cost and also used for the development of accelerated aging protocols necessary for later testing.

RESULTS

Chemical Hydrogen Storage Material Property Guidelines

Our objective was to develop a set of fluid-phase chemical hydrogen storage material property guidelines for automotive applications meeting the 2017 DOE technical targets. The fluid-phase chemical hydrogen storage media considered in the study were neat liquids, solutions, and non-settling homogeneous slurries. The fluid-phase material property guidelines are expected to aid material researchers in their materials development and/or discovery efforts. Until now, the materials researchers relied on system level targets to guide their materials research. Consequently, providing the materials research community with a viable set of chemical hydrogen storage materials properties fills a critical knowledge gap. Although the quantified set of material properties is not exhaustive, it is a necessary first step.

The ammonia borane system design developed by the Hydrogen Storage Engineering Center of Excellence was used as the boilerplate system design. The boilerplate system is presumed to contain the necessary components that will be common to all realizable fluid-phase chemical hydrogen storage media. Components of the ammonia borane system were identified as system independent (e.g., fuel cost), BOP/material independent (e.g., valves and pumps), and material-dependent (e.g., reactor).

System independent components are components invariant to the system design and vice-versa—examples include fuel cost and regeneration efficiency. Material-dependent components (MDC) include pumps, sensors, valves, tubing, etc. Because the BOP components were presumed to be material independent, the BOP components were grouped and treated as a constant with respect to mass, volume, durability, and operability. MDC are the components whose mass and volume are reliant upon the material properties, kinetics, and thermodynamics of the chemical hydrogen storage media. MDC of interest are reactor, heat exchanger, volume displacement tank, and hydrogen purification. To calculate viable material properties, the masses and volumes of the MDC were sized independent of the material. Given the *a priori* sizing of the MDC and the BOP sizing, the minimum gravimetric and volumetric hydrogen capacities for slurries, solutions and neat liquids were calculated that would meet the DOE 2017 gravimetric and volumetric system target. *A priori* sizing of the MDC permitted the calculation of material properties (e.g., kinetics and heat of reaction) that meet the mass and volume estimates of those components. The quantified list of chemical hydrogen storage material properties can be seen in Table 1.

TABLE 1. Chemical Hydrogen Storage Material Property Guidelines

Parameter	Symbol	Units	Range*	Assumptions
Minimum Material Capacity (liquids)	γ_{mat}	$g_{H2}/g_{material}$	~0.078 (*0.085*)†	• System mass (excludes media) = 30.6 kg (36.3 kg) • 5.6 kg of H_2 stored • Liquid media (neat) • Media density = 1.0 g/mL
Minimum Material Capacity (solutions)	γ_{mat}	$g_{H2}/g_{material}$	~0.098 (*0.106*) †	• System mass (excludes media) = 30.6 kg (36.3 kg) • Solute mass fraction = 0.35 ~ 0.80 • Solution density = 1.0 g/mL
Minimum Material Capacity (slurries)	γ_{mat}	$g_{H2}/g_{material}$	~0.112 (*0.121*) †	• System mass (excludes media) = 30.6 kg (36.3 kg) • Non-settling homogeneous slurry • Slurry mass fraction = 0.35 ~ 0.70 • Slurry volume fraction = 0 ~ 0.5 • Slurry density = 1.0 g/mL
Kinetics: Activation Energy	E_a	kJ/mol	117-150	• $V_{reactor}$ ≤ 4 L • Shelf life ≥ 60 days • Reaction order, n = 0 – 1
Kinetics: Pre-exponential Factor	A		$4 \times 10^9 - 1 \times 10^{16}$	
Endothermic Heat of Reaction	ΔH_{rxn}	kJ/mol H_2	≤ +17 (*15*) †	• Onboard Efficiency = 90% • # Cold Startups = 4 • ΔT = 150°C with no heat recovery • neat liquid (C_p = 1.6 J/g K) • Reactor mass = 2.5 kg SS (5.0 kg SS)
Exothermic Heat of Reaction	ΔH_{rxn}	kJ/mol H_2	≤ -27	• T_{max} = 250°C • Recycle ratio @ 50%
Maximum Reactor Outlet Temperature	T_{outlet}	°C	250	• Liquid Radiator = 2.08 kg • Gas Radiator = 0.3 kg • Ballast Tank = 2.6 kg
Impurities Concentration	y_i	ppm	No *a priori* estimates can be quantified	• $m_{adsorbent}$ ≤3.2 kg
Media H_2 Density	$(\gamma_{mat})(\phi_m)(\rho_{mat})$	kg H_2/L	≥0.07	• Heavy-duty polyethylene tank ≤ 6.2 kg
Regeneration Efficiency	η_{regen}	%	≥66.6%	• Onboard Efficiency = 90% • Well-to-power plant efficiency = 60%
Viscosity	η	cP	≤1,500	None

* (a) Parameter values are based on a specific system design and component performance with fixed masses and volumes. (b) Values outside these ranges do not imply that a material is not capable of meeting the system performance targets. (c) The material property ranges are subject to change as new or alternate technologies and/or new system designs are developed. (d) The minimum material capacities are subject to change as the density of the composition changes due to reductions in the mass and volume of the storage tank or reductions in system mass are realized.

† Values outside of parentheses are the values that correlate to the idealized system design (i.e., 30.6 kg) and the values in parentheses are those that correlate to the baseline system design (36.3 kg).

Flow-Through Reactor Studies with 50 and 60 wt% Alane Slurries

Alane is an attractive chemical hydrogen storage media because of its high net-usable hydrogen capacity of 10 wt%. Dehydrogenation of neat alane also produces impurity free, fuel cell-grade hydrogen. The disadvantage of alane is the fact that it is a solid; thus, resulting in a cumbersome technological task of moving solids onboard and off-board. Alane slurries offer a means to retain the advantages of alane dehydrogenation (i.e., hydrogen purity) but also a more facile means of moving the chemical hydrogen storage media onboard and off-board. The disadvantage of alane slurries (or any slurry) is the fact that the non-hydrogen bearing fluidizing media lowers the overall hydrogen capacity of the media composition. In order to achieve a net-usable hydrogen capacity of the alane slurry, alane loadings must approach 75-80 wt%. Shown in Figure 2 are the results of our flow-through reactor studies with 50 and 60 wt% alane loadings. High alane conversions (~90%) were achieved at the highest space-time (tau = 7.6 min), highest temperature (T = 210°C) and the lowest auger speed (auger = 12 rpm) for the 50 wt% alane slurry in silicon oil (Figure 2a). Impurities were observed when silicon oil was used as the fluidizing media. Chemical incompatibilities of alane and silicon oil resulted in a gas-phase impurity with "Si-H" infrared transitions. Alane slurries with silicon oil require reactor temperatures below 200°C in order to prevent the undesired side reactions.

Using mechanical pump fluid and the fluidizing media for alane slurries eliminated the production of the gas-phase impurity with the Si-H infrared transitions; thus, demonstrating the importance of slurry carrier. However, gas-phase impurities were still observed with 60 wt% alane

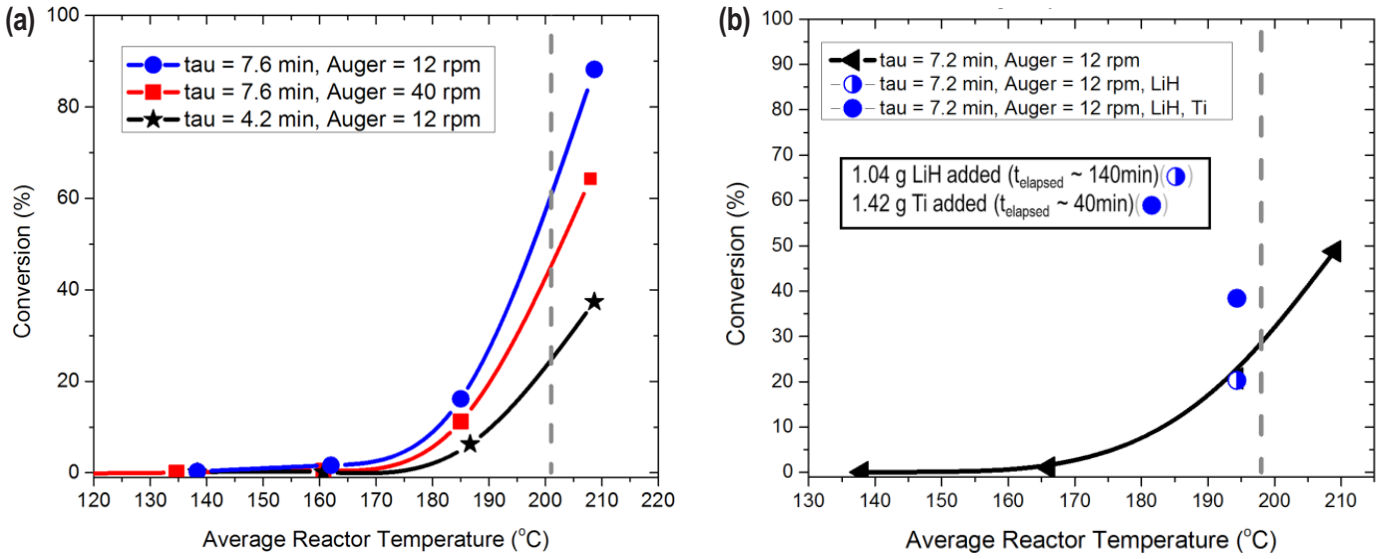

FIGURE 2. (a) Alane conversion as function of reactor temperature, space-time (tau), and auger speed for a 50 wt% alane slurry in silicon oil and (b) alane conversion as a function of reactor temperature, lithium hydride dopant, and titanium dopant for a 60 wt% alane slurry in mechanical pump fluid.

slurry in mechanical pump fluid. The highest conversion observed with the 60 wt% alane slurry was around 50% at 210°C (Figure 2b). Doping alane with LiH alone did not result in an increase the dehydrogenation kinetics. However, adding Ti (after doping with LiH) nearly doubled the conversion at an average reactor temperature of 195°C. Dopants and fluidizing media play an important role in alane slurry compositions. Optimizing alane slurries with respect to the carrier and dopants will prove critical in the further development of alane slurries.

SUMMARY

- Quantified chemical hydrogen storage material property guidelines
- Demonstrated 50 and 60 wt% alane slurries in flow through auger reactor

FY 2014 PUBLICATIONS AND PRESENTATIONS

1. K.P. Brooks,T.A. Semelsberger, K.L. Simmons, B.A. van Hassel, *Slurry-Based Chemical Hydrogen Storage Systems for Automotive Fuel Cell Applications*, Journal of Power Sources, DOI: 10.1016/j.jpowsour.2014.05.145.

2. T.A. Semelsberger, K.P. Brooks, *Chemical Hydrogen Storage Material Property Guidelines for Automotive Applications, Journal of Power Sources*, submitted.

3. T.A. Semelsberger, B.D. Rekken, B. Paik, E.L. Brosha, J.I. Tafoya, *Chemical Hydride Rate Modeling, Validation, and System Demonstration*, 2014 Annual Merit Review, Washington, D.C., June 2014.