

IV.E.6 Chemical and Environmental Reactivity Properties of Hydrogen Storage Materials within the Context of Systems

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Objectives

- Develop generalized methods and procedures required to quantify the effects of hydrogen storage material contamination in an automotive environment:
 - Quantify chemical processes and hazards associated with high and low level contamination of hydrogen storage materials.
 - Predict processes during accident scenarios of systems containing hydrogen storage materials.
 - Identify and demonstrate ex situ and in situ hazard mitigation strategies.
- Provide technical basis for codes and standards (C&S) efforts when appropriate technology maturity has been attained to enable the design, handling and operation of effective hydrogen storage systems for automotive applications.

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 On-Board Hydrogen Storage

- (D) Durability/Operability
- (F) Codes and Standards
- (Q) Reproducibility of Performance

Technical Targets

Technical targets addressed mainly focus on Environmental Health and Safety. This project is enabling the satisfaction of these targets by providing the technical basis for future C&S efforts, thus enabling the design, handling and operation of effective hydrogen storage systems.

Environmental Health & Safety

Toxicity	Meets or exceeds applicable standards
Safety	Meets or exceeds applicable standards

In addition to the above target, other storage technical targets are impacted by this effort as follows:

- Gravimetric and Volumetric Capacity - This parameter may be influenced by added weight and volume of developed safety systems and mitigation strategies; for example, contamination permeation barriers.
- Storage System Cost - System cost may be impacted by engineering controls that are developed.
- Fuel Purity - Current draft fuel purity standards are based on proton exchange membrane fuel cell requirements. Hydrogen storage materials may have higher hydrogen purity requirements.

Accomplishments

- Reactivity (Contamination) Properties of New Materials
 - The decomposition of four new materials was investigated in preparation for contamination experiments: alane from J. Greatz/Brookhaven National Laboratory (BNL), amino borane from T. Autrey/Pacific Northwest National Laboratory, calcium borohydride from E. Ronnebro/Sandia National Laboratories (SNL), and $2\text{LiBH}_4\text{-MgH}_2$.
 - New methods were developed to quantify reaction processes and kinetics between hydrogen storage materials and oxygen and water.
 - A contamination Sieverts apparatus was assembled to produce samples for analysis. The manifold was validated utilizing a complex metal hydride with well-characterized hydrogen sorption properties.

- New Methods for Characterizing Reactivity Properties
 - The flow-through reaction model validation manifold was designed, built, and utilized.
 - The manifold was utilized to investigate the bulk-scale contamination processes between alane and dry air as a first step to validate application-scale contamination models.
- Transport Modeling and Validation
 - Alane decomposition models were developed in preparation for oxidation modeling.
 - Species transport through a bed of alane was quantified and validated models were built.
 - Contamination reaction processes of alane ($\alpha\text{-AlH}_3$) with air were investigated at various scales.
 - Multi-phase flow field prediction was performed to investigate particle trajectories in reactive dust clouds utilizing Fuego, a code developed at SNL, as a first step towards dust cloud combustion modeling.



Introduction

This project is focused on developing generalized methods and procedures required to quantify the reactivity properties of hydrogen storage materials to enable the design, handling and operation of condensed-phase hydrogen storage systems for automotive applications. We are performing the experimental and theoretical efforts that are required to understand processes during high-level contamination events including accidents, and low-level contamination events experienced during the life cycle of the storage system. This effort provides the technical basis for the identification of hazard mitigation strategies, and eventually development of appropriate codes and standards. The effort is organized as follows: Task 1 - Quantify chemical processes and hazards during contamination; Task 2 - Predict chemical reactions and hazards during accident scenarios; and Task 3 - Identify and demonstrate hazard mitigation strategies. A successful effort in quantifying the reactivity properties of hydrogen storage materials will enable the safe design, production, handling, operation, and disposal of automotive hydrogen storage systems and provide the technical basis for eventual standards developed for safe hydrogen storage systems.

Approach

Rather than performing ad-hoc measurements on new hydrogen storage materials, we take a science-based approach to understanding, predicting, and

controlling contamination processes of hydrogen storage materials. We understand the fundamental contamination reaction processes and build chemical kinetic models using a combination of established and newly developed experimental techniques. These chemical kinetic models are then coupled with heat and mass transfer characteristics to assemble validated models of contamination scenarios. These validated models are then exercised to develop an understanding of the engineering and administrative controls required to mitigate the hazards caused by the contamination processes in the context of automotive systems.

Results

New methods were developed this year to: (1) characterize complex metal hydride and chemical hydride decomposition processes, (2) quantify oxidation processes, (3) validate contamination transport models, and (4) perform scoping calculations of H_2 storage material dust cloud releases.

Decomposition Studies

In preparation for the contamination model development, the decomposition of four new compounds was examined using Knudsen effusion cells coupled to a time-resolved mass spectrometer (this tool is called the simultaneous thermogravimetric modulated beam mass spectrometer, or STMBMS). The mass loss due to gas leaving the cell and the mass spectra of the evolving gases are measured as described in previous publications [1,2,3]. This allows the identities and concentrations of the gaseous species that are formed by the various reactions occurring within the reaction cell to be measured as a function of time during the course of an experiment. The data is used to calculate the number density of any gaseous species within the reaction cell as a function of time. This information may then be used to calculate the partial pressures of the various species, the rate of their evolution from the solid into the free volume within the reaction cell, and the flow rate of the various species out of the reaction cell. The compounds examined are listed in Table 1.

TABLE 1. Compounds Examined with STMBMS.

#	Compound	Source
1	$\alpha\text{-AlH}_3$	BNL, Dow
2	CaBH_4 (cat. & uncat.)	E. Ronnebro/SNL
3	$\text{LiBH}_4 \cdot \text{MgH}_2$	SNL
4	NH_3BH_3	T. Autrey/PNNL

Several experiments with $\alpha\text{-AlH}_3$ from BNL and Dow provide a baseline characterization of the thermal decomposition of alane. The rate of evolution of H_2

and H_2O from the BNL and Dow samples is shown in Figure 1. The Dow $\alpha\text{-AlH}_3$ evolves water over a wider temperature range when compared to the $\alpha\text{-AlH}_3$ produced by BNL. In addition, the rate of evolution of water from the former drops when H_2 evolves from the sample. This suggests that the reactions that lead to the evolution of water and H_2 are linked for this material. This behavior is not observed in the nano-size $\alpha\text{-AlH}_3$ powders made by BNL. The decomposition of the BNL $\alpha\text{-AlH}_3$ occurs at a lower temperature and has a more complex structure in the rate of evolution of hydrogen from the sample. This behavior suggests that the nano $\alpha\text{-AlH}_3$ sample may either be inhomogeneous or decompose through a series of phase transitions. For information on decomposition studies of the other metal hydrides $\text{Ca}(\text{BH}_4)_2$, $2\text{LiBH}_4 \cdot \text{MgH}_2$, and NH_3BH_3 , see the slides from the June 13, 2008 Annual Merit Review.

Oxidation Process Studies

This effort is structured to: (1) develop a means to identify the elements and determine the linkages that comprise the reaction network that controls the oxidation of hydrogen storage materials, and (2) provide the means to quantitatively characterize the reaction network with a mathematical model that can be used as

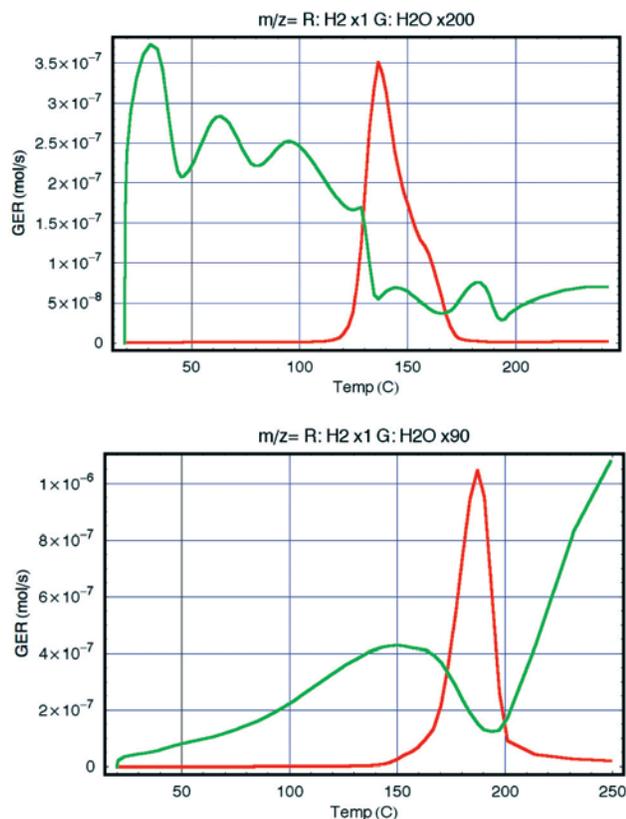


FIGURE 1. Gas Evolution Rates of H_2 (red) and H_2O (green) from $\alpha\text{-AlH}_3$ manufactured by BNL (top) and Dow (bottom)

input to simulate the reaction processes in large-scale modeling/simulation codes.

To collect the required data, a new flow reactor cell was designed and built for use in the STMBMS experiments. In this reaction cell design, a compound that generates the desired oxidizer gas is placed in the bottom of the cell and the hydrogen storage material of interest is loaded into the cell insert to form a packed bed of material. When the reaction cell is heated, gas (e.g., O_2) is released from the gas generator and flows through the bed of hydrogen storage material and then out of the reaction cell through the exit orifice. Our plans are to use these methods to investigate a variety of materials of interest to the hydrogen storage community. To develop the specific methodology for this purpose, we have focused on investigating the oxidation of nano $\alpha\text{-AlH}_3$ by O_2 . To develop the methods we first collected data on the decomposition of $\alpha\text{-AlH}_3$ and AgO and have constructed mathematical models characterizing their thermal decomposition.

The data showing the gas evolution rates of H_2 , O_2 , and H_2O from the reaction of O_2 with AlH_3 supplied by BNL is shown in Figure 2. The sample is heated through a series of four heating/cooling cycles and is then heated and held at isothermal temperatures of 150 and 200°C. The purpose of the four different heating/cooling cycles is to obtain temperature dependent data over a set of different temperature ranges and with varying extents of exposure to the oxidizer. The results show that most of the O_2 that flows through the bed of AlH_3 is converted to H_2O until the flow rate of H_2 from the AlH_3 sample slows at ~29,000 seconds. At this point the rate of evolution of H_2O decreases and the rate of evolution of O_2 increases.

Examination of the data during the first three cycles shows that the rate of evolution of O_2 is less than the rate of evolution of water. At these temperatures, the

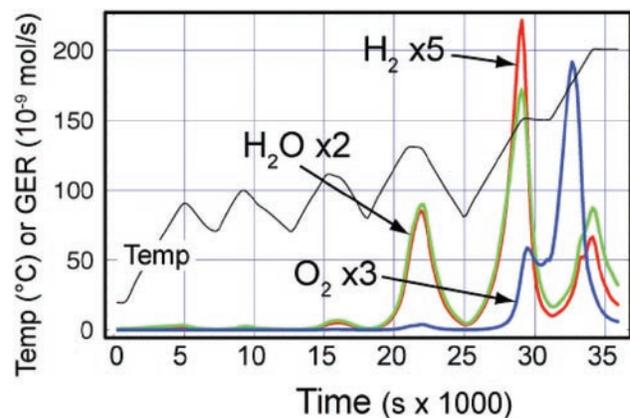


FIGURE 2. Gas evolution rates of H_2 , H_2O and O_2 from the oxidation of AlH_3 that was supplied by BNL. The black curve on each graph shows the temperature of the sample during the experiment.

oxidation rate of H_2 is slow and may be limited by the rate of evolution of hydrogen from the AlH_3 sample (note the low evolution rate of H_2 in this temperature range). When the sample is first heated to $120^\circ C$ the rates of evolution of H_2 and H_2O increase compared to the rate of evolution of O_2 . Note that the rates of evolution of the three gases are highly correlated in this thermal cycle.

Examination of the amount of oxygen that has evolved from the sample in these two experiments indicates that almost all of the oxygen released from the AgO sample evolves as either O_2 or H_2O . Mass balance analysis of the experiment indicates that only a very small fraction of the oxygen may be consumed by reaction with the aluminum. The results of these experiments are then utilized to define the chemical kinetic models of alane oxidation.

Contamination Transport Modeling

A flow manifold was designed to validate predictions of reactive flow through reactive porous media such as metal hydride beds. This effort extends the chemical kinetic models developed in Task 1 to bulk scale processes that will be experienced in automotive systems.

A set of transport equations were identified that can accommodate transport in reactive porous media for a variety of flow regimes (Young and Todd [4]). These transport equations are necessary to predict contamination processes during breach of tank/plumbing scenarios. These transport equations were utilized in a COMSOL™ finite element model of the flow-through reactor bed (Figure 3). Prior to applying these transport equations to reactive bed predictions, validation experiments must be completed to gain confidence in the model. Momentum transport calculations were validated using the flow manifold and reactor bed that contained a well-characterized porous frit assembly. The model accurately predicted pressure drop for a range of nitrogen and helium flow rates and pressures. After gaining confidence in the model with a well characterized material, the flow field was predicted for an 80% porous packed alane bed. Scanning electron microscopy was utilized to estimate the mean particle size and bed tortuosity for input parameters to the model. Predicted pressure drops as a function of nitrogen flow rate and pressure are in good agreement with experimental data as shown in Figure 3.

The manifold was also used for packed bed contamination experiments following the flow-field validation experiments. A 100 mg bed of BNL α -alane was contaminated at an increasing temperature ranging from room to $200^\circ C$ in dry air flowing at 0.05 SLPM. The experiments were carried out by first heating the

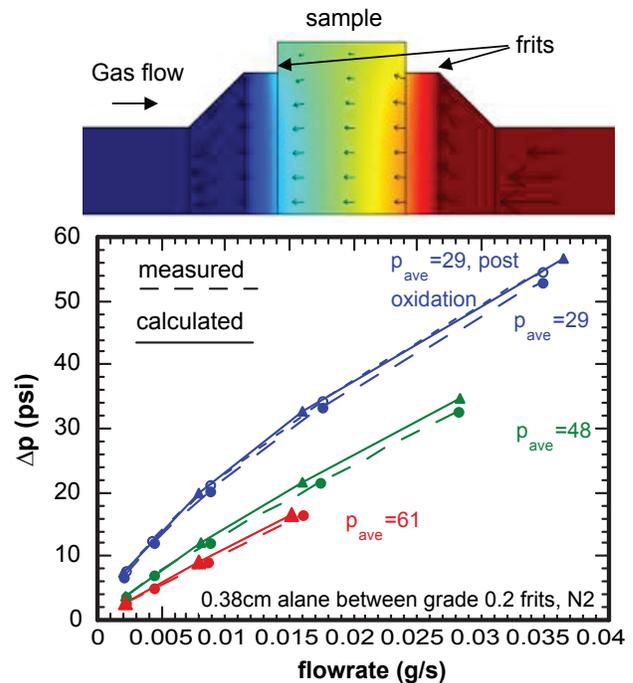


FIGURE 3. Validation data fit for nitrogen pressure drop predictions of an 80% porous packed alane bed.

bed under nitrogen flow to $100^\circ C$ while monitoring the gaseous product. After attaining steady flow conditions under nitrogen, dry air flow was initiated. After a brief induction period, the temperature of the bed was increased and thermal and mass spec data of the resulting bed contamination process was captured. Observations of physical processes during contamination with oxygen under these conditions are as follows:

- Oxygen exposure at low temperatures indicates that H_2O is the primary product.
- Oxygen exposure at higher temperatures indicates that H_2 is the dominant species.
- The only measurable self-heating event occurs during a significant reaction event at $\sim 150^\circ C$ resulting in a rapid rise in temperature.
- Only a small portion of the aluminum is oxidized, as indicated by thermal data and subsequent X-ray diffraction spectra.
- A portion of the original hydrogen remains on the sample in the form of aluminum hydroxide and AlH_3 .

These experiments (and other similar measurements) are being assembled to build fully validated models of automotive-scale packed bed contamination scenarios.

Dust Cloud Combustion Modeling

A dust jet modeling effort was performed during Fiscal Year 2008 in preparation for reactive hydrogen storage material modeling efforts. A two-phase flow consisting of a turbulent, isothermal, particle-laden jet was modeled with the SNL massively parallel Navier-Stokes code, Fuego. This code is being used at SNL currently to predict the transport processes in high pressure hydrogen jet flames and hydrocarbon fuel pool fires, including the radiation heat transfer from the high temperature regions. During FY 2008, the capability to predict transport processes in propellant fires is being included. In preparation for using the code to model metal hydride tank releases, a jet of air and sand with a mass loading ratio of 0.2 was modeled. This problem was studied experimentally by Shuen [5]. Distributions of gas and particle mean velocity as well as gas and particle turbulence quantities along the centerline of the jet and in the radial direction at several axial locations are available for model validation. The distribution of mean particle mass flux along the centerline of the jet was also measured. Flame propagation and potential flame acceleration in a hydride particle release depend to a large extent on the particle concentration and turbulence in the gas-particle flow. Thus it is important to be able to predict the evolution of the gas-particle flow in a turbulent jet. An example of the two-phase turbulent jet flow predicted using Fuego is shown in Figure 4. The centerline air velocity distribution is compared with the data from Shuen [5]. New capabilities for representative particle tracking and visualization of average particle properties have been added to Fuego recently; these capabilities will be utilized to compare particle fluxes and turbulence quantities with the data. Once the isothermal jet validation is completed, a particle-laden jet with heat transfer will be validated.

Conclusions and Future Directions

In the first year of this project we have developed methods for understanding contamination processes of hydrogen storage materials using computations validated with experimental measurements. We have begun to exercise these methods by utilizing α -AlH₃ sourced from BNL. In the upcoming year, we will continue efforts in the following areas:

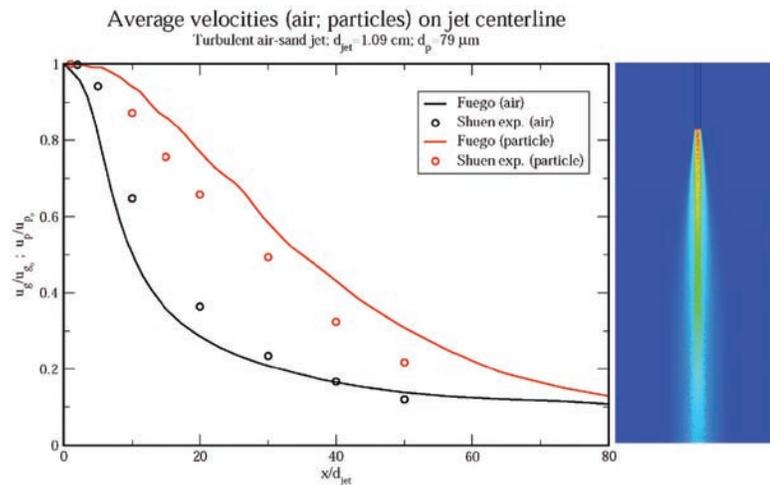


FIGURE 4. Distribution of axial component of air velocity along centerline of an air-sand turbulent jet with a mass loading ratio of 0.2.

Task 1 – Fundamental contamination processes:

- Continue alane contamination work by developing validated models for combined water and oxygen exposure.
- Continue to evaluate new materials such as amino boranes and Ca/Li borohydrides.

Task 2 – Scaling accident scenarios:

- Make validated predictions of large-scale alane air exposure scenarios.
- Evaluate capability of FLACS DESC to predict metal dust cloud combustion.

Task 3 – Hazard mitigation:

- Investigate use of novel materials and standard fire suppression chemicals for use with various H₂ storage materials.

FY 2008 Publications/Presentations

1. D. Dedrick, R. Behrens, B. Bradshaw, M. Kanouff, R. Larson, G. Evans, K. Stewart, "The contamination properties of hydrogen storage materials in the context of systems", IEA Task 22 Meeting, Quebec, Canada, March 2-5, 2008.
2. D. Dedrick, R. Behrens, B. Bradshaw, M. Kanouff, R. Larson, G. Evans, K. Stewart, "The safety properties of hydrogen storage materials in the context of systems", IEA Task 22 Meeting, Petten, The Netherlands, September 3-7, 2007.

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3. Behrens, R., Jr., Determination of the Rates of Formation of Gaseous Products from the Pyrolysis of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) by Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry. *International Journal of Chemical Kinetics* 1990, 22, 159-173.
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5. Shuen, *AIAA Journal*, v. 23, no. 3, pp. 396-404, March 1985.