IV.E.5 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 systems 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 consumer and industrial applications.

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:

(A) System Weight and Volume

(D) Durability/Operability

(F) Codes and Standards

(Q) Reproducibility of Performance

(K) System Life-Cycle Assessments

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 etc.
- 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 more stringent hydrogen purity requirements.

Accomplishments

Accomplishments can be organized into three focus areas; fundamentals of reactivity, accident scenarios, and hazard mitigation.

Fundamentals of Reactivity

- Reaction conditions resulting in the release of hydrogen from ammonia borane (AB) were identified. Vapor pressures were determined based on isothermal decomposition measurements.
- A bed of AB was exposed to air in the flow-through reactor manifold and was found to be un-reactive up to 103°C.
- Time-lapse images of the decomposition of AB were acquired to help determine the sequence of reactions associated with hydrogen release.
- A chemical kinetics model describing dehydrogenated-alane oxidation processes was developed and a report was distributed to International Partnership for the Hydrogen Economy collaborators.

Accident Scenarios

- We have completed our predictions of processes of a dehydrogenated alane tank at high temperature (150°C) for a variety of simulation variables.
- Model sensitivity studies were performed for the thermal, permeability, and chemical kinetic parameters to determine the confidence levels in breach-in-tank process predictions.
- Permeability models have been developed for a variety of materials including activated carbons, AB, and sodium alanates.
- Data has been acquired for the development of chemical kinetic models for sodium alanate oxidation.

Hazards Mitigation

- We identified a variety of aromatic hydrocarbons as high melting solids for use as non-homogenous reaction and ignition mitigating agents.
- Interactions between sodium alanates and anthracene were investigated through thermal decomposition analysis.
- We have synthesized a new cross-linking monomer with flame-retardant and char-formation properties to be used in microporous scaffolds for metal hydrides.
- Polymerization methods have been developed to encapsulate metal hydrides within a low density polymer scaffold.

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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 consumer and industrial 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 work is organized as following; 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 consumer and industrial hydrogen storage systems and provide the technical basis for eventual standards developed for safe hydrogen storage systems [1].

Approach

We take a science-based approach to understanding, predicting, and controlling contamination processes of hydrogen storage materials. By first understanding the fundamental contamination reaction processes using a combination of established and newly developed experimental techniques, we are able to build robust and useful chemical kinetic models. 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 systems.

Results

Fundamentals of Reactivity

The reactivity of AB was the focus of the fundamentals of reactivity efforts during Fiscal Year 2009. Qualitatively, AB and its decomposition products are much less sensitive to contamination such as air and water. That being said, AB has other aspects that make it interesting from a reactivity point of view. For example, if the decomposition conditions of AB are not carefully controlled, unfavorable products can be produced, such as diborane and borazine. We are performing experiments on AB that allow us to assess the main features of the reaction network that control the decomposition of AB. By understanding this network, engineers will be able to design systems that optimize the decomposition process and minimize the production of undesirable species that can degrade the reliability of the fuel cell system.

The reaction network of the AB decomposition process is more complex than previous hydrogen storage materials that we have investigated, such as AlH_3 and $NaAlH_4$. It involves both gas and condensed phase species and a multi-step process that controls the evolution of hydrogen. We continued our collaboration with the Pacific Northwest National Laboratory (T. Autrey) to perform isothermal decomposition experiments to elucidate reaction processes.

In our experiments, we examined the decomposition of AB under the very lowest and intermediate pressure conditions (see Behrens [2] for more information on the experimental method). Under the lowest pressure conditions, the sample decomposed by the

sublimation of NH_3BH_3. Under intermediate pressure conditions, the sample decomposes through a more complex reaction pathway than has been described in literature. From our initial experiments at intermediate confinement pressures, it is apparent that a complex nonlinear reaction network controls the evolution of the reaction process. A portion of the results from an experiment that probes the reaction process of AB as it is heated from room temperature to 1,000°C is shown in Figure 1. These data show what occurs in the first stage of the decomposition process. For example, at 90°C the NH_3BH_3 vapor is in equilibrium with the condensed phase AB. About 1,300 seconds after the sample has been held at 90°C, the first H_2 starts to evolve from the sample. Note that the change in the rate of evolution of NH_2BH_2 coincides with that of H_2. However, closer examination shows that NH_3 and B_2H_6 start to rise about 500 sec after the sample reaches 90°C. The delay in the release of all these species indicates that a local reaction environment is created in the sample that promotes the decomposition of NH_3BH_3 → NH_2BH_2 + H_2. The formation of this local reaction environment is likely to involve a process that results in the formation of NH_3 and B_2H_6 and takes place on the surface of the sample. Also note the evolution of borazine at a very low rate in this isothermal segment.

In addition to the gas-phase measurements, several hot-stage time-lapse movies were acquired of the decomposition of AB to assess whether geometrical and morphological features play a role in the reaction network. These movies showed that the reaction is not homogeneous throughout the sample and geometrical features play an important role in the decomposition of AB.

By assembling this reaction network we are able to provide insight that can be used to create new ideas on how to optimize and control reaction processes in AB and enable effective and reliable systems.
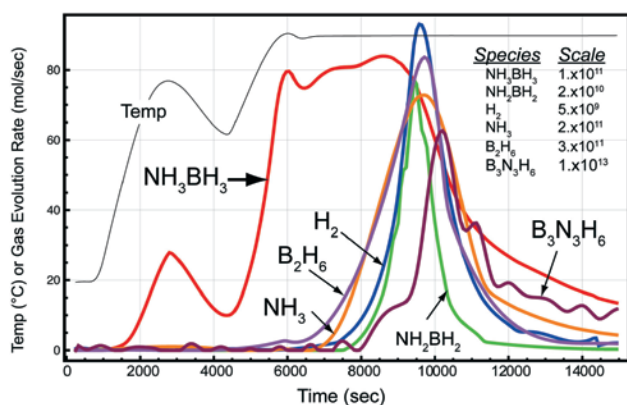

FIGURE 1. Rates of evolution of selected set of species as AB is heated to and held at 90°C.

Accident Scenarios

We are addressing two contamination scenarios in reactive hydrogen storage systems; breach-in-tank and contaminated refueling. For the past year, we have been considering alane-based systems (α-AlH$_3$ J. Graetz, Brookhaven National Laboratory). Due to its relatively simple chemistries and limited number of potential reaction pathways, alane provides a unique opportunity to investigate processes experienced during contamination of systems containing reactive high-surface area materials. We have coupled appropriate Knudsen-regime permeability models for flow through packed beds with the fundamental heat transfer and chemical kinetic processes occurring at the particle level (a report describing the oxidation of dehydrogenated-alane was distributed in FY 2009). Using experimental measurement to determine and validate model parameters with tools developed in FY 2008 [3], we have developed a robust numerical model that can be utilized to predict processes in arbitrary scaled-up geometries during scenarios such as breach-in-tank or contaminated refueling.

In FY 2009, we focused on the coupling of our validated mass transfer and chemical kinetic models to systems of scaled-up geometry. Model sensitivity studies were performed for the heat transfer, permeability, and chemical kinetic parameters to determine the confidence levels in process predictions. We have completed our predictions of processes of a dehydrogenated alane tank at high temperature (150°C) for a variety of simulation variables.

To illustrate the use of the coupled model, we chose a model geometry consisting of a cylinder 0.3 m in length and 0.0254 m in diameter with a 2 mm thick stainless steel wall. Simulations were performed with both heat loss to the environment (heat transfer coefficient, h_w = 5.5, 11 W/m^2-K) and also adiabatic conditions (h_w = 0). Porosity of the bed was varied between 0.5 and 0.76. The impact of radiation from the outer wall (ϵ = 0 to 0.3) and advection in the bed were also considered. The initial temperature and pressure were set to 150°C and $1.01 \cdot 10^{-5}$ Pa, respectively. The boundary conditions applied to the stem were a pressure of $1.01 \cdot 10^{-5}$ Pa for the momentum equation, a temperature of 25°C for the energy equation, and an oxygen concentration of 8.56 mol/m^3 (air) for the species transport equation.

Figure 2 shows six snap-shots in time of the thermal state of the alane cylinder during the contamination process where the cylinder is partially insulated and at an alane porosity of 0.755. A reaction front propagates through the bed with maximum temperatures of approximately 230°C at around 300 seconds. In general, a reaction zone propagates along the entire length of the bed with the exothermicity and extent of the reaction
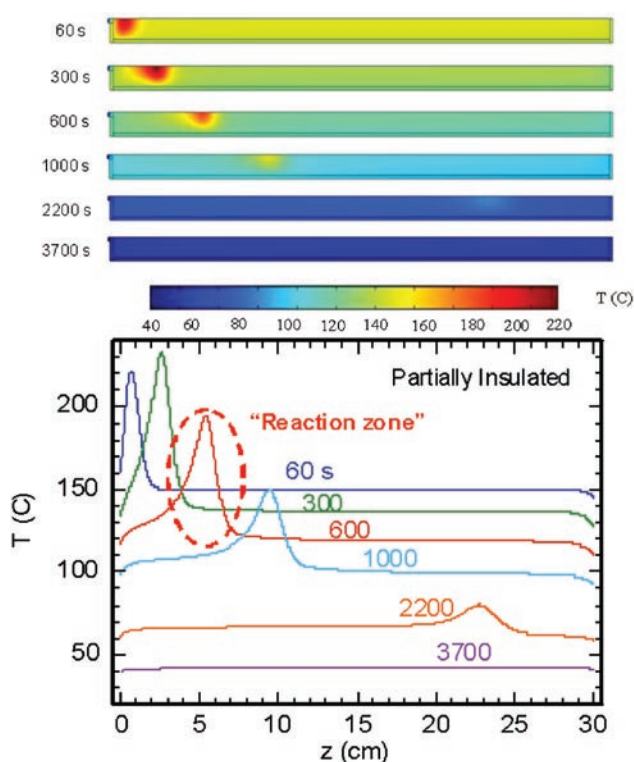
FIGURE 2. Results for the breach-in-tank scenario simulation for the 80% porous bed indicates a reaction front propagating though the system for 1 hour.

competing with the loss of heat to the environment. The temperature is a maximum within the reaction zone, but overall the temperature decreases with time due to the environmental losses. The maximum temperature in the reaction zone increases with time initially and then decreases for times greater than 300 seconds.

System sensitivities were analyzed by determining the influence of heat loss and packing density on the reaction front characteristics; specifically, the reaction zone temperature and its associated velocity. First, considering the impact of insulation for the 0.76 porous case, perfect insulation results in the highest reaction zone temperature, as might be expected. Interestingly, the reaction zone velocity decreases with increased insulation and temperature due to the kinetics of the reaction and the oxygen transport into the cylinder. As described in the kinetics model, the amount of aluminum that participates in the oxidation process increases with temperature. Meanwhile the transport of oxygen into the cylinder is limited by the small opening in the stem. Thus, as the amount of aluminum available increases it takes more time to consume it, which slows the rate of movement of the reaction zone. That is, the reaction zone velocity is determined by the amount of available aluminum and the transport rate of oxygen into the bed.

To investigate the impact of higher densities on the reaction processes, we considered a partially insulated system at 0.5 porosity as might be more appropriate for engineered systems. The properties for this case were calculated based on the thermal conductivity model and an empirical pore size model. In this case, the lower permeability limits the diffusion of oxygen gas significantly, resulting in lower temperatures compared to the 0.76 porosity case. Interestingly, the impact on reaction zone velocity is reversed compared to the insulation analysis; in this case, lower temperatures result in lower reaction zone velocities. However, the same mechanism that reduced the reaction zone velocity when the insulation was increased is at play when the packing density is increased, i.e. an increase in the amount of available aluminum. In the former case the amount of available aluminum increased due to a larger temperature, while in the latter case the larger packing density itself results in more available aluminum, in spite of the reduction in reaction zone temperature. In addition, the larger packing density reduces the permeability and effective diffusivity of oxygen in the bed, so the transport rate of oxygen is reduced, which also contributes to the slower reaction zone velocity.

Future efforts will consider the behavior of complex metal hydrides to quantify the breach-in-tank reaction processes for alkali-metal containing classes of systems. Additionally, by considering transport within a reversible material (such as sodium alanates [4] or magnesium amide/lithium hydride) we can investigate the impact of a contaminated refueling stream. In this scenario, a hydrogen depleted material is exposed to high-pressure hydrogen with entrained air. While the breach-in-tank contamination processes are dominated by diffusion, the contaminated refueling processes are dominated by convection and thus a larger concentration of reactants is available.

The alane system has provided a unique opportunity to observe the propagation of a reaction front through a hydrogen storage bed during a breach in tank scenario. Because the models were built with through experimental measurement, we are able to consider a variety of scenarios. For example, by coupling in chemical kinetics of hydrogen release, we can investigate the impact of de-hydrogenation of the alane during the breach in tank event. Considering the alane system, the hazard presented by the propagating reaction front is low, resulting in only a moderate exotherm. A complete description of the model and resulting simulation can be found in the proceedings from the 2009 International Conference on Hydrogen Safety by the same authors. Other, more reactive systems may result in a more significant hazard where, if un-mitigated, the breach-in-tank could lead to an over-temperature event causing containment vessel failure or other unfavorable outcomes.

Hazard Mitigation

We are developing low weight, low volume additives in the form of monomers/polymers to mitigate the hazards presented by exothermic bed reaction processes as described above and/or external heat source over-temperature events. We seek to identify low mass-loading additives that can be utilized with reactive solid-state hydrogen storage systems that a) provide a fail-safe during over temperature or contamination scenarios, b) do not detrimentally interact with the storage materials during normal operation, and c) do not inhibit but perhaps enhances, heat and mass transport into and out of the active material and composite structure.

Non-homogeneous mitigation solutions - We have selected potential materials for non-homogeneous solutions consisting of localized material that can be distributed strategically during the over-temperature event. This method could surround the bed to provide encapsulation. This approach involves using unreactive or mildly reactive organics that will melt during an extreme exotherm and flow into and around the storage bed, cutting off access of air to the bed. Two categories of materials are being examined to satisfy this role; crystalline small molecules, and high melting temperature polymers. We have identified a variety of aromatic hydrocarbons as high melting solids and are performing the experiments to determine the application of these materials.

Using sodium alanates as a prototype reactive hydride, a mixture of and anthracene was prepared in 1:1 weight ratios to determine the existence of any interactions between the two chemicals. Since any sodium alanate over-temperature events can occur at temperatures near 200°C, anthracene is an appropriate additive with a melting point of 210°C. The mixture was thermally decomposed thermo-gravimetrically and the results compared to un-modified sodium alanate. Considering pure sodium alanates, hydrogen evolution initiates near 100°C and proceeds with a two step decomposition reaction that completes near 180°C. When the sodium alanate is mixed with anthracene in a 1:1 mixture, the hydrogen evolution is qualitatively similar initially. However, the duration of hydrogen evolution is significantly longer compared to the un-modified sample. Hydrogen begins to evolve near 80°C (somewhat lower than the unmixed sample). At around 100°C, the first sign of reaction is observed though the formation and subsequent evolution of dihydroanthracene. Sublimation of anthracene is observed near 110°C. Higher molecular weight products begin forming at higher temperatures (~150°C). The hydrogen evolution characteristics from the sample are impacted significantly by the hydrogenation reaction.

Our continued efforts focus in two areas. First, we are investigating the reaction pathways that exist between alanates and the anthracene to guide us in our additive selection process. Secondly, we are performing similar experiments with pyrene and perylene and polymers (polypropylene) to determine the usefulness of these materials as additives. Additionally, we are exploring the option to functionalize these materials through the incorporation of halogenated hydrocarbons that can act as a fire retardant and the use of char forming intumescent materials to form a thick char during combustion.

Homogeneous mitigation solutions - Homogeneous additives that exist as a matrix with the hydrogen storage material are also being developed to act as an over-heat fail-safe. Ultimately, we are seeking to develop a matrix that is functionalized in the following three ways:

- Fire suppression – engineered polymer scaffolds can suppress fire via char formation.
- Scaffolding – immobilization of the bed to inhibit particle sintering, decrepitation, and dust release using low density, high surface area polymer xero/areo-gels.
- Surface catalysis – modification of hydrogen release/uptake with Lewis-basic monomer used in polymer formulation.

A schematic of the process is shown in Figure 3. Fire suppressants and char forming elements are incorporated into the monomers. An additional monomer with Lewis-basic functionality is included. By varying reaction conditions and monomer ratios, polymerization can yield a micro-porous cross-linked matrix. A number of challenges exist in the development of this tri-functional matrix: a) new monomers with
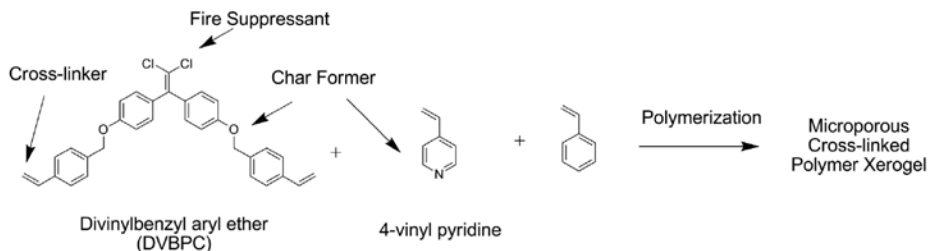

FIGURE 3. Potential tri-functionalized matrix performs as a hazard mitigation and performance enhancement.

fire-suppressing properties must be synthesized, b) the developed matrix must demonstrate structural rigidity to withstand the life-cycle of the hydrogen storage material, and c) monomers and functional groups must be unreactive during polymerization.

We have developed polymerization conditions for 4-vinyl pyridine and the cross-linking agent divinylbenzene. Low density foams have been made and show enhanced mechanical properties compared to the all-styrene containing foams. We have also synthesized the divinyl aryl ether monomer (DVBPC) as a potential matrix precursor. This monomer was accessed by treating vinyl-benzyl chloride with bis-phenol C in DMF (n, n-di-methyl formamide) in the presence of a base. Attempts to use DVBPC as the cross-linking agent, however, have not been successful. We have also developed conditions for polymerizing vinyl monomers in the presence of various metal hydrides and AB. These composite materials contain approximately 10–20 wt% polymer and appear as hard pucks. Thermal analysis and reactivity experiments are underway to compare hydrogen release properties and "breach-of-tank" scenarios with unsupported hydrides.

Conclusions and Future Directions

This project has demonstrated that, through the use of experiment-based model development of complex reaction and transport processes, hazard scenarios can be investigated for a variety of geometries and system configurations. Based on this understanding, hazard mitigation technologies can be developed to make systems reliable and effective. Towards this end we have discovered that:

- The transport of heat and mass can be well characterized for a variety of hydrogen storage materials including metal hydrides, chemical hydrides, and activated carbons.
- An over-temperature event originating from contamination or external sources could present a hazard during the operation of the hydrogen storage system.
- This impact of this over-temperature hazard may be minimized though the use of mitigating solutions such as reactant-excluding additives.

Based on current Presidential budget request, no additional data will be acquired in FY 2010. A significant amount of data has been accrued investigating the reactivity of complex metal hydrides, treatment of contaminated materials, and mitigating additives. These results will be compiled in a final FY 2010 report.

FY 2009 Publications/Presentations

1. D. Dedrick, M. Kanouff, R. Larson, R. Bradshaw, G. Sartor. "Heat and mass transport in hydride systems - Predictions of processes during operation and accident scenarios" HFC 2009, Vancouver BC, May 31st to June 3rd.

2. D. Dedrick, M. Kanouff, R. Larson, R. Bradshaw, J. Graetz, S. Hwang. "Predictions of solid-state hydrogen storage system contamination processes", Proceedings from the ICHS 2009, Corsica, Fr. Sept 16–18th, 2009, in press.

3. D. Dedrick, R. Behrens, M. Kanouff, R. Larson, R. Bradshaw, G. Sartor. "The reactivity of hydrogen storage materials in the context of systems" Presentation to the International Energy Agency Task 22, Roma, Italy, October 2008 and Jeju Island So. Korea, April 2009.

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1. D.E. Dedrick, "Chapter 4 - Solid-state hydrogen storage system design" SOLID-STATE HYDROGEN STORAGE: MATERIALS AND CHEMISTRY, Edited by G Walker, The University of Nottingham, UK, Woodhead Publishing Ltd, 2008. ISBN 1 84569 270 5.

2. Behrens, R., Jr., New simultaneous thermogravimetry and modulated molecular beam mass spectrometry apparatus for quantitative thermal decomposition studies. Review of Scientific Instruments 1987, 58, (3), 451-461.

3. D. Dedrick, R. Behrens, M. Kanouff, R. Larson, R. Bradshaw. "IV.E.6 Chemical and Environmental Reactivity Properties of Hydrogen Storage Materials within the Context of Systems" 2008 DOE Hydrogen program annual report.

4. D. Dedrick, M. Kanouff, R. Larson, T. Johnson, S. Jorgensen. "Heat and mass transport in metal hydride based hydrogen storage systems", Proceedings of HT2009 ASME Summer Heat Transfer Conference July 19–23, 2009, San Francisco, California, in press.