IV.D.1d Chemical Hydride Rate Modeling, Validation, and System Demonstration

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Project End Date: February 2014

Technical Objectives

- Develop fuel gauge sensors for solid-state hydrogen storage media.
- Mathematically model the aging characteristics (i.e., shelf-life) of candidate hydrogen storage materials.
- Develop rate models for hydrogen release on candidate chemical hydrides.
- Develop novel strategies for start-up and transient operation with candidate chemical hydrides.
- Identify hydrogen impurities and develop novel impurity mitigation strategies.
- Design, build, and demonstrate a subscale prototype reactor that releases hydrogen using chemical hydrides (technology area lead).

Management Objectives

- DOE Program Liaison: Coordinate/collaborate with the Chemical Hydrogen Storage Center of Excellence (CHSCoE).
- Chemical Hydride System Architect: Monitor and guide progress on chemical hydride systems.

Technical Barriers

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

(C) Efficiency
(A) System Weight and Volume
(D) Durability/Operability

Technical Targets (2015)

- Gravimetric Capacity: 3 kWh/kg
- Volumetric Capacity: 2.7 kWh/L
- H_2 Discharge Rate: minimum full flow rate 0.02 H_2 g/s kW
- H_2 Purity: 99.99 %H_2
- Start-Up Time to Full Flow: 5 s @ 20°C, 15 s @ -20°C
- Loss of Usable H_2: 0.05 g/hr-kg H_2 stored

Accomplishments

- Demonstrated novel acoustic fuel-gauge sensor with metal hydrides:
  - Patent submitted
- Developed and updated testing protocols for accurate shelf-life data acquisition.
- Collected shelf-life data for neat ammonia borane (AB) and liquid AB formulation.
- Screened approximately 20 catalysts for room temperature dehydrogenation of liquid-phase AB.
- Developed dual-catalyst bed reactor model to investigate start-up and transient operation.
- Quantified borazine and diborane impurities generated from neat AB.
- Demonstrated that borazine and diborane can be scrubbed to produce fuel-cell quality hydrogen.
- Developed preliminary system designs for liquid-phase chemical hydrides.

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Introduction

This project is a new start (Feburary 2009). 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.

One challenge in developing efficient reactor designs is in addressing the wide range of applicable variables, including reactant and product phases (solid, liquid, and gas are all possible); exothermic, endothermic, or autothermal reaction thermodynamics; catalyst effectiveness; selectivity; space-time; and reactor volume. The first objective of the LANL team is to quantify these variables for candidate chemical hydride materials through rate expressions modeled from tightly controlled, well-defined kinetics experiments free of mass and heat transfer effects. In LANL's Phase 1 work, these rate expressions will be applied in system-level models. In Phase 2, the rate expressions will be used with computation fluid dynamics codes to develop novel and efficient reactor designs in collaboration with other Hydrogen Storage Engineering Center of Excellence partners.

Kinetics experiments can be used to identify routes to optimize catalyst design, improve reactor efficiency, and reduce weight, volume, and cost. The experiments and the resulting rate models will therefore support achieving the objective of optimizing the reactor for an on-board automotive system. In addition, the engineering team will work with the CHSCoE to optimize the catalysts for candidate chemical hydride systems.

LANL will also address the unique requirements of on-board 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 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 hydrides) 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.

Technical Tasks

Technical Task 1: Design and Develop Fuel Gauge Sensors for Solid-State Hydrogen Storage Media

Approach: LANL will employ an inexpensive, simple, and robust method of using the natural properties of the hydrogen storage media to develop novel fuel gauge sensors.

Technical Task 2: Develop Models of the Aging Characteristics of Hydrogen Storage Materials

Approach: In collaboration with the material Centers of Excellence, aging experiments will be performed as a function of temperature (0°C–60°C), pressure (0 psig–5,000 psig), percent relative humidity (0%–90%), and percent air (0%–100%). Collected data will be regressed into a model for predicting the degradation of stored hydrogen storage media as function of geographic location, diurnal cycles, storage temperature, storage pressure, and storage atmosphere (such as humidity and air).

Technical Task 3: Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides

Approach: LANL's approach will be to collaborate with the CHSCoE on reactor testing candidate chemical hydrides under tightly controlled experimental conditions (such as temperature and pressure) using LANL's in-house designed and built reactors. Intrinsic rates will be determined over ranges of temperature (25°C–200°C), composition, pressure (0 psig–100 psig), and space-time (0.01 s–10 s). Reactor tests will also be performed to ensure that mass and heat transfer effects are negligible. The sought-after data will include selectivity, conversion, hydrogen yield, and mass balances of all reactants and products.

Technical Task 4: Develop Novel Strategies for Start-Up and Transient Operation with Candidate Chemical Hydrides

Approach: Exothermic reactions offer the greatest opportunities to meet the DOE technical targets of start time to full flow and transient response by taking advantage of the heat generated upon hydrogen release. The heat required to raise the reactor temperature to that of the desired operating temperature can be obtained on-board without external heat sources by designing novel thermal integration strategies coupled with exothermic hydrogen release reactions. Modeling efforts will be conducted to determine which approach has the largest impact on reducing startup time and transient response; additional decision criteria will include reactor mass, reactor volume, and reactor cost.

Technical Task 5: Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies

Approach: As materials are down selected and available, we will produce hydrogen from

candidate materials and operate small, 5 cm^2 single-cell proton exchange membrane (PEM) fuel cells to evaluate the quality of the hydrogen. This task will produce durability data on PEM fuel cell operation using hydrogen generated from hydrogen storage materials. Impurity identification can be accomplished by performing post-characterization studies on the PEM fuel cell, such as cyclic voltammetry, scanning electron microscopy, transmission electron microscopy, X-ray fluorescence, diffuse reflectance infrared Fourier transform spectroscopy, solid-state nuclear magnetic resonance, and high frequency resistance. LANL has previously demonstrated the catastrophic effects of hydrogen impurities generated from ammonia borane on PEM fuel cells. Prior to the PEM fuel cell test, the impurities generated from AB were unknown.

Results

Fuel Gauge Sensor Development (Task 1)

Experiments were performed to determine the viability of employing acoustic sensor technology on metal hydrides as a fuel gauge sensor. Data were collected on commercial and non-commercial steel cylindrical pressure vessels containing metal hydride storage materials. In each case, the mass of metal hydride was small compared to the total mass of the system. However, large differences in the swept frequency response were evident (Figure 1), thus establishing a proof-of-principle that a hydrogen level sensor based on acoustic principles is feasible.

Figure 2 shows changes in the measured acoustic response spectra of the fully charged, large Solid H™ cylinder as it was removed and replaced. A small amount of water-based gel couplant was added in between each measurement and the exact placement of the cylinder on the transducers (including rotation component) was subject to small variability. While there are differences in the recorded spectra, several resonance peaks (e.g. at 45, 87, 136, 191, 248 kHz, etc.) are present in each scan albeit with slightly different amplitudes.

These data strongly indicated the need for an improved method of controlling the charge state of the hydride without disturbing the position of the hydride cylinder or the acoustic couplant in between measurements. Moreover, the variability introduced into the measurement via the previous method would preclude tracking the acoustic response at intermediate levels of charge or discharge. Demonstration of this ability will be very important for the purposes of level gauge development. Furthermore, during initial reversibility experiments where the hydride was charged and discharged repeated, it found that the properties of the water-based gel couplant would change due to the large exotherms associated with incorporation of H into the crystalline lattice of the metal hydride. The gel became more viscous and overtime eventually became very tacky due to dehydration of the gel. It is known that this stiffening of the couplant would introduce changes

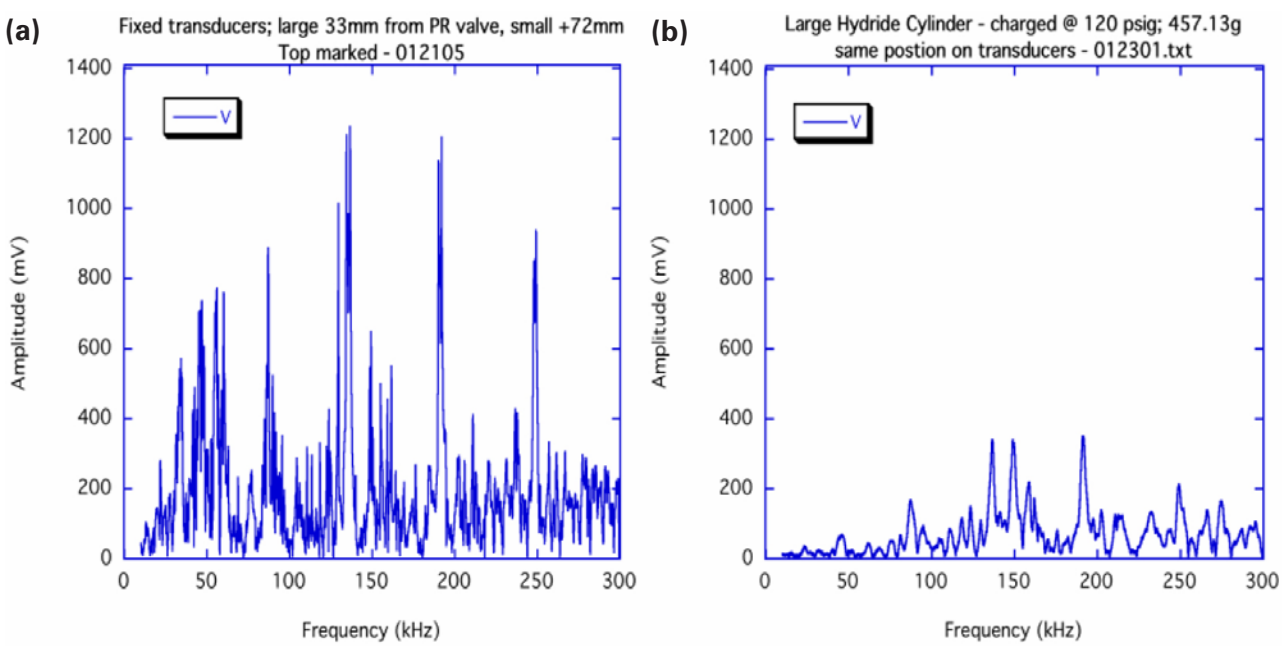

FIGURE 1. Acoustic Responses for (a) Fully-Discharged Metal Hydride and (b) Fully-Charged Metal Hydride

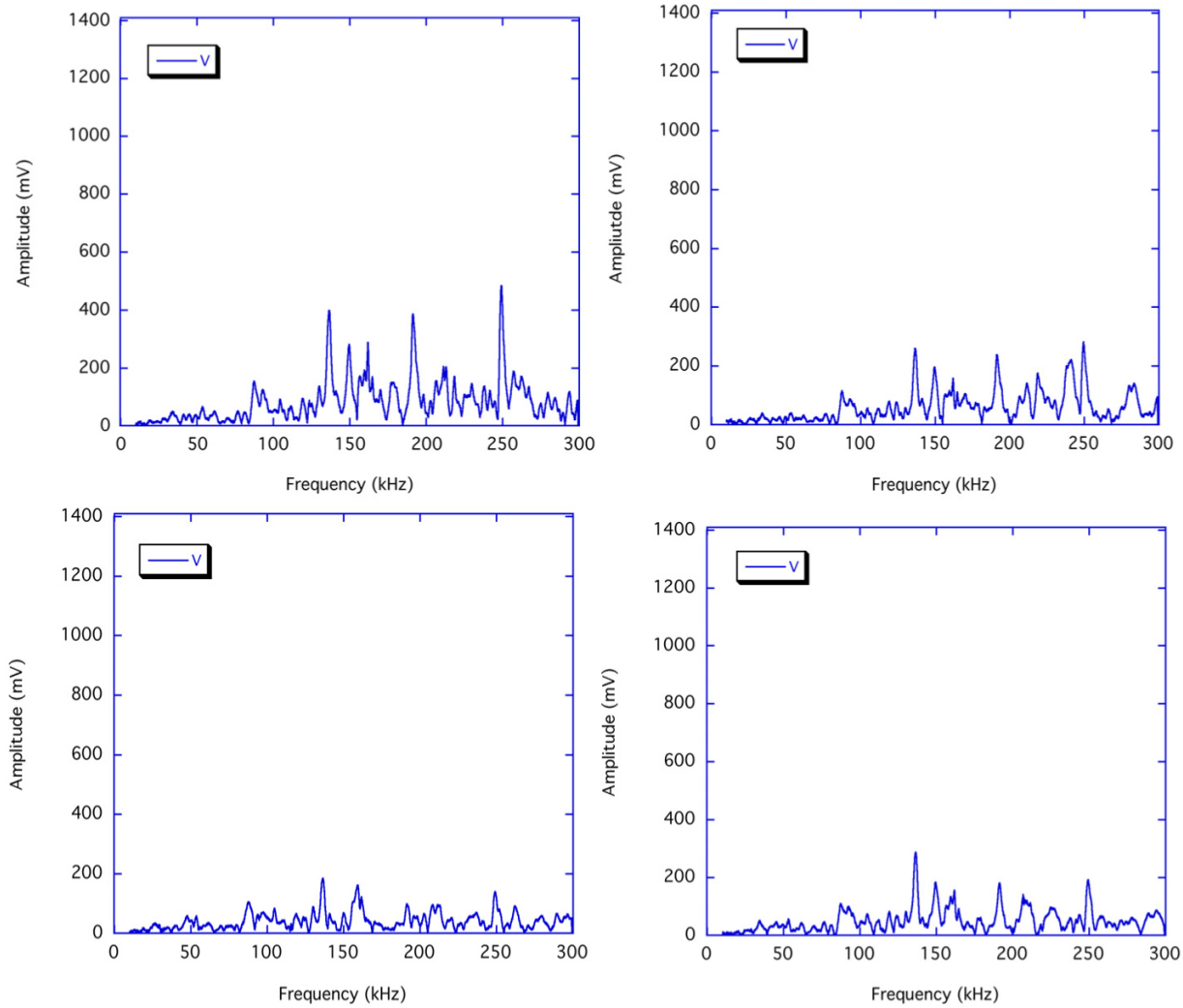

FIGURE 2. Four measurements of the Solid-H™ BL-30 storage cylinder, charged state, from 5 to 300 kHz conducted in succession with minor changes in placement of cylinder on top of the transducers, the possibility for slight rotation of cylinder, and variation in amount of water-based gel acoustic couplant.

in the resonance spectra and in particular, change which modes of vibration within the system were excited.

Mathematically Model the Aging Characteristics of Candidate Hydrogen Storage Materials (Task 2)

Shelf-life models were obtained for neat AB under non-isothermal reacting conditions. Differential scanning calorimetry (DSC) heat flow data were used to correlate dehydrogenation activity (or reaction progress) as a function of temperature. Models were generated using the Freidman analysis (or differential isoconversional technique). A shelf-life mode for neat AB was generated and is shown in Figure 3. Figure 3 shows the modeled reaction progress (i.e., extent of dehydrogenation) as a function of time and temperature. According to the model, AB will be stable

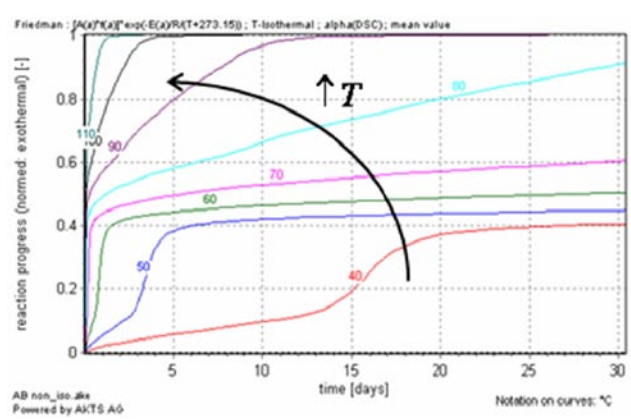

FIGURE 3. Shelf-Life Model for Neat AB

at 40°C for approximately 15 days before significant dehydrogenation occurs. This model, however, under predicts the shelf-life model of neat AB. Consequently, this model does not agree with experiment and therefore has been down-selected (or given a "no-go"). Disagreement between the experiment results and the current model can be attributed to the movement of the DSC pan upon dehydrogenation, giving rise to inaccurate heat flow results which translated into the model. Additional experiments are being performed that address this issue. Updated models will be generated and compared to the data to ensure agreement between them.

Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides (Task 3)

Rate models for the dehydrogenation of liquid phase AB have been generated using a limited data set. The data set primarily includes hydrogen production as a function of temperature. In addition, the data were collected in a batch reactor with hydrogen being the only measurable quantity. A complete set of kinetics data would include hydrogen production as a function of temperature, concentration, flow rate, and catalyst. In addition, mass balances resulting in selectivities and yields are necessary for an accurate and complete description of the reaction kinetics. We are working with the CHSCoE in obtaining these results for rate model regression.

Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies (Task 4)

Observed impurities generated from AB are ammonia, borazine and diborane. Impurities from the thermal decomposition of AB have been shown to be catastrophic to fuel cell operation and durability. We have quantified (via calibrations) borazine and diborane that are generated from neat AB, AB/methyl cellulose and AB dissolved in ionic liquids. The amount of borazine and diborane generated is strongly dependent upon temperature, catalyst, purity, additives, and physical phase (i.e., solid phase or liquid phase). Shown in Figure 4 are the gas phase infrared spectra of (a) neat borazine, (b) gas phase products observed from neat AB thermal decomposition, and (c) neat diborane. In contrast to neat AB, AB dissolved in ionic liquids only generates ammonia as the impurity. Borazine and diborane were successfully scrubbed using activated carbon (as shown in Figure 5) producing fuel cell grade hydrogen.

Develop Novel Strategies for Start-Up and Transient Operation with Candidate Chemical Hydrides (Task 5)

Start-up and transient operation are critical features that need to be addressed for all viable on-board hydrogen delivery systems. Our approach is to design and implement novel strategies that address these two DOE targets. We looked at a design where a room temperature dehydrogenation catalyst was homogeneously mixed with a high temperature catalyst (~70°C); refer to Figure 6. The room temperature catalyst provides a means to accommodate both the startup and transient operation of the fuel cell. The short coming of the room temperature catalyst is that it promotes the release of only one equivalent of hydrogen. This is in contrast to the high-temperature catalyst that allows for multiple equivalents of hydrogen to be released. In other words, there are two reaction pathways that are catalyzed by the different catalysts. Competing reaction pathways result in a trade-off scenario between hydrogen production efficiency, heat generation and transient response. The homogeneous dual catalyst bed design results in a hydrogen production efficiency that is below the DOE gravimetric targets.

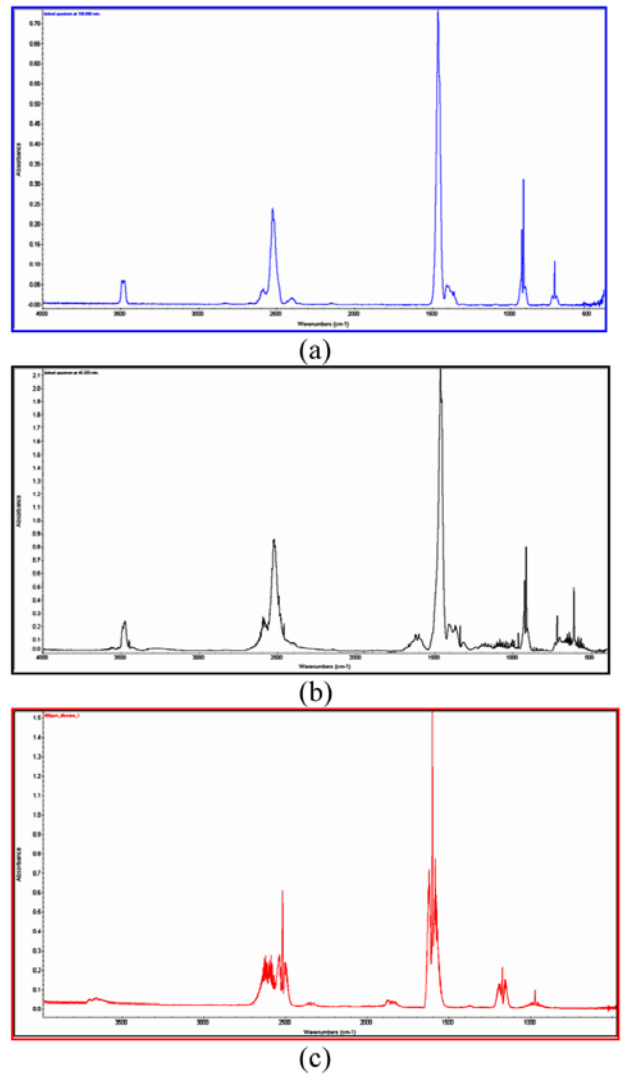

FIGURE 4. Gas Phase Infrared Spectra of (a) Borazine, (b) Products Generated from Neat AB (T_{max} = 200°C @ 5 °C/min) and (c) Diborane

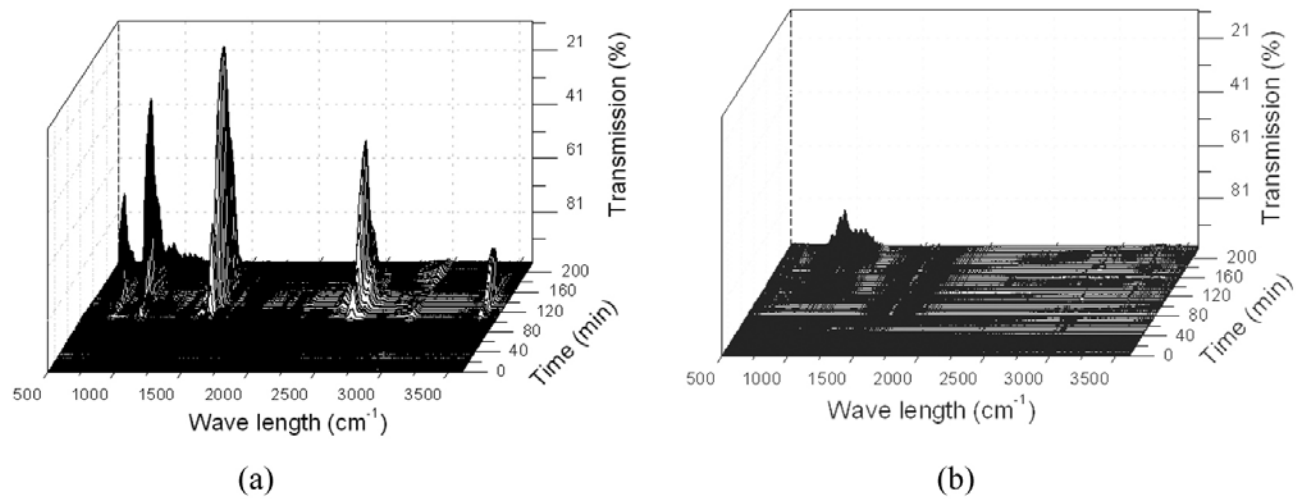

FIGURE 5. Gas Phase Infrared Spectra of Products Generated From Neat AB as a Function of Time (Temperature) (a) Without a Filter and (b) with Activated Carbon Filter

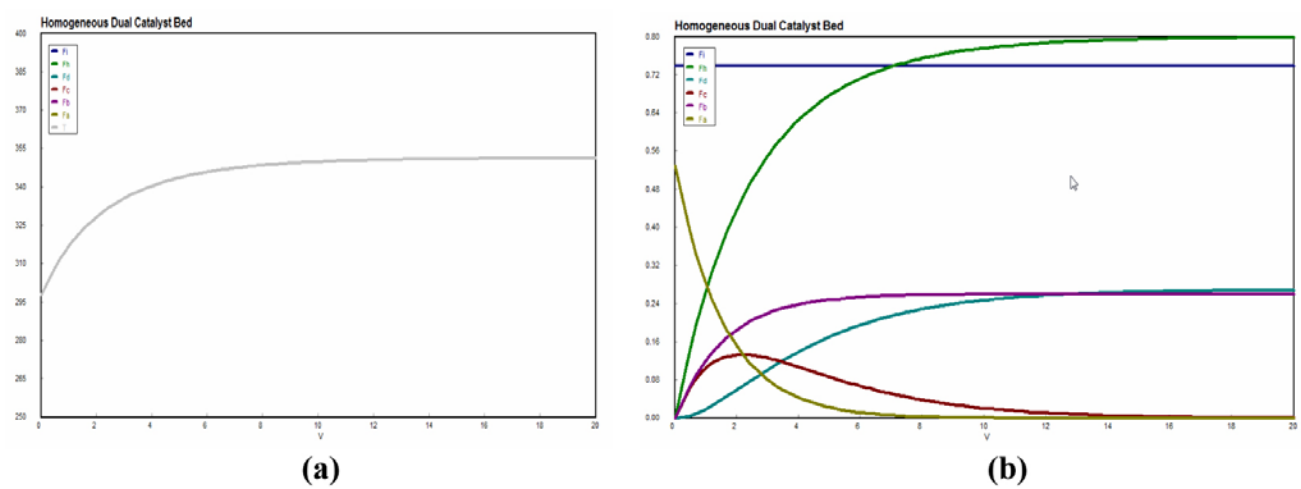

FIGURE 6. Temperature (a) and Concentration (b) Profiles for the Homogenous Dual Catalyst Bed Reactor Design

Consequently, this approach will not work and has been discarded as a viable design. We have also screened approximately 20 different catalysts for room temperature activity. None of the dehydrogenation catalysts proved to be viable room temperature catalysts. Results are shown in Figure 7. Because of the poor room temperature dehydrogenation activity observed with all of the catalysts tested, research on these catalysts has been discontinued.

Design, Build, and Demonstrate a Subscale Prototype Reactor Using Liquid or Slurry Phase Chemical Hydrides (Task 6)

In order to address the DOE targets we must first assess the current status via preliminary system designs. Shown in Figure 8 are two preliminary on-board system designs for liquid/slurry-phase AB. The preliminary system designs will be translated into a spider chart that compares the system to the DOE targets as a whole. We have identified areas that need to be addressed. These areas include impurity mitigation, startup and transient operation, and heat management. Preliminary costs and overall system efficiencies will also be calculated from the system designs.

Summary

- Level gauge milestones for Fiscal Year (FY) 2010 are on track and will be met by end of the fourth quarter.
- The change in swept acoustic frequency response with metal hydride hydrogenation/dehydrogenation observed in commercially prepared metal hydride

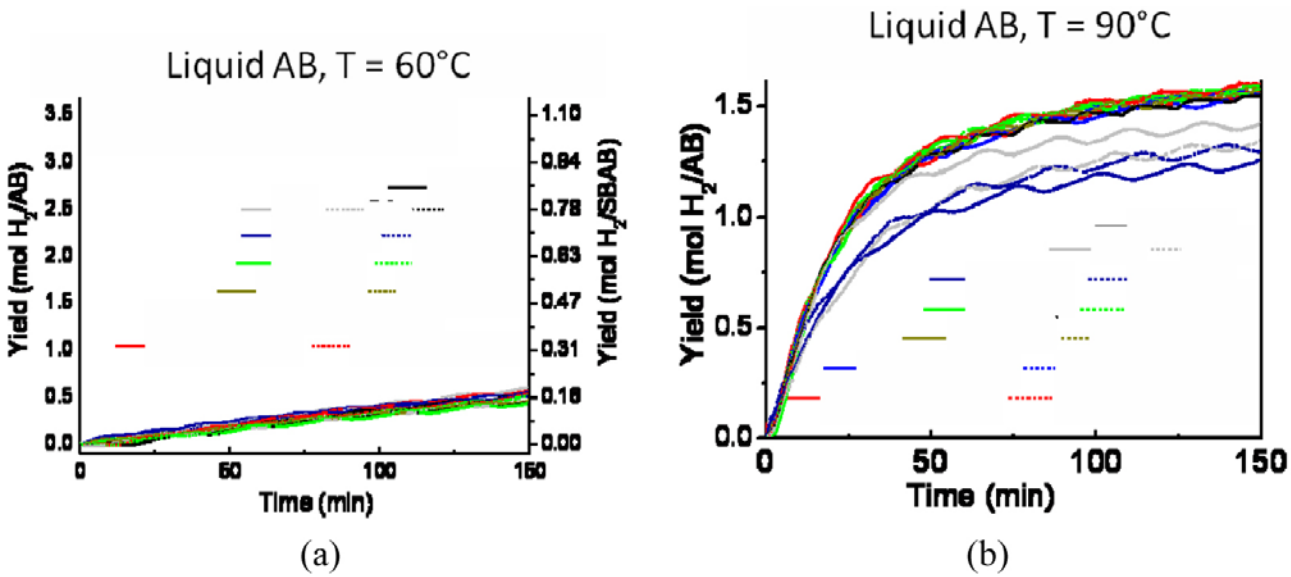

FIGURE 7. Catalyst Screening Results for the Room Temperature Dehydrogenation of Liquid Phase AB

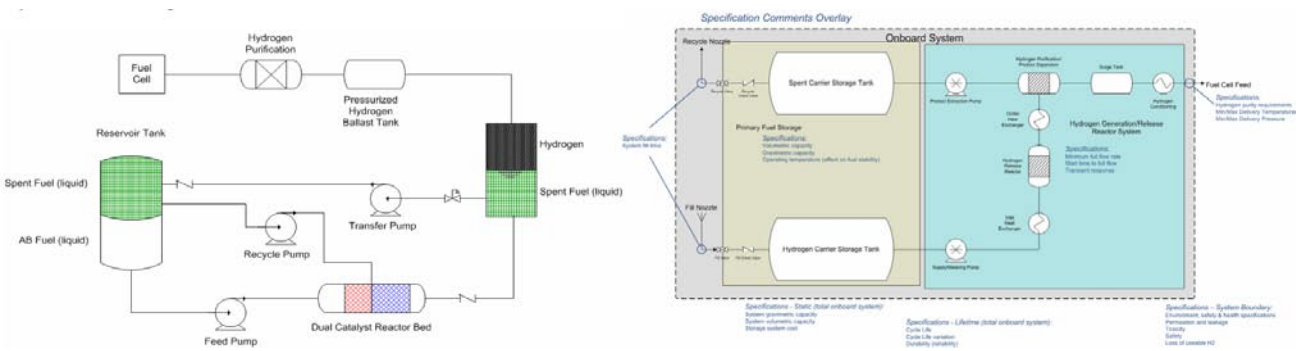

FIGURE 8. Preliminary On-Board System Designs for Liquid/Slurry-Phase Hydrogen Storage Media

cylinders has been reproduced in simple stainless steel vessels:

- Characteristic response observed for two different metal hydride alloys.
- Ergenics™ 208 and $LaNi_5$ alloy obtained from Aldrich in different cylinder masses/volumes show same effect.

- Experiments confirm that sound waves are coupling with, and interacting with, the metal hydride within the stainless steel pressure vessels and not due to secondary effects.
- Patent submitted.
- Acoustic sensor may be useful for metal hydride and adsorbent cycling studies.
- Developed and updated testing protocols for accurate shelf-life data acquisition.
- Collected shelf-life data for neat AB:
  - Shelf-life model for neat AB under predicts stability because of foaming issues, resulting in inaccurate data.
- Preliminary shelf-life data collected for a liquid AB formulation:
  - Liquid-AB formulations stable for 100 hrs @ 60°C; need to measure shelf-life for extended time periods (>1,000 hrs).
- The homogeneous dual catalyst bed design for handling the startup and transient operation of the fuel cell has been discontinued because the low temperature catalyst is too fast resulting in hydrogen production efficiencies equal to 0.4 (max is 1.0).
- Screened approximately 20 heterogeneous catalysts for room temperature activity:
  - Reactor tested catalysts cannot meet the startup requirement needed for an on-board hydrogen delivery system.

- Novel reactor designs (without auxiliary heating sources) addressing start-up and transient operation require the development of novel heterogeneous catalysts that are active at room temperature.
- Preliminary system designs for both liquid phase and solid phase chemical hydrides have been generated.

Future Directions

Acoustic Fuel Gauge Sensor

- Investigate the effects hydrogen head pressure on acoustic response.
- Investigate the effects valve positioning and supply lines on acoustic response.
- Perform compaction test to determine if acoustic coupling effects.
- Demonstrate tracking intermediate states of hydrogen charge of the commercial hydride cylinder and look at effects of temperature on the resonance spectra.
- Begin work with other H_2 storage media.

Shelf-Life Modeling

- Collect shelf-life data on solid AB with anti-foaming agent.
- Collect a complete set of shelf-life data on liquid-AB formulations.
- Update experimental setup and protocols as needed to ensure accurate data for model development.
- Verify model accurately predicts shelf-life models for extended time periods.

Reaction Rate Models for Hydrogen Release on Candidate Chemical Hydrides

- Acquire complete set of kinetics data:
  - Low-temperature catalyst route
  - High-temperature catalyst route
- Focus on segregated dual catalyst bed design.

Low Temperature Catalyst Development for Startup and Transient Operation

- Continued efforts will focus on converting the room temperature homogeneous catalysts into heterogeneous form while maintaining room temperature activity.

Hydrogen Impurities and Mitigation

- In collaboration with the CHSCoE, quantify impurities from liquid AB formulations as a function of temperature ramp.
- In collaboration with the CHSCoE, quantify impurities from solid AB formulations as a function of temperature ramp.
- In collaboration with MHSCoE, quantify impurities from candidate metal hydrides formulations as a function of temperature ramp.
- In collaboration with United Technologies Research Center, explore and test possible alternative scrubbing technologies for ammonia, diborane and borazine.