IV.D.3 Chemical Hydride Rate Modeling, Validation, and System Demonstration

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Fiscal Year (FY) 2011 Technical Objectives

- Develop fuel gauge sensors for solidstate 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).
- Develop an on-board fluid-phase chemical hydrogen storage system; system designer.

FY 2011 Accomplishments

- Demonstrated novel acoustic fuel-gauge sensor is capable of tracking hydrogen states-of-charge for metal hydrides and metal hydride cycling.
- Performed preliminary fuel cell tolerance test with diborane impurity.
- Quantified borazine and diborane impurities generated from neat ammonia-borane (AB).
- Demonstrated that borazine and diborane can be scrubbed to produce fuel cell quality hydrogen.
- Developed base-case system designs for fluid-phase chemical hydrogen storage materials.
- Developed space filled model of base-case fluid-phase system design.

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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 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.

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 noncommercial 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 observed, thus establishing a proof-of-principle that a hydrogen level sensor based on acoustic principles is feasible. Follow up experiments validated that the intermediate metal hydride state-of-charge can also be measured. Shown in Figure 1 are the resulting acoustic responses for various metal hydride states-of-charge. The acoustic response was observed to be inversely proportional to the metal hydride state-of-charge.

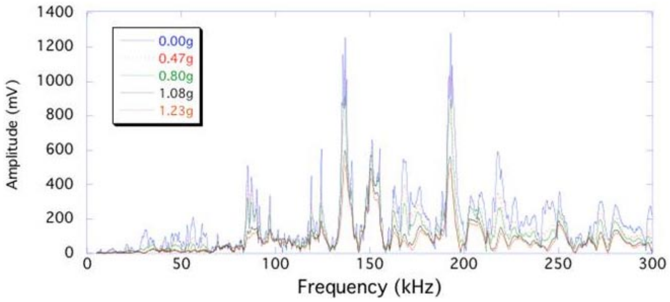

FIGURE 1. Acoustic Response as a Function of the Metal Hydride State-Of-Charge and Resonance Frequency

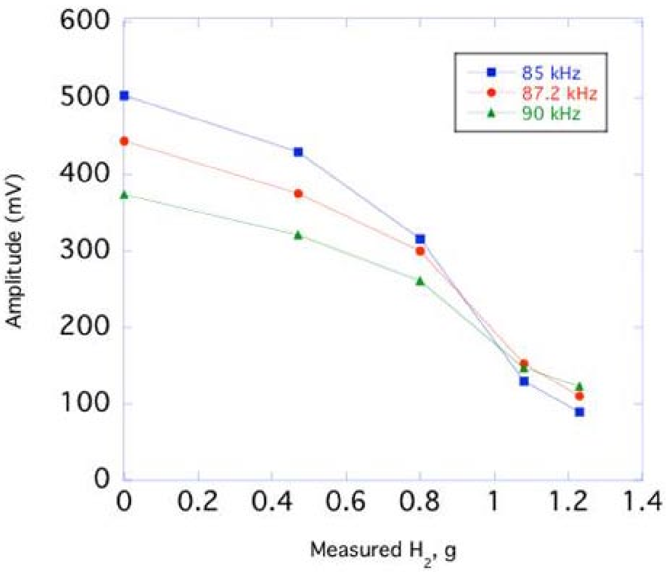

FIGURE 2. Acoustic Response for Three Resonance Frequencies as a Function of the Metal Hydride State-Of-Charge

The acoustic resonance frequencies were observed to be nonlinear with respect to the hydrogen state-of-charge. Figure 2 shows changes in three of the frequencies (85.0, 87.2, and 90.0 kHz) as a function of the metal hydride state-of-charge, with the lowest amplitudes occurring at the fully hydrided state-of-charge. The sensitivity in the acoustic amplitude was observed to be a function of not only the state-of-charge, but also the acoustic resonance frequency. The measured amplitude for a given resonance frequency exhibited monotonic behavior with respect to the state-of-charge, thus preventing multiple valued metal hydride states-of-charge.

Reproducibility of the state-of-charge is important if the sensor is to be commercialized. The sensor demonstrated reproducible results within 10%. The error is attributed to the fact that the metal hydride was in powder form. Performing acoustic measurements with engineered compacts will significantly lesson these errors.

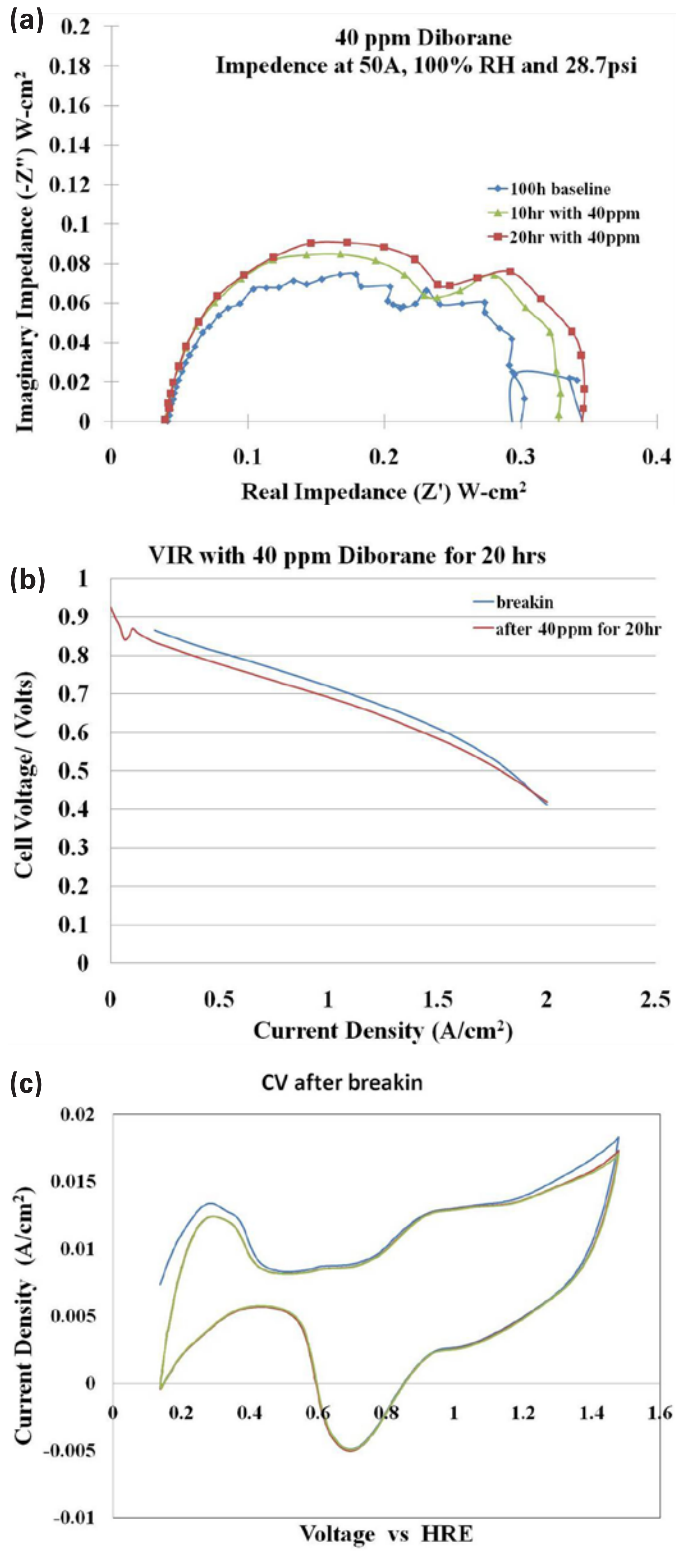

FIGURE 3. Fuel Cell Tolerance Test after 20 Hour Exposure with 40 ppm Diborane Impurity (a) Alternating Current Impendence, (b) Voltage-Current-Resistance Curve, and (c) Cyclic Voltammatry

Fuel Cell Tolerance Tests

In order accurately size an on-board hydrogen purification system for delivering fuel cell grade hydrogen, fuel cell tolerance levels for each of the impurities must be established. Diborane and borazine are known fuel cell impurities, but their levels for the safe and effective operation of a fuel cell are ill-defined. LANL performed preliminary fuel cell tolerance test with 2% diborane (balance ultra-high purity Ar) to investigate its effect on fuel cell performance. Shown in Figure 3 are the fuel cell tolerance test results after 20 hours of exposure with 40 ppm diborane. A decrease in fuel cell performance was observed after 20 hours of exposure to 40 ppm diborane, evidenced by a loss of 20 mV (Figure 3b). The electrochemical surface area remained constant throughout the preliminary 20 hour fuel cell tolerance test. The decrease in fuel cell performance can be attributed to an increase in the charge transfer resistance (Figure 3a). In addition, similar fuel cell tolerance tests are required for borazine.

Summary

- Successfully demonstrated that acoustic sensor technology can be used for tracking in real time the fully charged, fully discharged and the intermediate hydrogen state-of-charge of fixed metal hydride beds.
- Quantified impurities (diborane, ammonia, and borazine) generated from AB compositions.
- Performed preliminary fuel cell tolerance tests with diborane:
  - Fuel cell tolerance tests with 40 ppm diborane resulted in a 20 mV decrease in performance after 20 hours of exposure.
- Developed and designed automotive scale fluid-phase chemical hydrogen storage system.
- Developed and designed volume-based model of the automotive scale system design.
- Designed, built, and demonstrated a bench top fluid-phase chemical hydrogen validation test bed.

Future Directions

- Acoustic Fuel Gauge Sensor
  - Finish preliminary measurements on fluid-phase chemical hydrogen storage media
- Shelf-Life Modeling
  - Collect a complete set of shelf-life data on fluid-phase AB formulations.
  - 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
- 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 LANL Chemical Hydrogen Storage Center of Excellence, quantify impurities from liquid AB formulations as a function of temperature.
- Subscale Component Design and Validation
  - Gas-liquid separator
  - Reactor
  - Hydrogen purification train