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

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Objectives

- Act as the Chemical Hydrogen Storage Center of Excellence (CHSCoE) liaison.
- 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).

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
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(F) Codes and Standards

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 hydrogen fuel gauge sensor proof-of-concept.
- Provided chemical hydride empirical rate model for hydrogen release to Savannah River National Laboratory (SRNL).
- Finished setting up equipment to perform experiments on:
  - Shelf-life modeling
  - Impurity testing
- Collaboration onset with the CHSCoE:
  - Engineering data collection
  - Materials transfer for testing

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Introduction

This project is a new start (February 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 (HSECoE) 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.

Approach

Our approaches in fulfilling the needs and requirements for on-board hydrogen storage within LANL's research scope in the HSECoE will employ efforts in both experimental and modeling fronts. Our approaches are broken down based on our work objectives and they are:

1. **Design and Develop Fuel Gauge Sensors for Solid-State Hydrogen Storage Media**: LANL will employ an inexpensive, simple, and robust methods of using the natural properties of the hydrogen storage media to develop novel fuel gauge sensors.
2. **Mathematically Model the Aging Characteristics of Candidate Hydrogen Storage Materials (for example, complex metal hydrides or chemical hydrides):** 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).
3. **Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides Relevance to Technical Objectives:** 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.
4. **Develop Novel Strategies for Start-Up and Transient Operation with Candidate Chemical Hydrides:** 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.
5. **Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies Relevance to Technical Objectives:** 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 (SEM), 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 ammonia borane were unknown.

Results

Fuel Gauge Sensor Development

A novel fuel gauge sensor has been demonstrated for a mischmetal hydride. Results indicate that the fuel gauge sensor can detect changes in the hydrogen state-of-charge of the mischmetal hydride.

Mathematically Model the Aging Characteristics of Candidate Hydrogen Storage Materials (for example, complex metal hydrides or chemical hydrides)

Our lab is now equipped and ready to perform the aging experiments needed to model the shelf-lives of candidate hydrogen storage materials.

Develop Rate Models for Hydrogen Release on Candidate Chemical Hydrides Relevance to Technical Objectives

Empirical rate models have been provided to SRNL to begin zeroith order system modeling. Rate models are based on the power-law method and the design equation is for flowing systems.

Identify Hydrogen Impurities and Develop Novel Impurity Mitigation Strategies Relevance to Technical Objectives

Impurities of the dehydrogenation of ammonia borane have been identified as borazine, diborane and ammonia. Quantification of the impurities is in progress. Impurities from the thermal decomposition of ammonia borane have been shown to be catastrophic to fuel cell operation and durability.

Conclusions

- Empirical rate models have been transferred to SRNL to begin modeling.
- Novel fuel gauge sensor demonstrated encouraging results for mischmetal hydrides.
- Quantification of impurities will soon commence.
- Shelf-life experiments are currently underway.

Future Directions

Experimental and Characterization

- Develop preliminary reactor design to begin system modeling and integration.
- Continue shelf-life experiments for shelf-life modeling.
- Quantify hydrogen impurities resulting from chemical hydrogen storage media.
- Continue fuel gauge sensor develop and applicability to other relevant hydrogen storage media.