

IV.D.1c Advancement of Systems Designs and Key Engineering Technologies for Materials-Based Hydrogen Storage

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Objectives

- Collaborate closely with the Hydrogen Storage Engineering Center of Excellence (HSECoE) partners to advance materials-based hydrogen storage system technologies.
- Develop vehicle/power plant/storage system integrated system modeling elements to improve specification of storage system requirements and to predict performance for candidate designs.
- Establish detailed heat and mass transfer modeling and apply to design improved internal heat exchange configurations.
- Design and evaluate compacted/structured hydride powder beds including integration into the heat exchange configurations.
- Assess the viability of on-board purification for various storage material classes and purification approaches.

- Conduct risk assessments during the progression of the phased HSECoE efforts to evaluate concepts regarding the “Environmental Health and Safety” target.

Technical Barriers

This project is concerned with assessing and developing all aspects associated with viability of storage systems and therefore addresses a broad set of technical barriers from the Storage section (3.3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (G) Materials of Construction
- (H) Balance of Plant (BOP) Components
- (I) Dispensing Technology
- (J) Thermal Management
- (K) System Life-Cycle Assessments

Technical Targets

The goals of this project mirror those of the HSECoE which by the end of Phase I (March, 2011) seeks to define systems configurations which can fully meet four of the DOE 2010 numerical system storage targets as outlined in the Multi-Year Research, Development and Demonstration Plan and partially meet the remaining numerical targets to at least 40% of the target or higher.

Accomplishments

Accomplishments of the current project comprise:

- Demonstrated that powder compaction with a uniaxial press can simultaneously increase the density of sodium alanate materials by 63% (39% reduction in volume) and the thermal conductivity by a factor of seven in comparison to the properties of loose powder while maintaining comparable hydrogen absorption and desorption rates.
- Developed a biaxial flexure screening test for determining the strength of compressed pellets and changes in the pellet strength due to hydrogen absorption and desorption cycles.

- Designed and optimized a heat exchanger for a sodium alanate-based hydrogen storage system with a fast refueling time and developed a lumped parameter model of such a system for inclusion in vehicle level modeling.
- Demonstrated viability of an onboard hydrogen purification cartridge for ammonia, which addresses concerns about the presence of ammonia in hydrogen from chemical hydride (e.g. ammonia borane) and metal hydrides (e.g. $\text{LiNH}_2/\text{MgH}_2$ mixtures).
- Designed and implemented an integrated power plant storage system modeling framework in Simulink.



Introduction

Physical storage of hydrogen through compressed gas and cryogenic liquid approaches is well established, but has drawbacks regarding weight, volume, cost and efficiency which motivate the development of alternative, materials-based methods of hydrogen storage. Recent worldwide research efforts for improved storage materials have produced novel candidates and continue in the pursuit of materials with overall viability. While the characteristics of the storage materials are of primary importance, the additional system components required for the materials to function as desired can have a significant impact on the overall performance. Definition, analysis and improvement of such systems components and architectures, both for specific materials and for generalized material classes, are important technical elements to advance in the development of superior methods of hydrogen storage.

Approach

UTRC's approach involves a broad set of tasks which leverage prior experience, coordinate with other UTRC projects and extend to new areas of concept development. A graphical representation of our approach to conduct the research is shown in Figure 1. It shows material-related tasks at the base of the pyramid, component design tasks in the center, and system-related tasks near the top, which all tie in with the overall structure of the HSECoE. The results will be used by the HSECoE to determine the viability of materials-based hydrogen storage systems. The project is divided into three phases with the first covering two years. A Go/No-Go decision at the end of Phase 1 (March 31, 2011) will guide activities and concepts for deeper evaluation in Phase 2.

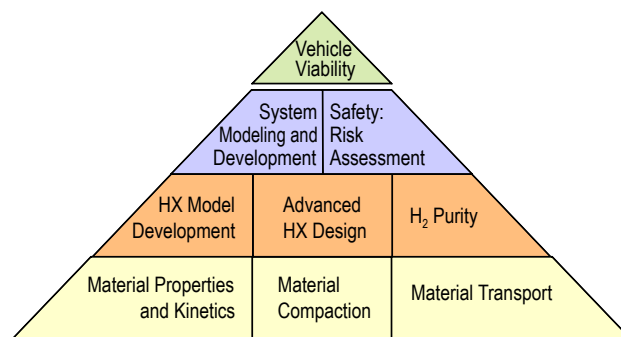


FIGURE 1. UTRC's approach to leveraging in-house expertise and prior experience with metal hydride system prototyping to advance materials based hydrogen storage.

Results

DOE's 2010 target for the volumetric capacity of a hydrogen storage system is 28 grams hydrogen per liter on a system basis. At the time of this study sodium alanate was a Tier 1 material in the HSECoE, and it was therefore selected as a model material for evaluating the impact of compaction on the density and thermal conductivity of a prototypical hydrogen storage material. Reaching the targeted volumetric capacity with sodium alanate requires powder compaction. For this purpose UTRC installed a heated platen uniaxial press inside a glovebox with an inert atmosphere. The density of the pressed pellets as a function of the compaction pressure is shown in Figure 2. The thermal conductivity of the compacted material was measured with a Hot Disk[®] Thermal Constants Analyzer and is shown in Figure 3 as a function of density. The results show that compaction of sodium alanate enables an increase in density of about 63% in comparison to loose powder (39% reduction in volume) which results in a seven fold increase of the thermal conductivity. Compacted sodium alanate appeared to have a slightly slower hydrogen absorption rate and this is subject of future research.

Sodium alanate pellets need to be strong for this automotive application. A biaxial flexure screening test was developed in order to measure the strength and determine any strength change after hydrogen absorption and desorption cycles. Initial results show a small volumetric expansion (~2%) of the pellets due to repeated cycling and the pellets maintained their strength (1.4 kpsi), but experiments will need to be repeated and performed over a larger number of cycles in order to better determine the significance of those results.

DOE's 2010 target of 4.2 minutes for system fill time (for 5 kg hydrogen) is challenging for a hydrogen storage system based on sodium alanate due to the relative high heat of hydrogen absorption (~40 kJ/mol hydrogen) and kinetic limitations. A COMSOL Multiphysics[™]

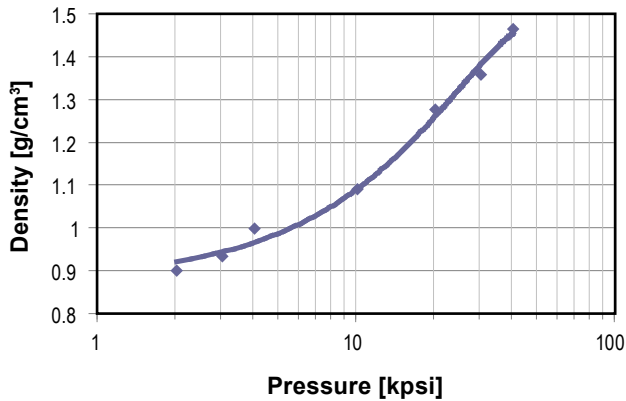


FIGURE 2. Impact of Applied Pressure during Compaction on Density of Sodium Alanate Pellets

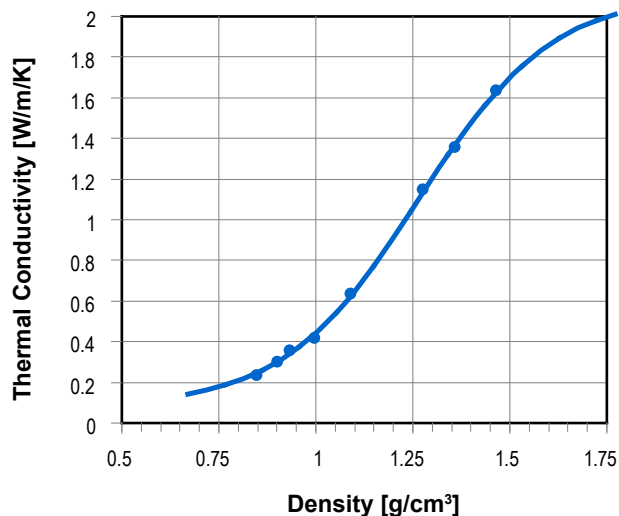


FIGURE 3. Thermal Conductivity of Sodium Alanate Pellets as a Function of Density

thermochemical simulation approach was co-developed with Savannah River National Laboratory and used to engineer a sodium alanate-based hydrogen storage system with such a short fill time, while maximizing gravimetric and volumetric capacities. It required an enhancement of the reaction kinetics beyond what is currently observed. The allowable temperature rise in the sodium alanate bed during refueling was restricted to 170°C. This constraint was imposed as a decrease of the hydrogen absorption rate was observed when holding the material at 180°C for an extended period of time (15-75 hrs), which is undesirable. The heat exchanger tubing diameter, aluminum content in the bed and the tube spacing were optimized with this model and the results are shown in Figure 4. It clearly shows the improvement of the volumetric capacity due to compaction and how a relative high volumetric capacity

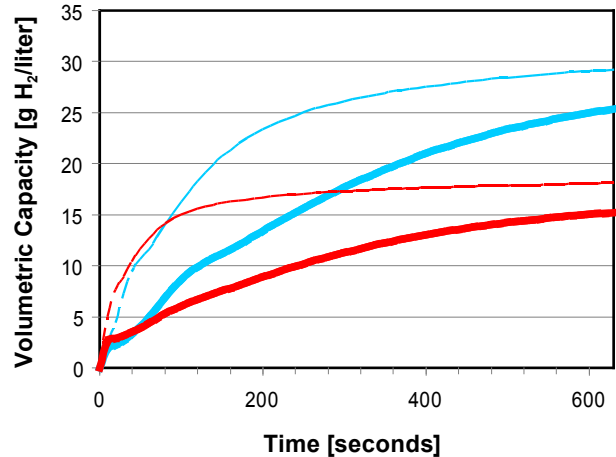


FIGURE 4. Volumetric capacity of hydrogen storage based on sodium alanate (sodium alanate + heat exchanger, but without pressure vessel and other system components) as a function of time for beds of which the gravimetric capacity had been optimized for a 10.5 minutes fill time. Red and blue lines show the results for powder and pellets, respectively. The drawn lines show the results with UTRC's Prototype 2 kinetics [3] and the dashed lines show the results with improved reaction kinetics (factor 10 for powder and factor 3 for pellet).

can be achieved even at a short fill time by using tightly spaced small diameter tubing (1/8") in the heat exchanger and improvement of the reaction rate beyond what is currently observed. However, compaction only reduces the volume of the hydrogen storage material and therefore the gravimetric capacity of the sodium alanate bed still remains low (<18 g H₂/kg) in comparison to DOE's 2010 target (45 g H₂/kg system).

UTRC is leading the Integrated Power Plant Storage System Modeling technical area of the HSECoE and with other partners has developed a simulation framework that was implemented in Simulink™. The framework is shown in Figure 5 in a graphical form. The team developed an interface matrix between the different simulation modules under guidance of Ford. The framework created a strong focus for the team members. Each member contributed models such as the lumped parameter model of a sodium alanate system by UTRC, the sodium alanate system with a different design by General Motors (GM), the cryo-adsorption system by GM, the chemical hydride system based on ammonia borane by the Pacific Northwest National Laboratory, the proton exchange membrane (PEM) fuel cell system by Ford and the vehicle level model by the National Renewable Energy Laboratory (NREL). The integrated framework enables a dynamic evaluation of the performance of a vehicle with a materials-based hydrogen storage system and a seamless comparison of various hydrogen storage systems on a common and quantitative basis, which is critical for the Go/No-Go decision in the end of Phase 1.

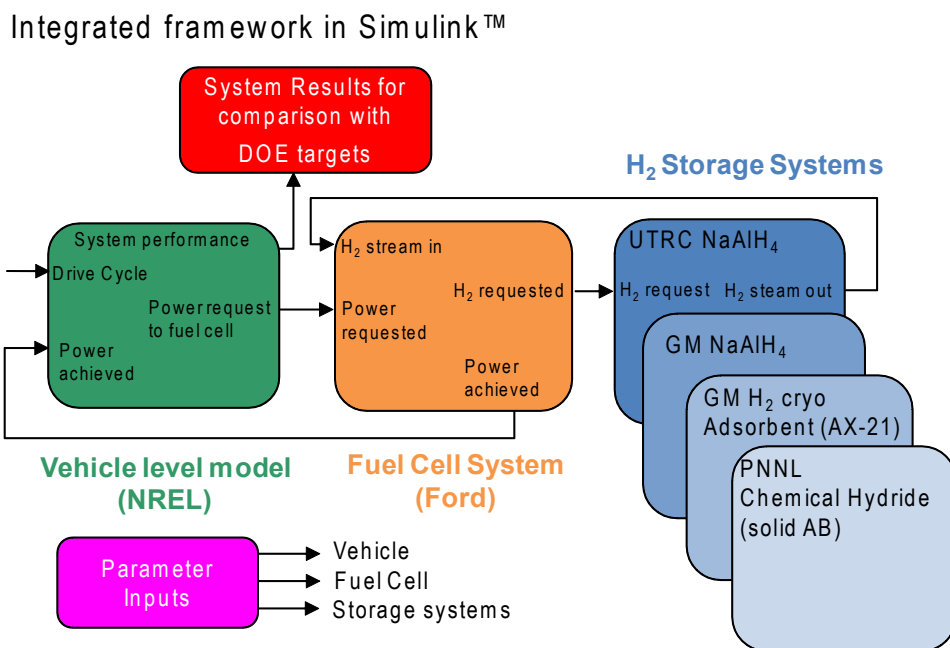


FIGURE 5. Integrated Power Plant Storage System Modeling Framework in Simulink™

Hydrogen from the hydrogen storage system needs to have a sufficient purity in order to enable high performance and long life of the PEM fuel cell system. The SAE J2719 guideline [1] was adopted as the hydrogen purity standard. This guideline not only specifies the total hydrogen content but also sets limits on the concentration of specific impurities such as ammonia. Ammonia was shown to be an impurity of concern by Keith Wipke from NREL [2] as part of the Hydrogen Fuel Cell Vehicle and Infrastructure Learning Demonstration project as some of the hydrogen that was tested contained 1 ppm ammonia, which exceeds the SAE guideline of 0.1 ppm. Ammonia is not only introduced on-board the vehicle by the hydrogen filling station but two candidate materials for hydrogen storage (ammonia borane and $\text{LiNH}_2\text{:Mg H}_2$ mixtures) have also been reported to release hydrogen that is contaminated with ammonia. Therefore, ammonia abatement was selected as an initial focus for the hydrogen purity task. A chemical adsorption cartridge was selected for an experimental evaluation as it has distinct benefits in terms of cost and low hydrogen loss in comparison to the two alternative purification approaches (palladium membrane and on-board regenerable physical adsorption). An experimental setup was designed and built to determine the dynamic sorption capacity of various sorbents. It uses a photo-acoustic analyzer to monitor the ammonia content in the effluent of the sorbent bed as a function of time. The breakthrough time was defined as the time at which the ammonia content would exceed 0.6 ppm, which is the detection limit of this analyzer. It was determined

experimentally that a commercially available sorbent had a dynamic sorption capacity for ammonia of about 2-2.5 wt% as a result of both physical and chemical adsorption under dry conditions (no humidification). A cartridge with about 4 kg of this sorbent would last about 3 months when processing 5 kg of hydrogen per week if the hydrogen would contain 200 ppm ammonia. This appears to be a viable approach and improving the capacity of the sorbent to reduce weight and volume is part of our future work. It is realized that abating hydrogen impurities with purification methods is only one approach and that it would be desirable to have an improved understanding and control over the hydrogen release mechanism to avoid the formation of impurities all together.

Qualitative risk analysis was performed on a chemical hydride system (based on ammonia borane) and on a cryo-adsorption system (based on AX21) and fault trees were developed for both.

Conclusions and Future Directions

Conclusions derived from the work in Fiscal Year 2010 are:

- Compaction of hydrogen storage materials, with sodium alanate as an example, is a valuable engineering tool for improving thermal conductivity and volumetric capacity of a hydrogen storage system but there is a trade-off between how much one can compact and when the decrease in permeability starts to become an issue. Also,

- verifying that strength and compact integrity is maintained, is important.
- Sodium alanate is a good model material for developing engineering tools (compaction method, multiphysics model) though it is recognized it cannot fulfill the DOE targets.
- Evaluating different hydrogen storage systems on a common basis, by establishing a common simulation framework, is important for down-selecting hydrogen storage systems for Phase 2 consistently across the center.
- On-board hydrogen purification with commercially available sorbents to remove ammonia is feasible as long as the ammonia content is low (e.g. <200 ppm).

Future work will comprise:

- Determine hydrogen permeability of compacted sodium alanate pellets and use results in COMSOL Multiphysics™ model to quantify impact of pressure gradients on hydrogen absorption and desorption rate.
- Develop a small test article of compacted sodium alanate to determine thermal performance with aspects of heat exchanger integration.
- Expand the compaction effort, thermal conductivity and permeability measurements, to other materials that are of interest to the HSECoE.
- Use the Simulink framework to compare performance of various hydrogen storage system designs on a common basis and evaluate against DOE targets in close cooperation with the HSECoE partners.

- Improve ammonia dynamic sorption capacity of sorbent material and expand hydrogen purification approach from ammonia to other impurities of concern.
- Qualitative risk assessment of hydrogen storage systems of interest to the HSECoE.

FY 2010 Publications/Presentations

1. Daniel A. Mosher, System Engineering for Materials Based Hydrogen Storage, IEA HIA TASK 22 Meeting, Fundamental and applied hydrogen storage materials development, April 11–15, 2010, Death Valley, California.

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