
Hydrogen Storage System Modeling: Public Access, Maintenance, and Enhancements

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Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Coordinate the public access of select models developed under the Hydrogen Storage Engineering Center of Excellence (HSECoE) activity, including web posting of documentation and tracking downloads and web activity.
- Maintain performance of existing storage system models and update and validate as new experimental data becomes available.
- Enhance and expand existing models to improve simulation speed and application to other uses. This will focus on expanding the parameterization of the models and their flexibility in evaluating new material candidates. This will initially include the development of pre-processor sizing routines for the adsorbent and chemical hydrogen systems followed by the metal hydride and cryo-compressed systems.

Fiscal Year (FY) 2019 Objectives

- Work with HSECoE partners to continue to update and improve center-developed models. Make these models available and accessible to the broader research and academic community

through a controlled web-based access portal and track downloads and website activity.

- Create stand-alone Microsoft Excel versions of the HSECoE-developed material storage models to provide first-order storage system estimates based on material property information.
- Update the hydrogen storage equations with additional, alternative theoretical storage system formulations to allow users to choose the most appropriate theory for their material.
- Develop tools to size/design storage systems based on available volume or desired hydrogen storage mass.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- System weight and volume
- System cost
- Efficiency
- Charging/discharging rates
- Dispensing technology
- Systems life-cycle assessments.

Technical Targets

This project is conducting simulation and modeling studies of advanced onboard materials-based hydrogen storage technologies. Insights gleaned from these studies are being applied toward the hydrogen storage vessel design and materials synthesis that meet the following DOE 2020 hydrogen storage for light-duty vehicle targets:

- Storage system cost: \$333/kg H₂ Stored
- System gravimetric capacity: 0.045 kg H₂/kg system

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- System volumetric capacity: 0.030 kg H₂/L system
- Charging/discharging rates: 3–5 min
- Well-to-power-plant efficiency: 60%.
- Developed a standalone Excel model for metal hydrides.
- Development of a standalone Excel model for chemical hydrogen storage.

FY 2019 Accomplishments

- Improved the adsorbent model with more user options, Dubinin-Astakhov (D-A) and UNILAN models, and specification of system volume or mass of hydrogen as starting point.
- Improved the metal hydride storage system in the Framework Model through addition of a two-step reversible kinetic model, user inputs for material properties and reaction parameters, and hydrogen mass or system volume as input parameters.
- Developed a standalone Excel model for adsorbents.
- Validated the Modular Adsorbent Tank Insert (MATI) Adsorbent Storage System.
- Provided possible pathways to meet gravimetric technical targets for NaAlH₄.
- Evaluated new materials relative to technical targets.
- Modified the Vehicle Framework to run the individual hydrogen storage models with either system volume or hydrogen mass.
- Tracked and monitored web activity and downloads.
- Updated website.

INTRODUCTION

Overcoming challenges associated with onboard hydrogen storage is critical to the widespread adoption of hydrogen-fueled vehicles. The overarching challenge is identifying a means to store enough hydrogen onboard to enable a driving range greater than 300 miles within vehicle-related packaging, cost, safety, and performance constraints. As new hydrogen storage materials are discovered and created, material developers must predict their full-scale vehicle performance and compare their performance with pure hydrogen storage (700-bar, cryo-compressed, and liquid H₂ storage). The goal of this work is to provide material developers with the modeling tools necessary to make these predictions based on the work done by the HSECoE.

APPROACH

The approach for FY 2019 is to complete updates, validate, enhance, troubleshoot, de-bug, and document the models developed by the HSECoE so that they can be made accessible to and useful for other researchers within the hydrogen storage community. These models will be updated with alternative storage system formulations, such as different isotherm models for adsorbents and alternative chemical reaction kinetic expressions for metal hydrides. In addition, standalone system design tools that do not require special software will be developed to serve as a scoping tool for the new hydrogen storage materials that may be developed.

RESULTS

The following provides results from work completed this year by the multi-lab team with a focus on Microsoft Excel-based storage system design tools. The team maintained public access of select HSECoE models, documented activities in several publications, and exercised the tools with other material data sets. The team also monitored/tracked web activity and model downloads. To date there have been 241 downloads of the Hydrogen Tank Mass and Cost Estimator model, 165 downloads of the Hydrogen Vehicle Simulation Framework model, 107 downloads of the Metal Hydride Finite Element Model, 66 downloads of the Metal Hydride Acceptability Envelope, 31 downloads of the Chemical Hydrogen Storage System Design Standalone model, and 30 downloads of the Adsorbent Storage System Design Standalone model.

Each of the hydrogen storage MATLAB executable standalone models were converted into visual basic in Microsoft Excel so they could be simplified by using a macro within Microsoft Excel without needing any additional software. This change simplifies the model operation to allow wider usage than was possible with MATLAB without the loss of functionality. In the MATLAB version of the models, the input and output files

were in Microsoft Excel and the calculation was done in an executable MATLAB file. In the new Microsoft Excel model, the input and output files are also Excel worksheets. As a result, there is little difference in these files relative to previous models. The only obvious difference is the “Run” button that is displayed next to the input data in the “Inputs” worksheet used to run the calculation macros. This is the primary improvement for all hydrogen storage material models. All other model updates and improvements are outlined below.

Adsorbent Model Improvements

Improvements to the adsorbent model are summarized in Table 1 and include more user-controlled options, D-A and UNILAN model options, and the ability to specify system volume or mass of hydrogen as a starting point. Each of the major model updates was made to improve model usability and/or functionality. The adsorbent hydrogen storage system design balance of plant (BOP) has been updated to include BOPs for room-temperature operation ($\sim 25^{\circ}\text{C}$), cold operation near dry ice temperatures, and an updated version of the cryogenic operation BOP. This will allow each user to tailor their adsorbent system design to the preferred operation of their chosen adsorbent. As a continuation of this capability, the user can also decide how thick to make their pressure vessel insulation as well as whether or not to include liquid nitrogen (LN_2) tank cooling channels in their system design.

The adsorbent isotherm theory is the backbone of the adsorbent system model, which is why the user can now choose which adsorbent isotherm theory they would like to use in the model. The two most prominent isotherm models are D-A and UNILAN isotherm theory options. In addition, the user can change the isotherm theory constants to match their specific adsorbent material so they can design the best hydrogen storage system for their material. Finally, the user can choose whether to base the system design on the mass of usable hydrogen or the maximum total storage system volume as the starting point. This allows the user to more easily answer the question of *how large* the adsorbent hydrogen storage system needs to be or *how much hydrogen* can the adsorbent hydrogen storage system store.

Table 1. Adsorbent Model Improvements

Original Model	Updated Model
BOP for cryogenic operation only	BOP options for room temperature, cold, and cryogenic operations
Insulation thickness hard coded to 1-inch	Insulation thickness is user controlled
LN_2 tank cooling channel always included	LN_2 tank cooling channels user controlled
D-A isotherm model used only	D-A and UNILAN isotherm model options
MOF-5 material properties hard coded	User defined adsorbent material properties (with MOF-5 default values)
Mass of usable hydrogen is the starting point of the calculation	Mass of usable hydrogen or maximum total storage system volume starting point

Metal Hydride Model Improvements

The metal hydride system framework model was also updated, with the improvements summarized in Table 2. These improvements include user inputs for material properties and reaction parameters, and the use of usable hydrogen mass or storage system volume as the starting point. A further improvement was the expansion of the kinetic model to include two reaction options: (1) a single-step irreversible reaction rate used for intermetallic compounds, and (2) a two-step series reaction model with reversible reactions used for complex metal hydrides. The versatility of these reaction models is the opportunities for user inputs, which include reaction parameters, material properties, and other key parameters to tailor the model to the user’s specific metal hydride and desired operating conditions. Similar to the Framework model, the stand-alone metal hydride system design tool also has the ability to start from either desired usable hydrogen or maximum storage system volume, just like the Framework and the adsorbent storage system design tool.

Table 2. Metal Hydride Model Improvements

Original Model	Updated Model
Single step irreversible reaction	Single step irreversible or two step reversible models selectable
Hard coded reaction rate and enthalpy (30 kJ/mol)	Reaction parameters and material properties as inputs
Mass of usable hydrogen is the starting point of the calculation	Mass of usable hydrogen or maximum total storage system volume starting point

Evaluation of Potential Pathway to Meet Gravimetric Technical Target for Metal Hydrides

The metal hydride system design tool was exercised to demonstrate alternative approaches that can be made in the properties of a metal hydride material to meet the DOE technical targets for gravimetric density of a hydrogen storage system for light-duty vehicles. While multiple pathways exist to achieve these targets, Figure 1 demonstrates that based on sodium alanate, the reaction enthalpy should be decreased and hydrogen capacity and density increased to reduce the system mass of the material. Despite these changes, it still required that a lighter tank be used to ultimately reach the final goal.

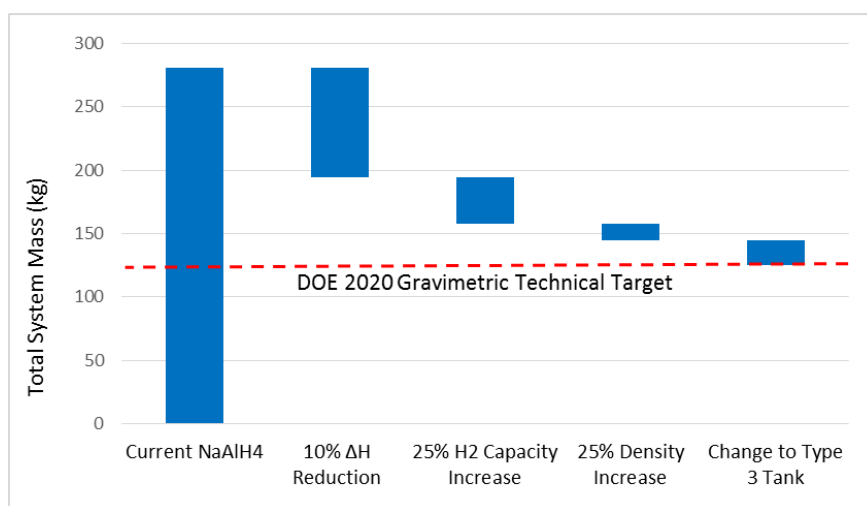


Figure 1. Potential pathway to meet gravimetric target for NaAlH4

Properties of nano-Li3N being developed by Sandia National Laboratories were compared to sodium alanate to demonstrate their benefits from a gravimetric density perspective. As can be seen in Figure 2, KH doping further reduces the system mass, but additional improvements in the reaction enthalpy, hydrogen capacity, density, and tank type may still be required to meet the DOE 2020 technical target for gravimetric capacity.

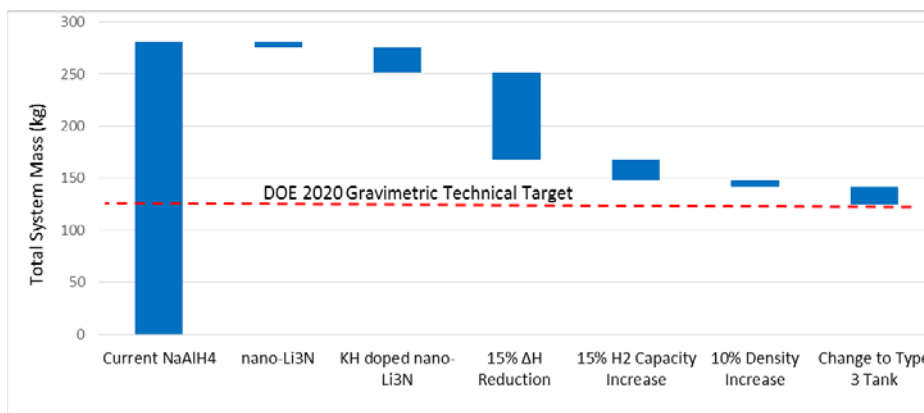


Figure 2. Evaluation of new materials relative to DOE targets

MATI Adsorbent Storage System Validation

Several comparisons to experimental data were made to validate the adsorbent hydrogen storage system designs. Total hydrogen storage, refueling from 1 bar to 100 bar at constant temperature, and desorption data from 100 bar to 1 bar at constant temperature taken from the 2-liter MATI prototype with compacted MOF-5 pucks built for the HSECoE provided the primary data sets used for validation. Constant temperature was maintained by submerging the prototype in an LN₂ bath. For refueling, the pressure was slowly ramped over 14 minutes to minimize the heat of pressurization. Desorption experiments were also performed with a similarly slow pressure decrease to maintain constant temperatures. The experimentally measured constant temperature boundary condition was approximately 83 K because tubing upstream of the prototype outside of the LN₂ bath was exposed to the ambient. Note that 83 K was measured at the MATI plates as well and can also be attributed to heat transfer from insulated tubing exposed to the ambient.

Table 3. MATI Adsorbent Storage System Validation

Operating Conditions	H _{2,in}	m _{tube,tot}	m _{proto,exp}	m _{proto,model}	%-Diff
(1.07 bar, 83.7 K) → (60.0 bar, 91.3 K)	86.85 g	41.69 g	45.16 g	45.45 g	0.639%
(1.09 bar, 83.7 K) → (100.0 bar, 84.5 K)	140.54 g	72.56 g	67.99 g	68.09 g	0.158%
(5.05 bar, 84.0 K) → (60.5 bar, 106.6 K)	59.55 g	28.51 g	31.04 g	24.57 g	-20.86%
(5.23 bar, 83.2 K) → (100.2 bar, 102.4 K)	107.24 g	58.10 g	49.14 g	49.00 g	-0.285%

Table 3 provides an overview of the MATI validation data as well as its corresponding computational results. The average error is 5.5% if the outlier is included but only 0.36% without the outlier. This outlier is most likely caused by a data fitting error of the hydrogen adsorption isotherms and is not indicative of an issue with the adsorbent hydrogen storage system design tool. Similar validation experiments with comparable results were shown for the HexCell-based adsorbent hydrogen storage system.

Vehicle Framework Model Updates

The vehicle framework was updated to include the individual storage sizing tools that can now design based on a given system volume or usable hydrogen mass as starting points as shown in Figure 3.

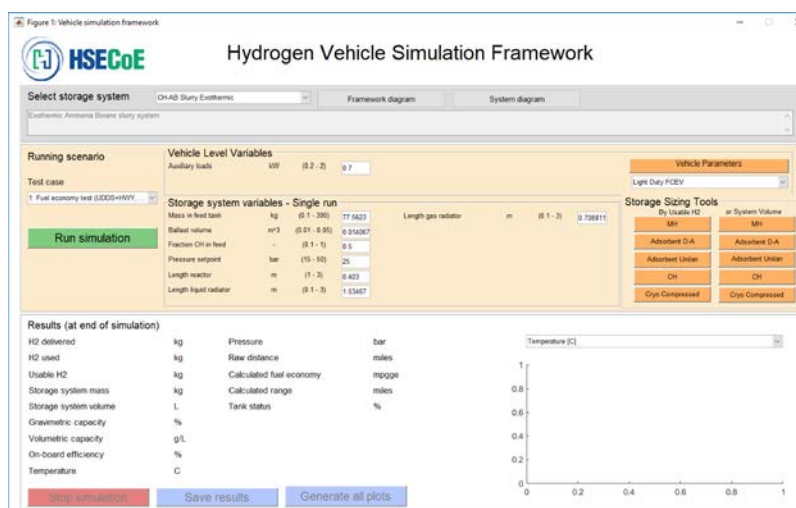


Figure 3. The Hydrogen Vehicle Simulation Framework now has individual storage sizing tools either by system volume or hydrogen mass

Website Activity

Visitors from across the globe continue to access our website, as seen in Figure 4. Most of the website visits access the models web page either on the first page they view or in subsequent page views.

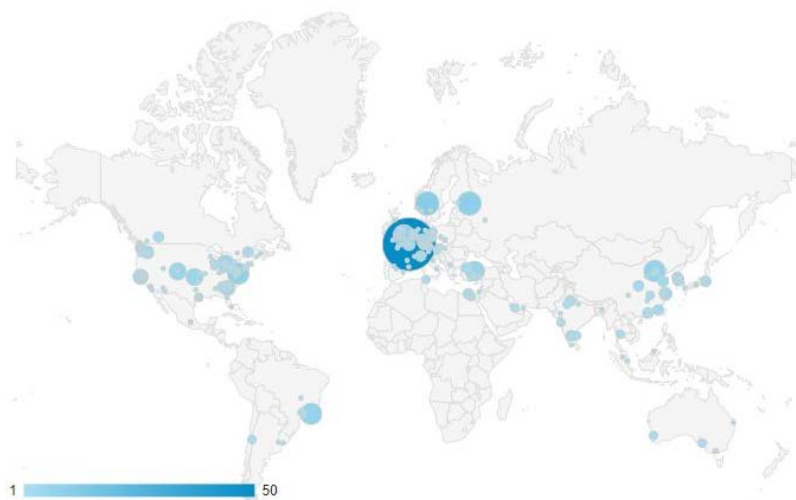


Figure 4. Global visits to our website for the period April 1, 2018, through March 1, 2019

The models currently developed and maintained by the team are listed in Table 4. These are either available on the website already or are in the process of being added for public download. The models are made available publicly through the HSECoE web page, where website activity and model downloads are tracked.

Table 4. HSECoE Models Available on Web Portal and Model Posting Status

Model Name	Lead	Status
Metal Hydride Acceptability Envelope	SRNL	Complete
Metal Hydride Finite Element Model	SRNL	Complete
Hydrogen Tank Mass and Cost Estimator Model	PNNL	Complete
Metal Hydride Framework Model	PNNL	Complete
Chemical Hydrogen Storage Framework Model	PNNL	Complete
Adsorption Data Framework Model	SRNL	Complete
Adsorption Data Finite Element Model	SRNL	Model Complete ^a
Adsorption Data Fitting Routine	SRNL	Model Complete ^a
Adsorption Data Standalone System Design Tool	SRNL	Complete
Chemical Hydrogen Storage Standalone System Design Tool	PNNL	Complete

^aAwaiting user's manual completion before the model is released to the public.

CONCLUSIONS AND UPCOMING ACTIVITIES

- HSECoE partners continue to update and improve center-developed models.
- Use of Visual Basic programs in Microsoft Excel have made these models available and accessible to the broader research and academic community.
- These standalone executable versions of the HSECoE-developed material storage models provide first-order storage system estimates based on material property information.
- The framework models have been updated with additional, alternative theoretical storage system formulations to allow users to choose the most appropriate theory for their material.
- Next year's work will focus on using the models to assist Hydrogen Materials Advanced Research Consortium materials researchers to evaluate their materials.

- The Framework storage, fuel cell, and vehicle models will be updated to accommodate medium-duty (vocational, class 4–6) and heavy-duty (line-haul, class 8) vehicle platforms in addition to the existing mid-sized passenger car option.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. David A. Tamburello, Anthony J. McWilliams, Bruce J. Hardy, and Matthew R. Kesterson, “Heat Transfer Unit and Method For Prefabricated Vessel,” US patent 9,957,103 B2. May 1, 2018.
2. David A. Tamburello, Matthew R. Kesterson, and Bruce J. Hardy, “Heat Transfer Unit and Method For Prefabricated Vessel,” US patent 9,809,380 B2. November 7, 2017.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. D. Tamburello, M. Thornton, S. Sprik, and K. Brooks, “Hydrogen Storage System Modeling: Public Access, Maintenance, and Enhancements,” U.S. Department of Energy Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, June 15, 2018.
2. D. Tamburello, M. Thornton, S. Sprik, and K. Brooks, “Hydrogen Storage System Modeling Support: HSECoE System Modeling Update,” Hydrogen Storage Technical Team Review, January 18, 2018.
3. Bruce Hardy, David Tamburello, and Claudio Corgnale, “Hydrogen Storage Adsorbent Systems Acceptability Envelope,” *International Journal of Hydrogen Energy* 43, no. 42 (2018): 19528–19539. <https://doi.org/10.1016/j.ijhydene.2018.08.140>.
4. David Tamburello, Bruce Hardy, Martin Sulic, Matthew Kesterson, Claudio Corgnale, and Donald Anton, “Compact Cryo-Adsorbent Hydrogen Storage Systems for Fuel Cell Vehicles,” *ASME Power Conference Proceedings* no. 51395 (2018): V001T06A025. <https://doi.org/10.1115/POWER2018-7474>.
5. Kriston P. Brooks, Samuel J. Sprik, David A. Tamburello, and Matthew J. Thornton, “Design Tool for Estimating Chemical Hydrogen Storage System Characteristics for Light-Duty Fuel Cell Vehicles,” *International Journal of Hydrogen Energy* 43 (2018): 8846–8858. <https://doi.org/10.1016/j.ijhydene.2018.03.090>.