IV.D.2 System Design, Analysis, Modeling, and Media Engineering Properties for Hydrogen Energy Storage

Matthew Thornton (Primary Contact), Lin Simpson, Aaron Brooker, and Jonathon Cosgrove
National Renewable Energy Laboratory (NREL)
1617 Cole Boulevard
Golden, CO 80401
Phone: (303) 275-4273
Email: Matthew.Thornton@nrel.gov

DOE Managers
HQ: Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

GO: Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@go.doe.gov

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Fiscal Year (FY) 2012 Objectives

- Perform vehicle-level modeling and simulations of various storage systems configurations.
- Lead the storage system energy analysis and provide results.
- Compile and obtain media engineering properties for adsorbent materials.

Technical Barriers

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

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(E) Charging/Discharging Rates
(I) Dispensing Technology
(K) 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 design and synthesis of hydrogen storage vessels that meet the following DOE 2015 hydrogen storage for light-duty vehicle targets:

- Cost: to be determined
- Specific energy: 0.055 kg H_2/kg system
- Energy density: 0.040 kg H_2/L system
- Charging/discharging rates: 3.3 min
- Well to power plant efficiency: 60%

FY 2012 Accomplishments

- Developed a vehicle model framework and test cycle matrix to aid in the analysis and understanding of hydrogen storage system requirements for light-duty vehicles.
- Integrated the hydrogen storage simulator (HSSIM) vehicle model with the center fuel cell and hydrogen storage models to create a model framework that could be used across the center to evaluate all storage system designs on a common basis and with consistent assumptions.
- Used the vehicle model and the center modeling framework to evaluate the performance of specific storage system designs across all material classes and assess the impact on vehicle performance to help guide specific system designs and focus engineering solutions that will overcome barriers to meeting the technical targets.
- Performed vehicle-level tradeoff analyses to better understand the impact of key engineering designs, for example, the tradeoff between mass, onboard hydrogen storage capacity, and vehicle range.
- Used Hydrogen Delivery Scenario Analysis Model (HDSAM) to calculate preliminary greenhouse gas (GHG) emissions and well-to-power plant (WTPP) efficiency figures for baseline physical storage systems and candidate materials-based storage systems for each material class.
- Identified potential materials for analysis and provided storage system design guidance to help meet DOE storage targets with adsorption materials.

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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. By means of systems analysis and modeling, hydrogen storage system requirements for light-duty vehicles can be assessed. With these findings and through collaboration with our Hydrogen Storage Engineering Center of Excellence (HSECoE) partners, optimal pathways for successful hydrogen storage system technology can be identified to enable future commercialization of hydrogen-fueled vehicles.

Approach

An array of tools and experience at NREL are being used to meet the objectives of the HSECoE. Specifically, extensive knowledge of multiple vehicle simulations, well-to-wheels analysis, and optimization are being employed and integrated with fuel cell and material-based hydrogen storage system models developed by other HSECoE partners. This integrated model framework allows for the evaluation of various hydrogen storage options on a common basis. Engineering requirements are defined from these studies thus enabling the design of hydrogen storage vessels that could meet DOE performance and cost targets in a vehicle system context.

In the area of media engineering, attaining the objectives of the HSECoE relies on NREL's leadership in developing custom analytical instrumentation for hydrogen sorption analysis. These tools are used to thoroughly characterize hydrogen storage sorbents so that an optimized storage vessel specific to the sorption material may be efficiently engineered. NREL uses these methods to analyze sorption materials identified by the HSECoE as holding promise for application in commercial on-vehicle refuelable hydrogen storage systems capable of meeting DOE targets.

Results

The following will provide results from work completed this year to support the HSECoE with a focus on five main tasks. In collaboration with our original equipment manufacturer (OEM) partners, NREL (1) worked on the development of HSSIM and final structure of a test cycle matrix used to support the overall modeling effort; (2) worked on the integration of the vehicle model with the center fuel cell and hydrogen storage models to create a model framework; (3) worked with the systems architects to perform simulations and tradeoff studies to help with the high-level storage systems design and engineering, including mass and volume trade-offs; (4) performed energy analysis on specific system designs being considered by the HSECoE; and (5) continued work in the area of adsorbent materials characterization and analysis.

To gain a better understanding of the interactions that exist between various materials-based hydrogen storage systems and the vehicle system as well as the engineering challenges that exist when integrating one of these systems with a vehicle, NREL has developed a vehicle-level model designed to be sensitive to these issues. The HSSIM vehicle model was developed as a specialized tool that could be used to assist in the design and engineering of materials-based hydrogen storage systems being considered by the HSECoE. This tool is designed to not only allow for understanding key trade-offs, but also to have a seamless integration with the HSECoE fuel cell and detailed hydrogen storage system models and to evaluate progress towards the DOE's hydrogen storage technical targets. This model has been integrated with a fuel cell model developed by Ford Motor Company in a HSECoE common modeling frame work developed by United Technologies Research Center and other HSECoE partners (Figure 1).

The HSSIM vehicle model is designed to evaluate high-level attribute improvements. To accomplish this, the inputs, such as the glider and powertrain components, are also defined at a high level. The vehicle glider is defined with a specific frontal area, drag coefficient, mass, center of gravity, front axle weight fraction, and wheelbase. The wheels are defined by inertia, a rolling resistance coefficient, coefficient of friction, and radius. The inputs for the motor are power, peak efficiency, mass per unit of power, cost per unit of power, and time to full power. The battery inputs include power, energy, mass per unit of energy, and round trip efficiency. Auxiliary loads are assumed to be a specified constant plus an amount required for the fuel cell and hydrogen storage systems. These inputs match the DOE's technical target units, such as battery kilograms per kilowatt hour, so that the impact of improvements can be evaluated over time as the targets change.

A key part of the vehicle model was working with the center OEMs on developing a test matrix that will be used to evaluate all the storage systems being considered across the center on a common basis. The test matrix was structured to evaluate the performance of the storage systems against the technical targets under standard and realistic transient driving conditions. The matrix was also designed to exercise a given system from full to empty to provide an understanding of its performance over the entire range of fill conditions. Therefore, the test cases were designed to repeat a drive cycle or set of drive cycles until the storage system being evaluated was empty. Standard drive cycles are typically not long enough to achieve this and would not even deplete a buffer tank in some systems. The important point here is that when evaluating the complex dynamics of hydrogen storage system, this approach of repeating drive cycles to create test cases is critical to gaining the feedback necessary to refine and improve the systems.

As shown in Table 1, the center test matrix includes five test cases:

The first case combines repeats of the urban dynamometer driving schedule (UDDS) and the highway fuel

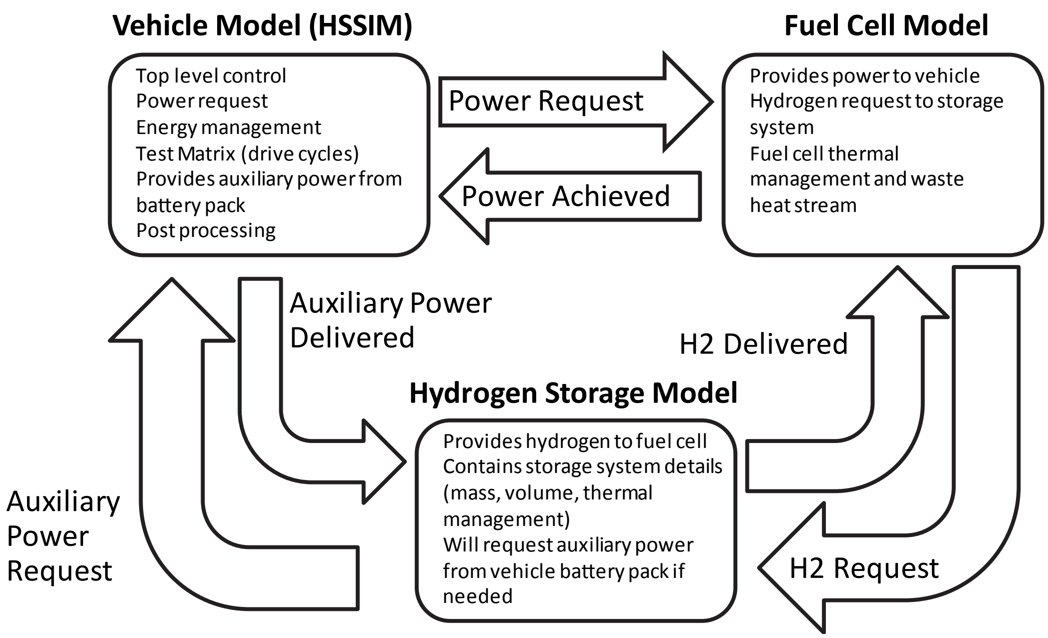

FIGURE 1. HSECoE integrated modeling framework

TABLE 1. Test matrix used across the center to evaluate the performance of all the storage systems

Case	Test Schedule	Cycles	Description	Test Temp (°F)	Distance per cycle (miles)	Duration per cycle (minutes)	Top Speed (mph)	Average Speed (mph)	Max. Acc. (mph /sec)	Stops	Idle	Avg. H2 Flow (g/s)*	Peak H2 Flow (g/s)*	Expected Usage
1	Ambient Drive Cycle - Repeat the EPA FE cycles from full to empty and adjust for 5 cycle post-2008	UDDS	Low speeds in stop-and-go urban traffic	75 (24 C)	7.5	22.8	56.7	19.6	3.3	17	19%	0.09	0.69	1. Establish baseline fuel economy (adjust for the 5 cycle based on the average from the cycles) 2. Establish vehicle attributes 3. Utilize for storage sizing
		HWFET	Free-flow traffic at highway speeds	75 (24 C)	10.26	12.75	60	48.3	3.2	0	0%	0.15	0.56	
2	Aggressive Drive Cycle - Repeat from full to empty	US06	Higher speeds; harder acceleration & braking	75 (24 C)	8	9.9	80	48.4	8.46	4	7%	0.20	1.60	Confirm fast transient response capability – adjust if system does not perform function
3	Cold Drive Cycle - Repeat from full to empty	FTP-75 (cold)	FTP-75 at colder ambient temperature	-4 (-20 C)	11.04	31.2	56	21.1	3.3	23	18%	0.07	0.66	1. Cold start criteria 2. Confirm cold ambient capability – adjust if system does not perform function
4	Hot Drive Cycle - Repeat from full to empty	SC03	AC use under hot ambient conditions	95 (35 C)	3.6	9.9	54.8	21.2	5.1	5	19%	0.09	0.97	Confirm hot ambient capability - adjust if system does not perform function
5	Dormancy Test	n/a	Static test to evaluate the stability of the storage system	95 (35 C)	0	31 days	0	0	0	100%	100%			Confirm loss of useable H2 target

economy test (HWFET) until the storage systems is depleted. This is used to determine the vehicle-level fuel economy and from that figure the vehicle range. The fuel economy is calculated using the current Environmental Protection Agency five-cycle procedure of adjusting and weighting the UDDS and HWFET to provide one fuel economy figure that represents real-world use—it is not the raw figures that come directly from running the cycles. Similarly, the range is then calculated from the adjusted and weighted UDDS and HWFET figure and not simply the cycles miles achieved until the storage systems is empty. Again, this test matrix is key to providing a means to evaluate the fuel economy, range, and other vehicle level performance features of the storage systems on a common and comparable basis.

NREL used these model outputs from the framework to evaluate the current status of various materials-based systems being evaluated by the HSECoE. Because this work is in progress, the results presented here are preliminary and may change over time as the storage systems are refined and the models are adjusted accordingly. That is, the intent is to show how the model outputs can be used to evaluate and compare different storage systems and support engineering solutions to particular barriers. The intent, at least at this time, is not to develop an argument for which system or materials class has the most promise for actual vehicle application. Vehicle-level results will be presented for a select group of these systems (i.e., this is not a comprehensive set of systems being evaluated under the HSECoE nor is it a complete set of storage models induced in the framework). For the model application, example results discussed in this section's simulations were run with the AX-21 and MOF-5 adsorbent systems, the $NaAlH_4$ and TiCrMn metal hydride systems, and the fluid ammonia borane (AB) chemical hydride system. In addition, 350-bar and 700-bar compressed gas systems are included for comparison to the materials-based systems.

For the following discussion, model applications and results reported are based on Test Case 1 of the framework exclusively (i.e. UDDS and HWFET combined test cycles). In addition, a midsize car class was selected as the initial baseline simulations within the framework. The intent was to be representative of a high sales volume midsize car, such as the Ford Fusion, Chevrolet Malibu, or Toyota Camry. The attributes associated with this size vehicle are a frontal area of 2.2 m^2, drag coefficient of 0.29, and tire size of P195/65R15. The electric motor was sized to 100 kW with 85% efficiency from the motor to the road. Consistent with most fuel cell vehicles, the vehicle includes a 20 kW/1 kWh battery pack for hybridization for capturing regenerative braking and assistance with propulsion. The state of charge of the battery is maintained between 40% and 80%, with the target state of charge varying throughout the cycle depending on driving conditions. The vehicle glider weight (excluding the hydrogen storage system and other drive components) is 1,104 kg. The motor and power electronics combined weight is 105 kg, the battery system weight is 51 kg, the fuel cell system with cooling weight is 214 kg, and the hydrogen storage systems weight varied. The remaining weight is the vehicle glider and other supporting subsystems. All of the following results are based on the vehicle configuration above, but the model is capable of simulating both larger and smaller vehicle classes and configurations.

For the example systems included in Table 2, the fuel economy for materials-based systems ranged from 49.3 miles per gallon gasoline equivalent (mpgge) for the MOF-5 system to 36.4 mpgge for the $NaAlH_4$ system. The $NaAlH_4$ system performed the worst in terms of fuel economy due its requirement for high temperature conditions to release hydrogen from the hydride material. As a result, the system burns hydrogen to create the needed temperatures for the storage system so that hydrogen can be released for use in the fuel cell. The use of hydrogen for system thermal management results in poor onboard efficiency and subsequently poor fuel economy, as up to 23% of the stored hydrogen is not used to generate tractive power. Alternatively, the fluid AB and MOF-5 systems performed better in this example due to their high gravimetric efficiency resulting in lower overall systems and vehicle mass and therefore better fuel economy. As a result, the MOF-5 system also offers the best range results of 276 miles based on the above vehicle configuration and 5.6 kg nominal usable hydrogen storage capacity. The $NaAlH_4$ system had a range of 204 miles, which is well below the target of 300 miles. All of the other systems in this example were near the 300-mile range target (ranging from 257 to 276 miles). This included the other metal hydride system. The compressed gas systems demonstrated slightly better, but comparable fuel economy and range relative to these example material-based systems.

TABLE 2. Vehicle Level Performance Summary

Hydrogen Storage System	Adjusted Fuel Economy (mpgge)	Range (mi) 5.6 kg H2	On-Board Efficiency (%) UDDS/HFET	Gravimetric Density (wt%)	Volumetric Density (g/l)
AX21 press FCHX	48.7	273	97	4.3	25.2
MOF5 Cmpct- FCHX	48.3	271	97	3.5	24.1
MOF5 Press FCHX	49.3	276	98	4.6	25.3
Fluid AB	45.3	254	96	4.6	38.9
Alane	42.6	239	88	4.6	38.9
$NaAlH_4$	36.4	204	77	1.2	11.4
TiCrMn	45.9	257	100	1.1	26.5
350-bar Compressed Gas	49.9	280	100	4.8	17.0
700-bar Compressed Gas	49.9	279	100	4.7	25.0

The MOF-5 adsorbent system and the fluid AB chemical hydride system both had a gravimetric density of 4.6 weight percent (i.e., the percent of hydrogen mass to the overall storage system mass; the DOE 2017 technical target for gravimetric density is 5.5 weight percent). These were the best performing materials-based systems and were comparable to the compressed gas systems, which had gravimetric densities of 4.7–4.8 weight percent. That said the fluid AB system outperformed the compressed gas systems and all of the other materials-based systems in terms of volumetric density with nearly 40g of hydrogen per system liter. The DOE's 2017 technical target for volumetric density is 40 g/L. For all the example materials-based systems included here, the MOF-5 system performed the best in terms of fuel economy, range, and gravimetric density and was comparable or better than the compressed gas systems. Also note the fluid AB system performed best in terms of volumetric density, but it is important to remember that the fluid AB system is an off-board regenerable system that is accompanied by unique refilling challenges, logistics, and costs that are not captured in the above analysis.

Another example application was working the center system architects to provide high-level feedback on the performance and design of their given material systems. The focus of this activity was an example of a trade-off study quantifying the relative range impacts resulting from a fixed volume study. Table 3 shows the results from the application of this type of study to four adsorbent systems.

In this fixed volume study four different adsorbent system designs were evaluated in conjunction with three different volume levels. The four adsorbent systems included powered MOF-5 operating at 60 bar and 80 K full tank conditions with an assumed aluminum tank, powdered MOF-5 operating at 60 bar and 40 K full tank conditions with an assumed carbon-fiber tank, compacted MOF-5 0.52 g/cc operating at 200 bar and 80 K full tank conditions with an assumed aluminum tank and compacted MOF-5 0.52 g/cc MOF-5 operating at 200 bar and 40 K full tank conditions with an assumed carbon-fiber tank. Each system was simulated in a mid-sized passenger vehicle using the integrated modeling framework for case one to provide range and fuel economy for three volume assumptions; 140 liters, 205 liters and 253 liters. These three volume levels were based on assumptions form the DOE 2017 hydrogen storage technical targets and represent the high, medium and low range of practical storage systems volume for passenger vehicles. For comparison, the usable capacity in the 350 bar

TABLE 3. Range and Vehicle Level Performance Results for Fixed Volume Study

Hydrogen Storage System	Adjusted Fuel Economy (mpgge)	Usable H2 (kg)	Range (mi) Usable H2	Gravimetric Capacity Weight Percent	Volumetric Capacity (g/l)	Volume (L)
Powder MOF-5 60-bar 80 K Al	51.11	2.00	102.20	2.80	12.86	140[1]
Powder MOF-5 60-bar 40 K CF	51.30	4.20	215.50	6.61	29.84	140
0.52g/cc MOF-5 200-bar 80 K Al	50.47	3.35	169.10	2.68	23.94	140
0.52g/cc MOF-5 200-bar 40 K CF	50.62	4.60	232.90	4.18	32.59	140
Powder MOF-5 60-bar 80 K Al	50.95	2.80	142.70	3.15	13.67	205
Powder MOF-5 60-bar 40 K CF	50.97	6.70	341.50	7.97	32.64	205
0.52g/cc MOF-5 200-bar 80 K Al	49.93	5.35	267.10	2.92	26.11	205
0.52g/cc MOF-5 200-bar 40 K CF	50.18	7.30	366.30	4.61	35.51	205
Powder MOF-5 60-bar 80 K Al	50.73	3.60	182.60	3.39	14.18	253
Powder MOF-5 60-bar 40 K CF	50.89	8.60	437.60	8.68	33.96	253
0.52g/cc MOF-5 200-bar 80 K Al	49.32	6.85	337.90	3.02	27.05	253
0.52g/cc MOF-5 200-bar 40 K CF	49.71	9.30	462.30	4.77	39.56	253

compressed gas storage system for the Ford Focus fuel cell vehicle was 4 kg with an external volume of about 230 liters.

This study shows that the volume target is much more sensitive to range than the gravimetric target. That is, storage systems that had high mass but allowed for more onboard hydrogen storage through compaction or low temperature operation had small fuel economy penalties but were accompanied by much higher ranges due to their ability to store more hydrogen onboard for a given volume. This information has been used by the adsorbent system architect and modeler to help refine their system designs.

NREL also continued to support the HSECoE by performing energy analyses on various storage system designs that have become available. These analyses provide the center system architects and other partners with high-level estimates about the overall energy inputs required by a given system, including WTPP efficiency (%), hydrogen cost ($/kg) and GHG emissions (carbon dioxide equivalent) on a gram per mile basis.

The HDSAM was used to estimate the above parameters for each system. To date the HDSAM model has been run for $NaAlH_2$ metal hydride system and the AX-21 and MOF-5 sorbent systems to produce preliminary WTPP efficiency, GHG emissions, and hydrogen cost figures. NREL is currently working with the center adsorbent and chemical hydride system architects to obtain these data and perform HDSAM runs for a fluid AB, Alane and various MOF-5 adsorbent storage systems.

For media engineering, NREL worked with engineering center partners to identify potential materials and configurations that can be optimized with the appropriate thermal conductivity, sorption, and mechanical properties needed for integration in a hydrogen storage system. Specific efforts included optimizing activated carbon pellet synthesis and capacities. Comparison of results between MSC-30, Missouri 3K, and pyrolyzed polyether ether ketone (PEEK) powders and pellets indicated similar behavior to MOF-5. Potentially, slightly higher volumetric capacities could be obtained with optimized PEEK materials, but is not warranted due to the additional material and synthesis costs. This work also identified that carbon fibers improve pellet structure and thermal conductivities.

NREL also measured hydrogen sorption using a He cryostat cooler to provide variable temperature capabilities. Initial analysis indicates that He and hydrogen measurements as a function of pressure of the empty sample holder provides a reasonable measure of zero adsorption at both 303 K and 75 K (Figure 2). Additional measurements at other temperatures will be performed to identify issues and limits on the experimental parameters. Hydrogen adsorption and desorption results for different temperatures and pressures where also obtained. Direct comparison between the use of water and liquid nitrogen baths to control temperature and the use of a He cryostat were made at 303 K and 75 K. In

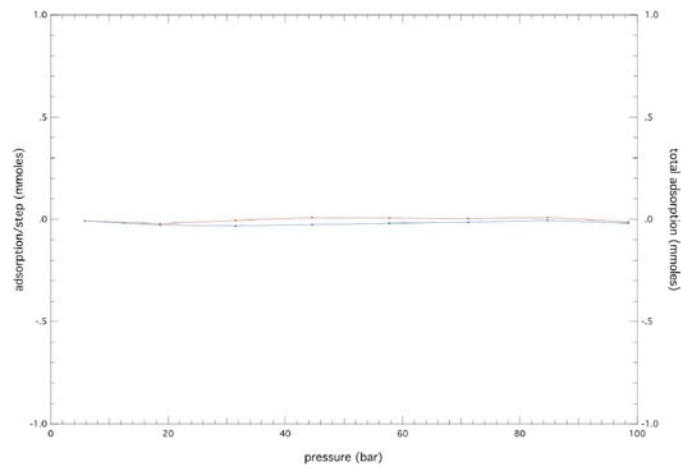

FIGURE 2. Hydrogen adsorption of empty sample holder at 303 K. The data show that the instrument is providing a reasonable measure of zero adsorption as a function of pressure. Red: Adsorption per step (left axis) Blue: Total Adsorption (right axis).

general the results from the measurements using the baths typically have uncertainties less than 20%. However, with the present cryostat configuration that limits sample size and has slightly higher volumes, the measurements have uncertainties above 20%. Significant modifications to the sample holder and crystat configuration are required to reduce uncertainties.

Future Direction

- Continue to run vehicle simulations to support engineering design and support the center modeling framework refinements and enhancements:
  - Run vehicle simulations to support high-level storage system design and engineering tradeoffs.
  - Run vehicle simulations to support storage systems sizing analyses.
- Evaluate storage system impacts on vehicle performance (e.g., fuel economy, range).
- Evaluate storage system progress toward tech targets. Run HDSAM to evaluate (fluid AB, Alane and various MOF-5 sdsorbent storage systems:
  - WTPP efficiency
  - GHG emissions
  - H_2 cost
- Provide additional material characterization specifically related to sorbents optimized for engineered hydrogen storage systems.

FY 2012 Publications/Presentations

1. Matthew Thornton, Aaron Brooker, Jonathon Cosgrove, National Renewable Energy Laboratory; Michael Veenstra, Ford Motor Company; Jose Miguel Pasini, United Technologies Research

Center, "Development of a Vehicle Level Simulation Model for Evaluating the Trade-off between Various Advanced On-board Hydrogen Storage Technologies for Fuel Cell Vehicles", SAE Paper 2012-01-1227, April 2012, Detroit Michigan.

2. System Design, Analysis, Modeling, and Media Engineering Properties for Hydrogen Energy Storage, Matthew Thornton, DOE Annual Merit Review Meeting, May 15, 2012, Washington, D.C.