

IV.D.6 Advancement of Systems Designs and Key Engineering Technologies for Materials Based-Hydrogen Storage

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- (A) System Weight and Volume
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (H) Balance of Plant (BOP) Components
- (J) Thermal Management

Technical Targets

The goals of this project mirror those of the HSECoE to advance hydrogen storage system technologies toward the DOE Hydrogen Program's 2017 storage targets [1].

TABLE 1. Current status of three system-related targets

Characteristic	Units	HSECoE Goals	Storage System Type	UTRC 2012 Status
Gas Liquid Separator	kg	5.4	Chemical Hydride	5.9
	L	19		2.7
Ammonia Filter	kg	1.2	Chemical Hydride	1.1
	L	1.6		1.6
SAC Density	g/cm ³	>0.6	Adsorbent	0.76
	m ² /g	2,800		1,698

SAC – super activated carbon

Fiscal Year (FY) 2012 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.
- Engineer and test specialty components for H₂ storage systems.
- Assess the viability of onboard purification for various storage material classes and purification approaches.
- Compact super activated carbon and metal-organic framework (MOF) materials without binder.
- Conduct risk assessments during the progression of the phased HSECoE efforts.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

FY 2012 Accomplishments

Accomplishments of the current project comprise:

- Used Simulink[®] framework and metal hydride system model to identify ideal onboard reversible metal hydride material properties.
- Identified high contact resistance in combination with slow two-step hydrogen absorption kinetics as obstacle to meet 2017 DOE refueling time target if using sodium aluminum hydride (SAH) pellets integrated with a heat exchanger tube.
- Selected gas-liquid separator (GLS) for chemical hydride system and designed test rig.
- Developed high capacity and regenerable H₂ purification cartridge that enables NH₃ removal down to 0.1 ppm, as required by the SAE J2719 APR2008 guideline.
- Evaluated porous metal filters for containment of cryo-adsorbent material into storage tank and for particulate mitigation.
- Performed Qualitative Risk Analysis of HSECoE designs/materials.

- Developed method to assess thermal conductivity anisotropy of compacted H₂ storage materials.
- Improved volumetric capacity and thermal conductivity of MOF-5 through uniaxial compaction and additives.
- Improved volumetric capacity and thermal conductivity of super activated carbons MaxSorb and IRH-33 through spark plasma sintering and additives.



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 is to leverage in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials based H₂ storage for automotive applications. UTRC continued to focus during the third year of the HSECoE project on developing tools for comparing H₂ storage systems on a common basis that could also be used by a wider audience. UTRC screened H₂ storage system improvement ideas resulting from compaction, thermal conductivity enhancement, H₂ purification, compact and low weight heat exchanger design, and gas liquid separator technology. Results contributed to the quantification of ideal on-board reversible metal hydride properties that would enable meeting the DOE 2017 system targets [1].

Results

UTRC, in collaboration with Savannah River National Laboratory, General Motors, Lincoln Composites and the Pacific Northwest National Laboratory (PNNL), performed a study with the aim of quantifying the ideal metal hydride properties of an onboard reversible metal hydride storage system that would be capable of meeting the DOE 2017

targets for onboard hydrogen storage systems for light-duty vehicles [1]. Figure 1 shows the gravimetric capacity of metal hydride materials as a function of the hydrogenation enthalpy. It also shows two targeted areas, one enclosed by a green line for regular metal hydrides and one enclosed by a blue line for destabilized metal hydrides. Details about the results of this analysis can be found in [2,3].

DOE targets [1] are specific, quantitative, and timely and have to be met simultaneously. One important target is the onboard efficiency target that specifies that 90% of the hydrogen that has been stored in the hydrogen storage system needs to be delivered to the fuel cell. This greatly limits the hydrogenation enthalpy of metal hydrides that can be considered for this application. UTRC estimated that this target can only be met when the hydrogenation enthalpy is less than 30 kJ/mole-H₂ for regular metal hydrides. Such a material will make hydrogen available to the fuel cell at the minimum delivery pressure of 5 bar at 60°C by using waste heat from the fuel cell. Such a metal hydride should have a minimum gravimetric capacity of 11 wt% in order for the hydrogen storage system to be able to meet DOE's weight and volume targets for light-duty vehicles. The hydrogenation enthalpy can also not be too low as the equilibrium pressure of the material would be too high and require a much heavier pressure vessel. It was decided in this study to limit the hydrogen pressure in the storage system to less than 100 bar in order to maintain the benefit of a lower pressure H₂ storage system that would require less carbon fiber than high pressure physical storage systems and that would require less compression energy and have safety benefits. Metal hydrides with a higher hydrogenation enthalpy (>30 kJ/mole-H₂) will not be able to meet the onboard efficiency target as more than 10% of the stored hydrogen would need to be combusted in order to generate heat for H₂ desorption before the H₂ could be made available to the fuel cell. Such a combustion system increases the weight of the H₂ storage system and this has to be compensated for by having a H₂ storage material with an even higher gravimetric capacity (dashed green line). A similar box has been drawn in Figure 1 for destabilized metal hydride materials. The difference in hydrogenation entropy in comparison to the regular metal hydride materials causes the blue box to be in a different location. Currently, the HSECoE is not aware of any metal hydride materials that fit within the green or blue box and the onboard reversible metal hydride system development was discontinued within the HSECoE for this light-duty vehicle application. Some materials appear to be close to the desired regions but either will result in a H₂ storage system with a lower than targeted onboard efficiency when used in combination with a conventional proton exchange membrane fuel cell system or will be heavier or larger in volume than the DOE targets allow.

As part of an orderly completion of the onboard reversible metal hydride work, heat transfer characteristics were determined of SAH pellets integrated with a heat

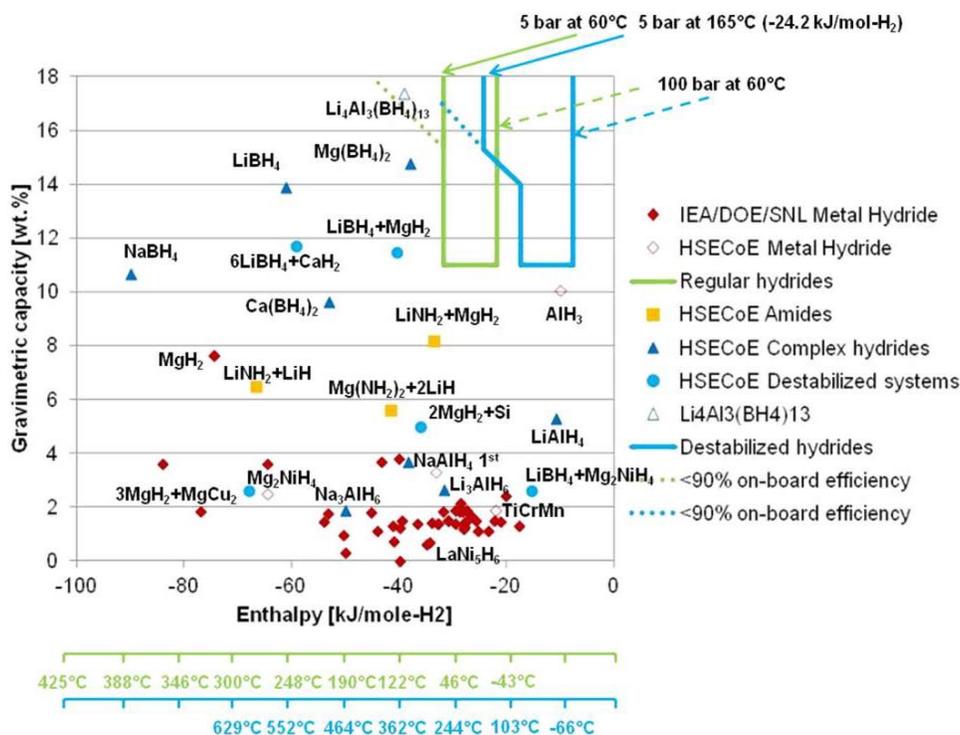


FIGURE 1. Ideal metal hydride properties for light-duty vehicle application

exchanger tube. The results show that the contact resistance between the SAH pellets and the heat exchanger tube was significant and this in combination with the relatively slow two step H₂ adsorption mechanism limited the H₂ adsorption rate that could be achieved. Reaching 90% of the storage capacity in DOE’s 2017 refueling time target of 3.3 minutes was not feasible. A more detailed comparison between the experimental data and a COMSOL model is being pursued.

A fluid-based chemical hydride system, such as for instance ammonia borane (AB) dissolved in ionic liquids (Los Alamos National Laboratory) or suspended in a slurry (PNNL), requires a GLS. It separates hydrogen gas produced during AB thermolysis from the fluids that will also contain the AB thermolysis byproducts (e.g. BNH_x). UTRC selected a passive GLS design with a low profile and no moving parts that deploys three different separation mechanism: coalescence, gravity and centrifugal action. UTRC also designed a laboratory system for testing the GLS performance, as shown in Figures 2 and 3, which has the following key components: 1) feed tank with mixing impeller, 2) Coriolis mass flow meter, 3) metering pump, 4) tube-in-tube heat exchanger (heating), 5) GLS, 6) drain with actuated drain valve, 7) magnetic level indicator, 8) sloped bottom collection tank, 9) tube-in-tube heat exchanger (cooling), 10) coalescing filter, 11) transfer pump, 12) vent silencer. Construction of the GLS test facility is in progress. UTRC will report out on the ability of this GLS and its modified form(s) to reach the performance target of producing a H₂

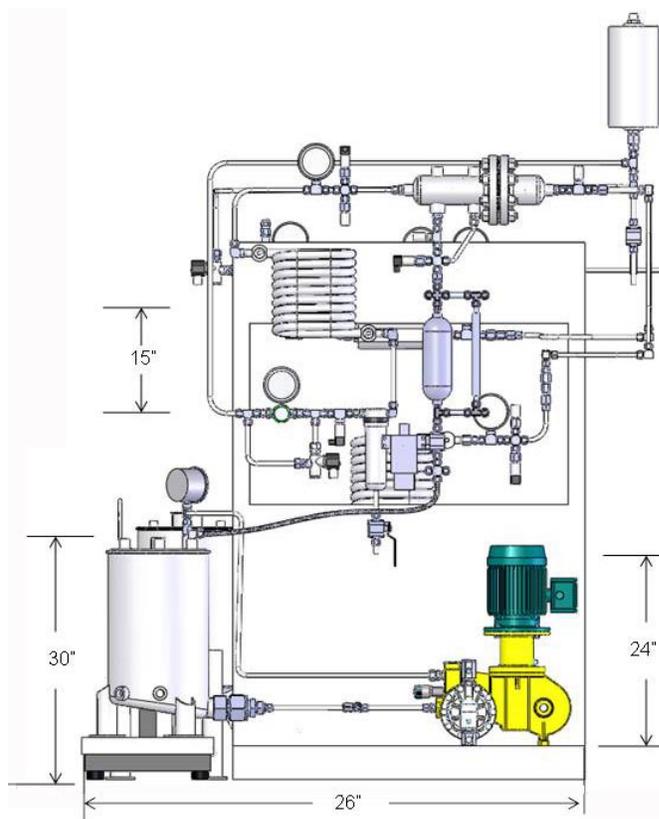


FIGURE 2. Front view gas liquid separator test rig

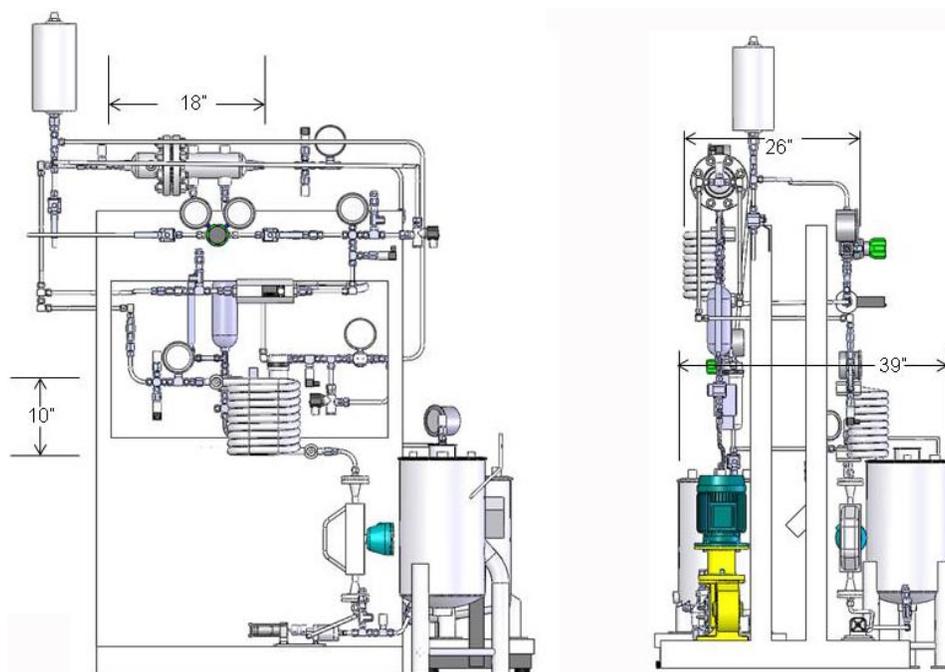


FIGURE 3. Back and side view of gas liquid separator test rig

gas with less than 100 ppm aerosol when handling a fluid comprising 720 mL/min liquid phase and 600 slpm of H₂ gas phase (from 40 wt% AB @ 2.35 Eq H₂ and max H₂ flow of 0.8 g/s H₂) that has a viscosity less than 1,500 cp with a GLS mass and volume less than 5.4 kg and 19 liters, respectively.

Hydrogen produced during AB thermolysis contains various impurities [4]. One of those impurities is ammonia (NH₃), which has to be removed down to 0.1 ppm level according to the SAE International J2719 guideline [5]. UTRC developed a high capacity regenerable ammonia adsorbent in collaboration with Université du Québec à Trois-Rivières (UQTR), Canada. The sorbent comprises metal chlorides (e.g. ZnCl₂, MgCl₂, and MnCl₂) that have been deposited on the super activated carbon IRH-33. Its dynamic sorption capacity is shown in Figure 4 as a function of the number of cycles. The sorbent makes it possible to scrub NH₃ down to 0.1 ppm with a replacement/regeneration interval of 1,800 miles of driving at an inlet concentration of 500 ppm while having a mass and volume of 1.2 kg and 1.6 liters, respectively, which is an important goal for the chemical hydride system development within the HSECoE.

H₂ quality from cryo-adsorption systems is impacted by adsorbent particulates that can get entrained into the hydrogen that is being supplied to the fuel cell system. UTRC evaluated the performance of porous metal particulate filters to mitigate particulates and for containing the adsorbent material in its storage tank. The particulate concentration was measured by means of a Engine Exhaust Particle Sizer™ spectrometer on the outlet of a packed bed of MaxSorb powder inside a sample cylinder with and without the filter.

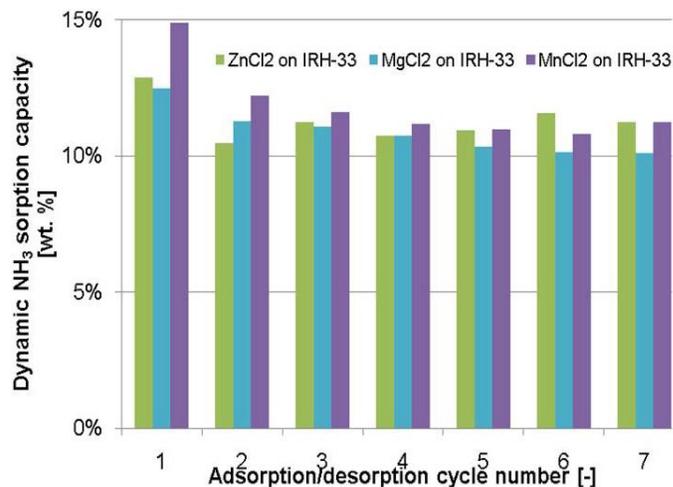


FIGURE 4. High capacity and regenerable NH₃ adsorbent based on IRH-33 + metal chlorides

The results indicate that a 0.5 μm porous metal filter is capable of reducing the particulate concentration to a level of 400 μg/m³, which is below the SAE J2719 guideline [5] of 1,000 μg/m³.

Adsorbents like MaxSorb, IRH-33 and MOF-5, which are being considered for the cryo-adsorption system, have a high specific surface area on a gravimetric basis but a relative low specific surface area on a volumetric basis when deployed as a powder due to their low tap density. UTRC evaluated several methods for compacting these materials in

order to reduce the volume of the storage system: 1) uniaxial compaction, 2) uniaxial compaction inside an aluminum foam, 3) vibration packing, 4) filter press and 5) spark plasma sintering (SPS). Uniaxial compaction was found to be applicable to MOF-5 and thermal conductivity samples were prepared that contained 10 wt% expanded natural graphite (ENG) worms and had a density of $(0.604 \pm 0.004) \text{ g/cm}^3$ after compaction at 25 MPa. SPS was successful in compacting MaxSorb and IRH-33 to densities $>0.6 \text{ g/cm}^3$ but all other techniques that were evaluated yielded densities equal to the tap density of 0.3 g/cm^3 of those SACs due to spring-back. SPS processing conditions were optimized in order to minimize loss of specific surface area on a gravimetric basis upon compaction. The results for IRH-33 are shown in Table 2. SPS was found to be scalable to large size samples, as shown in Figure 5. Samples with a 4-cm diameter and 2-cm thickness were successfully prepared and were used for thermal conductivity measurements.

UTRC developed a test method to assess the thermal conductivity anisotropy of compacted materials after introducing ENG worms [6]. The method is based on performing measurements according to the transient plane source method in each of the orthogonal directions of the sample and a subsequent inverse analysis with a COMSOL multiphysics model of the experiment in order to extract thermal conductivity parameters. The method was applied to MOF-5 with 10 wt% ENG worms at room temperature. The results from the analysis are shown in Table 3. The thermal conductivity of the MOF-5 sample with ENG was a factor 5-12 higher in the direction perpendicular to the compaction direction. This has been ascribed to the alignment of ENG platelets perpendicular to that compaction direction, which was first observed in $\text{MgH}_2 + \text{ENG}$ composites [7]. UTRC observed similar improvements of the thermal conductivity with IRH-33 + ENG composite samples that had been compacted through SPS.

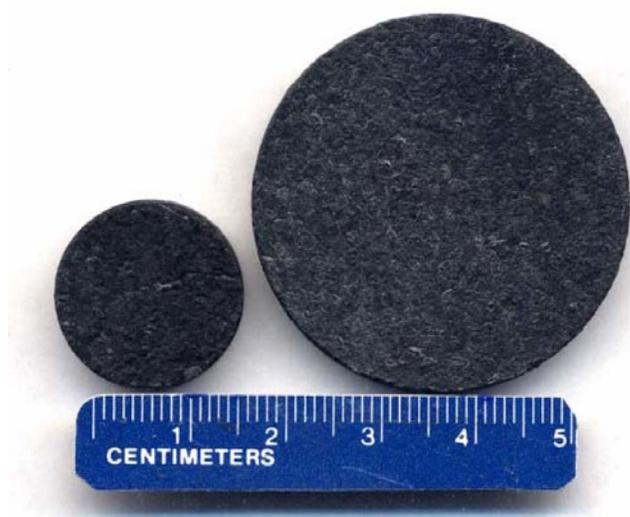


FIGURE 5. SPS of SAC IRH-33

TABLE 3. Thermal conductivity anisotropy of compacted MOF-5 + 10 wt% ENG worms at a density of $(0.604 \pm 0.004) \text{ g/cm}^3$

Parameter	95% confidence interval	Unit
k_x	$3.32 < 3.45 < 3.58$	W/m/K
k_y	$1.44 < 1.49 < 1.55$	W/m/K
k_z	$0.280 < 0.286 < 0.292$	W/m/K
C_p	$1,395 < 1,438 < 1,484$	J/kg/K

UTRC developed a plan for measuring the dust explosion characteristics of MOF-5 powder in air and air/ H_2 mixtures, building on its experience with such tests from a separate DOE contract. UTRC performed a limited number of experiments to assess the risks associated with AB dissolved in or mixed with ionic liquids. AB phase separated from the three ionic liquids that were evaluated and an AB mixture with ionic liquids that would stay liquid before and after

TABLE 2. SPS results of SACIRH-33

Material	Form	Temp. (°C)	Pressure (MPa)	Density (g/cm^3)	Surface Area		Micropore Vol. (cm^3/g)	Mesopore Vol. (cm^3/g)	Total Vol. ($P/P_0=0.9$) (cm^3/g)
					(m^2/g)	(m^2/cm^3)			
IRH-33	Granular	N.A.		0.22	2,334	513	0.81	0.85	1.44
	Pellet (HRI binder)			0.84	1,381	1,160	0.49	0.18	0.68
	SPS	900	40	0.63	1,558	982	0.56	0.44	0.92
		900	80	0.76	1,698	1,290	0.60	0.34	0.92
		1000	40	0.70	1,401	981	0.50	0.40	0.82
		1200	10	N.A.	1,400	N.A.	0.51	0.65	0.94
		1200	40	0.84	1,046	879	0.37	0.31	0.63
		1200	80	1.13	993	1,122	0.35	0.17	0.52
1200	80	0.94	1,094	1,028	0.38	0.22	0.59		

thermolysis was not found. Kidde-Fenwal made flammability test equipment available to UTRC. It will be used to evaluate the flammability of AB in a slurry form with silicone oil, as is going to be prepared by PNNL. In collaboration with members of the HSECoE, UTRC participated in face-to-face failure mode and effect analysis (FMEA) of both the proposed chemical hydride and cryo-adsorption system. The focus of both FMEAs was to identify additional experiments that would need to be performed in order to make sure that each of HSECoE's systems would meet the DOE requirements.

Conclusions and Future Directions

Conclusions derived from the work in FY 2012 are:

- System engineering shows that onboard reversible metal hydride materials need to meet stringent requirements in terms of gravimetric capacity and hydrogenation enthalpy in order to meet the DOE 2017 targets for light-duty vehicles. HSECoE discontinued such a system development when such materials could not be identified.
- GLS became a new unit operation in the chemical hydride system as a result of selecting AB in a fluid form for Phase 2 of HSCoE. UTRC is taking the lead on this topic and selected a passive GLS design with low profile and is building a test rig.
- The NH₃ impurity in H₂ produced from the thermolysis of AB can be effectively removed with a high capacity and regenerable adsorbent filter that comprises metal chlorides deposited on the super activated carbon IRH-33 from UQTR.
- ENG 'worms' are effective additives that increase the thermal conductivity of not only metal hydride materials but also adsorbents like MOF-5, and IRH-33.
- SPS is an effective technique that can be used to compact super activated carbon while minimizing the loss of its gravimetric specific surface area.

Future work will comprise:

- Graphical user interface development of Simulink[®] framework in order to promote wider usage.
- Lead Integrated Power Plant/Storage System Modeling technical area.
- Qualitative risk assessments of each of the remaining materials based hydrogen storage systems and tests in support of the qualitative risk assessment.
- Engineering and testing of specialty components for H₂ storage systems and their experimental evaluation, such as the gas liquid separator in the chemical hydride system.
- Experimental evaluation of NH₃ filter connected to H₂ generated from the thermolysis of liquid AB.

FY 2012 Publications/Presentations

1. Bart A. van Hassel, Daniel A. Mosher, José Miguel Pasini, Mikhail Gorbounov, John Holowczak, Xia Tang, Robert Brown, Bruce Laube, and Lawrence Pryor, "Engineering improvement of NaAlH₄ system," *Int. J. Hydrogen Energy* **37**, 2756–2766 (2012).
2. José Miguel Pasini, Bart A. van Hassel, Daniel A. Mosher and Michael J. Veenstra, "System modeling methodology and analyses for materials-based hydrogen storage," *Int. J. Hydrogen Energy* **37**, 2874–2884 (2012).
3. Matthew Thornton, Jon Cosgrove, Aaron Brooker, José Miguel Pasini, and Michael J. Veenstra, "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 Technical Paper 2012-01-1227, *SAE 2012 World Congress & Exhibition*, April 2012, Detroit, MI, USA (2012).
4. Bart A. van Hassel, J.M. Pasini, D. Mosher, M. Gorbounov, J. Holowczak, I. Fechenia, J. Khalil, F. Sun, X. Tang, R. Brown, B. Laube and L. Pryor, "Advancement of Systems Designs and Key Engineering Technologies for Materials-Based Hydrogen Storage", Gordon Research Conference, July 17–22, 2011 Stonehill College, Easton, Massachusetts.
5. Igor Fechenia and Bart A. Van Hassel. "Solution of Inverse Thermal Problem for Assessment of Thermal Parameters of Engineered H₂ Storage Material", COMSOL Conference, Boston, October 13–15, 2011.
6. Bart A. van Hassel, D. Mosher, J.M. Pasini, M. Gorbounov, J. Holowczak, X. Tang, R. Brown, Fanping Sun, Igor Fedchenia and A.E. Kuczek, Engineering progress in materials based H₂ storage for light-duty vehicles, IEA HIA Task 22, Copenhagen, Denmark, September 4–8, 2011.
7. Bart A. van Hassel, D. Mosher, J.M. Pasini, M. Gorbounov, J. Holowczak, X. Tang, R. Brown, Fanping Sun, Igor Fedchenia and A.E. Kuczek, Engineering progress in materials based H₂ storage for light-duty vehicles, IEA HIA Task 22, Copenhagen, Heidelberg, May 6–10, 2012.
8. Bart A. van Hassel, J.M. Pasini, R.C. McGee, J.R. Karra, A.M. Limarga, J. Holowczak, I. Fedchenia, J. Khalil, J.C. Rampone and R. Brown, Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage, Annual Merit Review, Crystal City, Virginia, May 14–18, 2012.
9. José Miguel Pasini, Claudio Corgnale, Bart A. van Hassel, Theodore Motyka, Sudarshan Kumar, and Kevin L. Simmons, "Metal hydride material requirements for automotive hydrogen storage systems," *submitted to Int. J. Hydrogen Energy*.

References

1. <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/storage.pdf>
2. Bart A. van Hassel, J.M. Pasini, R.C. McGee, J.R. Karra, A.M. Limarga, J. Holowczak, I. Fedchenia, J. Khalil, J.C. Rampone and R. Brown, Advancement of Systems Designs and Key Engineering

Technologies for Materials Based Hydrogen Storage, Annual Merit Review, Crystal City, Virginia, May 14–18, 2012.

3. José Miguel Pasini, Claudio Corgnale, Bart A. van Hassel, Theodore Motyka, Sudarshan Kumar, and Kevin L. Simmons, “Metal hydride material requirements for automotive hydrogen storage systems,” *submitted to Int. J. Hydrogen Energy*.

4. T.A. Semelsberger, Ben Davis, Biswajit Paik, Jose Tafoya, Gerie Purdy, and Tessui Nakagawa, Chemical Hydride Rate Modeling, Validation, and System Demonstration, Annual Merit Review, Crystal City, Virginia, May 14–18, 2012.

5. Information Report on the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles, SAE International Surface Vehicle Information Report, J2719 APR2008, Revised 2008-04.

6. Igor Fechenia and Bart A. Van Hassel. “Solution of Inverse Thermal Problem for Assessment of Thermal Parameters of Engineered H₂ Storage Material”, COMSOL Conference, Boston, October 13–15, 2011.

7. A. Chaise, P. de Rango, Ph. Marty, D. Fruchart, S. Miraglia, R. Olive's, S. Garrier, Enhancement of hydrogen sorption in magnesium hydride using expanded natural graphite, *International journal of hydrogen energy*, 34 (2009), pp. 8589 – 8596.