IV.E.1 On-Board and Off-Board Analyses of Hydrogen Storage Options

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Objectives

The overall objective of this effort is to support DOE with independent system level analyses of various H_2 storage approaches, to help to assess and down-select options, and to determine the feasibility of meeting DOE targets. Specific objectives in Fiscal Year (FY) 2010 included:

- Model various developmental hydrogen storage systems.
- Provide results to Centers of Excellence for assessment of performance targets and goals.
- Develop models to "reverse-engineer" particular approaches.
- Identify interface issues, opportunities, and data needs for technology development.

Technical Barriers

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

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(E) Charging/Discharging Rates
(J) Thermal Management
(K) System Life Cycle Assessments

Technical Targets

This project is conducting system level analyses to address the DOE 2010 and 2015 technical targets for on-board hydrogen storage systems:

- System gravimetric capacity: 1.5 kWh/kg in 2010, 1.8 kWh/kg in 2015
- System volumetric capacity: 0.9 kWh/L in 2010, 1.3 kWh/L in 2015
- Minimum H_2 delivery pressure: 4 atm in 2010, 3 atm in 2015
- Refueling rate: 1.2 kg/min in 2010, 1.5 kg/min in 2015
- Minimum full flow rate of H_2: 0.02 g/s/kW (2010 and 2015)

Accomplishments

- Analyzed the gravimetric and volumetric capacities of Type-3 (metal liner) and Type-4 (high density polyethylene [HDPE] liner), 350- and 700-bar compressed hydrogen (cH_2) physical storage systems.
- Updated the analysis of storage capacity and system performance of the cryo-compressed hydrogen (CcH_2) storage systems to include liner fatigue considerations.
- Analyzing the storage capacity of liquid hydrogen storage systems (LH_2) with advanced vapor shields to extend dormancy.
- Revised the on-board and off-board analyses of the metal-organic framework (MOF-177) system with adiabatic LH_2 refueling and cryogenic liner fatigue considerations.
- Initiated system analysis of on-board hydrogen storage systems that use ammonia borane (AB) in ionic liquids (ILs) as the hydrogen storage medium.
- Conducting off-board analysis of AB regeneration using hydrazine.

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Introduction

Several different approaches are being pursued to develop on-board hydrogen storage systems with the goal of meeting the DOE targets for light-duty vehicular applications. Each approach has unique characteristics, such as the thermal energy and temperature of charge and discharge, kinetics of the physical and chemical process steps involved, and requirements for the materials and energy interfaces between the storage

system and the fuel supply system on the one hand, and the fuel user on the other. Other storage system design and operating parameters influence the projected system costs as well. We are developing models to understand the characteristics of storage systems based on the various approaches and to evaluate their potential to meet the DOE targets for on-board applications.

Approach

Our approach is to develop thermodynamic, kinetic, and engineering models of the various hydrogen storage systems being developed under DOE sponsorship. We then use these models to identify significant component and performance issues, and to assist DOE and its contractors in evaluating alternative system configurations and design and operating parameters. We establish performance criteria that may be used, for example, in developing storage system cost models. We refine and validate the models as data become available from the various developers. We work with the Hydrogen Storage Systems Analysis Working Group to coordinate our research activities with other analysis projects to assure consistency and to avoid duplication. An important aspect of our work is to develop overall systems models that include the interfaces between hydrogen production and delivery, hydrogen storage, and the hydrogen user.

Results

Figure 1 summarizes the storage capacities and well-to-engine efficiencies of some storage options that have been analyzed. The results in Figure 1 are only for reference and should not be compared directly since the systems are at different stages of development and have been analyzed to different levels of sophistication. The specific results given here are subject to revision as the models continue to be refined and additional data become available to help validate them.

Physical Storage

We modified our physical storage model to include the effects of autofrettage on the fatigue life of metal liners in Type-3 pressure vessels and on the load distribution between the liner and the carbon fiber (CF). We modeled the autofrettage process applied to composite tanks for service at ambient and cryogenic temperatures [1]. For service at ambient temperatures, we determined the induced residual compressive stresses in the metal liner and tensile stresses in the CF. We also modeled the post-autofrettage thermal stresses, the reversal of the residual stresses, and the resulting liner yield at lower loads even though the liner yield and tensile strength are higher at cryogenic temperatures. We used the model to determine the liner and CF
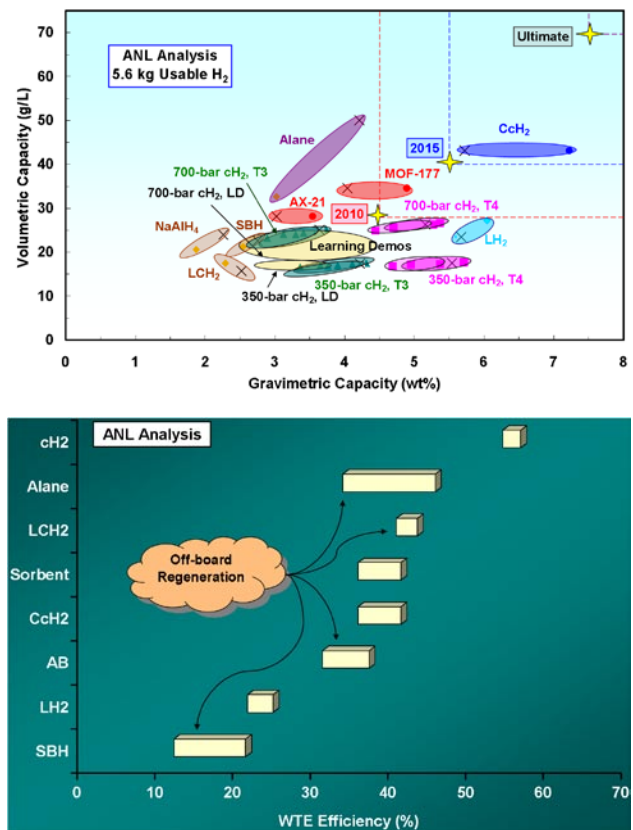

FIGURE 1. Storage Capacities and Well-to-Engine Efficiencies of Hydrogen Storage Options

thicknesses to meet the target life of 5,500 pressure cycles at 25% over the normal working pressure (SAE J2579). In addition, based on recent data and feedback from tank developers, we reduced the CF strength in our analysis by 10% to account for the variability in CF quality at high-volume manufacturing, and significantly increased the CF translation efficiency from 63% to 82% for 700-bar storage.

The fraction of the tensile load borne by the CF in Type-3 tanks affects the weight and cost of the tank. It is desirable to shift as much of the load to the CF as possible within the constraint of the autofrettage proof pressure. Figure 2 shows the calculated gravimetric and volumetric capacities for the Type-3 and Type-4, cH_2, single-tank systems. We calculate that the CF in a 350-bar, 5.6-kg usable H_2, Type-3 tank system can carry 90% of the total load, the Al liner thickness is 7.4 mm, and the usable storage capacities are 4.2 wt% and 17.4 g/L. The corresponding capacities for the Type-4 tank system (5-mm HDPE liner) are higher, 5.5 wt% and 17.6 g/L. At 700-bar storage pressure, the liner thickness for the Type-3 tank increases to 12.1 mm, the gravimetric capacity decreases to 3.6 wt%, and the volumetric capacity increases to 25 g/L. The storage capacities for the 700 bar, Type-4 tank system are higher,
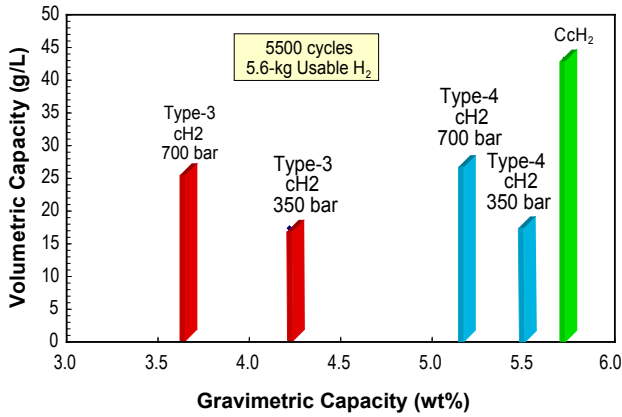
FIGURE 2. Usable Gravimetric and Volumetric Capacities of cH$_2$ and CcH$_2$ Systems

5.2 wt% and 26.3 g/L. Because the HDPE liner carries negligible load, the liner thickness is unchanged between 350-bar and 700-bar pressures. We conclude that among the various cH$_2$ tank systems analyzed, only the 350 bar, Type-4 system can potentially meet the 2015 gravimetric target of 5.5 wt% for 5.6 kg of recoverable hydrogen. None of the analyzed systems was found capable of meeting the 2015 volumetric target of 40 g/L.

We used the autofrettage model to revise the projected capacities of the Gen-3 CcH$_2$ system with an in-tank heat exchanger and a 276-bar pressure vessel rating [2,3]. We determined that the unloading of the residual stresses during post-autofrettage cooling to cryogenic temperatures limits the maximum CF load share to 85%. The maximum load share is constrained by the proof pressure, which in turn depends on the

safety factor (2.25) and the assumed approach to the burst pressure (80%). We estimate that a 9.3-mm liner is needed to withstand 5,500 pressure cycles. The liner thickness would increase if the analysis had considered deep temperature cycling due to refueling with compressed and liquid hydrogen (dual-mode storage). As shown in Figure 2, we project that a 5.6-kg recoverable CcH$_2$ system can achieve capacities of 5.5 wt% and 41.1 g/L, meeting the DOE 2015 targets. Furthermore, with an aluminum outer shell instead of the steel shell, the gravimetric capacity of the 5.6-kg CcH$_2$ system can exceed 9 wt% (but at a higher cost).

Sorption Storage

We updated and expanded our analysis of on-board hydrogen storage in MOF-177. We investigated the adiabatic refueling option in which the MOF tank is evaporatively cooled by refueling it with LH$_2$. We considered that hydrogen is recirculated through a small ex-tank heat exchanger during discharge to provide the heat of desorption and the temperature swing in the sorbent bed. We conducted fatigue analyses to estimate the required liner and CF thicknesses to meet the target life of 5,500 pressure cycles. We performed life cycle analyses to determine the well-to-tank energy efficiency, greenhouse gas emissions and fuel and ownership costs.

Figure 3 shows the calculated system gravimetric and volumetric capacities and the optimum storage temperature and temperature swing as functions of storage pressure. The optimum storage temperature and temperature swing depend on the storage pressure. The maximum gravimetric capacity of ~5.2 wt% is achieved at 150 atm and 80 K. The maximum volumetric capacity
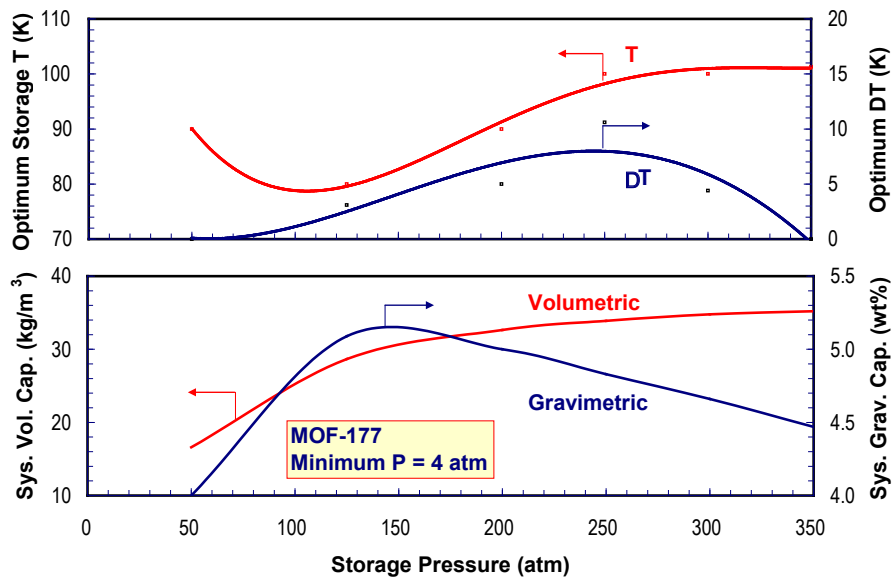

FIGURE 3. Usable Storage Capacity of Adiabatic, LH$_2$ Refueled MOF-177 System

increases with increasing pressure, reaching ~35 g-H_2/L at 350 atm and 100 K.

We estimated that 29% of the weight of the MOF-177 system (250-bar storage pressure, 80-K storage temperature) is in the storage medium, 25% in the liner, 11% in the CF composite, 11% in the aluminum shell, 1% in the multi-layer vacuum superinsulation, and 23% in other miscellaneous components. The corresponding volume distribution is 68% for MOF-177 bed, 6% for the liner, 5% for CF, 3% for the shell, 11% for the multi-layer vacuum superinsulation, and 7% for other miscellaneous components.

Analysis of the refueling dynamics showed that the total cooling load is 7.1 MJ (maximum, from completely empty to completely full). Of this, 62% is to remove the heat of hydrogen adsorption on MOF-177 and 38% is for sensible cooling of the thermal mass and the pressure-volume work of compressing the hydrogen in the tank. During discharge, a constant heat input rate of 1.9 kW is needed to provide H_2 continuously at 1.6 g/s full flow rate for an 80-kW fuel cell system. The peak heat input rate increases to 6.3 kW if the heat is supplied only as the tank pressure tends to fall below 4 atm. The system dormancy is a function of the amount of H_2 stored in the tank and the tank pressure and temperature at the start of the dormancy period. The minimum dormancy is 16 W-days, or ~3 days with a 5-W heat in-leakage rate.

The effects of varying different parameters on the system gravimetric and volumetric capacities were assessed. The parameter values (base case value in boldface) in the sensitivity study were 100, **250** and 300 atm storage pressure; 3, **4** and 8 atm minimum discharge pressure; and 0.4, **0.6** and 0.8 MOF packing fraction. In addition, the effects of a hypothetical increase in the absolute adsorption capacity by **0%**, 20%, and 50% were evaluated. The resultant gravimetric capacities ranged from 4.6 to 5.75 wt% and the volumetric capacities ranged from 24 to 43 g/L. The sensitivity analyses showed that the adsorption capacity was the most significant parameter for the gravimetric capacity, whereas the storage pressure and the adsorption capacity were the two most significant parameters for volumetric capacity. Over the range of parameter values studied, the gravimetric capacity was the least affected by the minimum H_2 delivery pressure and the storage pressure, while the volumetric capacity was the least sensitive to the minimum H_2 delivery pressure and the MOF packing fraction.

The MOF-177 system, as analyzed, can meet the 2010 storage targets, but a 30% increase in sorption capacity is needed to meet the 2015 targets. With hydrogen obtained by steam-methane reforming and electricity drawn from the Energy Information Agency-projected U.S. grid mix for 2015, our analysis showed that the well-to-tank efficiency is about 41%, which falls well short of the DOE target of 60%. The

total greenhouse gas emissions were estimated to be 19.7 kg CO_2 equivalent/kg-H_2, or ~0.31 kg CO_2/mile (63-gasoline gallon equivalent fuel economy) which is slightly less than the emissions for a conventional gasoline internal combustion engine vehicle (~0.35 kg CO_2/mile for 30 mpg fuel economy). The ownership cost was $0.15/mile, which is 50% higher than that for conventional gasoline vehicles ($0.10/mile, 30 mpg and $3/gallon gasoline untaxed).

Chemical Storage

We performed a preliminary on-board analysis for hydrogen storage in a 50:50 liquid mixture by weight of AB and an IL, bmimCl (1-butyl-3-methylimidazolium chloride, $C_8H_{15}ClN_2$). This AB solution is a stirrable, viscous liquid at room temperature, with a freezing point below –10ºC. However, the solution foams once H_2 is released from the AB in the exothermic process; the foam begins to convert to a white solid after releasing 1 H_2 equivalent, with the entire mixture becoming solid after releasing 2 H_2 equivalents [4]. We fitted the dehydrogenation kinetics data [4] to the Avrami-Erofeyev kinetics model with n=1.5 for the first H_2 equivalent released (Step 1) and n=2.5 for the next 1.35 H_2 equivalents released (Step 2). In our model, 100% AB conversion implies the release of 2.35 H_2 equivalents from AB. The kinetics model fits the measured data well for temperatures of 75°C, 85°C, 95°C, 105°C, and 110°C. The model could then be used to estimate hydrogen release at higher temperatures. The modeled kinetics showed that a temperature higher than 150ºC is needed to release 2 equivalents of H_2 in 30 s (average release rate of 67 mEq/s) with a liquid-hourly space velocity (LHSV) of 120 h^{-1}; for comparison, the highest measured release rate is 6 mEq/s at 110°C.

Assuming that an alternate IL (or mixture of ILs) is found such that the solution does not foam or solidify, we developed a conceptual on-board dehydrogenation reactor model using the kinetic data for the AB-bmimCl mixture. The main challenge is to control the peak temperature in this exothermic process, as too high a temperature may lead to undesirable side reactions, as well as issues of solvent stability and AB conversion (complete AB conversion would impede regenerability). The adiabatic temperature rise is in excess of 500ºC, which, with an inlet temperature of 150ºC, would lead to peak temperatures of 650ºC or higher. The reactor temperatures can be controlled by using a heat transfer coolant, product recycle, or a combination of the two, as shown in the system schematic diagram in Figure 4. The reactor model was set up to yield 1.6 g/s of H_2 at 100% conversion using ethylene glycol as the coolant with a 10ºC temperature rise through the reactor. To limit the maximum temperature to 200ºC, the recycle ratio needs to be between 0.90 and 0.95 for an inlet temperature of 150ºC and an LHSV of 150 h^{-1}. The

LTC: Low Temperature Coolant
HTC: High Temperature Coolant
PLV: Pressure Letdown Valve
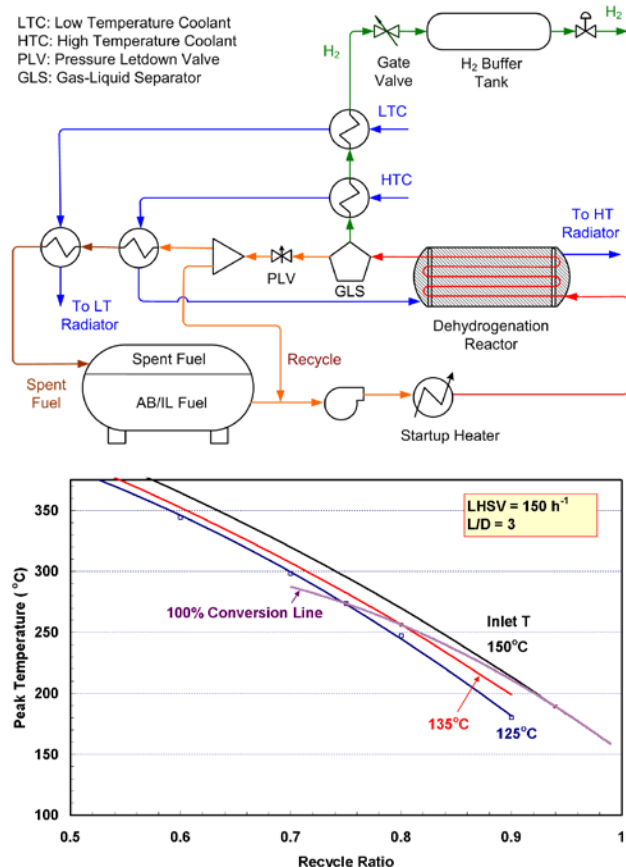GLS: Gas-Liquid Separator

FIGURE 4. On-Board AB System Configuration and Performance of Adiabatic Dehydrogenation Reactor

peak reactor temperature is a function of the solution inlet temperature and the recycle ratio. For a specified conversion, it may not be possible to control the peak temperature adequately by just reducing the inlet temperature.

The reactor may also be operated adiabatically without the need for ethylene glycol coolant. In this mode of operation, the 100% conversion line determines the maximum recycle ratio as a function of the inlet temperature (Figure 4). Adiabatic operation also leads to a simpler reactor design, but the entire heat of reaction (26.4 kW at full flow) will have to be removed elsewhere in the system. This heat rejection and reactor startup and shutdown will be addressed in future work.

Conclusions and Future Directions

- Our analysis of cH_2 storage in Type-3 tanks indicates that the maximum load share in carbon fiber is limited to 90% because of the liner fatigue life requirement and the constraint on proof pressure. We project a gravimetric capacity of 4.2 wt% at 350 bar, decreasing to 3.6 wt% at 700 bar for 5.6 kg recoverable hydrogen. The corresponding

volumetric capacity is 17.4 g/L at 350 bar, increasing to 25 g/L at 700 bar. With Type-4 tanks, the gravimetric capacity improves to 5.5 wt% at 350 bar and 5.2 wt% at 700 bar; the volumetric capacity is marginally higher at 350 bar and improves to 26.3 g/L at 700 bar.

- Our analysis of CcH_2 storage in Type-3 tanks indicates that the maximum load share in carbon fiber is limited to 85% because of the unloading of residual stresses at cryogenic conditions. We project a gravimetric capacity of 5.5 wt% and a volumetric capacity of 41.8 g/L for 5.6 kg recoverable hydrogen. The gravimetric capacity can be significantly higher if the steel outer shell is replaced with an aluminum shell.

- We project that an on-board MOF-177 system with adiabatic LH_2 refueling and 5.6 kg recoverable H_2 can achieve 4.8 wt% gravimetric capacity and 34.6 g/L volumetric capacity at 250 bar. The loss-free time and hydrogen loss rate are functions of the amount of hydrogen stored and the pressure and temperature at the start of the dormancy event.

- In FY 2011, we will continue our system analysis of hydrogen storage in liquid ammonia boranes. We will investigate reactor startup, buffer hydrogen storage, fuel stability, and supplemental heat rejection.

- In FY 2011, we will complete our analysis of the single-pot scheme developed by CHCoE for regenerating AB with hydrazine. We will determine the process efficiencies, well-to-tank efficiency and greenhouse gas emissions.

- Also in FY 2011, we will further extend our systems analysis work on physical, sorbent and metal-hydride storage methods.

FY 2010 Publications/Presentations

1. R.K. Ahluwalia and J.K. Peng, "Automotive Hydrogen Storage System Using Cryo-Adsorption on Activated Carbon," International Journal of Hydrogen Energy, 34 (2009), 5476-5487.

2. R.K. Ahluwalia T.Q. Hua and J.K. Peng, "Automotive Storage of Hydrogen in Alane," International Journal of Hydrogen Energy, 34 (2009), 7731-7740.

3. R.K. Ahluwalia T.Q. Hua, J.K. Peng, S. Lasher, K. McKenney, J. Sinha and M. Gardiner "Technical Assessment of Cryo-Compressed Hydrogen Storage Systems with Automotive Applications," International Journal of Hydrogen Energy, 35 (2010), 4171-4184.

4. R.K. Ahluwalia T.Q. Hua, J.K. Peng, S. Lasher, K. McKenney and J. Sinha "Technical Assessment of Cryo-Compressed Hydrogen Storage Tank Systems for Automotive Applications," Argonne National Laboratory Report, ANL/09-33, December 2009.

5. S. Lasher, K. McKenney, J. Sinha, R.K. Ahluwalia T.Q. Hua and J.K. Peng "Technical Assessment of Compressed Hydrogen Storage Tank Systems for Automotive Applications," TIAX LLC Report, December 2009.

6. R.K. Ahluwalia, J.K. Peng and T.Q. Hua "Hydrogen Storage Using Ammonia Borane in Ionic Liquids – Preliminary Results," Storage System Analysis Working Group, ANL, March 2010.

7. T.Q. Hua and R.K. Ahluwalia, "Fatigue Life Analysis of Type 3 Hydrogen Storage Tanks," Storage System Analysis Working Group, ANL, February 2010.

8. R.K. Ahluwalia, T.Q. Hua and J.K. Peng, "On-board and Off-board Performance of Hydrogen Storage in Metal-Organic Frameworks," Storage System Analysis Working Group, ANL, February 2010.

9. R.K. Ahluwalia T.Q. Hua and J.K. Peng, S. Lasher, K. McKenney and J. Sinha "Analysis of Cryo-Compressed Hydrogen Storage Options," Hydrogen Storage Tech Team Meeting, Detroit, December 2009.

10. T.Q. Hua, R.K. Ahluwalia and J.K. Peng, "Analysis of Compressed Hydrogen Storage System," Storage System Analysis Working Group, ANL, December 2009.

References

1. J.C. Thesken, P.L.N. Murthy and S.L. Phoenix, "Composite Overwrap Pressure Vessels: Mechanics and Stress Rupture Lifting Philosophy," NASA/TM–2009-215683, September 2009.

2. S.M. Aceves, F. Espinosa-Loza, E. Ladesma-Orozco, T.O. Ross, A.H. Weisberg, T.C. Brunner and O. Kircher, "High-Density Automotive Hydrogen Storage with Cryogenic Capable Pressure Vessels," International Journal of Hydrogen Energy, 35 (2010), 1219-1226.

3. R.K. Ahluwalia T.Q. Hua, J.K. Peng, S. Lasher, K. McKenney, J. Sinha and M. Gardiner "Technical Assessment of Cryo-Compressed Hydrogen Storage Systems with Automotive Applications," International Journal of Hydrogen Energy, 35 (2010), 4171-4184.

4. D.W. Himmelberger, L.R. Alden, M.E. Bluhm and L.G. Sneddon, "Ammonia Borane Hydrogen Release in Ionic Liquids," Inorganic Chemistry, 48 (2009), 9883-9889.