Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage

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DOE Hydrogen Program



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Overview

Timeline

- Start: February 2009
- End Phase 1: March 2011
- End Phase 2: July 2013
- End Phase 3 / Project: June 2014
- Percent complete: 32% (spending)

Budget

- \$6.86M Total Program
 - \$5.32M DOE
 - \$1.55M (22.5%) UTRC
- FY10: \$1.00M DOE
- FY11: \$950k DOE

Barriers*

- A J
- A. System Weight & Volume
- E. Charging / Discharging Rates
- J. Thermal Management

Targets*

• All

Partners





* DOE EERE HFCIT Program Multi-year Plan for Storage

Objectives

 Design of materials based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles

Performance Measure	Units	2010	2015	Ultimate	
System Gravimetric Capacity	g H ₂ /kg system	45	55	75	
System Volumetric Capacity	g H ₂ /L system	28	40	70	
System fill time (for 5 kg H_2)	minutes	4.2	3.3	2.5	
Fuel Purity	% H ₂	SAE J2719 guideline (99.97% dry basis)			

- Major project impact:
 - H₂ storage systems comparison on common basis for Go/No-Go decision:
 - Integrated Power Plant Storage System Modeling
 - Volumetric capacity (compaction)
 - System fill time (thermal conductivity, HX design)
 - Fuel purity (purification cartridge to remove NH₃)

Qualitative risk analysis (QLRA)

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Approach

Approach



Collaborations

IPPSSM framework development



Quantitative comparison of H_2 storage systems on a common basis achieved by team effort



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Compaction of (complex) metal hydrides



to low powder density through compaction and higher capacity materials.

Li-Mg-N-H system requires binder (e.g. Expanded Natural Graphite (ENG)).

Technical Accomplishments and Progress



Stabilization of NaAlH₄ (SAH) pellets



Mesh reinforcement reduces volumetric expansion and yields stronger pellets after absorption/desorption cycles but DOE target is 1,500 cycles

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Compaction of SAH without

additives is not sufficient

(AMR 2010)

Thermal conductivity enhancement

 Fast refueling time with SAH requires an effective bed thermal conductivity of 4-8 W/m/K

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Aluminum powder is ineffective; Use aluminum fins. Expanded Natural Graphite can be effective when used as 'worms' causing thermal conductivity anisotropy

Thermal conductivity anisotropy with ENG 'worms'



■ COMSOL[™] model development

Technical Accomplishments and Progress



Results for 8 LiH : 3 Mg(NH₂)₂

r it to oxperimental data		ENG	k radial	k axial
Objective = \longrightarrow Matlab [®]		wt.%	[W/m/K]	[W/m/K]
(Experiment _{radial} -Comsol _{radial}) ²	SAH	5	10.8	1.54
	LiMgNH	5	1.56	1.13
	LiMgNH	10	2.64	1.95
	LiMgNH	15	11.6	0.75



Induce high thermal conductivity towards the heat exchanger tube

Heat exchanger optimization for fast refueling



Performance modeling (COMSOL[™])

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Pelletized SAH kinetics (updated) in combination with HX design enables 90% of storage capacity in 10.5 minutes.

SAH pellets around HX tube

Concept evaluation (Lab-scale)

Integration with HX



Concept evaluation (Lab-scale)

 Repaired/Modified PCT control system Adjusted COMSOL[™] model with updated kinetics and axi-symmetry of test article



Validate key components and concepts at an appropriate scale for Phase 2

Framework results

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NaAlH_₄ powder and compacted pellets systems

- Maximum operating temperature: 170°C
- System starts at 20°C and delivers 5.6 kg H₂ to fuel cell
- Back-to-back EPA Fuel Economy test drive cycles
- Pressure drops during heat-up as gas in voids is sent to combustor to bring the system to operating temperature.



NaAlH₄ powder system running Fuel Economy Test drive cycles



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Framework results



Framework results

Weight and volume*: main contributors

- Effect of increased capacity:
 - BOP weight and volume become increasingly important when using a higher capacity material.
- Guidance:
 - BOP weight and volume reduction important when using higher capacity material
 - Make buffer tank separate from hydride storage system



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* Using BOP components library developed by PNL



Enabling technology: H₂ quality

 Objective: Develop system methods to improve discharged hydrogen purity / quality for acceptable PEM fuel cell durability (SAE J2719 APR2008 guideline)



Qualitative risk analysis (QLRA)

Objective: Identify the critical risks, failure modes and technical challenges of three H₂ storage systems.



Examples of Critical Risks, Failure Modes and Technical Challenges

<u>Risk</u> : Potential for dust explosion in air (wet/dry). Also, fire and/or explosion of released H ₂ gas. <u>Failure mechanism</u> : accidental rupture of storage vessel upon collision	Risk: Runaway chemical reaction during AB thermolysis. Failure mechanism: Loss of thermolysis exothermic heat removal capability	Risk: Loss of vacuum insulation enhances heat influx through the tank wall causing boil off of stored H_2 , pressurizing the storage tank, loss of H_2 inventory via PRD venting and potential for tank failure by overpressurization if PRD venting rate is not sufficient. Note: Loss of H_2 via PRD venting and permeation through the tank wall reduce the mass of stored H_2 available to feed the on-board fuel calls.
Risk: material reactivity with water and subsequent fire and vessel failure by overpressurization. Failure mechanism: water	Risk: Release of toxic gases (diborane and borazine) during solid AB thermolysis.Failure mechanism: Rupture of the on-board spent fuel tank or	Failure mechanism: Stored H ₂ gradually permeates / diffuses to the vacuum insulation gap leading to pressurizing the gap with H ₂ .



Safety categorization of H₂ storage media

Objective: develop a framework for safety categorization of H_2 storage media for on-board vehicular applications.

- The storage media can be solid, liquid, or slurry and include: Metal hydrides, chemical hydrides and adsorbents
- Categorization is based on risk assessment of: Material reactivity, pyrophoricity, sensitivity to mechanical impact, toxicity, chemical stability, ability to cause runaway chemical reaction, on-board vehicular use & handling and off-board regeneration/recycling.
- Material risk includes adverse impact on human safety, health and environment impact.
- Four categories of material risk: Green, Yellow, Orange and Red.

Safety Categories of Storage Media	Classification Criteria
GREEN	Material's chemistry is green, i.e., causes no risks to human health and/or the environment. Qualifying features: 1) No release of toxic chemicals during its manufacturing, on-board vehicular use or regeneration/recycling. 2) Material is chemically stable, i.e., nonpyrophoric, non-water reactive. 3) Non-corrosive and no material compatibility concerns. 4) Not sensitive to mechanical impact.
	 Low-to-moderate-risk material. Qualifying features: 1) Material may release very low concentrations of toxic chemicals during its manufacturing, use or regeneration/recycling. Releases are of no harm to humans and/or the environment. 2) Risk can be eliminated through risk mitigation. Examples: Material's pyrophoricity and water reactivity can be eliminated by powder compaction. Material's temperature sensitivity can be eliminated by stabilizing the material using additives with green chemistry features.
	High-risk material. Qualifying features: 1) Material releases high concentrations of toxic chemical during its manufacturing, use or regeneration/recycling. Releases are harmful to human health and/or the environment. 2) Risk may be eliminated/reduced through risk mitigation but cost would be high, process is complex, additive are of non-green chemistry, additives adversely impact the volumetric and/or gravimetric storage capacity.
RED (Material's risk is unacceptable to human health and/or the environment. Qualifying features: 1) Material may release unacceptably high concentrations of toxic chemicals during its manufacturing, use or regeneration/recycling. Releases are harmful to human health and/or the environment. 2) Risk cannot be eliminated through risk mitigation. Examples: • Material's pyrophoricity and water reactivity cannot be eliminated by powder compaction. • Material's temperature sensitivity cannot be eliminated by stabilizing the material using additives with green chemistry features. • Material may cause a runaway chemical reaction.

Phase-II risk analysis activities

- Perform failure modes and effects analysis (FMEA) to rank material and system risks based on the probability of occurrence and severity of consequences.
- Populate the safety categorization framework.

Collaborations

- Continue to incorporate risk insights from UTRC materials reactivity contract.
- Continue to incorporate quantitative insights from SNL and SRNL reactivity contracts.



FY11 and FY12 Plan

	FY11		FY12			
	2Q	3Q	4Q	1Q	2Q	3Q
Go/No-Go meeting for Phase 1 to Phase 2 transition	$\overrightarrow{\mathbf{x}}$					
Design FMEA of H ₂ storage systems: improve levels of quantitative risk assessment						
Improve understanding of DOT requirements						
Framework maintenance and support and updating models						
LiMgNH system implementation in Framework						
Enable sensitivity studies with Framework						
Address data gaps in material properties						
Further develop internal mesh reinforcement path of compacted hydrides						
Evaluation hydride pellet / HX tube concept	_					
Screen NH ₃ sorbent with higher capacity that is regenerable	-					
Fabricate and evaluate test article for impurity mitigation	-					
Evaluate particulate mitigation strategies	-					
Prioritize tasks after DOE's review of Go/No-Go presentation materials		\bigstar				
Solid transport quantification with surrogate material						
Gas/liquid separation design for liquid chemical hydride system						
Engineer specialty components and their evaluation		_				
Support material and system selection of best technology for Phase 3						$\overrightarrow{\mathbf{x}}$

Summary

- Relevance: Design of materials based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles
- Approach: 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

Technical Accomplishments and Progress:

- Simulink framework generated a quantitative comparison of all three hydrogen storage systems on a common basis for the Go/No-Go decision.
- Compaction know-how transferred from SAH to LiMgNH system; Identified need for binder; SAH pellet stabilization with internal mesh demonstrated.
- Additives evaluated for thermal conductivity enhancement; introduced preferred thermal conductivity enhancement towards HX tube (anisotropy)
- Designed heat exchanger with minimal weight for fast refueling of SAH tank
- Revitalized PCT for evaluating concept of SAH pellet integration with HX tube
- Screened ammonia sorbents and particulate filter to enable sufficient H₂ purity
- Qualitative risk assessment of all three H₂ storage systems

Collaboration: Simulink framework recognized as successful effort of HSECoE as it enabled a team effort and yielded results at a critical time (Go/No-Go)

HSECOE Future Work: Work towards milestones and next phase Go/No-Go decision

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Technical Back-Up Slides

Collaborations

Center structure – roles & collaborations



Vibration packing

Objective: Evaluate whether vibration packing of adsorbent material like AX21/Maxsorb can improve density from 0.3 g/cm³ to 0.6 g/cm³ without binder additions

Expectations for packing density:

Model	Description	Packing density
Dense regular packing	Monodisperse spheres	0.7405
Random close packing	Bimodal particle size distribution	0.75-0.68
Random close packing	E.g. the bed vibrated	0.641-0.625
Random loose packing		0.58



Vibration packing principle



Shakers in two directions





Time and frequency dependence



Vibration packing did not improve density of AX21/Maxsorb above 0.3 g/cm³. AX21/Maxsorb needs to be kept under compression to yield 0.6 g/cm³.



Kinetics of NaAlH₄ + 4 mol% TiCl₃ remeasured

H₂ Absorption Rate

 Capacity loss upon aging at 180°C, 110-100 bar H₂ partial pressure



SAH + 4 mol% TiCl₃ has considerably higher kinetics than Prototype 2 material.

Consider 170°C upper limit for SAH to avoid capacity loss

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Kinetics and heat transfer for LiMgNH system

- Requirement
 - A fast system fill time

	System Fill Time [min]
2010	4.2
2015	3.3
Ultimate	2.5

- Enablers:
 - Kinetics yields 90% of materials capacity at targeted fill time
 - Not reduced by compaction
 - (Complex) metal hydride bed effective thermal conductivity 4-8 W/m/K





Solid hydride transport: requirements and concepts

Objectives:

- Functionally demonstrate solid hydride transport
- Identify key challenges to on board bulk material handling
- Support March 2011 go/no-go decision (BMH)

Scope:

- Material: surrogate representative of solid candidate fuels
- Engineering forms: powder and encapsulated pellets
- Through reactor and fuel tanks

Evaluation metric

- Distance over which the material is transported
- Elevation that one needs to be able to achieve
- Section with curvature and hot zone
- Rate at which the material is transported
- Absolute pressure and/or pressure difference
- Scalability





Solid hydride transport: experiment with flexible screw

- Flexible rectangular coil screw as primary propulsion element
- Teflon outer tube and inner core forming an annular passage to minimize flow back
- Curved material passage to mimic for reactor
- Low speed feeding and metering by variable speed drive (up to 600 rpm of screw speed)
- Microthene G polyolefin powders (50 mesh) used as surrogated material for Ammonia Borane



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-135

Flexible coil screw



Weight & volume correlation for 100 bar pressure vessels

- To quickly obtain weight and volume of a Type IV pressure vessel, Lincoln Composites provided some cases for different internal volumes at 100 bar.
 - Type IV tank.
 - Rated for 100 bar (2.25 FS)
- A simple linear correlation is used to determine the additional weight and volume due to the pressure vessel at intermediate points.





Drive cycles & test conditions for use in the framework

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
Amb Drive Cycle - Rep the E	Ambient Drive Cycle - Repeat the EPA FE	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
T	cycles from full to empty and adjust for 5 cycle post-2008	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	the cycles) 2. Establish vehicle attributes 3. Utilize for storage sizing
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 (F1))	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



*Based on NREL simulation with compact vehicle, 5.6 kg usable H2, 80 kW fuel cell with a 20 kW battery

NaAlH₄ (uncompacted powder) system diagram

- 243 kg hydride needed to deliver 5.6 kg to the fuel cell.
- System: 410 kg, 438 liters = 1.37 wt%, 13 g-H₂/L
- No separate buffer tank. All gas comes from the pores.



Adapted from the GM alanate system diagram



NaAlH₄ powder system: Case 1 for sizing

Mair	n parameters			8
	Usable H ₂	5.6	ka	
	Total weight	410.2	ka	
	Total volume	438	L	
	Gravimetric capacity	1.37%		
	Volumetric capacity	12.8	g/L	
Mate	erial (pelletized)			0
	Gravimetric capacity	3.1%		200 -
	Porosity	56%		
Weight	ghts			
	Material	243	kg	
	Heat exchanger	41.6	kg	्य व
	Pressure vessel (additional)	45.8	kg	50
	Heat transfer fluid loop	70.53	kg	temperature [C]
	Hydrogen loop	7.61	kg	0 pressure [bar]
	Isolation valve	1.65	kg	0 1 2 3 4 time (s) x 10 ⁴
 Volu 	imes			 Other targets
	Tank internal volume	307	L	 On-board efficiency 70%
	Pressure vessel (additional)	42.3	L	 Cold/hot cases OK
	Heat transfer fluid loop	47.7	L	 Dormancy N/A
	Hydrogen loop	40.2	L	 Delivery temperature < 85C
<u> </u>	Isolation valve	0.26	L	 Min delivery pressure 5 bar
(FJ) HSECOE				 Min full flow rate 1.6 g/s
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NaAlH₄ (compacted pellets) system diagram

- 255 kg hydride needed to deliver 5.6 kg to the fuel cell.
- System: 395 kg, 377 liters = 1.42 wt%, 15 g-H₂/L
- No separate buffer tank: additional 53 L in-tank provided.



Adapted from the GM alanate system diagram



NaAlH₄ compacted system: Case 1 for sizing

- N	/lair	n parameters			8 د
		Usable H ₂	5.6	kg	ت 2 6
		Total weight	394.8	kg	E E
		Total volume	376.6	L	
		Gravimetric capacity	1.42%		° 7
		Volumetric capacity	15	g/L	\$ 2 \$ 2
• N	/late	erial (pelletized)			0
		Gravimetric capacity	3.1%		200
		Porosity	29%		
• V	Vei	ghts			150
		Material	255	kg	state state
		Heat exchanger	21.5	kg	ž 100
		Pressure vessel (additional)	38.5	kg	
		Heat transfer fluid loop	70.53	kg	50
		Hydrogen loop	7.61	kg	temperature [C]
		Isolation valve	1.65	kg	0 pressure [bar]
• \	/olu	imes			0 1 2 3 4 $O time (s) x 10^4$
		Tank internal volume	253.7	L	 Other targets
		Pressure vessel (additional)	34.7	L	 On-board efficiency 69%
		Heat transfer fluid loop	47.7	L	 Cold/hot cases OK
		Hydrogen loop	40.2	L	Dormancy N/A
		Isolation valve	0.26	L	 Delivery temperature < 85C
	`o E				 Min delivery pressure 5 bar
JISEL	JUE				 Min full flow rate 1.6 g/s

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Comparison of NaAlH₄ powder and compacted pellets systems

- There is a trade-off in compacting the material.
 - A reduction in pore volume can be effective up to a point.
 - Further compaction results in insufficient gas initially to heat the system to operating conditions → additional buffer space must be provided.





1:1 Li-Mg-N-H (uncompacted powder) system

- 92 kg hydride needed to deliver 5.6 kg to the fuel cell.
- System: 240 kg, 348 liters = 2.33 wt%, 16.1 g-H₂/L
- No separate buffer tank: additional 90 L in-tank provided for cold start.



Gravimetric improvement is driven by the material. Volumetric improvement is marginal due to need for extra volume for cold start.



1:1 Li-Mg-N-H powder Case 1 for sizing

Main parameters

Usable H2	5.6	kg
Total weight	240	kg
Total volume	348	L
Gravimetric capacity	2.33%	
Volumetric capacity	16.1	g/L
erial (pelletized)		
Gravimetric capacity	7.5%	
Porosity	50%	
ghts		
Material	92	kg
Heat exchanger	32	kg
Pressure vessel (additional)	35	kg
Heat transfer fluid loop	70.5	kg
Hydrogen loop	7.6	kg
Isolation valve	1.65	kg
imes		
Tank internal volume	229	L
Pressure vessel (additional)	31.1	L
Heat transfer fluid loop	47.7	L
Hydrogen loop	40.2	L
Isolation valve	0.26	L
	Usable H2 Total weight Total volume Gravimetric capacity Volumetric capacity erial (pelletized) Gravimetric capacity Porosity ghts Material Heat exchanger Pressure vessel (additional) Heat transfer fluid loop Hydrogen loop Isolation valve IMES Tank internal volume Pressure vessel (additional) Heat transfer fluid loop Hydrogen loop Isolation valve	Usable H25.6Total weight240Total volume348Gravimetric capacity2.33%Volumetric capacity16.1erial (pelletized)Gravimetric capacity7.5%Porosity50%ghts32Material92Heat exchanger32Pressure vessel (additional)35Heat transfer fluid loop70.5Hydrogen loop7.6Isolation valve1.65Tank internal volume229Pressure vessel (additional)31.1Heat transfer fluid loop47.7Hydrogen loop40.2Isolation valve0.26





1:1 Li-Mg-N-H (compacted pellets) system

- 92.5 kg hydride needed to deliver 5.6 kg to the fuel cell.
- System: 218 kg, 311 liters = 2.75 wt%, 18 g-H₂/L
- No separate buffer tank: additional 90 L in-tank provided for cold start.



Gravimetric improvement is driven by the material. Volumetric improvement is marginal due to need for extra volume.

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 In-tank buffer is inefficient for this case: a separate buffer with colder H₂ may be more effective.

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1:1 Li-Mg-N-H compacted Case 1 for sizing

	Mair	n parameters		
		Usable H2	5.6	kg
		Total weight	218	kg
		Total volume	311	L
		Gravimetric capacity	2.75%	
		Volumetric capacity	18	g/L
	Mate	erial (pelletized)		
		Gravimetric capacity	7.5%	
		Porosity	25%	
	Wei	ghts		
		Material	92.5	kg
		Heat exchanger	15	kg
		Pressure vessel (additional)	30.7	kg
		Heat transfer fluid loop	70.53	kg
		Hydrogen loop	7.61	kg
		Isolation valve	1.65	kg
	Volu	mes		
		Tank internal volume	196	L
		Pressure vessel (additional)	26.7	L
		Heat transfer fluid loop	47.7	L
		Hydrogen loop	40.2	L
		Isolation valve	0.26	L
HS	ECoE			



Other targets

- On-board efficiency 75%
- Cold/hot cases
 OK
- Dormancy N/A
- Delivery temperature < 85C
- Min delivery pressure 5 bar
- Min full flow rate
 1.6 g/s

Capacity comparison summary



- Independent alanate powder system analyses (GM & UTRC) give comparable results. The difference in gravimetric capacity is due to the pressure vessel assumption: Composite tank + Steel liner (GM) vs Type IV (UTRC).
- Most promising is the 1:1 Li-Mg-N-H compacted system:
 - Gravimetric capacity: 61% of 2010 target, 50% of 2015 target
- **HSECOE** Volumetric capacity: 64% of 2010 target, 45% of 2015 target

Weight and volume: main contributors

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