Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Metal Hydrides

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DOE Materials-Based Hydrogen Storage Summit
Defining Pathways for Onboard Automotive Applications

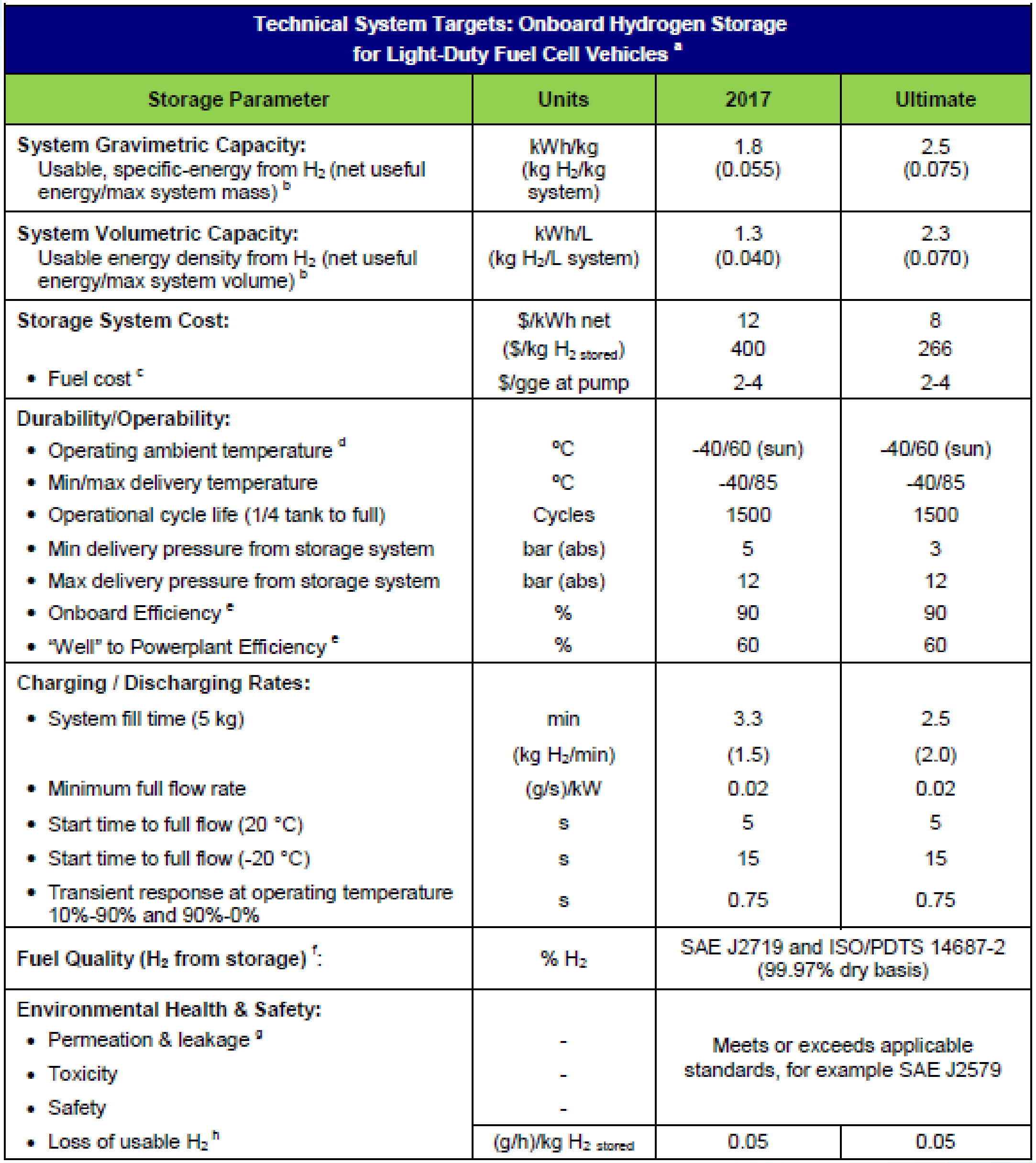
Outline

- **Background and MH History**
- **MH HSECoE Results**
    - Material Operating Requirements
    - Modeling and Analyses
    - BOP and Cost Estimation
- **Discussion of Results**
    - Phase 1 to Phase 2 Transition
    - “Ideal” MH Study
    - 700 bar Tank Comparison
- **Conclusion and Path Forward**

Background

- **The HSECoE Project began in 2009 and involved 3 Phase – each approx. 2 years in length.**
- **A HSECoE Phase 1 to Phase 2 transition meeting was held in DC in February 2011.**
- **A decision was made by DOE to provide a conditional "GO" decision for MH Systems but a final Go No-Go decision would be decided based on the results and discussions from an "Ideal" MH study.**
- **In August 31, 2011, upon DOE review of the information provided by the HSECoE on completion of Phase 1 activities, which included comparisons of all targets, required for light-duty vehicles, work on reversible metal hydrides was recommended not to continue into Phase 2.**
  - **Analyses for highly optimized vessel configurations that could adequately manage thermal and mass flow rates needed for reversible onboard hydrogen storage to meet the DOE performance targets imposed requirements substantially exceeding the properties and behavior of any single, currently existing candidate hydride.**
  - **The necessary combination of gravimetric and volumetric capacities, reaction kinetics, thermodynamics properties, and reversibility have not been found simultaneously in any hydride investigated to date.**
  - **Novel engineering solutions that will allow any currently known hydride, when incorporated into a complete system, have not been identified.**
- **A report summarizing the HSECoE activities on Metal Hydrides was submitted to DOE in May 2014.**

Background – Targets



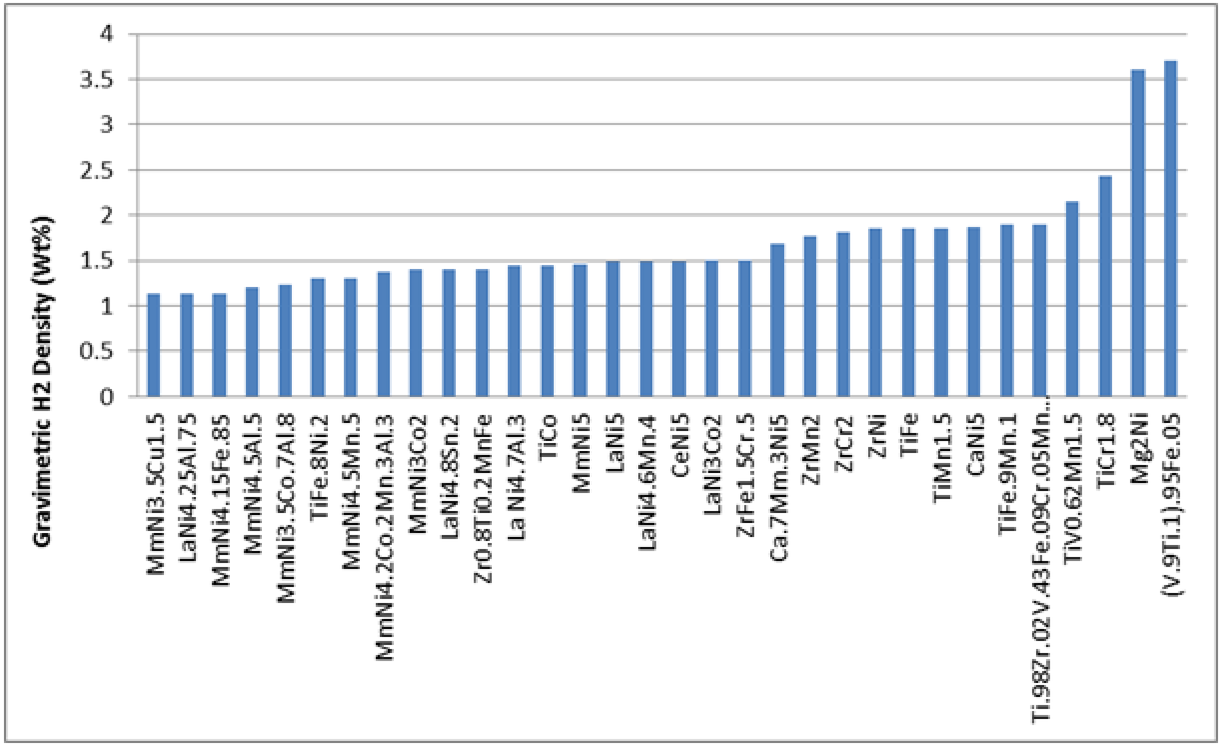
Technical System Targets: Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles [a]

Storage Parameter	Units	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass) [b]	kWh/kg (kg H_2/kg system)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume) [b]	kWh/L (kg H_2/L system)	1.3 (0.040)	2.3 (0.070)
Storage System Cost:	$/kWh net ($/kg $H_{2\ \text{stored}}$)	12 400	8 266
• Fuel cost [c]	$/gge at pump	2-4	2-4
Durability/Operability:			
• Operating ambient temperature [d]	°C	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85
• Operational cycle life (1/4 tank to full)	Cycles	1500	1500
• Min delivery pressure from storage system	bar (abs)	5	3
• Max delivery pressure from storage system	bar (abs)	12	12
• Onboard Efficiency [e]	%	90	90
• "Well" to Powerplant Efficiency [e]	%	60	60
Charging / Discharging Rates:			
• System fill time (5 kg)	min	3.3	2.5
	(kg H_2/min)	(1.5)	(2.0)
• Minimum full flow rate	(g/s)/kW	0.02	0.02
• Start time to full flow (20 °C)	s	5	5
• Start time to full flow (-20 °C)	s	15	15
• Transient response at operating temperature 10%-90% and 90%-0%	s	0.75	0.75
Fuel Quality (H_2 from storage) [f]:	% H_2	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)	
Environmental Health & Safety:			
• Permeation & leakage [g]	-	Meets or exceeds applicable standards, for example SAE J2579	
• Toxicity	-		
• Safety	-		
• Loss of usable H_2 [h]	(g/h)/kg $H_{2\ \text{stored}}$	0.05	0.05

US DOE Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles; http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf.

MH History

Intermetallic Hydrides versus Hydrogen Capacity



Most intermetallic MHs typically < 2wt%

United States Department of Energy, Hydrogen storage materials database, URL: http://hydrogenmaterialssearch.govtools.us/; 2011.

Complex Metal Hydrides

- In 1997 Bodganovic and Schwickardi* showed $NaAlH_4$ to be reversible
- Opened 10 to 15 years of new material R&D
- Some candidate materials had high gravimetric H_2 capacities near 20%
- Issues still existed with respect to
  - high operating temperatures,
  - slow kinetics
  - reversibility and
  - decomposition products (borane, ammonia etc.)

Material	Decomp. Starting T (°C)	H2 Content (wt. %)
$NaAlH_4$	230	7.5
$LiAH_4$	170	10.6
$Mg(AlH_4)_2$	110-130	9.3
$LiBH_4$	320	18.4
$NaBH_4$	450	10.6
$Mg(BH_4)_2$	320	14.8

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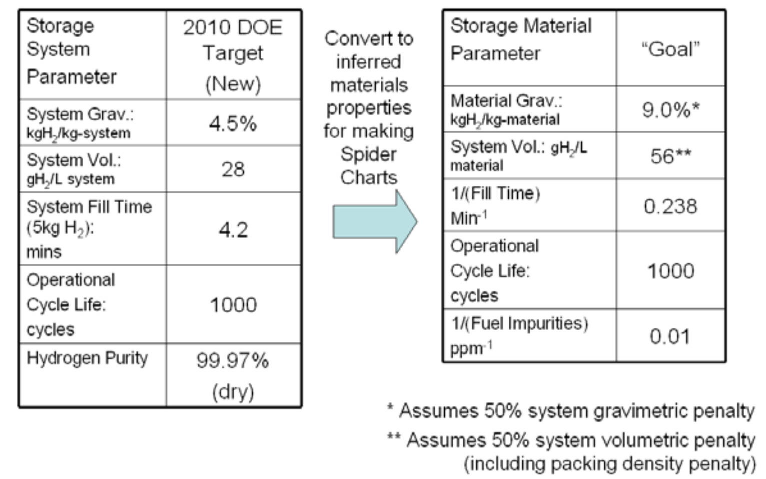
* Bogdanovic, B.; Schwickardi, M. Ti-doped alkali metal aluminum hydrides as potential novel reversible hydrogen storage materials. J. Alloys Compd. 1997, 253–254.

Metal Hydride Center of Excellence – Material Recommendations*



Storage System Parameter	2010 DOE Target (New)
System Grav.: kgH_2/kg-system	4.5%
System Vol.: gH_2/L system	28
System Fill Time (5kg H_2): mins	4.2
Operational Cycle Life: cycles	1000
Hydrogen Purity	99.97% (dry)

Convert to inferred materials properties for making Spider Charts

Storage Material Parameter	"Goal"
Material Grav.: kgH_2/kg-material	9.0%*
System Vol.: gH_2/L material	56**
1/(Fill Time) Min^{-1}	0.238
Operational Cycle Life: cycles	1000
1/(Fuel Impurities) ppm^{-1}	0.01

* Assumes 50% system gravimetric penalty

** Assumes 50% system volumetric penalty (including packing density penalty)

		A	B	C	D	E	F	G
2010 Materials "Goals"		**$LiBH_4/MgH_2$**	**$LiBH_4/Mg_2NiH_4$**	**$2LiNH_2/MgH_2$**	**$Mg(BH_4)_2$**	**$LiNH_2/MgH_2$**	**AB_2H_3** A = Ti, Zr B = V, Cr, Mn	**$NaAlH_4$**
Gravimetric Density (wt. %)	9%	10%	1.7%	5%	11%	6.5%	2.1%	4%
Volumetric Density (gH_2/L)	56	95	48	70	147	107	110	80
Min. Delivery Pressure @ 85 °C (PEMFC) (bar)	5	0.022	10	1.2	0.035	0.2	70	0
Cycle Life	1000	10	10	235	2	10	1000	100
Minimum Flow Rate (gH_2/sec) @ 85 °C	1	~0	~0	~0	~0	~0	1.5	~0
1/(Recharge Time = 4.2 min), min^{-1}	0.238	0.0333	0.0083	0.1667	0.0028	0.0110	0.0660	0.1
1/(Fuel Impurities = 100 ppm), ppm^{-1}	0.010	unknown	unknown	0.0056	0.0005	0.0088	∞	∞

Material A was a material that was developed prior to the start of the MHCoE and was included in the chart but ***not recommend*** to the HSECoE because of it very slow kinetics and its decomposition to diborane on cycling.

Material B is a new material that was included because of its lower decomposition temperature but it was also ***not recommended*** for the HSECoE because of its low gravimetric density and its diborane decomposition product similar to Material A.

Materials C, D and E ***were recommended*** for further investigation by the HSECoE and these will be discussed in more detail

Material F was also not evaluated by the MHCoE but was ***included here for comparison*** because it is one of the better gravimetric density intermetallic materials with excellent kinetics and cycling abilities at low temperatures. The investigation of TiCrMn one of the materials in this class of materials was investigated by the HSECoE.

Material G, $NaAlH_4$, was included in the chart because as mentioned earlier - it is still the best complex metal hydride candidate material today and despite only having a reversible hydrogen capacity of 4 wt% it makes a ***good surrogate material for future studies and material comparisons***

* Klebanoff, L.; Keller, J. 5-Year Review of Metal Hydride Center of Excellence. Int. J. Hydrogen Energy 38 (2013) 4533-4576.
In Proceedings of the 2010 U.S. DOE Hydrogen Program Annual Merit Review, Washington, DC, USA, 7–11 June 2010; Available online:
http://www.hydrogen.energy.gov/pdfs/review10/st029_klebanoff_ 2010_o_web.pdf.*

History of MH Systems

Vehicle Demonstrations Using Metal Hydride Tanks*

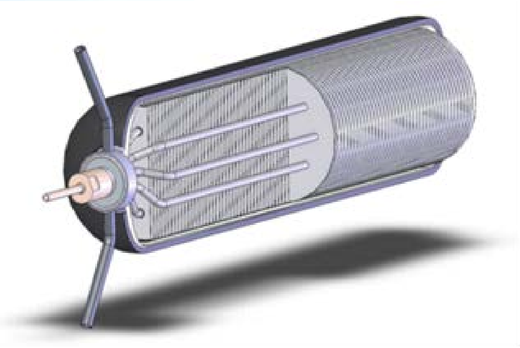
Maker	**Designation**	**Power**	**Size (kW)**	**Hydride**	**Year**
GM Opel	Precept FCEV	FC	75	?	2000
Honda	FCX-V1	FC	60	JMC	1999
Mazda	Cappela	ICE	?	JMC	1994
Mazda	Demio	FC	50	?	1997
Toyota	RAV4 FCEV	FC	20	?	1996
Toyota	FCHV-3	FC	90	JMC	2001
John Deere	Gator 1	FC hybrid	8.5	Mm(Ni,Al)	1998
John Deere	Gator 2	FC hybrid	8.5	Ti(Fe,Mn)	1998
SRTC Bus	Augusta	ICE hybrid	75	$Lm(Ni,Al)_5$	1996
FCPI /SNL	Mine Locomotive	FC	12	(Ti,Zr)(Mn,V,Cr,Fe)	2001
ECD	Motor Scooter	ICE	?	ECD	2002
Germany	U212 Submarine	FC hybrid	300	GfEh	2004

Most Demonstrations used Intermetallic MHs

* Sandrock G, Bowman Jr RC. Gas-based hydride applications: recent progress and future needs. J Alloy Compd 2003; 356e357:794e9, http://dx.doi.org/10.1016/S0925-8388(03)00090-2.

Note: the above table is not intended to be a complete list and a few additional vehicle demonstrations have been carried out during the past few years since this table was published.

History of MH Systems: Large-scale SAH Demonstrations



UTRC

SNL/GM

GKSS Research Center (Dornheim)

	UTRC (1/8 kg H2) Prototype II	SNL/GM (3 kg H_2)	GKSS (~0.3 kg H_2)	DOE 2017 Target
H_2 Storage Capacity (kg/l)	0.021	0.0105	~0.01**	0.040
H_2 Storage Capacity (kg/kg)	0.020	0.0085	~0.011**	0.055
H_2 filling time (min)	30	30*	10	3.3

* 10 min filling times were achieved at about 13% lower capacities

** values estimated from figures and tables in references [22], [23] and [24]

UTRC system (MH in shell) emphasized capacity, SNL/GM and GKSS (MH in tube) emphasized charging rate

HSECoE – Summary of MH Systems Results

- **Material Operating Requirements**
    - Material Database
    - Material Engineering Data
- **Modeling and Analysis**
    - Preliminary/Screening Models
    - Detailed Transport Models
    - System Models & Performance Analyses
- **Balance of Plant and Cost Estimation**
    - Component Database
    - Component Development and Optimization
    - System and Component Cost Estimation
- **“Ideal” MH and 700 bar Comparison Study**

HSECoE MH Results: Material Operating Requirements

HSCoE Metal Hydride Material Categories

	Tier 1 **Developed Materials**	*Tier 2* **Developing Materials**	**Down-selected Materials**
Metal Hydrides	$NaAlH_4$ $2LiNH_2+MgH_2$	$Mg(NH_2)_2+MgH_2+2LiH$ $TiCr(Mn)H_2$	MgH_2 Mg_2NiH_4

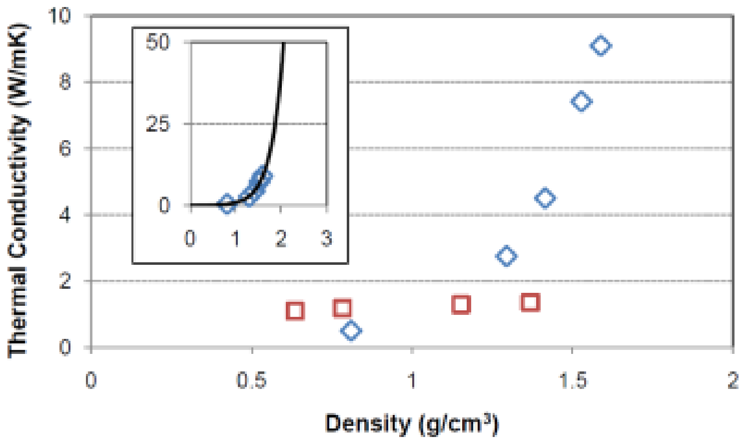
Minimum Screening Criteria for Metal Hydrides
Capacity: > 9wt% materials capacity to be able to meet the DOE 2015 system target
Absorption: RT to 250°C at 1-700 bar H_2 pressure, rate >20g/s (storing 5 kg accessible H_2)
Desorption: 80°C to 250°C at 1-3 bar H_2-pressure, rate >20g/s (storing 5 kg accessible H_2)
Enthalpy: <50kJ/mol
Crystal density: > 1g/cm^3
Availability: (quantitative cost & time i.e. <$10,000/kg in 30 day delivery)

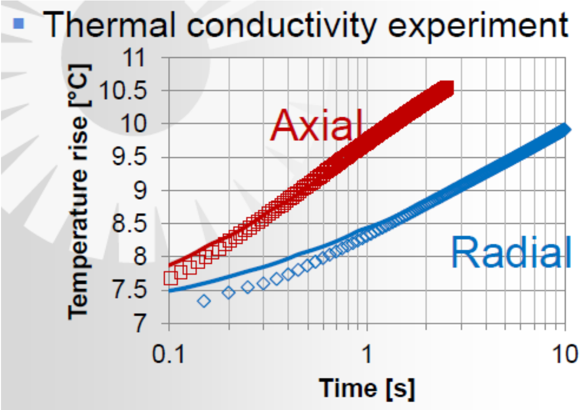
These key material properties included:

1. Chemical kinetics parameters and types of reactions (as functions of temperature and species concentration). Not necessary for mass transfer limited systems (i.e. very rapid kinetics).
2. Hydrogen capacity (isotherms).
3. Bulk density.
4. Material density (sometimes called crystal density).
5. Total porosity.
6. Inter-particle porosity (same as total porosity for non-porous particles).
7. Intra-particle porosity (if the particles are porous).
8. Heats of reaction.
9. Bulk thermal conductivity.
10. Specific heat.

These material properties of the selected MHs were included in an extensive MH Material Database.

Material Engineering Data: Thermal Conductivity & Density





	ENG wt.%	k radial [W/m/K]	k axial [W/m/K]
* SAH	5	10.8	1.54
LiMgNH	5	1.56	1.13
LiMgNH	10	2.64	1.95
LiMgNH	15	11.6	0.75

* $NaAlH_4$

Both GM and UTRC measured increasing TC for Complex MHs with compaction and addition of Al and ENG

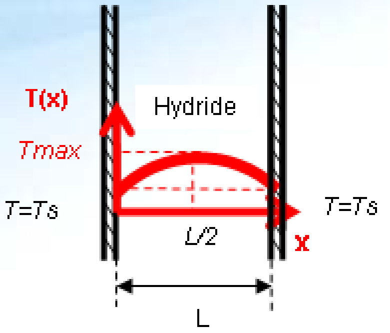
van Hassel BA, Mosher D, Pasini JM, Gorbounov M, Holowczak, J, Tang X, Brown R, Laube B, Pryor L, Engineering improvement of NaAlH4 system, Int J Hydrogen Energy 2012; 37: 2756- 2766.

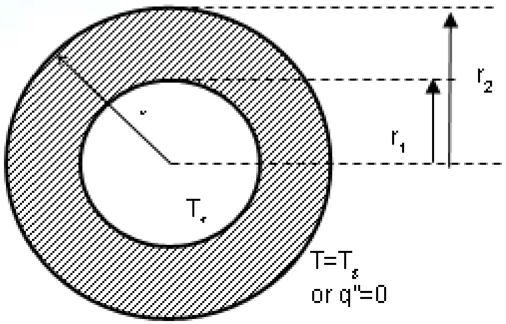
van Hassel BA, ,Gorbounov M, Holowczak, J, Tang X, Brown R, Advancement of system designs and key engineering technologies for materials-based hydrogen storage, Journal of Alloys and Compounds, 580, 2013, S337- S342.

Sulic M, Cai M, Kumar S, Cycling and engineering properties of highly compacted sodium alanate pellets, Int J Hydrogen Energy 2012; 37: 15187- 15195.

Sulic M, Cai M, Kumar S, Controlled degradation of highly compacted sodium alanate pellets, Int J Hydrogen Energy 2013; 38: 3019- 3023.

Modeling and Analyses: Preliminary and Scoping Models





$$y = \left(\frac{1}{L^2}\right)\left(\frac{k\ M_{Hyd\_eff}\ \Delta T}{-\Delta H_{overall}\ \rho_{Hydride}}\right) = \frac{1}{mM_{H2}}\frac{\Delta m_{H2}}{\Delta t}$$

Vessel parameter

Media parameters

$$\Delta T = \frac{L^2 \cdot \rho_{Bed} \cdot \frac{\Delta H_{overall}}{MW_{H_2}} \cdot \frac{\Delta M_{H_2}}{\Delta t}}{m \cdot k_{eff} \cdot M_{Hydride}}$$

$$\Delta T = T_{max} - T_{min}$$

Cylindrical

$$L^2 = r_1^2 - r_2^2$$

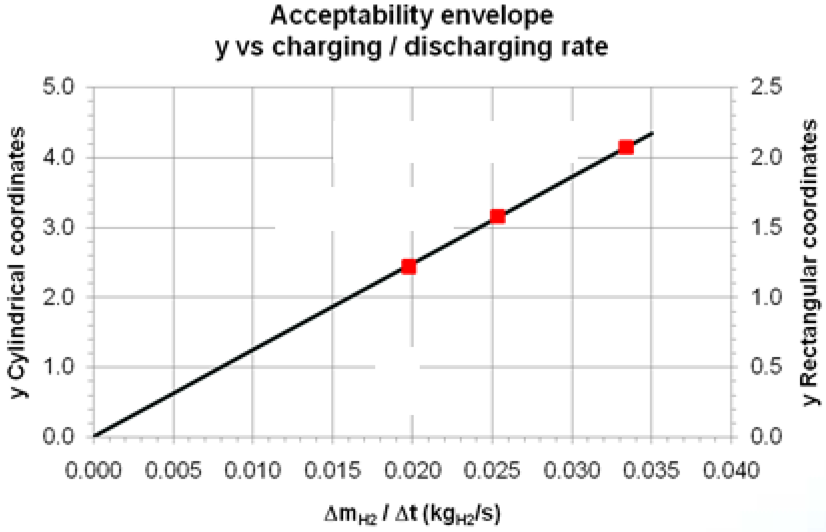
$$m = 8$$

Rectangular

L= (fin spacing)

$$m = 4$$

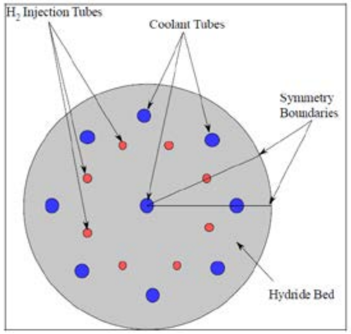
L	Distance between heat transfer surfaces (m)
ΔT	Temperature range required for acceptable chemical kinetics (to give specified charge/discharge rate) (K)
$\Delta H_{overall}$	Overall heat of reaction (kJ/mol H_2)
ρ_{Bed}	Hydride bed density (kg/m³)
k_{eff}	Effective bed thermal conductivity (W/m K)
$M_{Hydride}$	Mass of hydride required to load target amount of hydrogen (kg)
MW_{H_2}	Molecular Weight of Hydrogen (kg H_2/mol H_2)
$\frac{\Delta M_{H_2}}{\Delta t}$	Rate of charging/discharging (kg H_2/s)

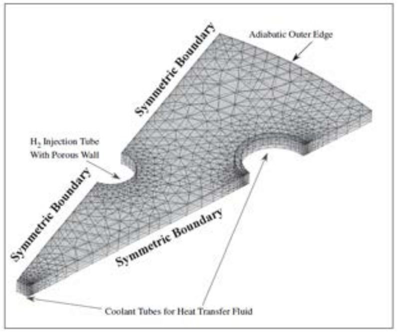


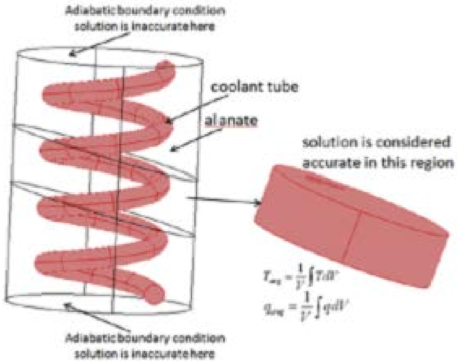
The Acceptability Envelope analysis uses a one-dimensional energy balance to relate the characteristics of the MH media and the system to the storage system performance targets.

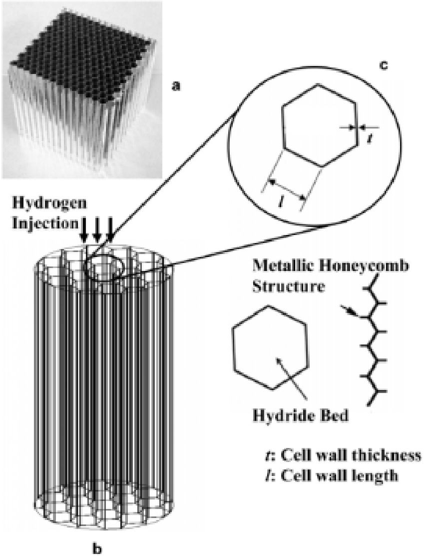
Corgnale C, Hardy BJ, Tamburello DA, Garrison SL, Anton DL, Acceptability envelope for metal hydride-based hydrogen storage systems. Int J Hydrogen Energy 2012;37:2812e24 http://dx.doi.org/10.1016/j.ijhydene.2011.07.037.

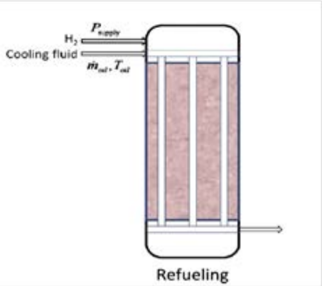
Detailed Transport Models

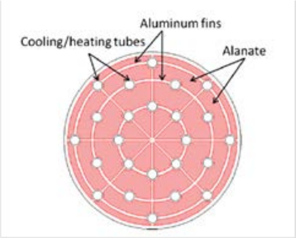










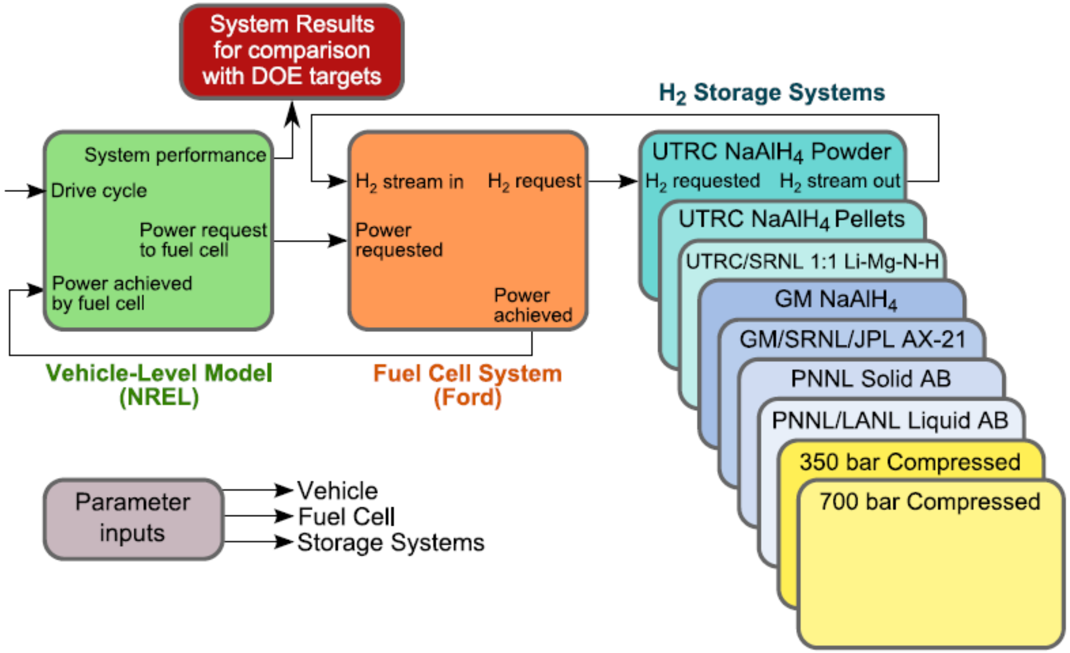


SRNL/UQTR and GM conducted detail transport models to fully understand the complex processes occurring during charging and discharging processes in hydrogen storage systems.

- Input to the detailed models included the transport equations along with temperature, pressure, and composition-dependent hydrogen uptake/discharge kinetics relations.
- Output from the detailed models will include temperatures, pressures, concentrations of media species, hydrogen velocities, correlation-based parameters, and any quantity that can be derived from these parameters, including derivatives and integrals.

Bhouri M, Goyette J, Hardy B, Anton D, Numerical modeling and performance evaluation of multi-tubular sodium alanate hydride finned reactor, Int J Hydrogen Energy 2012; 37: 1551-1567.
Bhouri M, Goyette J, Hardy B, Anton D, Honeycomb metallic structure for improving heat exchange in hydrogen storage system, Int J Hydrogen Energy 2011; 36: 6723-6738.
Raju M. and Kumar S. (2011) System Simulation Modeling and Heat Transfer in Sodium Alanate based Hydrogen Storage Systems, Int J Hydrogen Energy 2011; 36: 1578-1591.
Raju M. and Kumar S. (2010) Optimization of heat exchanger designs in metal hydride based hydrogen storage systems, Int J Hydrogen Energy 2012; 37: 2767-2778.

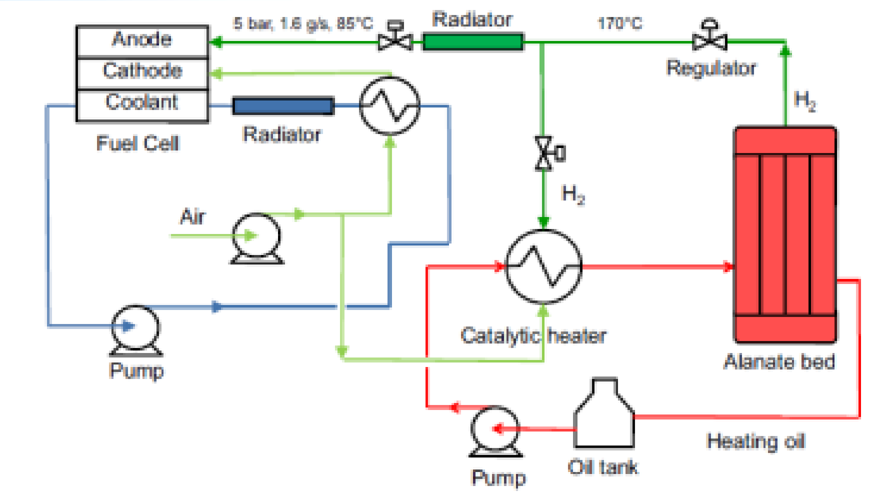
System Models: Modeling Framework



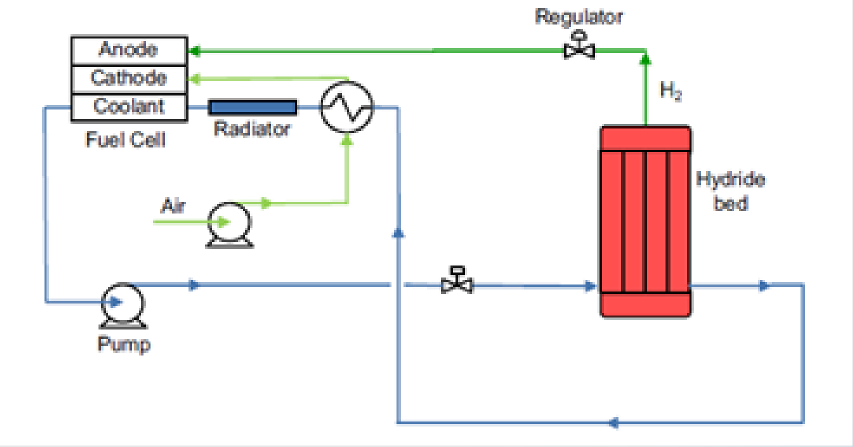
- To meet the objectives of the HSECoE a quick and efficient method was needed to evaluate various material-based storage systems and to compare their performance against DOE light duty vehicle targets.
- To accomplish this task a modeling approach was created that enabled the exchange of one hydrogen storage system for another while keeping the vehicle and fuel cell systems constant.
- The block diagram of the modeling “framework” was used for system evaluation and comparison and to implement the integrated power plant and storage system model (IPPSSM)

Pasini, JM, van Hassel BA, Mosher DA, Veenstra MJ, System modeling methodology and analyses for materials-based hydrogen storage, Intl. J. Hydrog. Energy, 37 (2012) 2874-2884.

MH System Baseline Designs



Baseline designs for various higher temperature MHs ($NaAlH_4$) were evaluated.



Baseline design for a high pressure MH system (TiCrMn) was evaluated.

Comparison of System Designs

Comparison of Material Properties and System Parameters for TiCrMn and $NaAlH_4$ Systems (system values based on results obtained from framework model)

	TiCrMn	$NaAlH_4$	DOE 2017 System Targets
Material Properties			
Crystal density (kg/m^3)	6200	1400	
Bulk density (kg/ m^3)	4000[1]	1000	
Reaction enthalpy (kJ/mole H_2)	22	37[2]/47[3]	
Specific heat (J/kg K)	500	1230	
H2 gravimetric capacity (wt%)	1.9	3.7	
System Parameters			
System maximum temperature (C)	65[4]	180	
System maximum pressure (bar)	500	150	
Effective thermal conductivity (W/m K)	9.5[5]	8.5[5]	
H2 gravimetric capacity (wt%)	1.2	1.2	5.5
H2 volumetric capacity (kg H2/l)	0.03	0.0115	0.04
Charging time - 5.5 kg useable H2 (min)	<5	10.5	3.3
Onboard efficiency (%)	99	78	90

Notes:

1. assuming 0.35 void fraction
2. reaction enthalpy for tetrahydride
3. reaction enthalpy for hexahydride
4. based on maximum radiator coolant temperature
5. assuming the addition of graphite or other thermal conductivity enhancement

Vehicle Performance Studies

Hydrogen Storage System	Adjusted Fuel Economy (mpgge)	Range (mi) 5.6kg H2	On-Board Efficiency (%) UDDS/HFET	Gravimetric Density (wt. %)	Volumetric Density (g/l)
$NaAlH_4$	**36.4**	**204**	**77**	**1.2**	**11.39**
TiCrMn	**45.9**	**257**	**100**	**1.1**	**26.53**
350 bar Compressed Gas	**49.9**	**280**	**100**	**4.8**	**17.03**
700 bar Compressed Gas	**49.9**	**279**	**100**	**4.7**	**25.01**

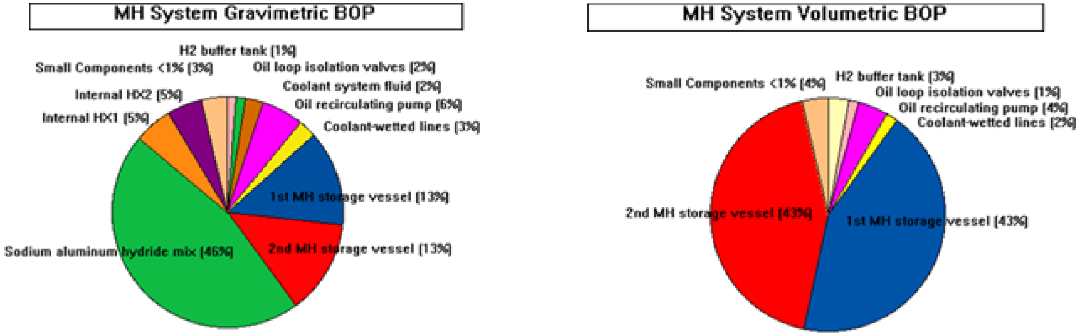
Vehicle Performance results for $NaAlH_4$ and TiCrMn compared to Compressed Gas.

Hydrogen Storage System	**WTW H2 Cost ($/kg)**	**WTW Energy Efficiency (%)**	**WTW GHG Emissions (g/mile)**
$NaAlH_4$	**$7.32**	**44.1**	**198**
350 bar Compressed Gas	**$4.26**	**56.7**	**197**
700 bar Compressed Gas	**$4.71**	**54.2**	**208**

Vehicle WTW results for NaAlH4 compared to Compressed Gas

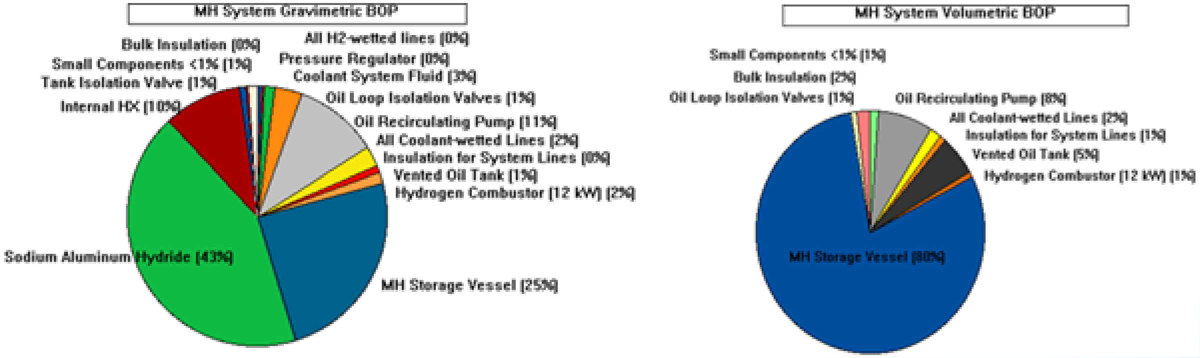
BOP Analyses and Studies

	Calculated	System	2010 Goal	2015 Goal		Fraction of 2010 Goal
Gravimetric Density	457.5 kg	.0122	.045	.055	Kg/Kg	27%
Volumetric Density	488.7 L	.0115	.028	.040	Kg/L	41%



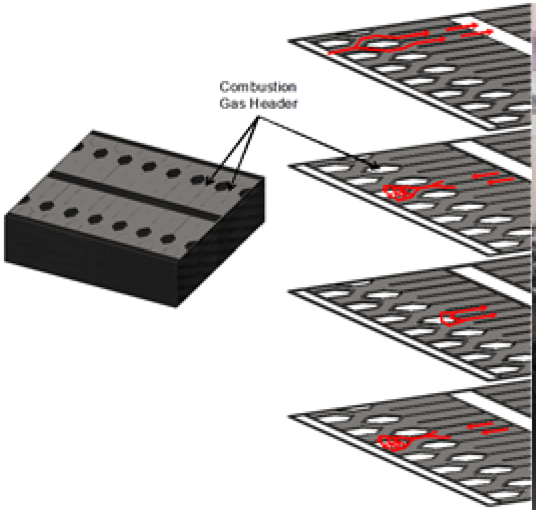
Baseline metal hydride system and BOP mass and volume projections

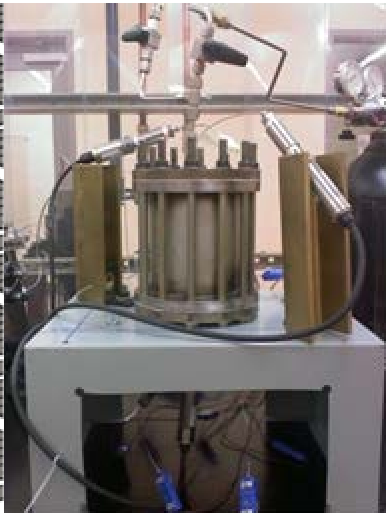
	Calculated	System	2010 Goal	2015 Goal		Fraction of 2010 Goal
Gravimetric Density	247.6 kg	.0226	.045	.055	Kg/Kg	50%
Volumetric Density	243.1 L	.0230	.028	.040	Kg/L	82%



Reduced mass and volume scenario analysis for a metal hydride system

BOP & Enabling Technologies: Microchannel Combustor





- OSU led team, using microchannel architecture, developed a test-cell combustor that had a projected system design of only 1 liter and 3.8 kg for the 12kW baseline metal hydride storage system.
- This is a 9X improvement in volume and 6X improvement in weight over a conventional design
- Testing of the single unit cell resulted in a measured efficiency of 92% (thermal energy transferred to the oil/chemical energy in the feed stream).

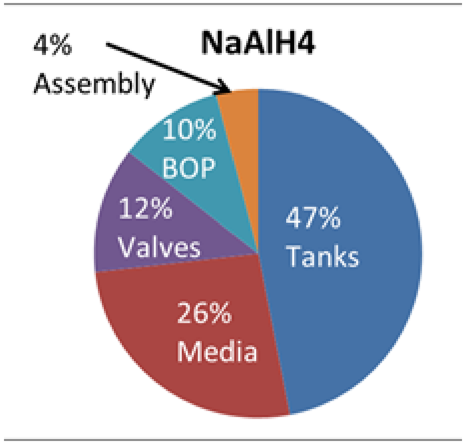
DOE Hydrogen and Fuel Cell 2011 Annual Progress Reports, IV.D.10, Microscale Enhancement of Heat and Mass Transfer for Hydrogen Energy Storage, www.hydrogen.energy.gov/pdfs/progress11/iv_d_10_drost_2011.pdf.

System Cost Estimation and Analyses

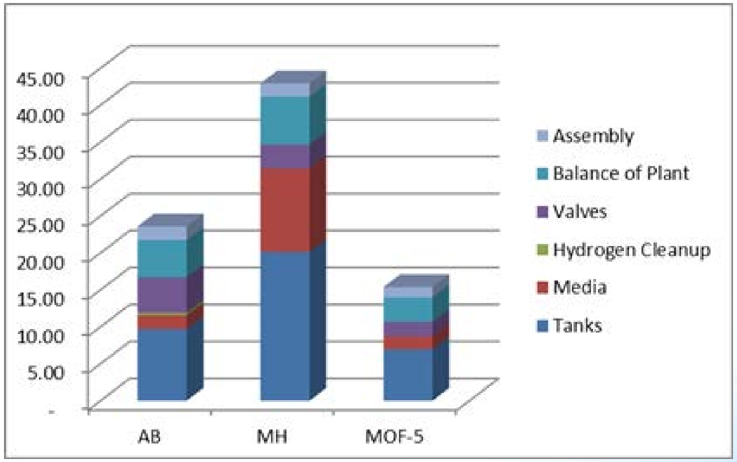
Metal hydride system cost across all production levels for baseline NaAlH4 system case

	Production Amount				
	10,000	**30,000**	**80,000**	**130,000**	**500,000**
Total Costs	20,201	18,267	16,679	14,804	8,008
$/kWh					42.9

Item	**10,000**	**30,000**	**80,000**	**130,000**	**500,000**
Tanks	5,187	4,652	4,250	4,073	3,756
Media	9,016	8,843	8,588	7,373	2,105
Media Cost/kg	39	38	37	32	9
Balance of Plant	4,347	3,307	2,570	2,290	1,817
Assembly	1,652	1,465	1,271	1,068	329



MH System Cost Breakdown for Major Components

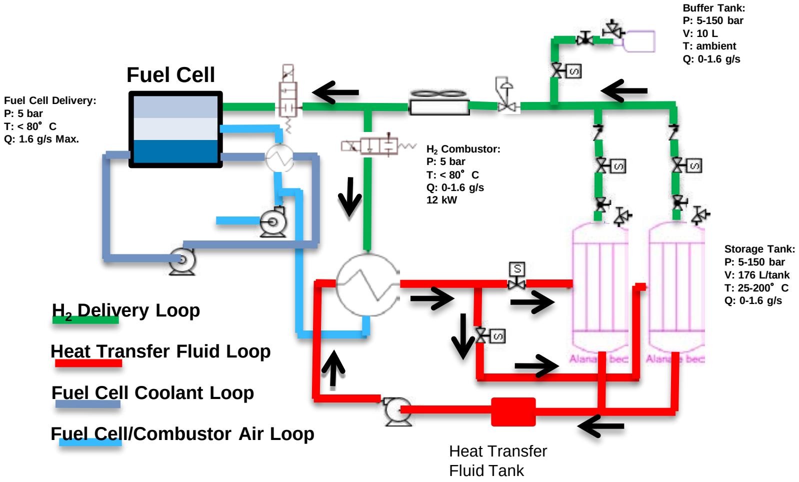


Comparison of Phase 1 System Cost Estimate

Phase 1 Metal Hydride System Projection

2017 Targets

- Dual Vessel Sodium Alanate Design (w. 4 mol%$TiCl_3$ & 5 wt% ENG)
- GM1 Design: fin and tube heat exchanger optimized to meet 10.5 min refueling time at the expense of wt %
- 2 Type 3 composite tanks with SS liners
- System includes a 10 l buffer tank and a 12 kW H_2 combustor

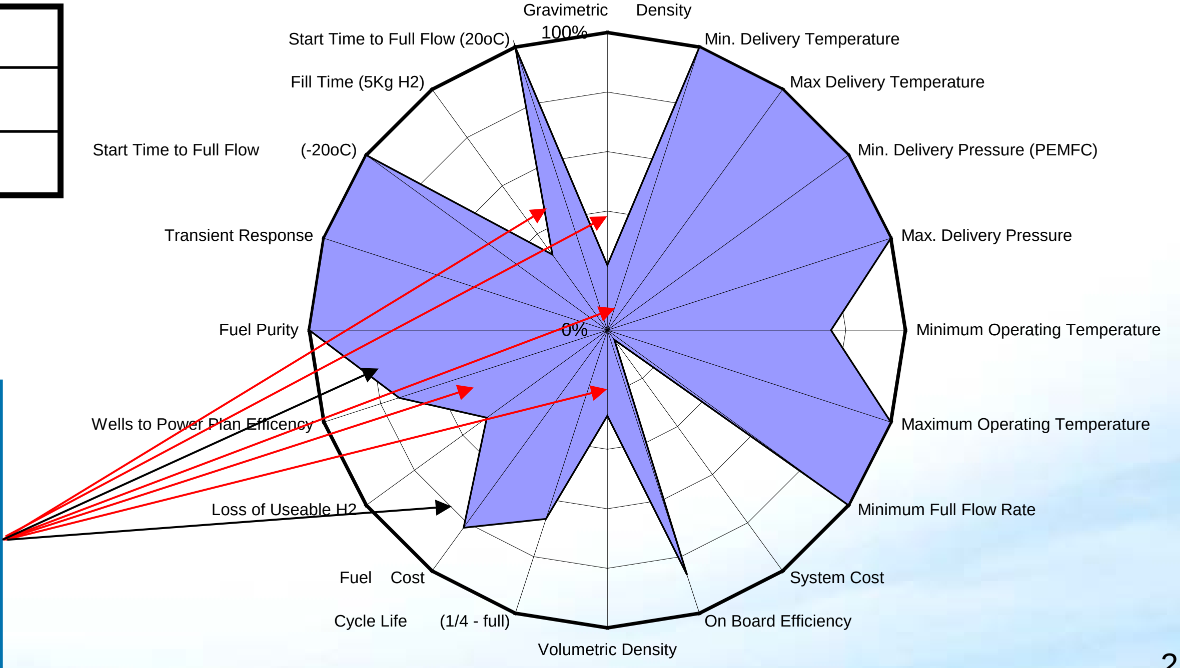


Gravimetric Density (wt.%)

Current	**1.2%**
2017	**5.5%**
Ultimate	**7.5%**

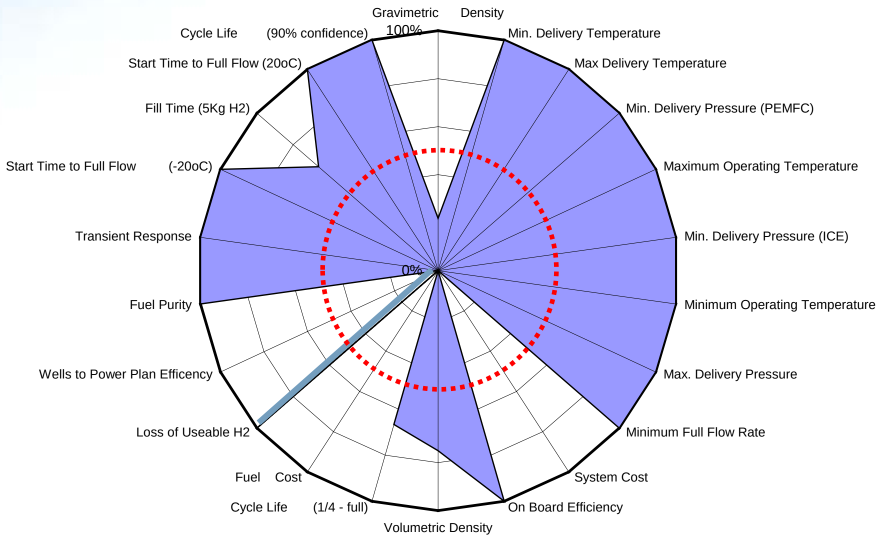
Volumetric Density (kg/l)

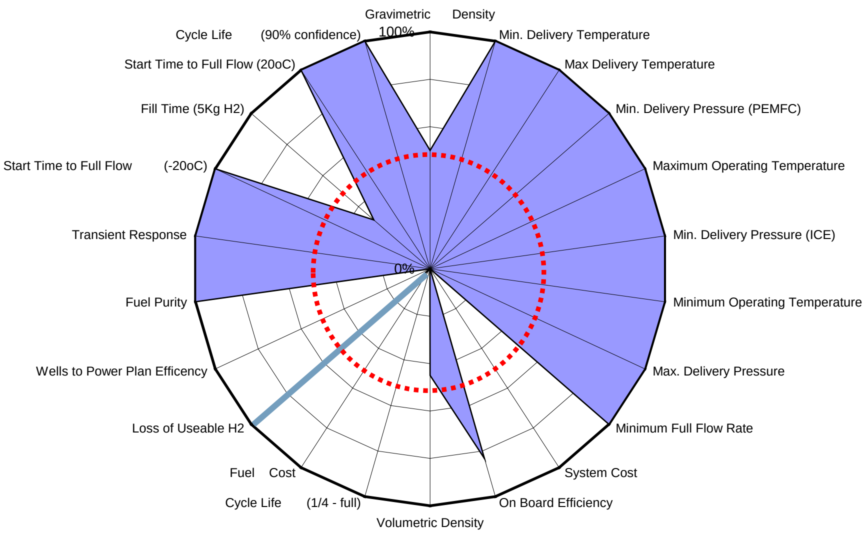
Current	**0.012**
2017	**0.040**
Ultimate	**0.070**



1. **Gravimetric Density**
2. **System Cost**
3. **Onboard Efficiency**
4. **Volumetric Density**
5. **Fill Time**
6. Fuel Cost

Phase 1 Go/No-Go: Alternative Systems


TiCrMn Hydride


1:1 LiAmide/MgH2

<ins>Targets below 50%</ins>
Gravimetric density (22%)
Cost (not calculated)

<ins>Targets below 50%</ins>
Volumetric density (45%)
Fill time (31% due to kinetics)
Cycle Life (<10)
Cost (not calculated)

Proposed “Ideal” MH Study

Approach

- The following system engineering tools were used to estimate the minimum material requirements required to meet the 2017 storage system targets:
  - Acceptability Envelope for vessel sizing and sensitivity analyses
  - Simulink/Framework for determining desorption heating and gas delivery requirements and for sizing BOP components (catalytic burner, buffer tank etc.)
  - Material and equipment specifications and expert opinion for sizing BOP components (tanks, piping, pumps, valves etc.)

J.M. Pasini, C. Corgnale, B.A. van Hassel, T. Motyka, S. Kumar, K. L. Simmons, Metal hydride material requirements for automotive hydrogen storage systems, Intl. J. Hydrogen Energy 2013; 38:9755-9765.

Major Assumptions – “Ideal” Material Study

- Charging and discharging kinetics follow a similar form used to describe sodium alanate (single reaction). A similar expression was used for both charging and discharging
- 85% of theoretical material gravimetric capacity is used to meet the 3.3 minute fill time
- 10% ENG used to justify 10 w/m-K bed thermal conductivity
- Compacted media yields a 30% bed porosity
- System pressure is 100 bar.
- Type IV tank, with small heat exchanger tubes and no baffles due to enhanced thermal conductivity
- ΔH of 27kJ/mol only requires waste heat from fuel cell - higher ΔH’s required a combination of fuel cell waste heat and some catalytic hydrogen combustion
- A minimum BOP for the non-tank associated components (piping valves, regulators etc.) is comparable that for compressed gas systems.

Sample Kinetic Charging Simulation

22 kJ/mol, 1406 kg/m^3, 9–16wt%, 0% H_2 combusted, $\Delta T=35°C$

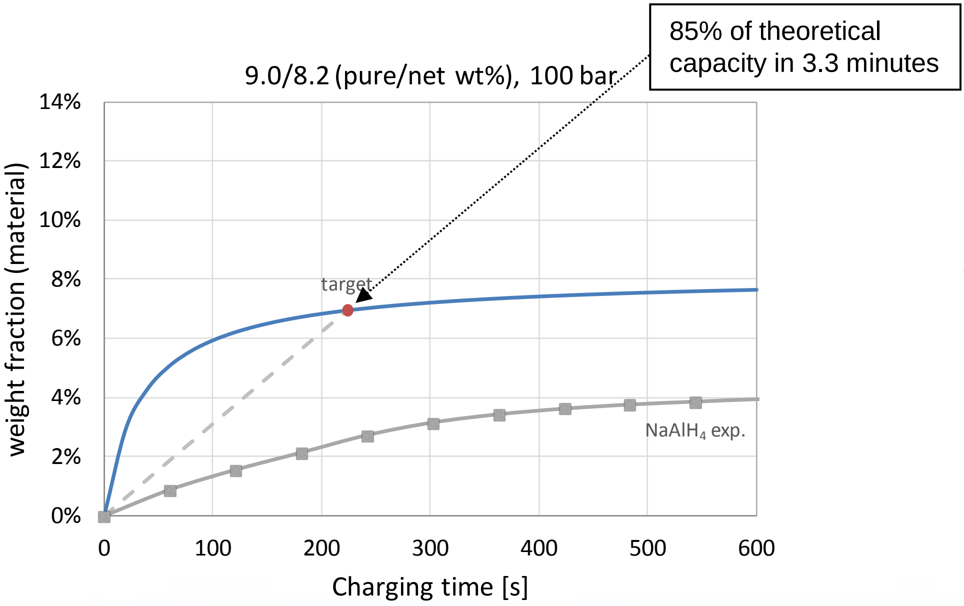
Kinetic expression

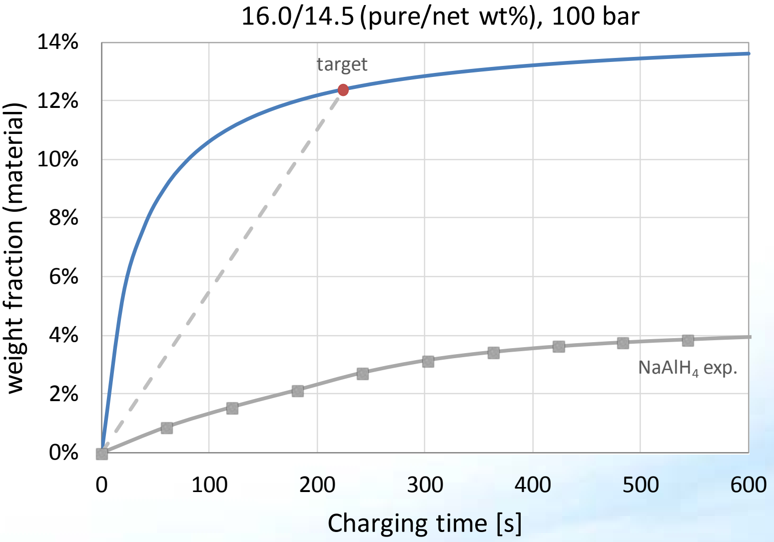
$$\frac{dwf}{dt} = -\operatorname{sgn}\left(\frac{wf}{wf_{\text{full}}} - x_{\text{sat}}\right) wf_{\text{full}} A e^{-E_a/RT} \left|\ln\left(\frac{P}{P_{\text{sat}}(T)}\right)\right| \left|\frac{wf}{wf_{\text{full}}} - x_{\text{sat}}\right|^{\chi}$$

wf = weight fraction

$x_{\text{sat}} = 1$ if $P > P_{\text{sat}}$ and $x_{\text{sat}} = 0$ if $P < P_{\text{sat}}$

Note – Simulation kinetic charge rate to 3.3 minute target is approx 3 to 6 times SAH*

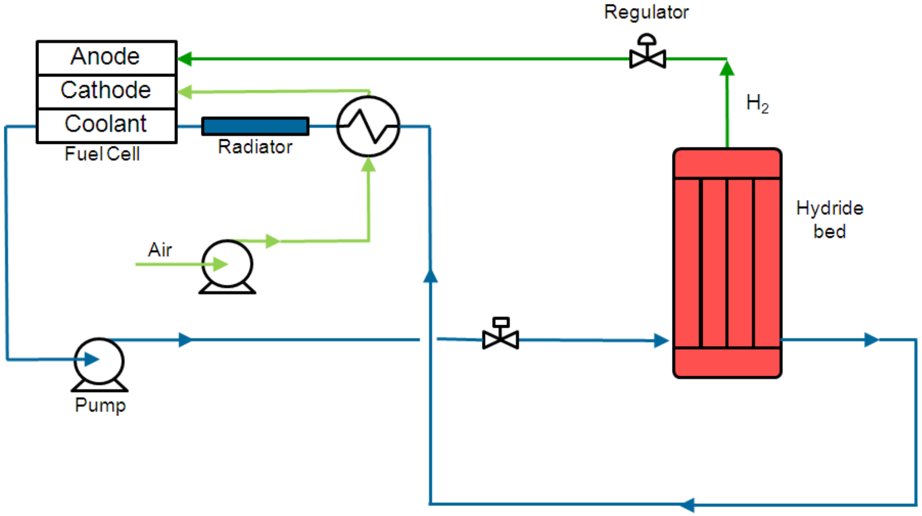

85% of theoretical capacity in 3.3 minutes

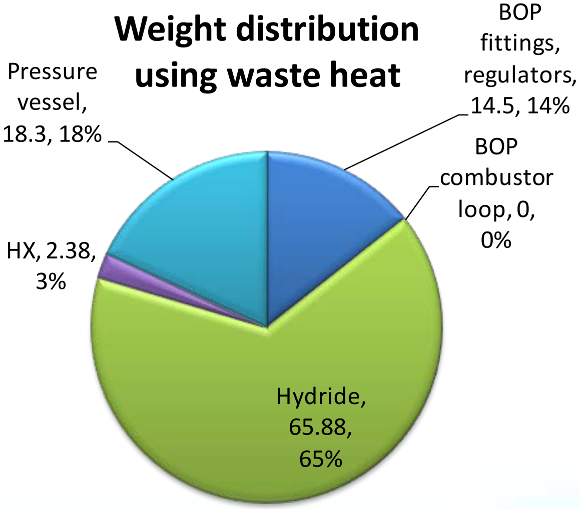


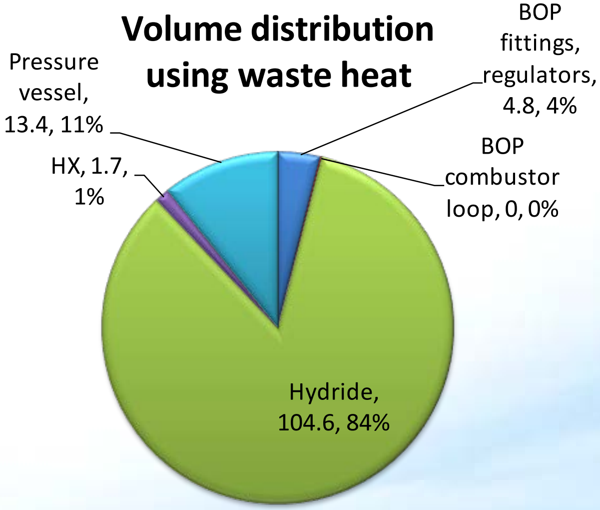
* SAH kinetic data, experimental data measured during HSECoE project and reported at AIChE conference by UTRC.

Metal Hydride System 1: Use Waste Heat Only

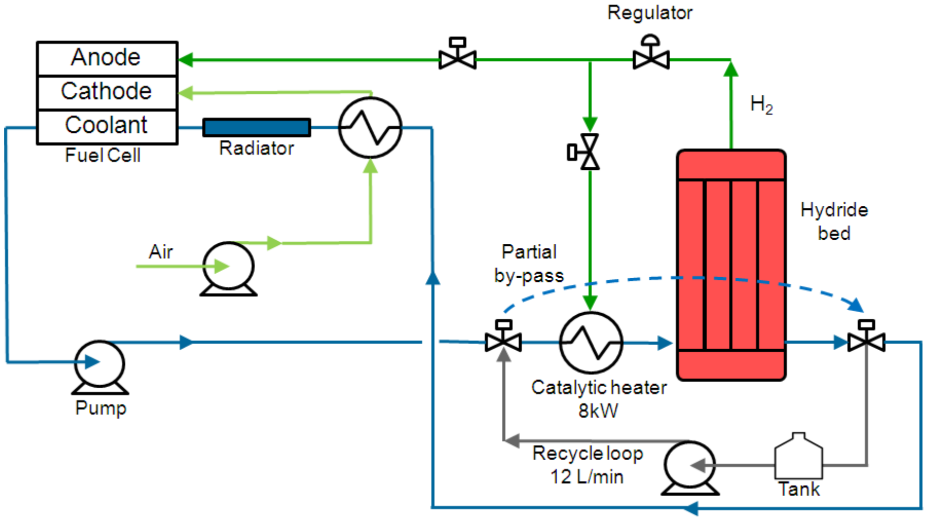
- Attributes
  - Very simple system.
  - Fuel cell waste heat stream used
  - No separate buffer tank: use H_2 in pores.
- Media Characteristics
  - $\Delta H = 27$ kJ/mol-H_2 ($T_{5\ bar} = 20.7\ ^oC$)
  - **11 wt.% pure material capacity**
- Results
  - Satisfies all targets.
  - On-board efficiency: ~100%
  - System: 101 kg, 124 liters



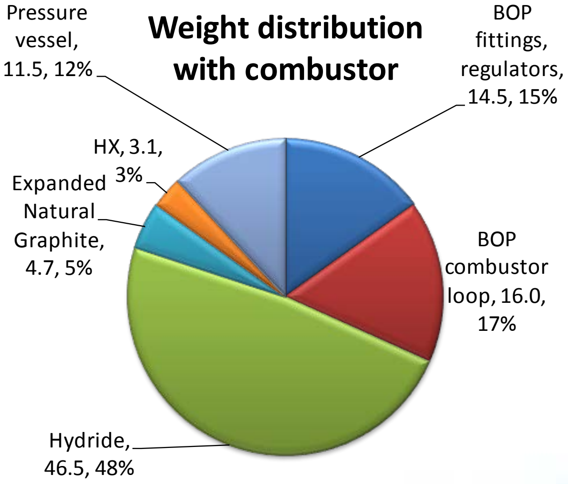


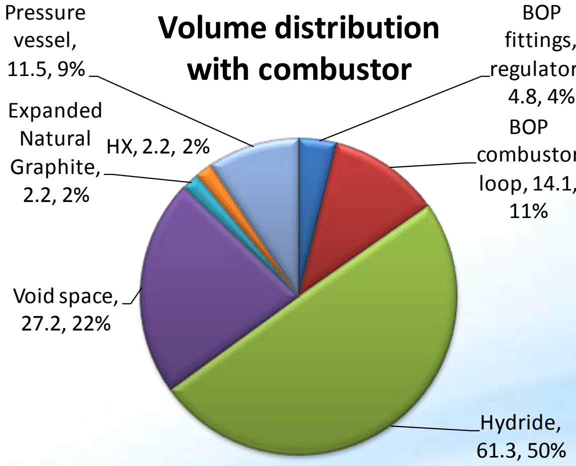


Metal Hydride System 2: Combust Some H_2

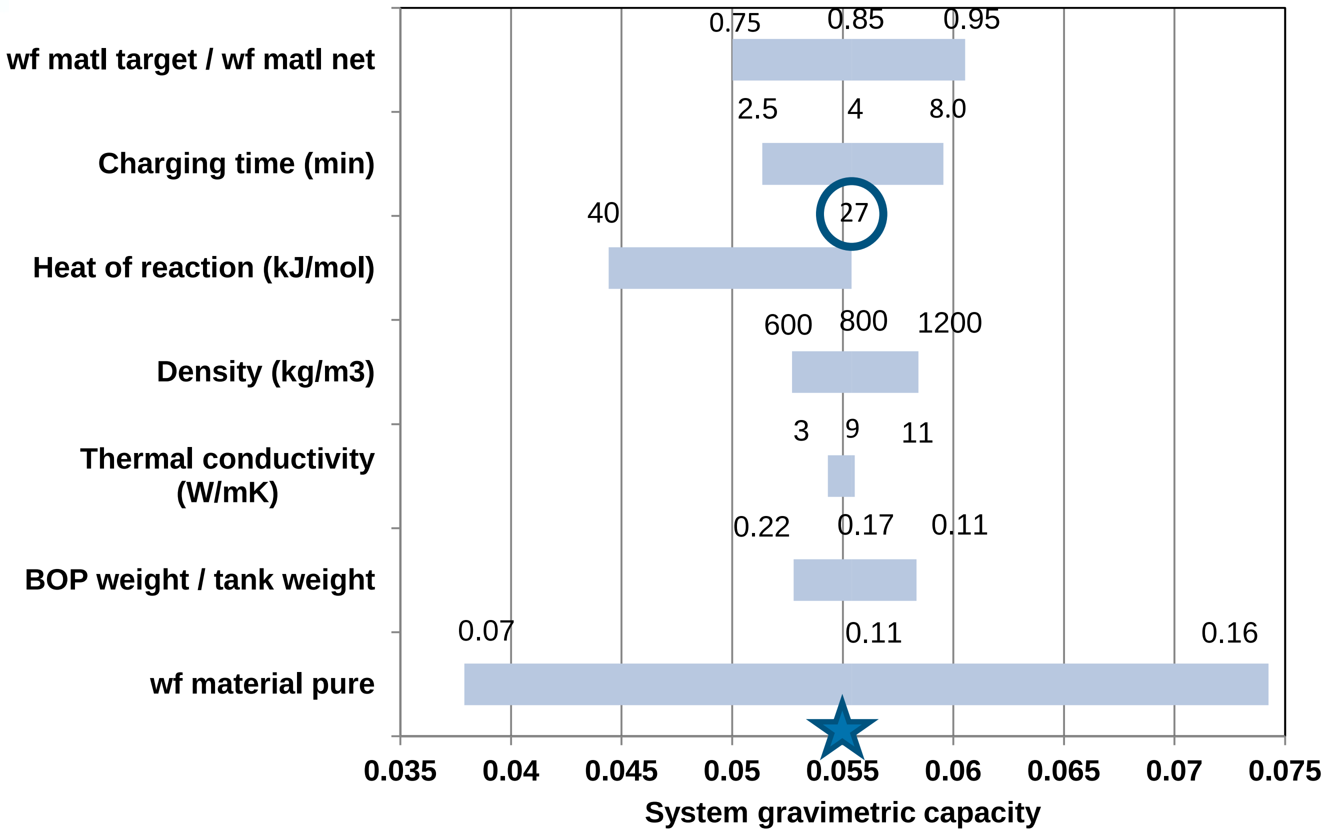


- Attributes
  - Mix of fuel cell coolant and recycled fluid used for warm-up and to maintain T_{tank}.
  - No separate buffer tank: use H_2 in pores.
- Media Characteristics
  - $\Delta H = -40$ kJ/mol-H_2 ($T_{5\ bar} = 122.8\ ^oC$)
  - **17 wt.% pure material capacity**
- Results
  - Satisfies all targets except on-board system efficiency.
  - On-board efficiency: ~81%
  - System: 103 kg, 126 liters
  - Operating at 130°C delivers 5.4 kg-H_2 (delivered + combusted: 6.6 kg-H_2)

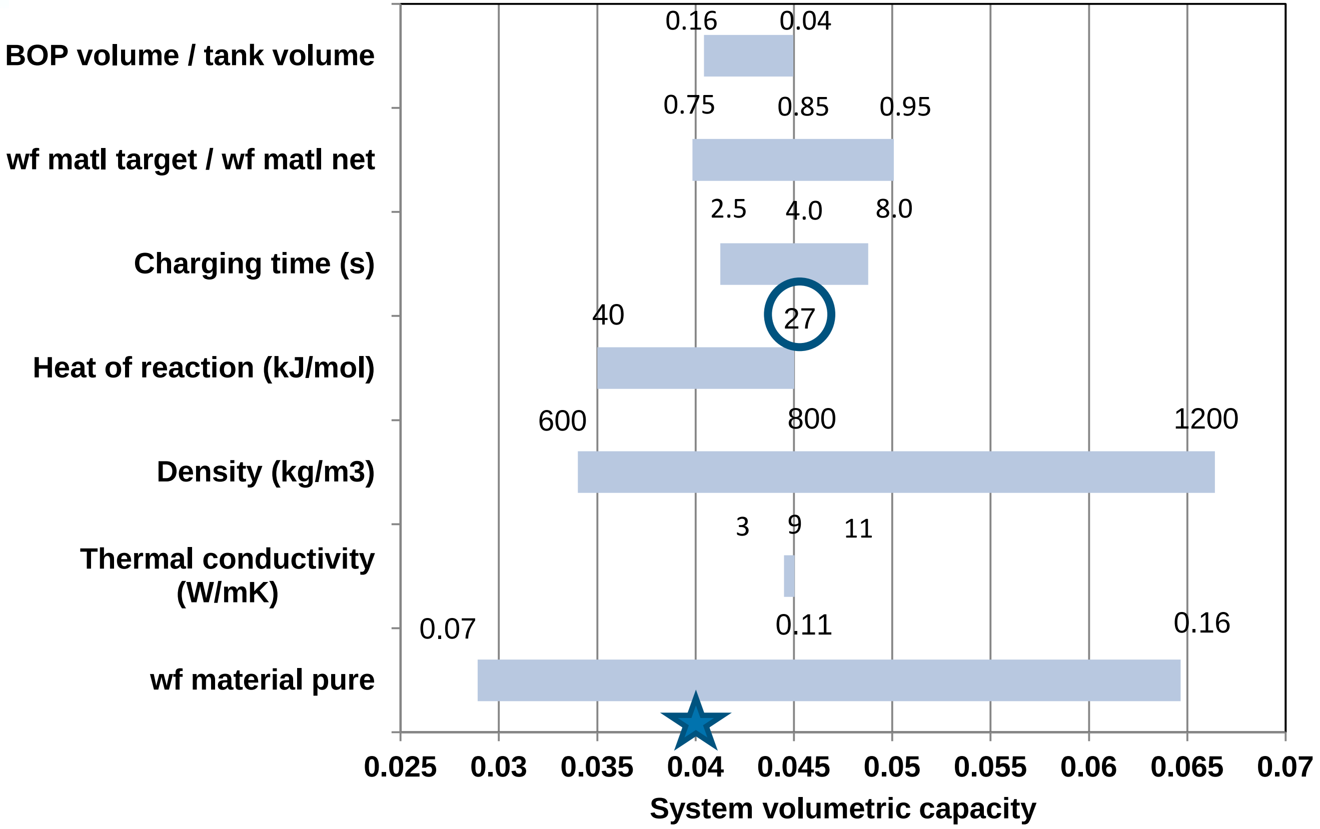




Sensitivity Analysis: System Gravimetric Capacity



Sensitivity Analysis: System Volumetric Capacity



Ideal MH Summary and Conclusions

- A material will need reasonably fast charging kinetics (3-8X better than SAH), preferably at moderate pressures (~ 100 bar).
- Any additional hydrogen capacity (1 to 1.5 wt%) gained by using higher pressure, hybrid tanks would be negated by the additional weight associated with the additional carbon fiber needed to reinforce the tank walls.
- For many material densities (>1100 to 1600 kg/m^3)* – the volumetric target can be easily met if the gravimetric target is met
- A minimum material H_2 capacity to meet the DOE 2017 Targets is 11 wt% (with no hydrogen combusted i.e. $\Delta H < 27$ kJ/mol-H2)
- For materials with a higher ΔH (some H_2 combustion required i.e. >30 kJ/mol-H2) a minimum material capacity would need to be approx. 17wt%

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* assumes a bulk or packed density of at least 800 kg/m^3 with a bed void fraction of 0.5 to 0.7

Metal Hydrides vs 700 bar Compressed H2 Performance (similar to “Ideal MH Study)

Objective:

- Determine the material requirements needed for a MH material to meet the 700 bar compressed gas performance.

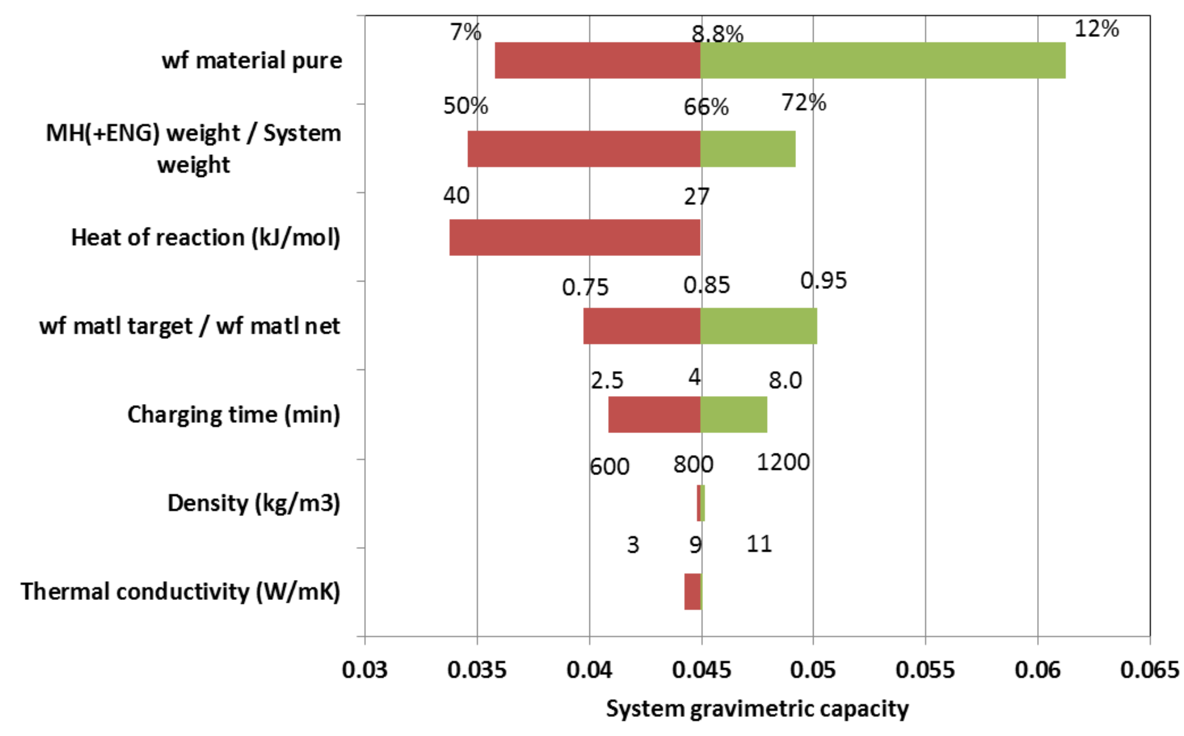
Based on previous “Ideal” MH Study and private discussions and analyses with Dr. Claudio Corgnale, December, 2014

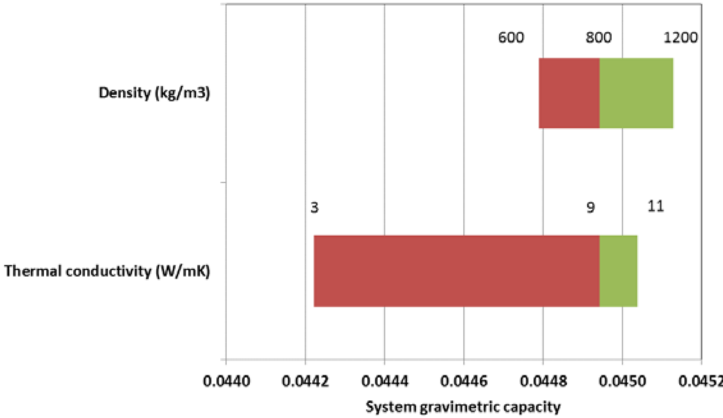
MH Analysis Assumptions

- **Baseline material data and assumed degrees of freedom**
  - **Bulk Density = 800 kg/m³ ***
  - **Thermal conductivity = 9 W/mK ***
  - **ΔH = 27 kJ/molH2 → No need for burner ***
    - Sensitivity analysis with ΔH = 40 kJ/molH2 → burner included in the BOP equipment *
  - **Max temperature difference inside the MH material ΔT = 40°C, based on the kinetics law assumed and reported in Reference ***
  - **Void fraction = 0.5**
  - **Charging time = 4 min**
  - **ENG weight % = 10%**
  - **Target MH weight capacity = 85% net MH weight capacity (including ENG)***
  - **Low pressure storage → gaseous H2 negligible**
- **Further system assumptions and inputs**
  - **Weight ratio (MH+ENG/system) = 66%***
  - **Volume ratio (MH+ENG/system) = 59%***
    - Sensitivity analyses carried out with values of weight and volume ratio down to about 50% to account for possible additional equipment
- **Unknown quantity**
  - **MH weight capacity (pure MH material) to meet the 700 bar gas performance (system weight capacity of 4.5%; system volume capacity of 0.025 kg H2/l)**

* Pasini JM, Corgnale C, van Hassel B, Motyka T, et at ‘Metal hydride material requirements for automotive hydrogen storage systems’ Int J Hydrogen Energy, 38 (23), 2013, 9755–9765

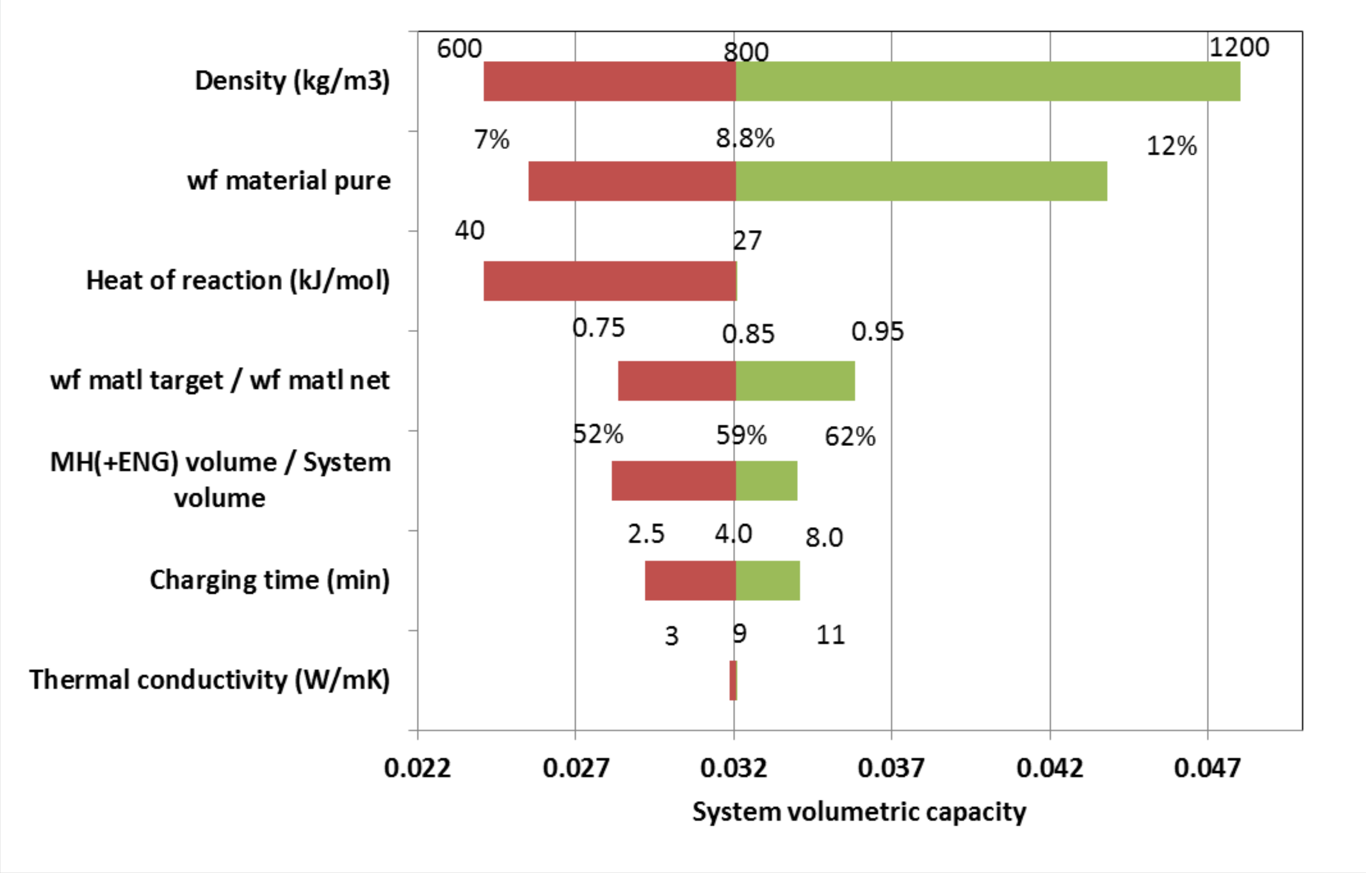
Sensitivity Analysis - Gravimetric





- **MH material wt% of 8.8% needed to meet 700 bar gravimetric capacity**

Sensitivity Analysis - Volumetric



- **MH can reach a volumetric capacity (0.032 kg/l) about 28% higher than the 700 bar tank at the baseline MH weight capacity (8.8%)**
- **MH can achieve the 700 bar volume capacity (0.025 kg/l) at a weight capacity about 20% lower than the baseline value (8.8% or about 7%)**

Summary and Conclusions of 700 bar Comparison Study

- A minimum material H_2 capacity to meet the 700 bar gas performance is about 8.8 wt%.
- For most reasonable bulk material densities (on the order of 800 kg/m^3) – the volumetric 700 bar values can be met if the gravimetric value is met.
- The gravimetric target is heavily influenced by material H_2 capacity but also by the material/system weight fraction.
- The volumetric values are heavily influenced by the material density.
- Also assumes ΔH = 27 kJ/molH2 (no burner needed) and that the material is highly reversible and has reasonably fast kinetics, especially to charge in 3-4 minutes.