

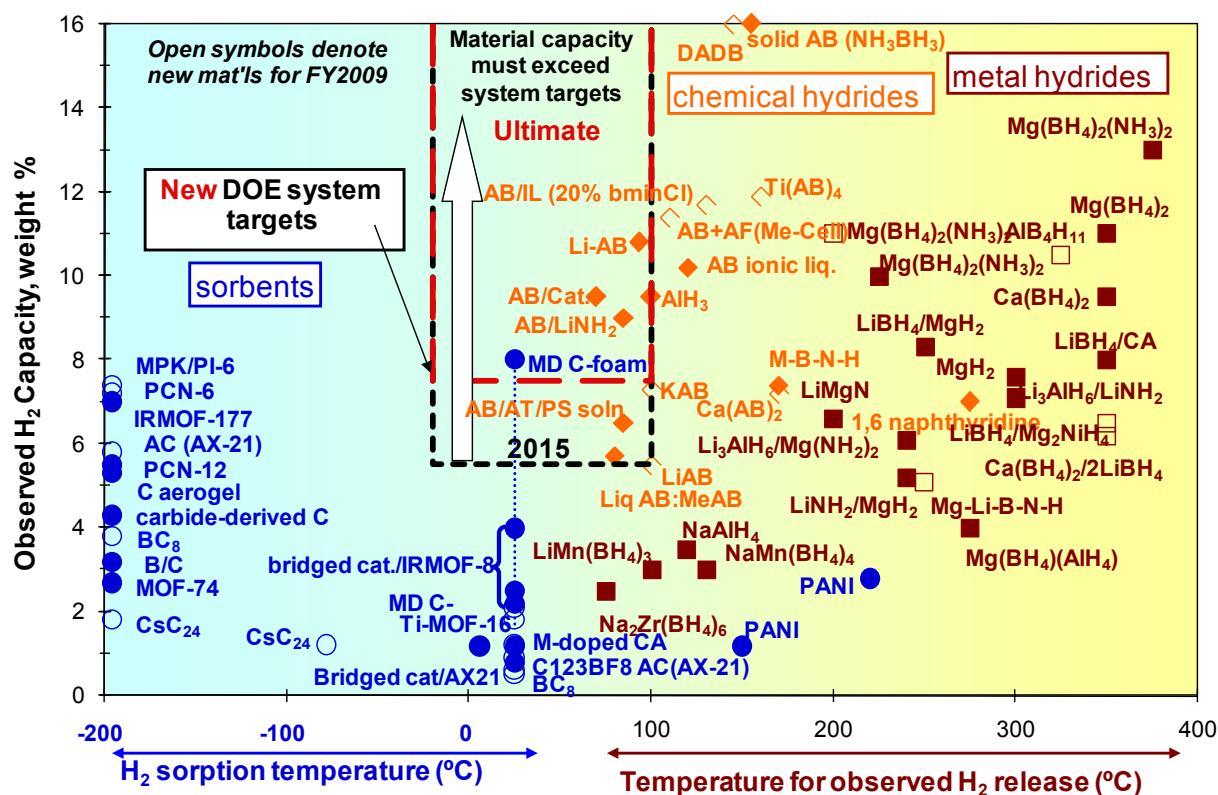
DOE Hydrogen and Fuel Cells Program Record	
Record #: 9014	Date: December 02, 2009
Title: Hydrogen Storage Materials: 2007 – 2009	
Originator: Robert C. Bowman, Ned T. Stetson	
Approved by: Sunita Satyapal	Date: December 02, 2009



Item:

This record summarizes the status of hydrogen (H₂) storage capacities that were determined for materials investigated between 2007 and 2009 within the Hydrogen Storage sub-program. Figure 1 shows the current status of materials development in terms of their gravimetric (in wt.%) capacities for just the materials themselves as a function of H₂ release or uptake temperature. The system targets for weight and temperatures as recently revised [1] for the 2015 and ultimate metrics are the areas enclosed by dashed lines in Figure 1. The arrow within the “windows” defined by these dashed lines is used to illustrate that storage capacities for the materials alone must be substantially greater than the system targets in order to meet the overall system weight requirements. Although some materials lie within the windows, other requirements (e.g. kinetics, reversibility, etc.) have not been met.

Figure 1. Hydrogen Storage Gravimetric Capacity Versus Temperature for Different Materials.



Background:

The hydrogen storing materials are separated into three broad categories:

- Chemical Hydrides (i.e., Hydrogen containing materials with strong chemical bonding exhibiting “irreversible” H₂ release that usually require catalysts for desorption. These materials typically involve off-board regeneration, requiring chemical reactions and/or high pressure/temperature.).
- Metal Hydrides (i.e., Materials that absorb hydrogen within the host itself by the disassociation of H₂ molecules and usually exhibit “reversible” reactions with H₂ gas under moderate conditions of temperature and pressure that can be done on-board. These materials are typically limited by slow kinetics and the need for high temperatures for desorption of hydrogen).
- Sorbents (i.e., Hydrogen storage is primarily via physisorption of H₂ species with rather weak bonding that generally permits storage only at much lower “cryogenic” temperatures. Volumetric capacities of these materials are typically very limited at ambient temperatures).

There are also some “borderline” materials with behavior intermediate between any two of these categories. One example would be porous nanocrystalline materials with selective metal catalysts (i.e., Pt or Pd) where the “hydrogen spillover mechanism” promotes disassociation of the H₂ molecules to form C-H chemical bonds in addition to altering the physisorption process [2], which potentially enhances storage capacities at ambient temperature but can also include penalties with the desorption behavior and kinetics [3].

Data Sources, Assumptions, and Current Status:

Since 2006, numerous new materials have been developed and the performance of previously identified materials improved through the materials Centers of Excellence (CoE) and independent projects of DOE’s Hydrogen Storage sub-program. The hydrogen capacities in Figure 1 are (with the exception of MgH₂ and NaAlH₄ as noted in Table 1) from these projects where all capacities are derived from experimental studies that used either volumetric or gravimetric methods [4] to determine the amount of hydrogen taken up or released by each material. It should be emphasized that these reported capacities are for the material alone and would be reduced significantly (i.e., often by a factor or two or more) for storage system level capacities (See the DOE/FreedomCAR targets [1]) that will include contributions from the storage media, containment vessel, and all balance-of-plant components necessary for a vehicular system. In addition, much more R&D is needed to modify the properties of high hydrogen capacity materials to meet the required range of operating temperature and pressure. For some materials, the limitations in temperature are mainly due to their thermodynamics (e.g., enthalpies or binding energy that are either too high or too low) while in many cases the kinetic rates are too slow at the desired operating temperatures. For hydrides in general, the optimal scenario would be to use the waste heat from the fuel cell powerplant for the endothermic desorption of hydrogen from the storage material without the need for burning released H₂ to produce the necessary elevated temperatures for those reactions with greater binding energies, or to enhance reaction kinetics. While a nominal release temperature is used for each material

plotted in Figure 1, there is typically a temperature range across which hydrogen is discharged or charged that can sometimes be altered by additives or catalysts.

The values of gravimetric capacities and release temperatures for the materials presented in Figure 1 are given along with some other key parameters in Tables 1-3 located at the end of this record. The metal hydrides, chemical hydrides, and sorbents are given in Table 1, Table 2, and Table 3, respectively. The original data contained in these tables were, with the two exceptions noted, compiled from the on-line Proceedings of the DOE Hydrogen Program's Annual Merit Reviews (AMR) [5] and Annual Progress Reports (APR) [6] along with other publications issued by DOE or published in peer-reviewed journal articles. The theoretical weight capacities of most hydrides listed in Tables 1 and 2 usually assumed that their entire hydrogen content is released except when decomposition products include highly stable phases (i.e., LiH, NaH, CaH₂, etc.). In this case, a corresponding portion of the hydrogen is retained by the storage material. Partial or total lack of reversibility at moderate pressure (i.e., < 150 bar) and temperature (i.e., < 350 °C) conditions has been found for many of the potentially high content hydrides as noted in Table 1.

Because the adsorption capacities of porous materials are usually quite dependent on their surface areas and the applied H₂ pressure, these parameters are included in Table 3 when available from the original sources. Since some of the sorption materials were evaluated using either small or incompletely characterized samples, rather large errors in reported capacities are possible as described more thoroughly by Gross and Carrington [4]. Furthermore, for all materials, results can be misleading when H₂ desorption is into vacuum or flowing inert gases, which are usually poor approximations to the "equilibrium" desorption for release into an overpressure of H₂ gas. Finally, hydrogen contents can be seriously overestimated if weight losses are solely attributed to H₂ evolution when heavier species (e.g., H₂O, NH₃, CH₄, B₂H₆, etc.) are significant components in the decomposition products [4]. In the DOE program, efforts are generally taken to ensure results are given only for H₂ desorption; however, some researchers have reported measurements without fully accounting for possible impurity species. Additional studies are needed to see whether these materials are truly viable candidates for storage.

To help accelerate progress in the identification and development of the most promising candidates, each of the materials COEs has conducted down-selection assessments eliminating the less promising materials against performance criteria. The Metal Hydride CoE (MHCoE) made a first series of down selects in 2007 [7] with a second one conducted in early 2009 [8]. Further work on more than 50 % of the evaluated materials was terminated due to reasons such as limited reversibility, too large enthalpies, too slow kinetics, or excessive impurities (i.e., NH₃, B₂H₆, etc.). The Go/No-Go status imposed on various hydrides by the MHCoE are included in Table 1. A down selection [9] was performed in 2008 by the Chemical Hydrogen Storage CoE (CHSCoE) using criteria that included the efficiency of regenerating the spent fuel in addition to capacities, release kinetics, and high release temperatures. Table 2 shows the Go/No-Go status of the CHSCoE materials that have been evaluated to date. In 2009 the Hydrogen Sorption CoE (HSCoE) completed its down-select process [10] that discontinued efforts on various candidates where a number of theoretically predicted systems could not be synthesized or else had capacities or adsorption binding energies which were too low. The status of the materials evaluated by HSCoE is shown in Table 3. Note that some entries in Tables 1 – 3 are listed as TBD. As R&D progresses, these results will be updated.

References:

- [1] DOE Targets for On-Board Hydrogen Storage Systems for Light-Duty Vehicles, February 2009, published on DOE/EERE Program website:
http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf
- [2] L. Wang and R. T. Yang, “New sorbents for hydrogen storage by hydrogen spillover – a review”, *J. Energy Environ. Sci.* **1** (2008) 268-279.
- [3] C. I. Contescu, et al., “Detection of hydrogen spillover in palladium-modified activated carbon fibers during hydrogen adsorption”, *J. Phys. Chem. C* **113** (2009) 5886-5890.
- [4] K. J. Gross and K. R. Carrington, “Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials”, December 2008, published on DOE/EERE Program website:
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/bestpractices_h2_storage_materials.pdf
- [5] DOE Hydrogen Program Annual Merit Review and Peer Evaluation, Proceedings published on the DOE Program website: http://www.hydrogen.energy.gov/annual_review.html
- [6] DOE Hydrogen Program Annual Progress Reports, published on the DOE Program website: http://www.hydrogen.energy.gov/annual_progress.html
- [7] L. Klebanoff, “Materials Go/No-Go Decisions Made Within the Department of Energy Metal Hydride Center of Excellence (MHCoe)”, September/October 2007, published on DOE/EERE Program website:
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/mhcoe_materials_downselect_report_fy07.pdf
- [8] L. Klebanoff, Metal Hydride Center of Excellence, DOE Hydrogen Program Annual Merit Review, Arlington VA, May, 2009, published on DOE Program website:
http://www.hydrogen.energy.gov/pdfs/review09/st_01_klebanoff.pdf
- [9] K. C. Ott, S. Linehan, F. Lipiecki, C. L. Aardahl, “Down Select Report of Chemical Hydrogen Storage Materials, Catalyst, and Spent Fuel Regeneration Processes”, May, 2008,, published on DOE/EERE Program website:
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/chs_coe_down_select.pdf
- [10] L. Simpson, “Materials Go/No-Go Recommendation Document” – November 30, 2009.

Table 1. Metal Hydrides: Summary of gravimetric capacities of materials (**NOT** system capacities) from indicated reference sources along with their reported reversibility and R&D status from MHCoe down selections.

metal hydrides	theor.wt.%	obs. wt.%	rel. temp. (°C)	reference source ¹	Organization	Reversible	Status
Mg(BH ₄) ₂	14.8	11	350	sl 18 FY07 ST-16	GE-GRC	Partial	Go
Mg(BH ₄) ₂ (NH ₃) ₂	16	10	225	sl 14 FY07 ST-16	GE-GRC	Partial	Go
Mg(BH ₄) ₂ (NH ₃) ₂	16	13	375	sl 14 FY07 ST-16	GE-GRC	Partial	Go
Mg(BH ₄)(AlH ₄)	11.4	4	275	sl 17 FY07 ST-16	GE-GRC	No	TBD
Ca(BH ₄) ₂	11.5	9.5	350	sl 9&10 FY07 ST-15	SNL	Partial	No-Go
LiMn(BH ₄) ₃	10.4	3	100	sl 10 FY07 ST-19	UH	No	No-Go
LiBH ₄ /C aerogel	10	8	350	sl 8&10 FY07 ST-18	HRL	Yes	Go
MgH ₂	7.6	7.6	300	hydride database ²	N/A	Yes	TBD
LiNH ₂ -MgH ₂	5.6	5.2	240	sl 19 FY07 ST-21	Utah	Yes	No-Go
NaAlH ₄	5.6	3.5	119	hydride database ²	N/A	Yes	No-Go
Li ₃ AlH ₆ /Mg(NH ₂) ₂	6.5	6.1	240	sl 19 FY07 ST-21	Utah	Yes	Go
Li ₃ AlH ₆ /LiNH ₂	7.3	7.1	300	sl 19 FY07 ST-21	Utah	Yes	No-Go
LiBH ₄ /MgH ₂	11.4	8.3	250	sl 22, FY08 ST-14	U.Conn	Yes	No-Go
LiMgN	8.2	6.6	200	sl 13 FY08 ST-29	CoE/Utah	Yes	Go
NaMn(BH ₄) ₄	11	3	130	sl 8 FY08 ST38	UH	No	No-Go
Na ₂ Zr(BH ₄) ₆	9.8	2.5	75	sl 8 FY08 ST38	UH	No	No-Go
AlB ₄ H ₁₁	13.5	10.5	325	sl 13 FY09 STP-42	OSU/JPL/ORNL	Partial	Go
Ca(BH ₄) ₂ +2LiBH ₄	6.7	6.2	350	sl 13 FY09 ST-03	SNL	Partial	TBD
Mg-Li-B-N-H	TBD	5.1	250	sl 23 FY09 STP-45	USF/SWRI	Yes	TBD
Al(BH ₄) ₃ -NH ₃	TBD	11	200	sl 8, FY09 STP-37	ORNL	TBD	Go
Mg ₂ NiH ₄ +4LiBH ₄	8.3	6.5	350	sl 20 FY09 ST-09	HRL	Yes	Go

¹The reference sources primarily refer to presentations given at DOE's Annual Merit Reviews (e.g., sl 18 FY07 AMR ST-16 denotes Slide #18 from Fiscal Year 2007 Annual Merit Review presentation ST-16) on the DOE website: http://www.hydrogen.energy.gov/annual_review.html

²Hydride Information Center on the Sandia National Laboratories website: <http://hydpark.ca.sandia.gov/>

Table 2. Chemical Hydrides: Summary of gravimetric and volumetric capacities of materials (**NOT** system capacities) from indicated reference sources along with R&D status from CHSCoe down selections.

chemical storage	theor.wt.%	obs. wt.%	rel. temp. (°C)	Vol. dens. (gH ₂ /L)	reference source ¹	Organization	Status
solid AB	19.4	16	155	48	sl 20&26 FY07 ST-28	PNNL	Go
liq. AB/cat. (AB:MeAB)	10.5	5.7	80	60	sl 10 FY07 ST-29	LANL	TBD
M-B-N-H (IPHE)	10	7.4	170	72	sl 21 FY07 ST-29	LANL	TBD
AlH ₃	10	9.5	100	143	sl 19 FY07 ST-20	BNL	Go
AB/LiNH ₂	TBD	9	85	76	sl 14 FY07 ST-27	UPenn	No-Go
Li-AB	TBD	10.8	93	TBD	sl 8, FY08 ST-5	PNNL	Go
AB ionic liquid	TBD	10.2	120	86	sl 10 FY08 ST-7	Penn	TBD
AB/AT/PS solution	TBD	6.5	85	60	sl 17-18 FY07 ST-27	Penn	TBD
1,6 naphthyridine	7.1	7	275	70	sl 14 FY07 ST-23	APCI	No-Go
AB/cat.	TBD	9.5	70	TBD	sl 11, FY08 ST-6	LANL	TBD
AB/IL (+20% bminCl)	TBD	11.4	110	95	sl 16, FY09 ST-16	Penn	TBD
AB + AF (methyl cellulose)	15.5	11.7	130	102	sl 28, FY-09 ST-18	PNNL	TBD
DADB	19.4	16	145	TBD	sl 28, FY-09 ST-18	PNNL	TBD
KAB	7.4	7.3	100	TBD	sl 8&10, FY-09 ST-17	LANL	TBD
Ca(AB) ₂	10.1	7.2	170	TBD	p.27, Reference 8	CHSCoe	TBD
Ti(AB) ₄	12.1	11.9	160	TBD	p.27, Reference 8	CHSCoe	Go
LiAB	13.7	5.5	100	52	sl 18, FY-09 ST-15 & sl 28, FY-09 ST-18	CHSCoe	Go

¹The reference sources primarily refer to presentations given at DOE's Annual Merit Reviews (e.g., sl 10 FY07 AMR ST-29 denotes Slide #10 from Fiscal Year 2007 Annual Merit Review presentation ST-29) on the DOE website: http://www.hydrogen.energy.gov/annual_review.html

Table 3. Hydrogen Sorbents: Summary of gravimetric and volumetric capacities of adsorbent materials (**NOT** system capacities) from indicated reference sources along with applied H₂ pressure and BET surface area (SA) when available. The R&D status from the HSCoE down selections is also shown.

adsorbents	obs. wt.%	rel. temp. (°C)	Vol. dens. (gH ₂ /L)	reference source ¹	Organization	H2 Pressure (bar)	SA (m ² /g)	status
IRMOF-177	7	-196	33	sl 27&28 FY07 ST-10	UCLA	50	~5700	Go
C aerogel	5.3	-196	29.2	sl 7 FY07 ST-6	LLNL/Caltech	30	3200	No-Go
bridged cat/IRMOF8	4	25	40.8	sl 18 FY07 ST-3	U Mich	100	TBD	Go
bridged cat/IRMOF8	2.2	25	TBD	sl 18 FY07 ST-3	U Mich	100	TBD	Go
bridged cat/IRMOF8	2.5	25	TBD	sl 8 FY07 STP-36	SwRI/INER	74	TBD	Go
PANI	2.8	220	TBD	sl 10&11 FY07 STP-2	U Penn	350	TBD	No-Go
PANI	1.2	150	TBD	sl 10&11 FY07 STP-2	U Penn	200	TBD	No-Go
metal doped C aerogel	1.2	25	TBD	sl 16 FY08 ST-24	LLNL/Caltech	100	~2400	Go
bridgedcat/AX21	1.2	5.6	TBD	sl 18 FY07 ST-3	U Mich	100	TBD	Go
carbide derived C	4.3	-196	34	sl 17&18 FY07 ST-9	U Penn	55	2350	TBD
MOF-74	2.7	-196	33	sl 4&15 FY08 ST23	Caltech	30	870	No-Go
PCN-12	5.5	-196	44.9	sl 18 FY08 ST-16	Miami U.	50	1960	Go
B-doped C	3.2	-196	TBD	sl 10 FY08 STP-11	Penn St.	60	TBD	Go
M-doped C-foam	8	25	TBD	sl 13 FY08 ST-28	Greece/SwRI	80	~500	TBD
M-doped C-foam	2.1	25	TBD	sl 13 FY09 STP-45	SwRI	88	TBD	TBD
PANI	0.8	25	TBD	sl 8 FY09 STP-45	UNLV/SwRI	73	TBD	TBD
Ti-MOF-16	1.8	25	TBD	sl 21 FY09 STP-45	SwRI	80	TBD	TBD
BC8	3.8	-196	30.4	sl 18 FY09 STP-29	Penn St.	50	330	Go
BC8	0.5	25	4.2	sl 18 FY09 STP-29	Penn St.	50	330	Go
PCN-6	7.2	-196	40.2	sl 20 FY09 STP-23	TA&M	50	TBD	Go
PCN-6	0.9	25	5.1	sl 20 FY09 STP-23	TA&M	50	TBD	Go
Ru, Pt, Pd-AC	1.2	25	6	sl 20 FY09 ST-26	NREL	80	TBD	Go
MPK/PI-6	7.4	-196	32	sl 12 FY09 STP-03	SUNY	60	3035	TBD
C123BF8 AC (AX-21)	0.6	25	TBD	sl 11 FY09 ST-28	AP&C	100	2390	Go
AC (AX-21)	5.8	-196	25	sl 19 FY09 STP-27	Caltech	60	TBD	TBD
CsC24	1.8	-196	21	sl 9 FY09 STP-27	Caltech	20	TBD	TBD
CsC24	1.2	-78	TBD	sl 9 FY09 STP-27	Caltech	48	TBD	TBD

¹The reference sources primarily refer to presentations given at DOE's Annual Merit Reviews (e.g., sl 7 FY07 AMR ST-6 denotes Slide #7 from Fiscal Year 2007 Annual Merit Review presentation ST-6) on the DOE website: http://www.hydrogen.energy.gov/annual_review.html