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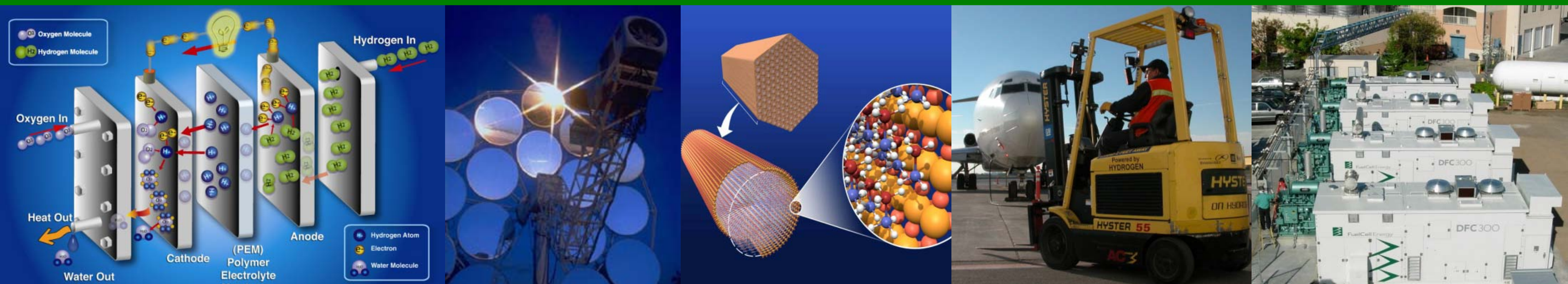

Hydrogen Storage

Ned T. Stetson

2010 Annual Merit Review and Peer Evaluation Meeting

(8 June 2010)

Goal & Objectives

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Goal: On-board hydrogen storage for > 300 mile driving range across different vehicle platforms, without compromising passenger/cargo space or performance

Develop on-board storage systems that meet ***all*** DOE system targets simultaneously.

- **System Engineering / Systems Analysis**
  - Demonstrate the technologies required to achieve the 2015 DOE on-board vehicle hydrogen storage goals
  - Continue storage system analysis/projections for advanced storage system capabilities & development of system models for on-board storage systems
  - Increase emphasis on early market applications
- **Continue R&D on materials for breakthrough storage technologies**
  - Continue new hydrogen storage material discovery R&D for advanced storage systems
  - Strengthen coordination between basic & applied research within DOE and across agencies

Budget

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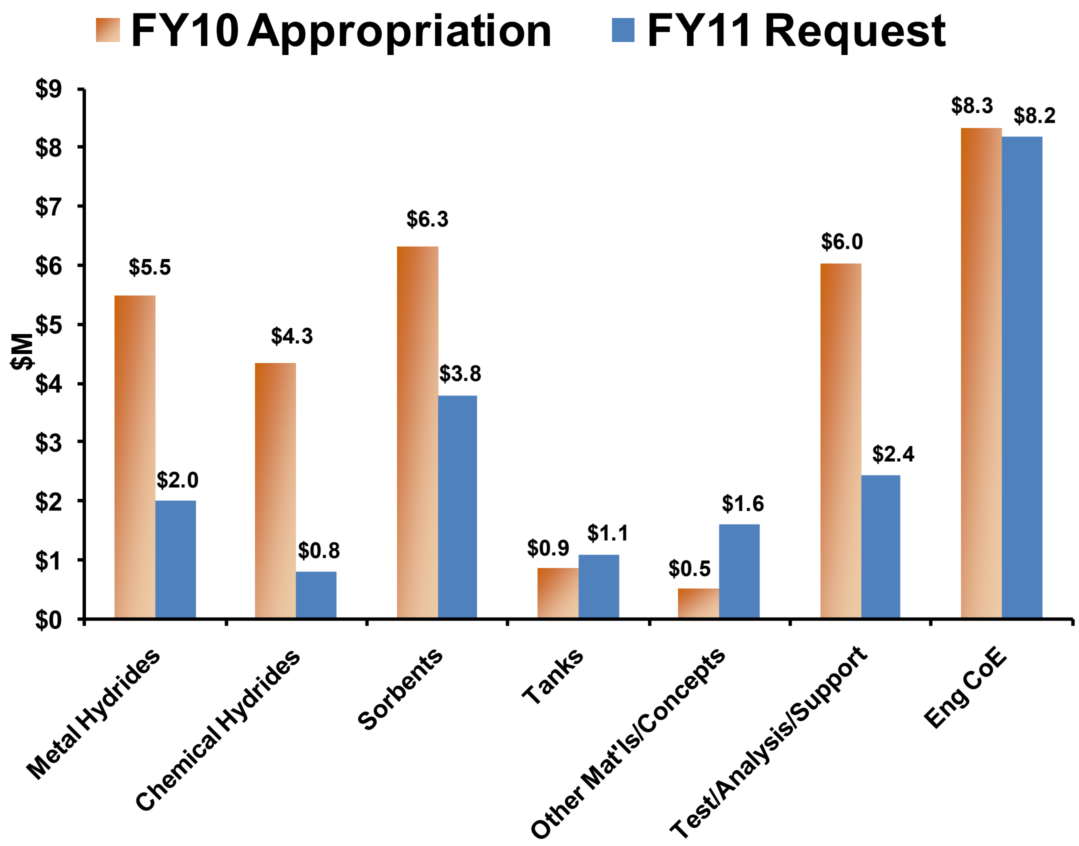
FY 2010 Appropriation = $32.0M
FY 2011 Request = $20.0M



Material Centers are being completed as planned at the end of Fiscal Year 2010

EMPHASIS

- Systems approach through the Engineering CoE, in collaboration with independent materials development projects, to achieve light-duty vehicle targets
- Continued close coordination with Basic Energy Science in 2010 & 2011 and improve coordination with National Science Foundation, Advanced Research Projects Agency - Energy, and Energy Frontier Research Centers activities
- Focus on cost reduction for high pressure tanks
- Increased analysis efforts for low to high production volumes
- Increase emphasis on early market storage applications

Challenges

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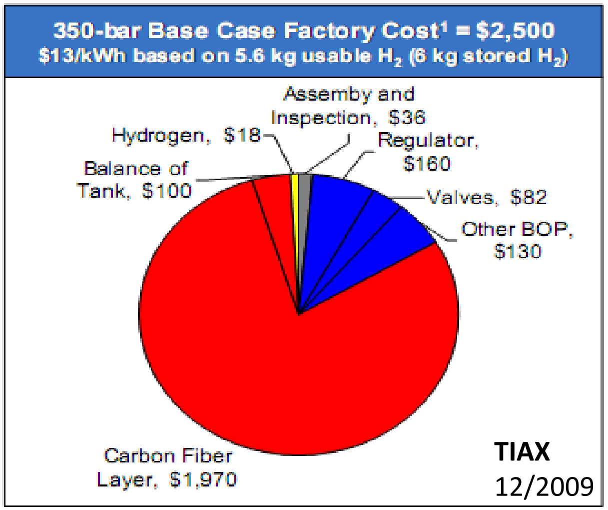
Compressed gas offers a near- term option, but cost is an issue

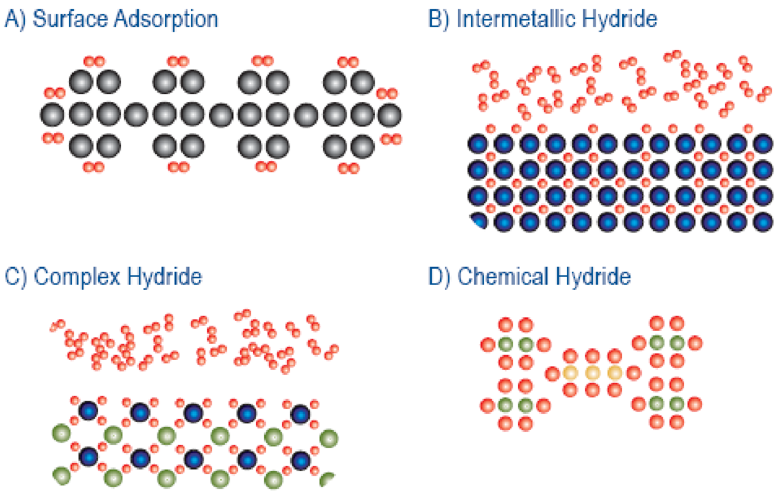
Compressed gas storage offers a near-term option for initial vehicle commercialization and early markets

- **Cost of composite tanks is challenging**
- **> 75% of the cost is projected to be due to the carbon fiber layer**
- **Additional analysis is needed to better understand costs at lower manufacturing volumes**



[1] Cost estimate in 2005 USD. Includes processing costs.

Advanced materials development is still needed for long-term solutions

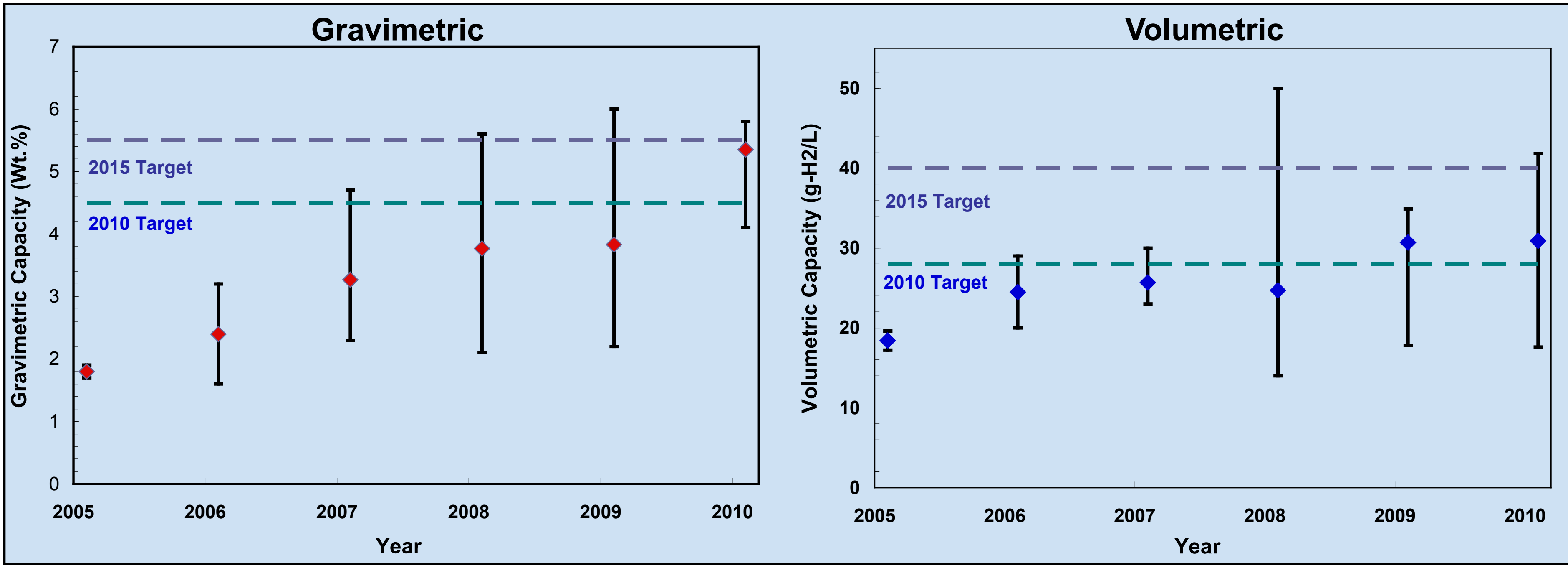


Materials discovery research is still needed for long-term, advanced materials with full set of properties for materials-based hydrogen storage options!

Progress in Storage Capacity

In just *five years* of accelerated investment, DOE has made significant progress in near- and long-term approaches.

Projected Capacities for Complete 5.6-kg H_2 Storage Systems



- *Projections performed by Argonne National Laboratory using the best available materials data and engineering analysis at the time of modeling*
- *Analyses included for:*
  - *Physical storage – liquid, 350 & 700 bar compressed and cryo-compressed*
  - *Materials-based – reversible sorbents and metal hydrides and off-board regenerable chemical hydrogen systems*

However no one system is yet able to meet all targets simultaneously

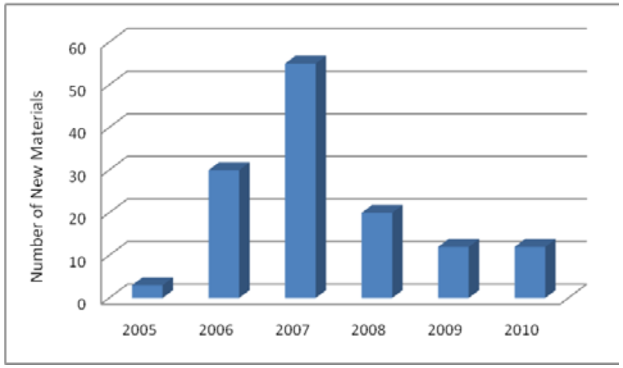
Portfolio Management & Progress

U.S. DEPARTMENT OF ENERGY

Many new material systems have been investigated through the three Materials Centers of Excellence.

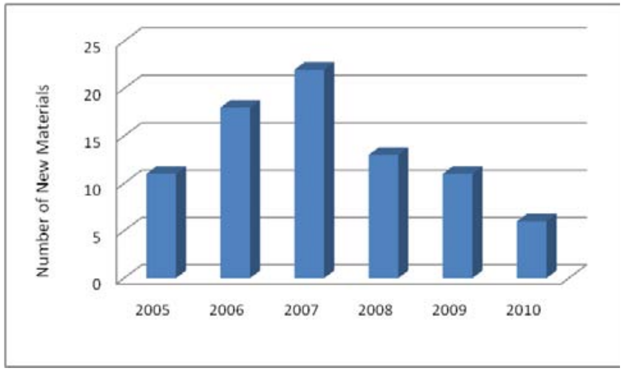
Chemical Hydrogen Storage

> 130 materials/combinations have been examined
~ 95% discontinued
~ 5% still being investigated-Ammonia Borane (AB) solid, ammonium borohydride, or mixture of AB with ionic liquids as liquid fuels



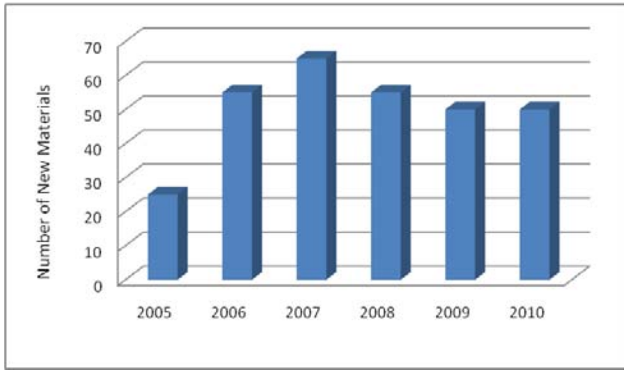
Metal Hydrides

More than 81 distinct material systems assessed experimentally—not including catalyst/additive studies
~ 75% discontinued
~ 25% still being investigated
Computational/theoretical screening done on more than 20 million reaction conditions for metal hydrides



Hydrogen Sorption

~ 210 materials investigated
~ 80% discontinued
~ 20% still being investigated



Hydrogen Storage Materials Database

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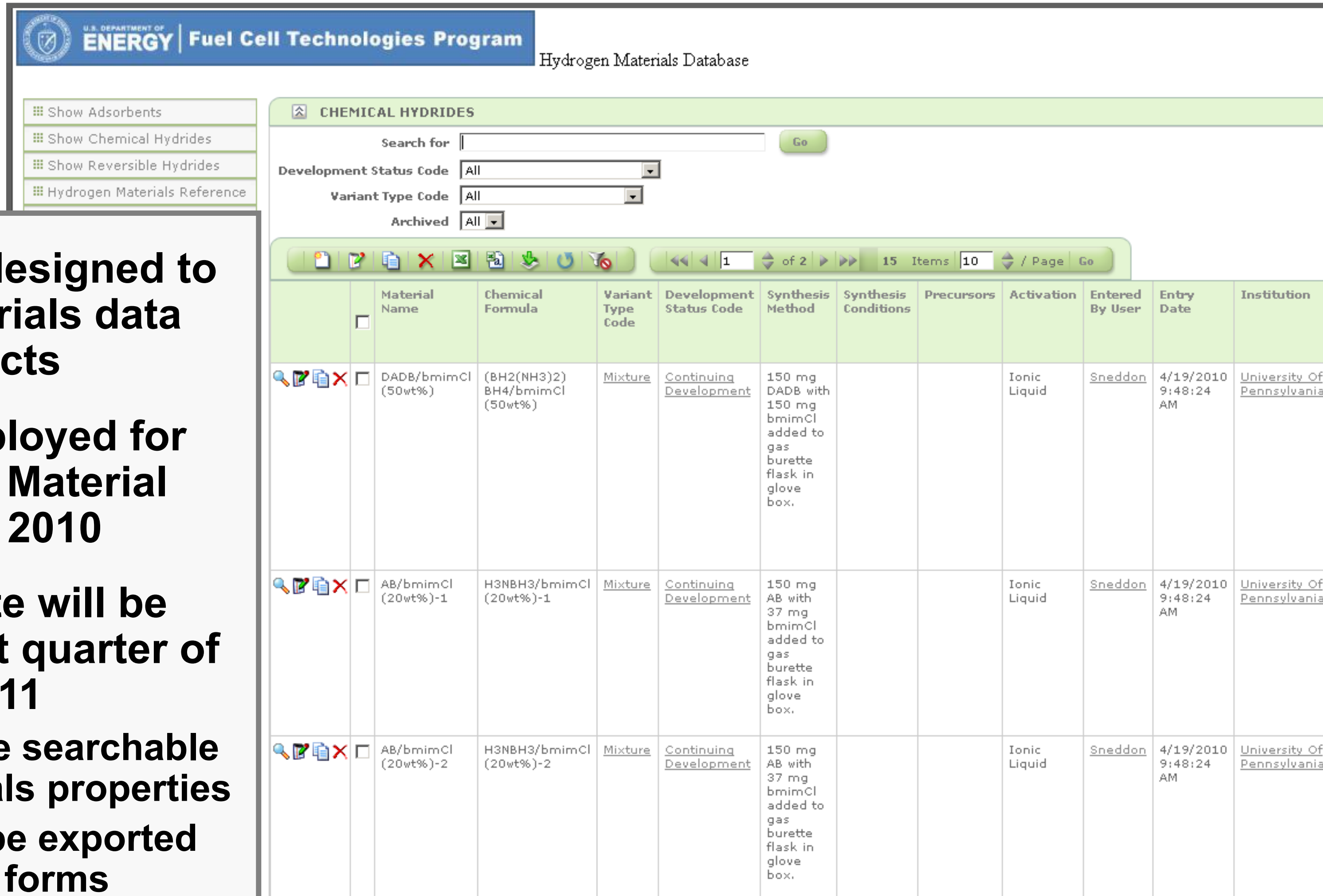
A database has been created to capture materials data from the research projects


Fuel Cell Technologies Program

Hydrogen Materials Database

- Show Adsorbents
- Show Chemical Hydrides
- Show Reversible Hydrides
- Hydrogen Materials Reference

CHEMICAL HYDRIDES

Search for: [ ] Go

Development Status Code: All

Variant Type Code: All

Archived: All

1 of 2 15 Items 10 / Page Go

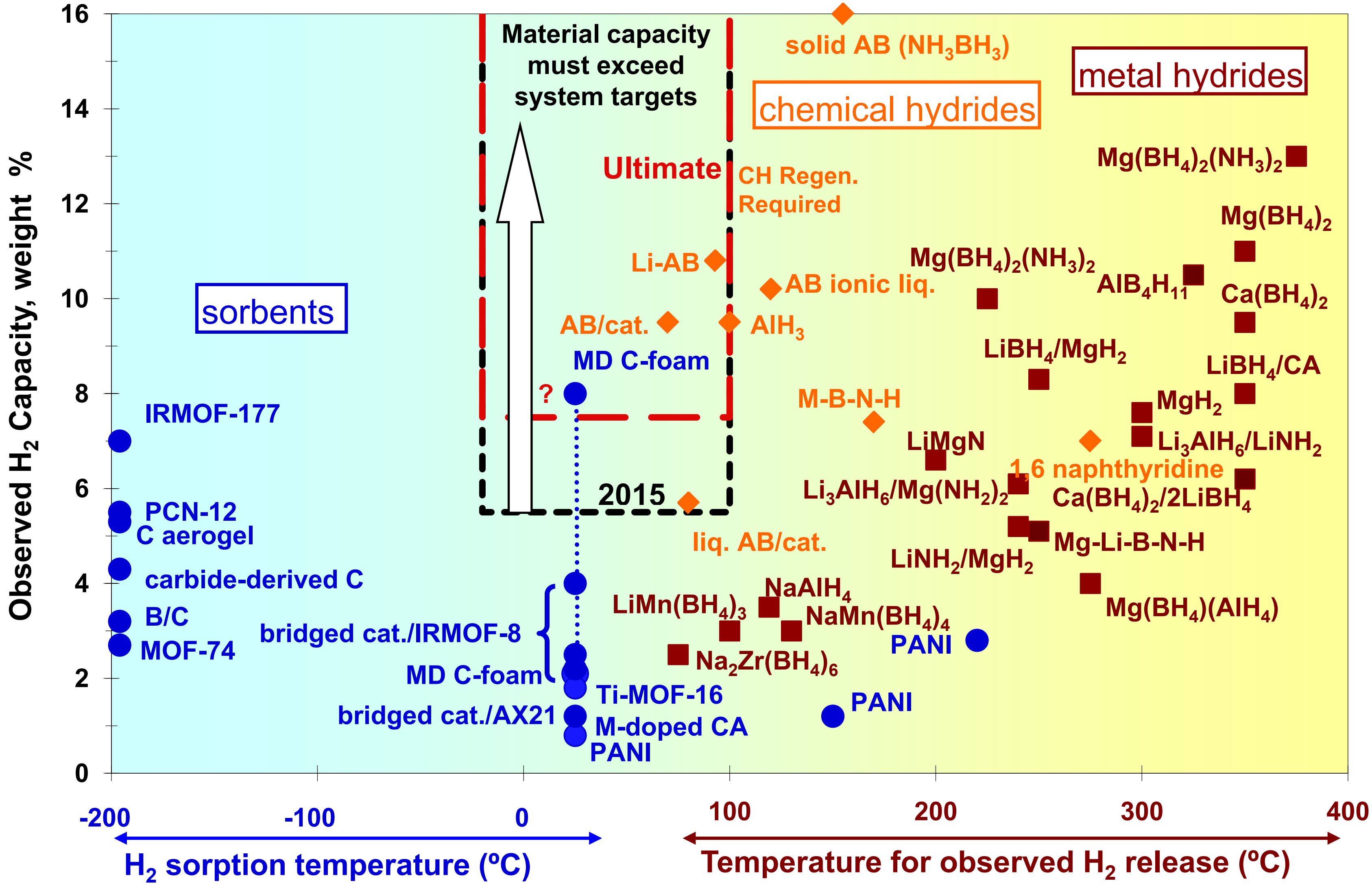
		Material Name	Chemical Formula	Variant Type Code	Development Status Code	Synthesis Method	Synthesis Conditions	Precursors	Activation	Entered By User	Entry Date	Institution
		DADB/bmimCl (50wt%)	(BH2(NH3)2) BH4/bmimCl (50wt%)	Mixture	Continuing Development	150 mg DADB with 150 mg bmimCl added to gas burette flask in glove box.			Ionic Liquid	Sneddon	4/19/2010 9:48:24 AM	University Of Pennsylvania
		AB/bmimCl (20wt%)-1	H3NBH3/bmimCl (20wt%)-1	Mixture	Continuing Development	150 mg AB with 37 mg bmimCl added to gas burette flask in glove box.			Ionic Liquid	Sneddon	4/19/2010 9:48:24 AM	University Of Pennsylvania
		AB/bmimCl (20wt%)-2	H3NBH3/bmimCl (20wt%)-2	Mixture	Continuing Development	150 mg AB with 37 mg bmimCl added to gas burette flask in glove box.			Ionic Liquid	Sneddon	4/19/2010 9:48:24 AM	University Of Pennsylvania

- **Database is designed to capture materials data from all projects**
- **Database deployed for data input by Material Centers April 2010**
- **Public website will be launched first quarter of fiscal year 2011**
  - **Site will be searchable by materials properties**
  - **Data can be exported in various forms**
  - **New materials data can be submitted for addition to public site**

2009 Progress & Accomplishments

U.S. DEPARTMENT OF ENERGY

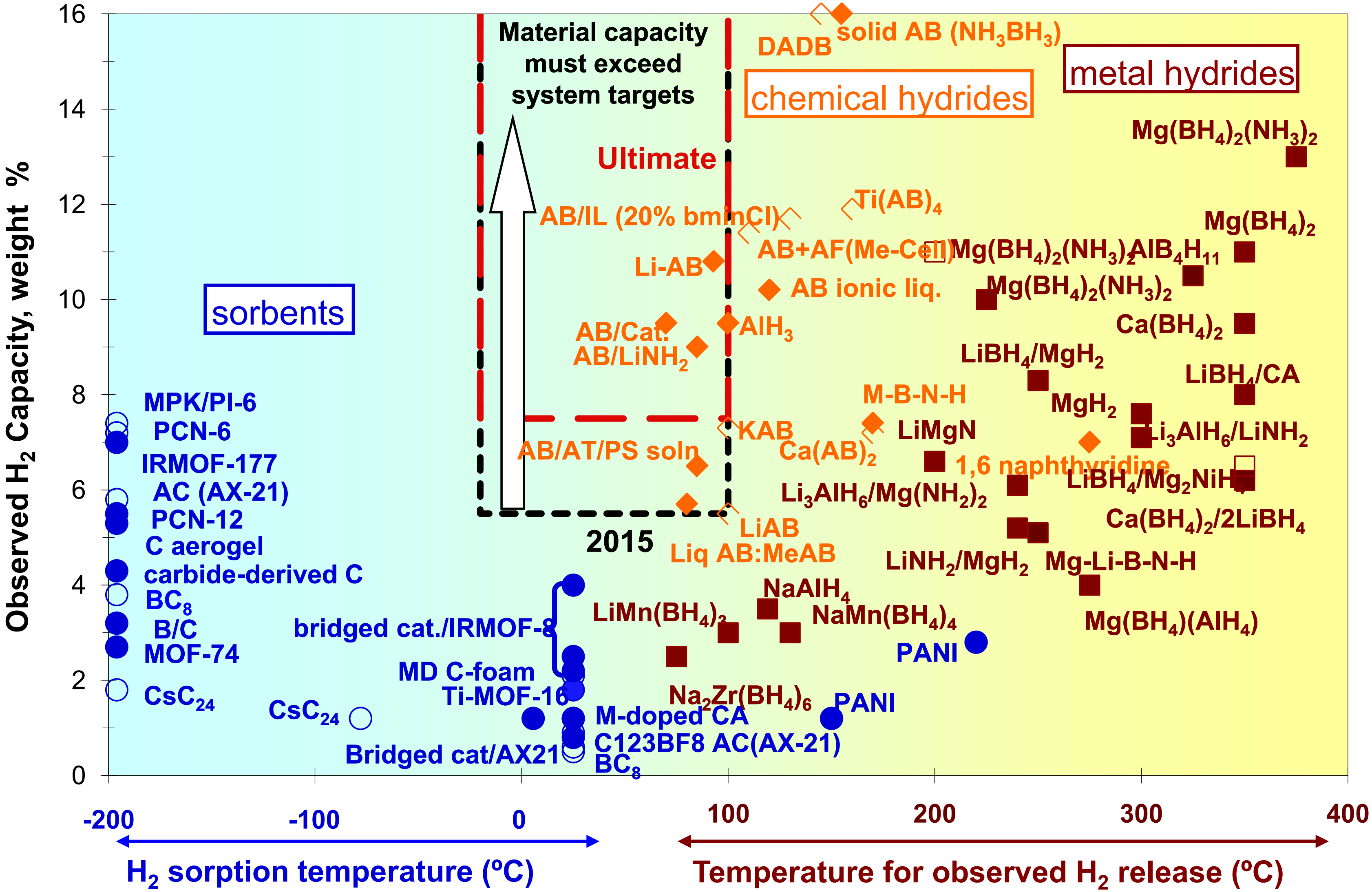
Status at 2009 AMR Review



2010 Progress & Accomplishments

U.S. DEPARTMENT OF ENERGY

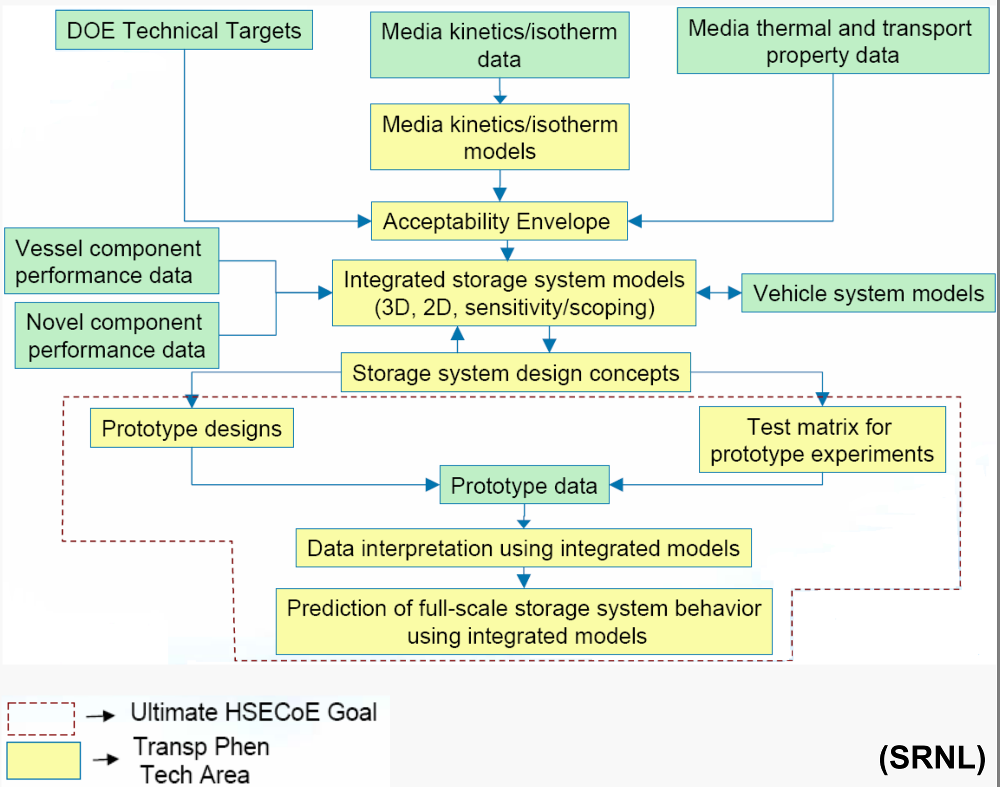
Open symbols denote new materials since 2009 AMR



2010 Progress: Engineering CoE

Focus on model development and material evaluation

Modeling of Storage Systems

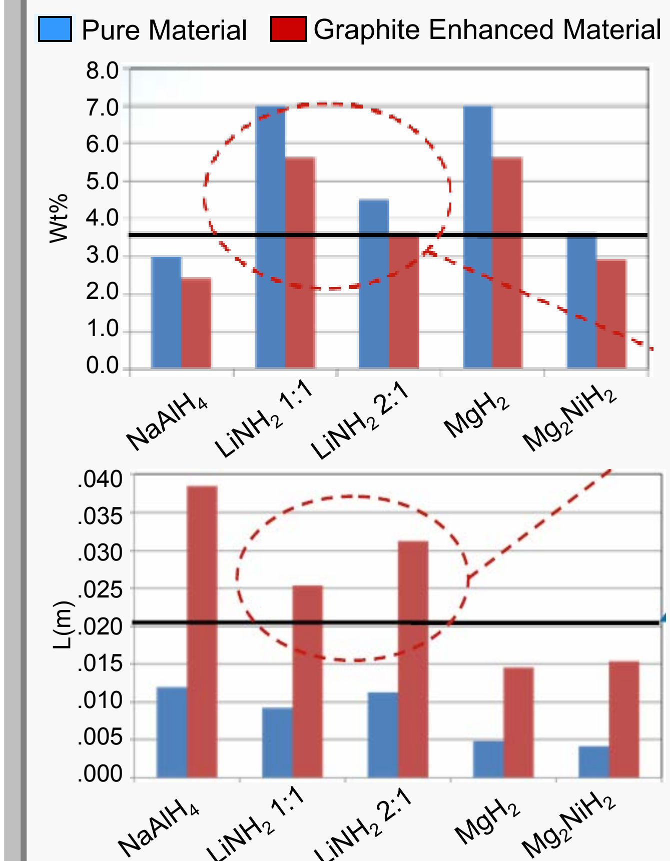


(SRNL)

Acceptability Envelope

The “Acceptability Envelope” or “BlackBox Analysis” determines range of characteristics necessary for coupled media and system to meet storage system performance targets

System Architect Analysis Applying Acceptability Envelope Model to Various Materials



Suggests that Li-Mg-N materials may be the most promising metal hydrides for further consideration

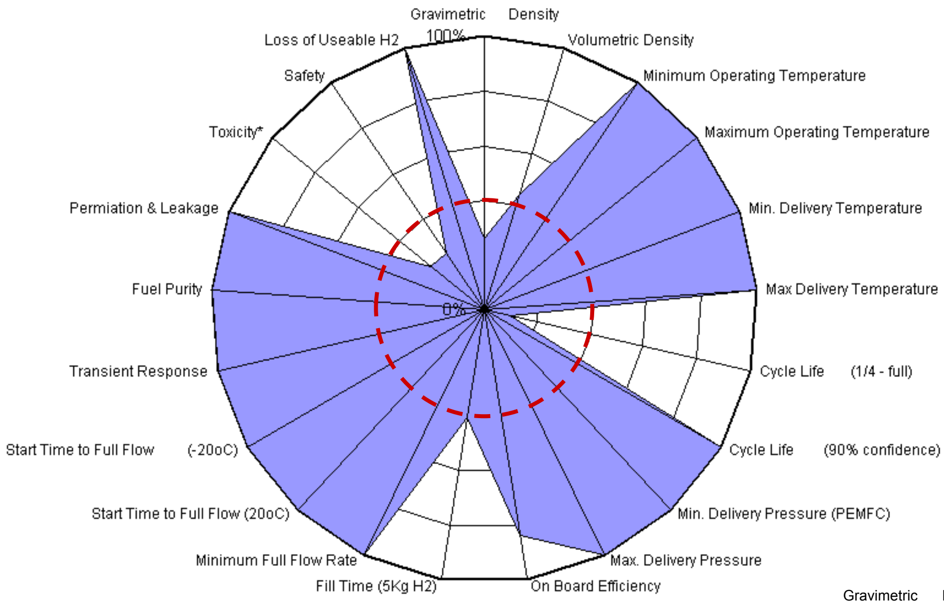
(SRNL)

L(m) is the distance between heat transfer elements in meters

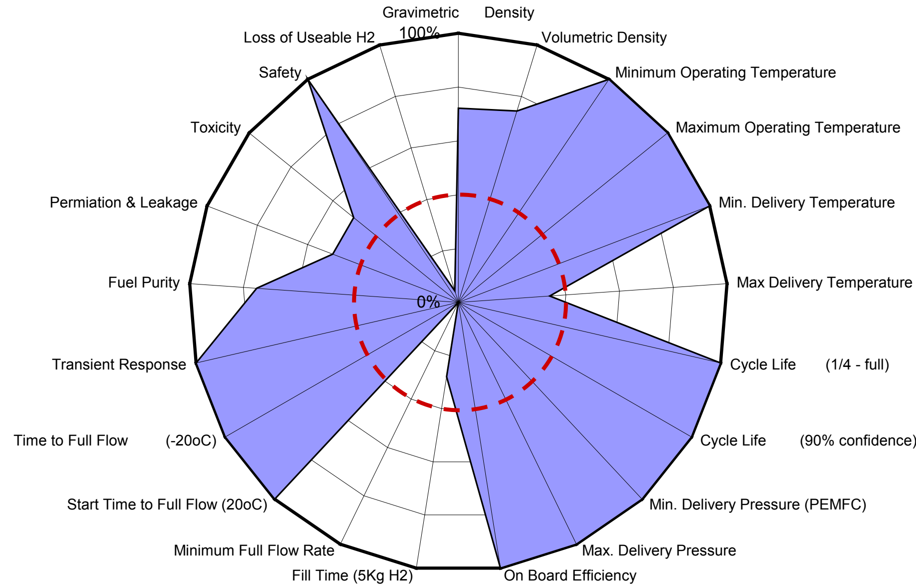
2010 Progress: Engineering CoE

U.S. DEPARTMENT OF ENERGY

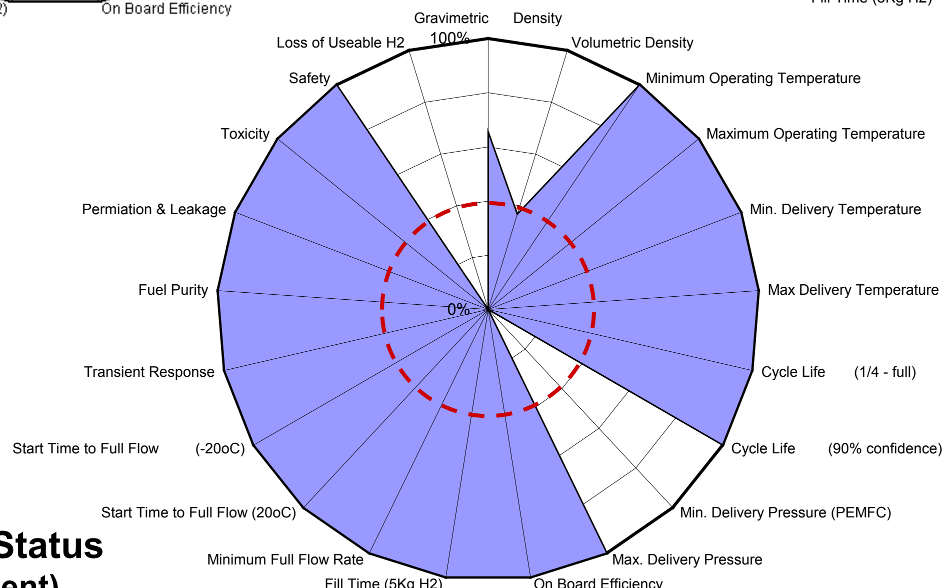
Systems evaluated against complete set of performance targets



Metal Hydrides
($NaAlH_4$)



Chemical Hydride System
(Solid Ammonia-Borane Bed)



Adsorbent System Status
(AX-21 Cryo-Adsorbent)

2010 Progress: Materials

U.S. DEPARTMENT OF ENERGY

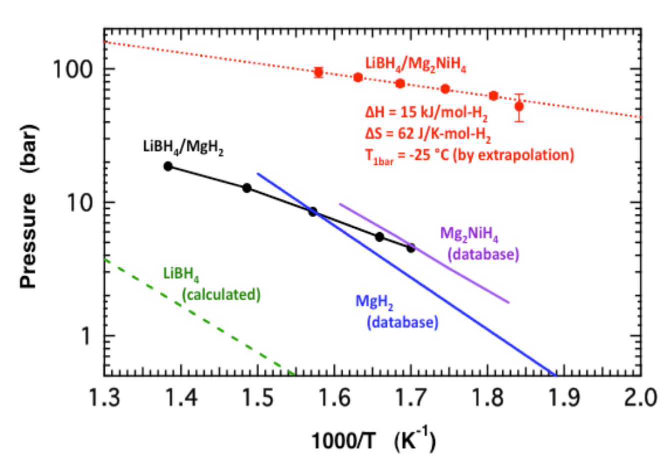
Progress being made in reversible metal hydride material discovery

Hydride Destabilization

- *Destabilization results in lower ΔH and $T_{1\ bar}$*

$LiBH_4/Mg_2NiH_4$ system

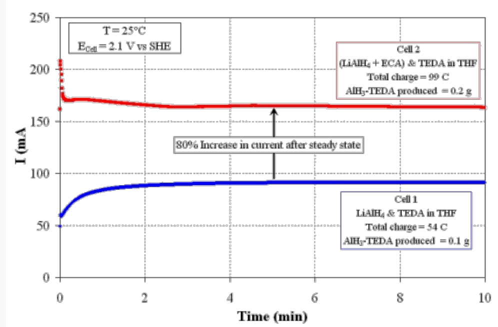
- ΔH (= *15 kJ/mol-H_2*) and ΔS (= *62 J/ K-mol-H_2*) are the lowest reported so far for a reversible system



(HRL)

AlH_3 Generated Electrochemically

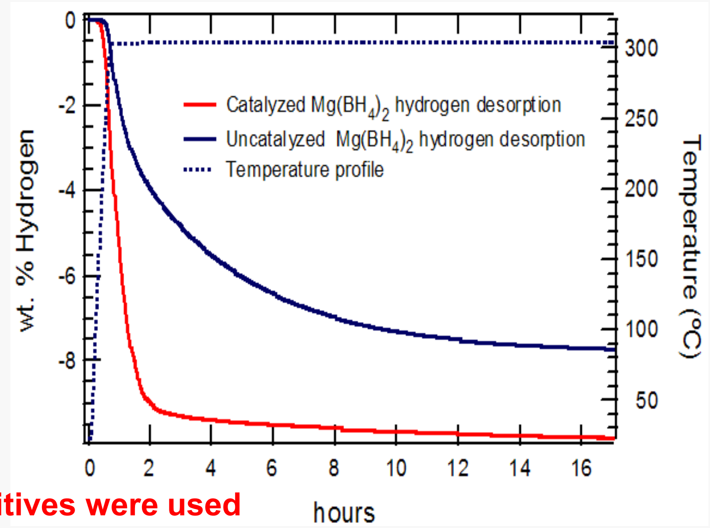
- ElectroCatalytic Additive found to increase steady-state current by 80%
- Dramatic increase in production rates.



(SRNL)

Role of Additives on H_2 release from $Mg(BH_4)_2$

- Small amount of boron hydrides (15 – 58 amu) (<0.2wt%) is released
- Other transition metal halides were tested but were not as effective
- The catalysts have little or no effect on rehydrogenation



Sandia National Laboratories

List what additives were used

AlH_3 Regeneration

Step 1: Five pathways identified to form AlH_3 adducts from H_2 and Al

Step 2: Transamination demonstrated with high yields for DMEA and TMA.

Step 3: TEA-AlH_3 separated with ~70% recovered AlH_3

ANL analysis of WTT efficiency suggests 55% possible with TMA route using waste heat

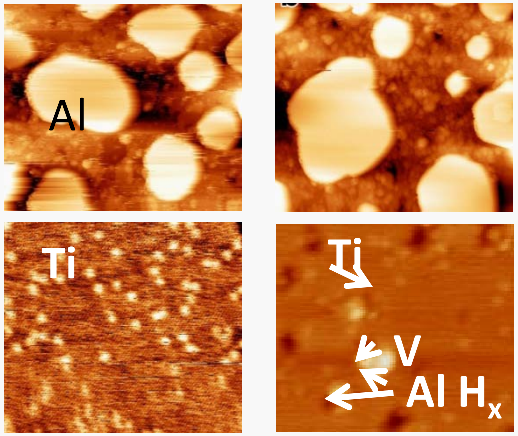
(BNL)

Understanding the role of additives in hydrogen uptake reactions

Role of Ti on the reaction of H_2 with Al

- Ti on clean Al surface critical for dissociating molecular hydrogen.
- Enables formation of mobile AlH_x entities on the surface

	No Hydrogen exposure	With Hydrogen exposure
Aluminum on Silicon with no Ti		
Aluminum on Silicon with Ti		

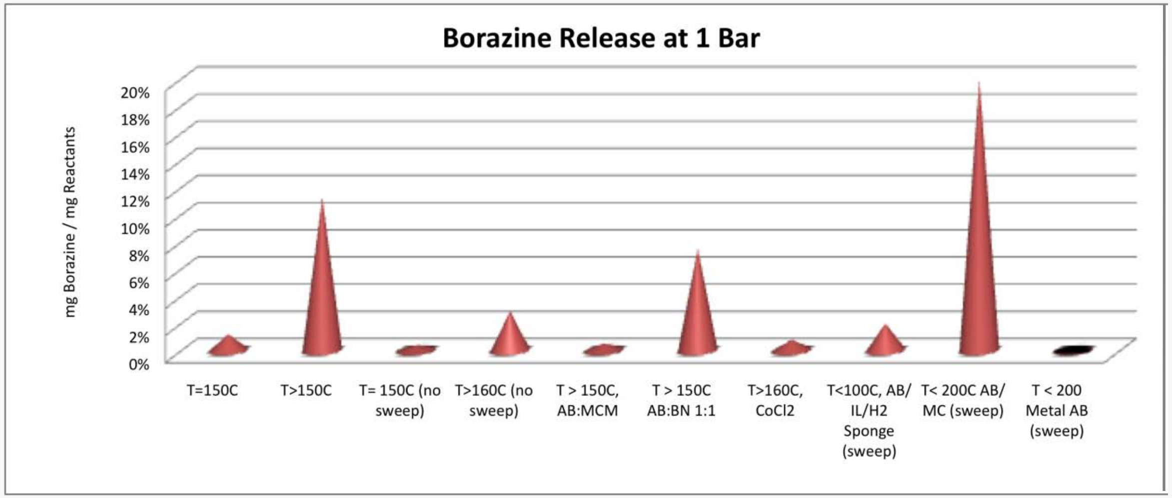


Chemical Hydrogen Storage Material

Impurities

PNNL and LANL developed methods for quantification and strategies for mitigation of impurities released during hydrogen release from ammonia borane.

Catalysts and additives reduce the release of borazine into the gas stream.



2010 Progress: Materials

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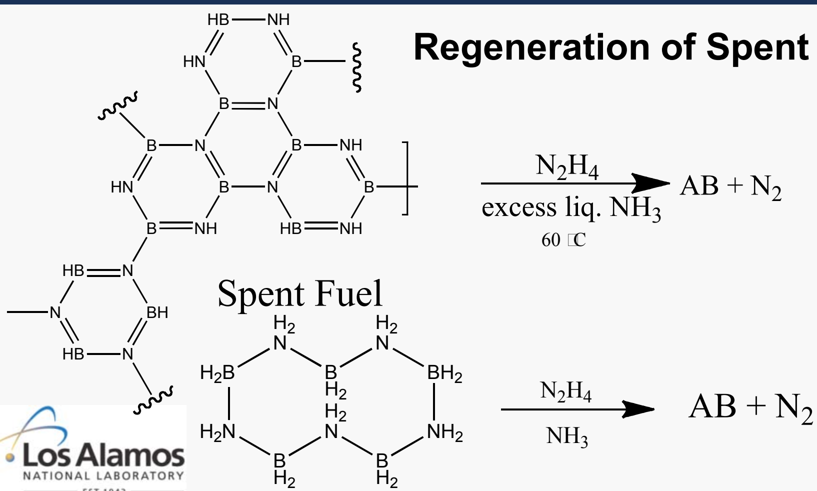
Chemical Hydrogen Storage Material

Regeneration of Spent Fuels



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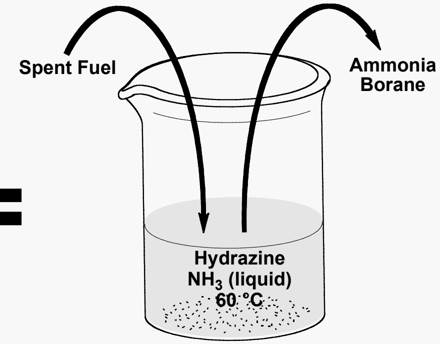


"one-pot" regen

Quantitative conversion by NMR

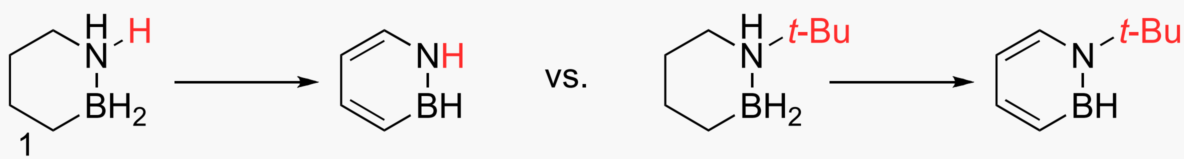
- Method gives ammonia borane for multiple spent fuel forms.
- Improvements in process efficiency and capital cost should result from the lower mass throughput (relative to previous process)

Los Alamos NATIONAL LABORATORY EST. 1943

New Materials from University of Oregon:

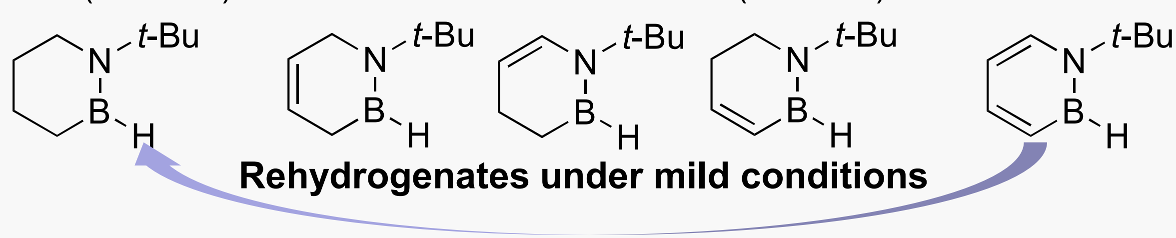
Coupling exothermic BHNH release with endothermic H-C-C-H in the same molecule is a successful approach

Material (1) | more readily available model of (1)



G at 298K (kcal/mol) = –2.3

G at 298K (kcal/mol) = –0.4



Rehydrogenates under mild conditions

- Prepared models of compound 1 at stages of dehydrogenation
- Demonstrated simple regeneration chemistry

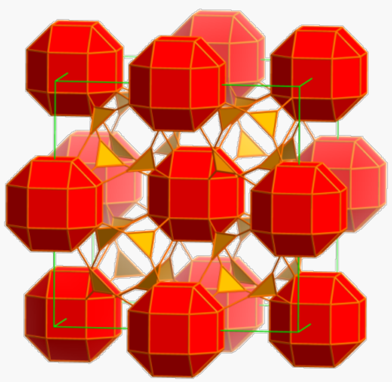
THE UNIVERSITY OF ALABAMA

UNIVERSITY OF WASHINGTON

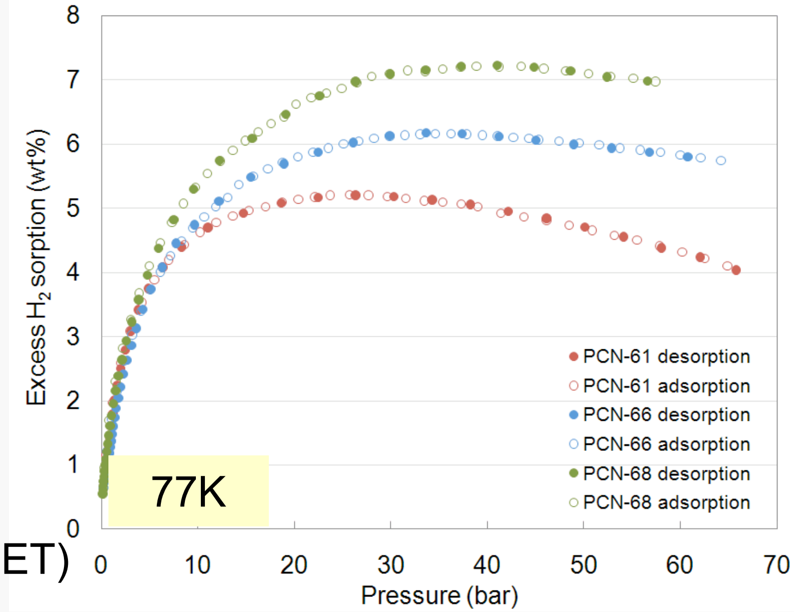
2010 Progress: Sorbents

Accomplishments: Cryosorbents

Stabilization of MOFs with High Surface Areas by the Incorporation of Mesocavities with Microwindows



PCN-61 PCN-66 PCN-68

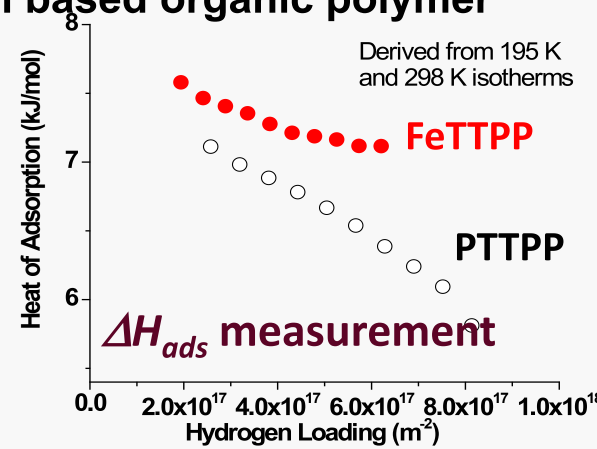


PCN-68: 6033 m2/g Langmuir (5109 m2/g BET) and ~ 7.2 wt% excess H2 capacity

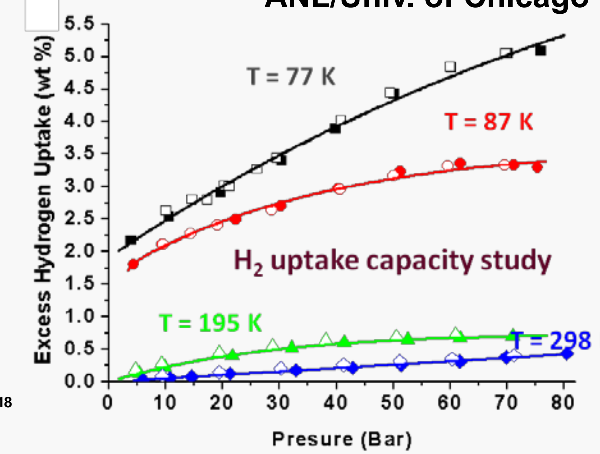
TAMU; Data by GM

Nanostructured polyporphyrin based organic polymer

- Achieved H_2 uptake of 5.1w% at 77K and 0.6w% at RT
- Observed H_2 isosteric heat of adsorption up to ~10 kJ/mol over selected POPs
- Polyporphyrin can serve as platform for exchanging transition metals for H-M interaction



ANL/Univ. of Chicago



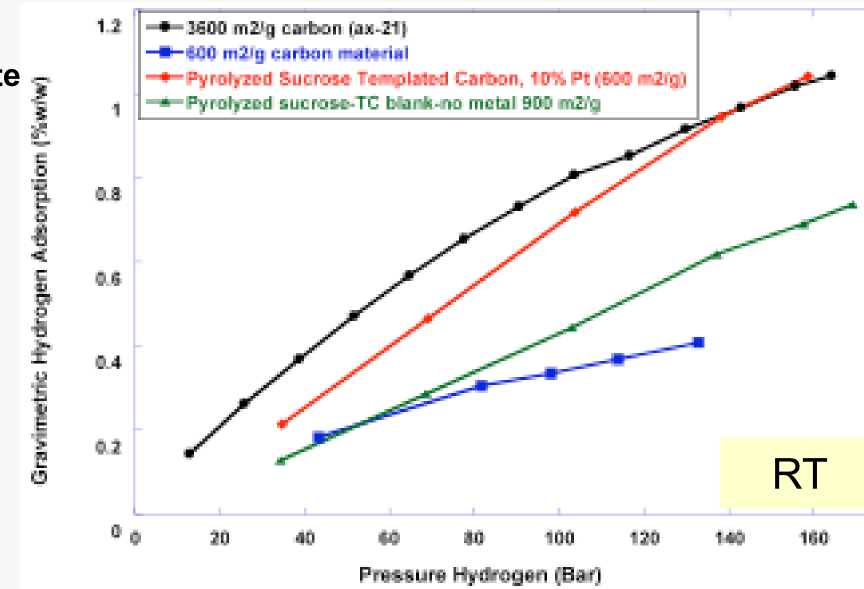
2010 Progress: Sorbents

Accomplishments: Towards Room Temperature & Moderate Pressure Conditions

Weak Chemisorption Materials

Pt/ Carbon from Pyrolyzed Sucrose on Silica Sphere Template

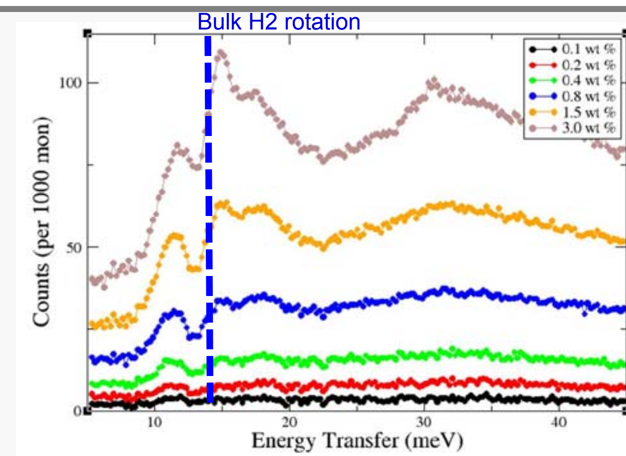
- **Excellent Kinetics: < 5 min to saturation**
- Adsorption of hydrogen still increasing at 150 bar
- Minimal irreversibility. Multiple cycles with no loss of sorption capacity or water formation.
- Demonstrates unique features of pyrolized sucrose that is used for “bridging” to MOFs
- Unexpected capacity on “small” surface area, 600 m2/g (Pt content 10wt%)
- Possibility of “hidden” pore structure needs to be determined



NREL

Boron substituted carbons

- **Quantitative B-H interactions observed for the first time**
  - Neutron data shows, for the first time, a large rotational splitting indicative of enhanced H_2 interactions in a substituted carbon
  - DRIFTS observes reversible H interaction in B-C materials
- Experimental results confirm calculations that B-C increases ΔH values



NIST and Penn State INS: H2 rotational spectra

2010 Status: Compressed Gas

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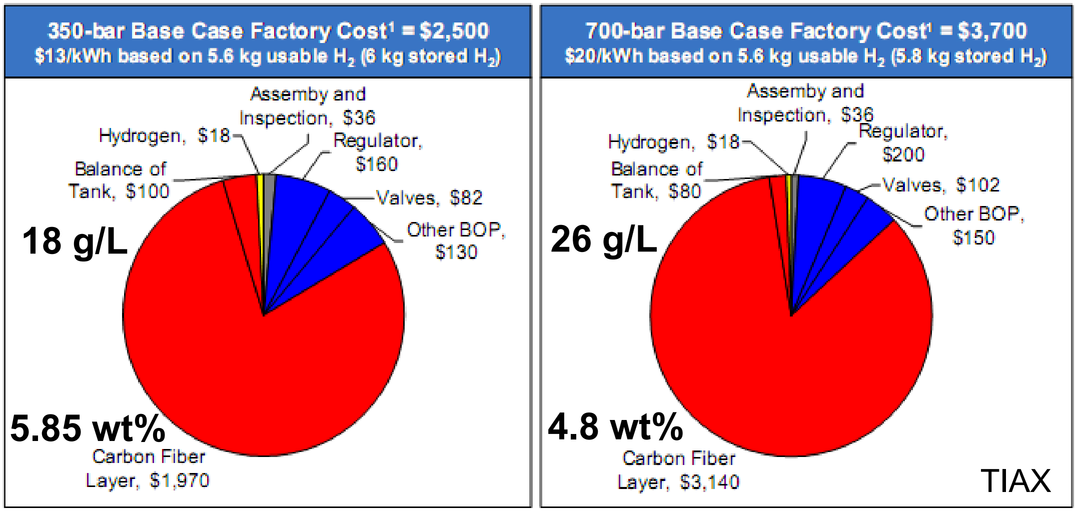
The carbon fiber composite layer accounts for about 75% and 80% of the 350-bar and 700-bar base case system costs, respectively.

With conventional processing using a carbon fiber-grade (CF) PAN, precursor is over 50% of the carbon fiber cost



[1] Cost estimate in 2005 USD. Includes processing costs.

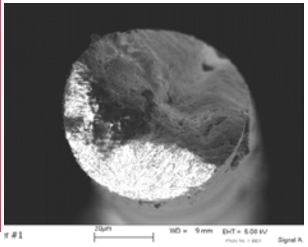
Based on manufacturing volumes of 500,000 units per annum., weight and volume under review

4 Elements of Cost Reduction

1. Scale of Operations
2. Precursors
3. Conversion
4. Manufacturing of Composite

The Storage Program is currently funding ORNL to develop lower cost precursors (i.e., melt spinnable PAN and polyolefins) and reduced production costs for high-strength carbon fibers.

ORNL early runs produced melt-spun PAN filaments of moderate quality



Precursor and Conversion	Estimated CF Cost $/lb CF
Baseline – Wet spun PAN precursor conventionally converted	$11.43
Melt spun PAN, advanced ORNL conversion	$ 6.11

2010 Progress: Analysis

U.S. DEPARTMENT OF ENERGY

Cryogenic pressure vessels offer potential to exceed 2015 H2 storage goals

3rd generation cryogenic pressure vessel prototype

2nd generation cryogenic pressure vessel prototype

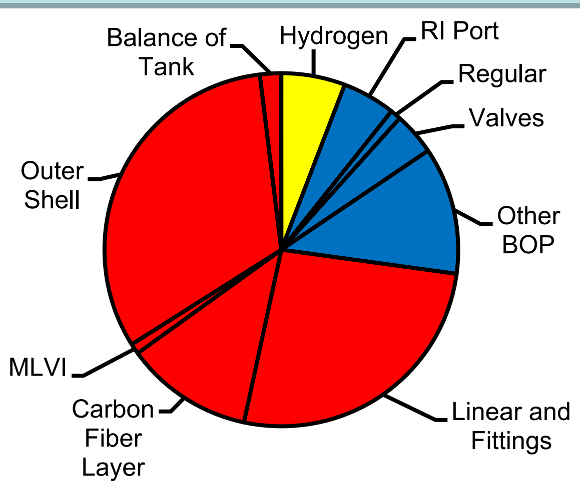
The 3rd generation cryogenic pressure vessel prototype saves 25 kg and 70 L compared to the previous 2nd generation prototype for storing 10.7 kg H_2 at 7.1 wt% H_2 and 44.5 kg H_2/L (LLNL)

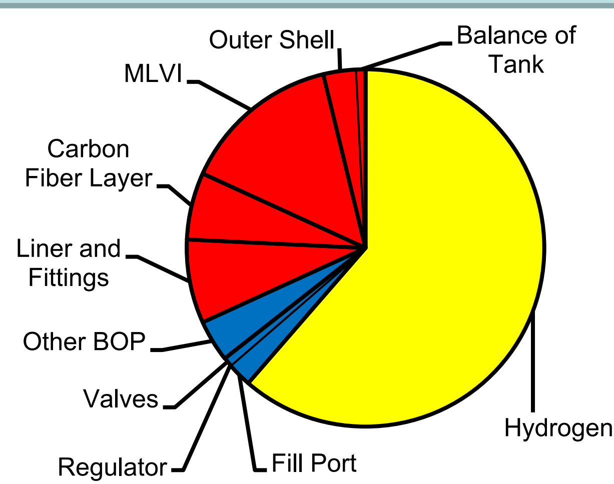
ANL/TIAX analyses indicate that scaling vessel size to store 5.6 kg H_2 for a passenger vehicle reduces capacities to 5.5 wt% H_2 at 42 g H_2/L at lower cost than a 700-bar Compressed gas tank.

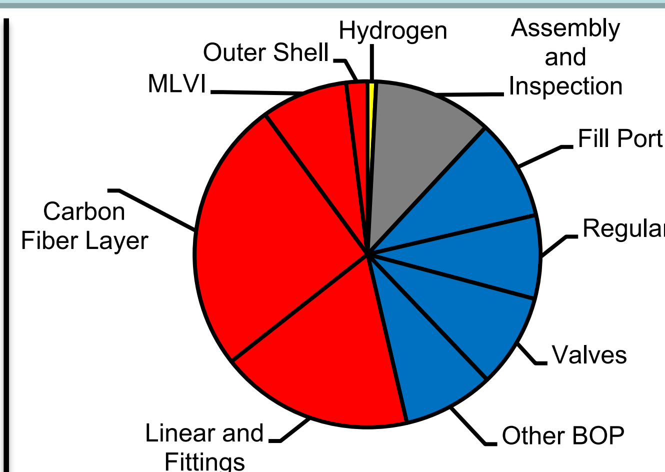
5.8 kg Base Case Weight = 102 kg
5.5 wt% based on 5.6 kg usage LH_2

5.8 kg Base Case Volume = 131 L
43 g H2/L based on 5.6 kg usable LH_2

5.8 kg Base Case Factory Cost[1] = $2,200
$12/kWh based on 5.6 kg useable LH_2

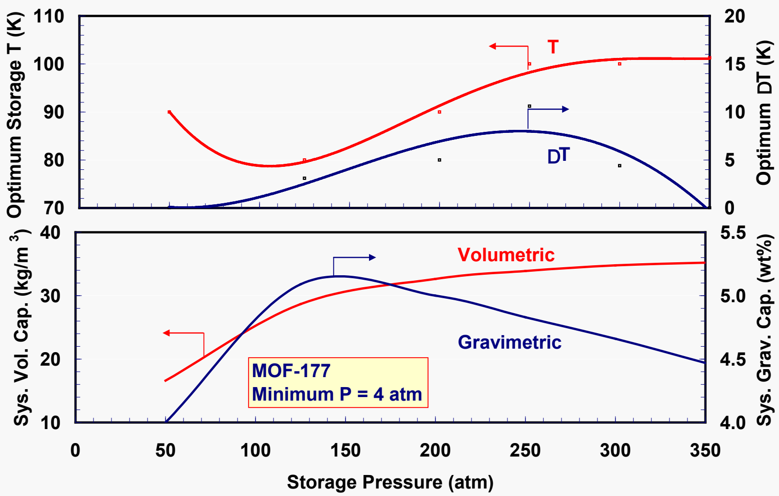






2010 Progress: Analysis

Metal Organic Frameworks Adiabatic Liquid H_2 Refueling Analysis



System gravimetric capacity peaks at ~150 atm but the volumetric capacity increases slowly with storage pressure

Refueling: 7.1 MJ evaporative cooling load

- 62% for ΔH, 38% for sensible cooling and PV work

Discharge options

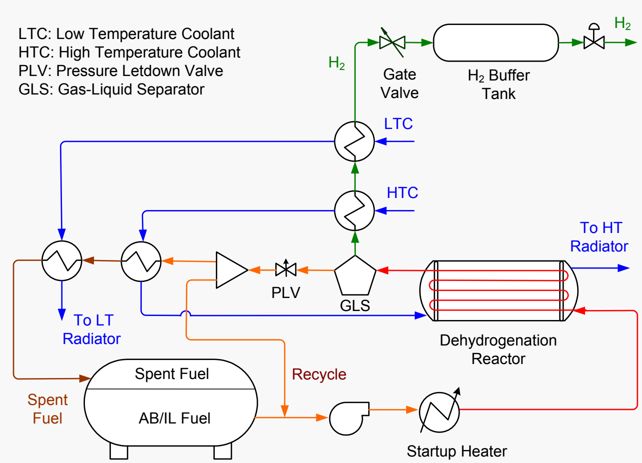
- Constant Q (1.2 kJ/g of H_2 discharged), 1.9 kW
- Variable Q, heat supplied only if tank P < 4 atm, 6.3-kW peak Q

Performance & Cost Metric	MOF -177	Units
System Gravimetric Capacity	4.1	Wt%
System Volumetric Capacity	34.1	Kg-H_2/m^3
Storage System Cost	18	$/kWh
Fuel Cost	4.6	$/gge
Cycle Life (1/4 full tank)	5500	Cycles
Min Delivery Pressure	4	atm
System Fill Rate	1.5 – 2	Kg-H_2/min
Min Dormancy (full tank)	2.8	W – d
H_2 Loss Rate (Max)	0.9	g/h/kg-H_2
WTT Efficiency	41.1	%
GHG Emissions (CO_2 eq)	19.7	kg/kg-H_2
Ownership Cost	0.15	$/mile

Borane Liquid Mixture Analysis

Onboard release system: Preliminary ANL analysis of ionic liquid/ammonia borane liquid mixtures developed in Sneddon's group at U. Penn with material capacities up to 11 wt. %, and fast release rates above 85 C identified:

- **Substantial spent fuel recycle to manage exothermic release**
- **Heat rejection and startup/shutdown are key challenges**



2009 Presidential Awardees in Program

Congratulations to the 3 Presidential Awardees:

- **Professor Susan Kauzlarich** – UC Davis, a 2009 recipient of the ***Presidential Award for Excellence in Science, Mathematics and Engineering Mentoring***—and a partner of the Chemical Hydrogen Storage Center of Excellence

- **Dr. Jason Graetz** – Brookhaven National Laboratory, a 2009 recipient of the ***Presidential Early Career Award for Scientists and Engineers***—and a partner of the Metal Hydride Center of Excellence
- **Dr. Craig Brown** – NIST, a 2009 recipient of the ***Presidential Early Career Award for Scientists and Engineers***—and a Partner of the Hydrogen Sorption Center of Excellence

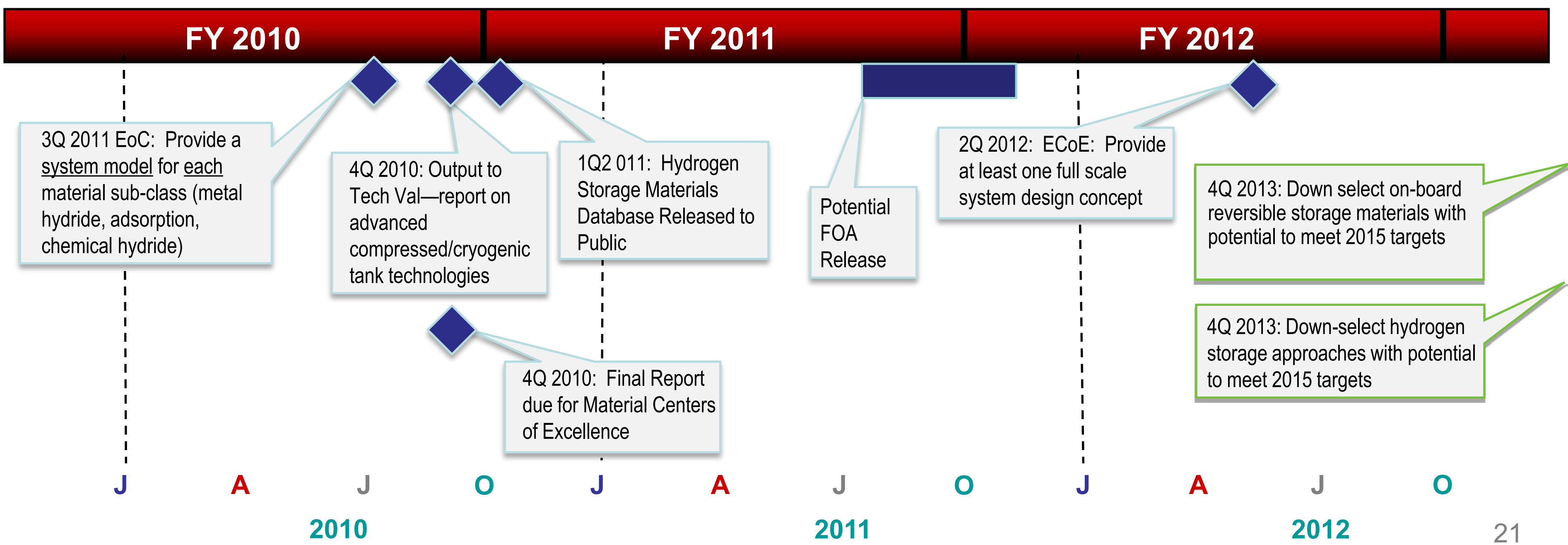
Major Upcoming Milestones

Physical Storage

- Initially tasks were not planned beyond FY2010 because physical storage was not seen as a pathway towards meeting the ultimate targets.
    - Physical Storage will be used for early automotive market penetration as well as other early markets;
    - Additional tasks will be planned and added for out years, especially focusing on cost reduction.

Material-based Storage

- Three Material-based Centers of Excellence established in FY2004 and are being completed in FY2010;
- Hydrogen Storage Engineering Center of Excellence established in FY2009 as a 5-year effort;
- New materials R&D efforts are needed to further develop storage materials and to support the engineering efforts.



Session Instructions

U.S. DEPARTMENT OF ENERGY

- This is a review, not a conference.
- Presentations will begin precisely at the scheduled times.
- Talks will be **20 minutes** and **Q&A 10 minutes**.
- Reviewers have priority for questions over the general audience.
- Reviewers should be seated in front of the room for convenient access by the microphone attendants during the Q&A.
- Please mute all cell phones, BlackBerries, etc.

Reviewer Reminders

U.S. DEPARTMENT OF ENERGY

- Deadline for final review form submittal is **June 18th**.
- ORISE personnel are available on-site for assistance. A reviewer lab is set-up in room 8216 and will be open Tuesday –Thursday from 7:30 AM to 6:00 PM and Friday 7:30 AM to 3:00 PM.
- Reviewer feedback session – **Thursday, at 6:15pm (after last Hydrogen Storage session), in this room.**

For More Information

U.S. DEPARTMENT OF ENERGY

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