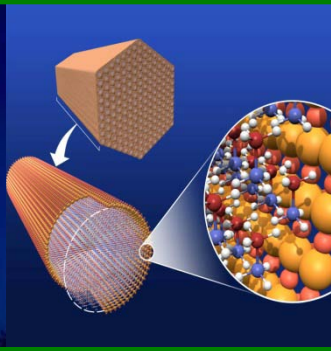
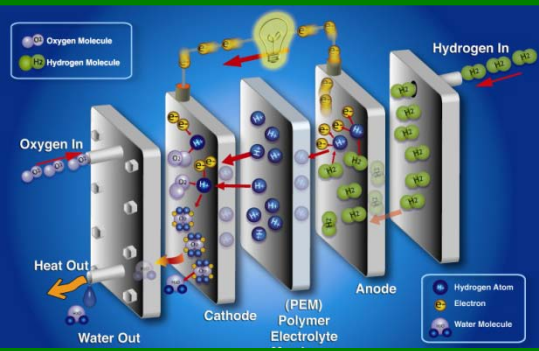




U.S. DEPARTMENT OF  
**ENERGY**



# Hydrogen Storage

Ned T. Stetson

*2010 Annual Merit Review and Peer Evaluation Meeting  
(8 June 2010)*

# Goal & Objectives

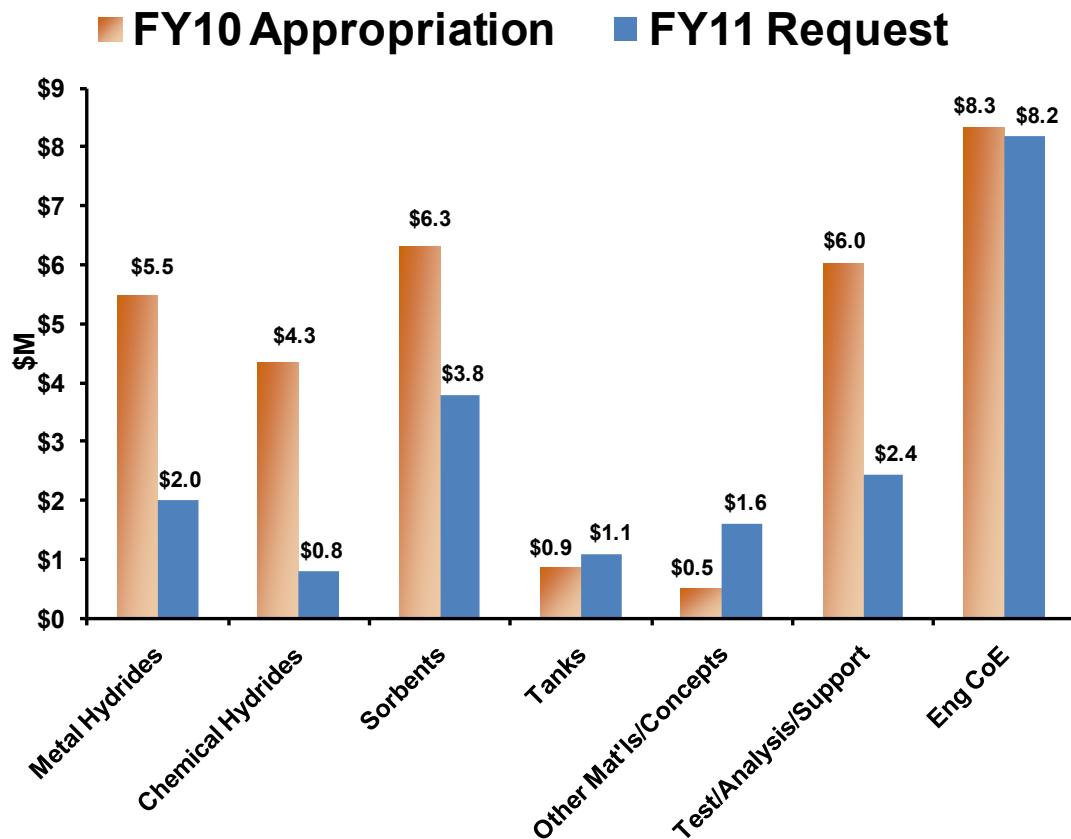
**Goal: On-board hydrogen storage for > 300 mile driving range across different vehicle platforms, without compromising passenger/cargo space or performance**

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

**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

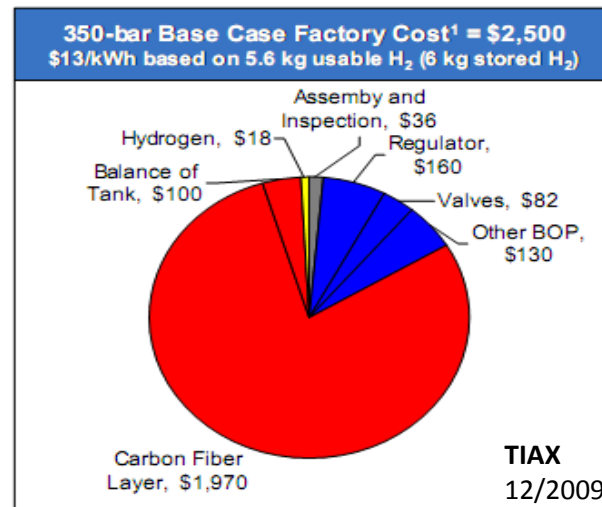
- Systems approach through the Engineering CoE, in collaboration with independent materials development projects, to achieve light-duty vehicle targets
- Continued close coordination with Basic Energy Science in 2010 & 2011 and improve coordination with National Science Foundation, Advanced Research 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

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**

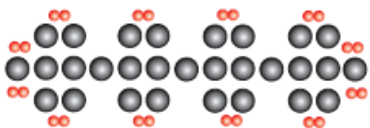
- Cost of composite tanks is challenging
- > 75% of the cost is projected to be due to the carbon fiber layer
- Additional analysis is needed to better understand costs at lower manufacturing volumes



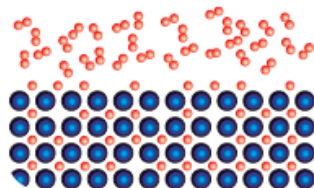
<sup>1</sup> Cost estimate in 2005 USD. Includes processing costs.

Advanced materials development is still needed for long-term solutions

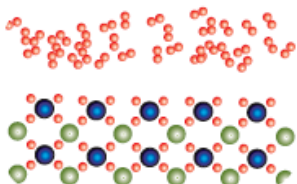
A) Surface Adsorption



B) Intermetallic Hydride



C) Complex Hydride



D) Chemical Hydride

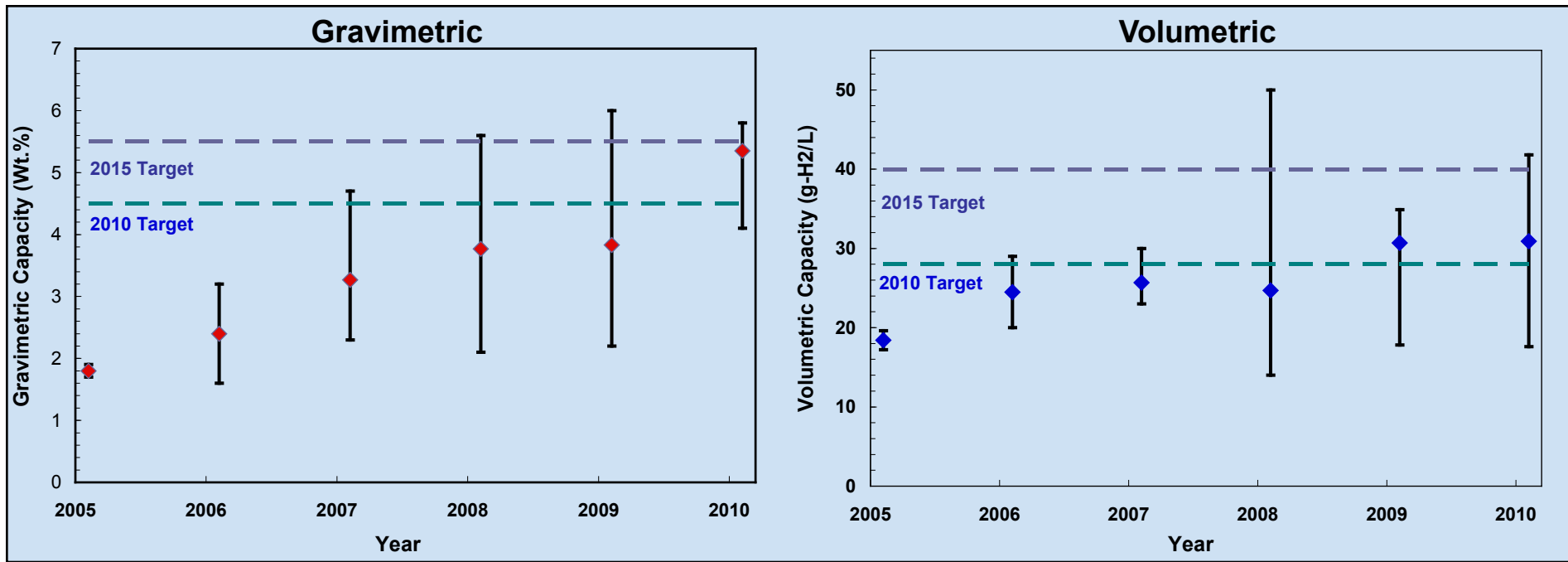


**Materials discovery research is still needed for long-term, advanced materials with full set of properties for materials-based hydrogen storage options!**

# 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<sub>2</sub> 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**

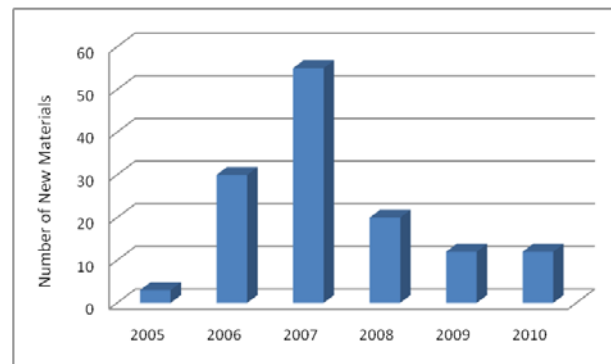
**However no one system is yet able to meet all targets simultaneously**

# Portfolio Management & Progress

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

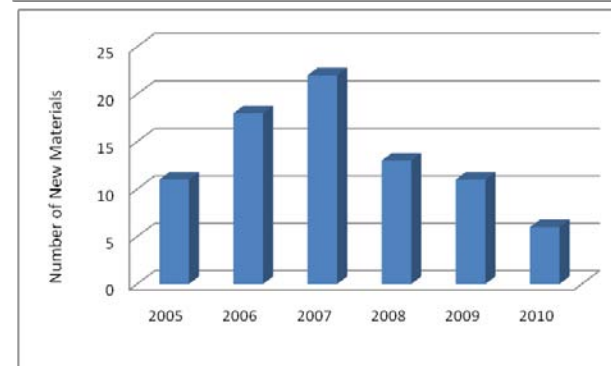


## Metal Hydrides

More than 81 distinct material systems assessed experimentally—not including catalyst/additive studies

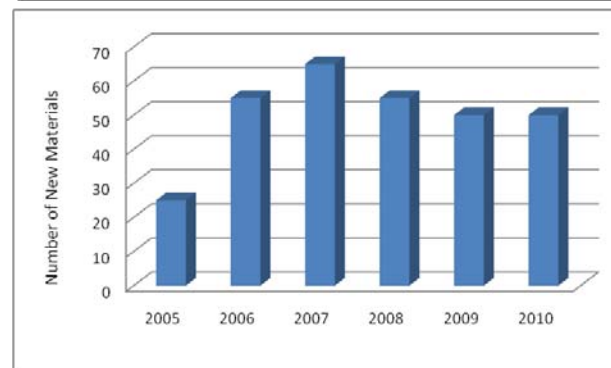
- ~ 75% discontinued
- ~ 25% still being investigated

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



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

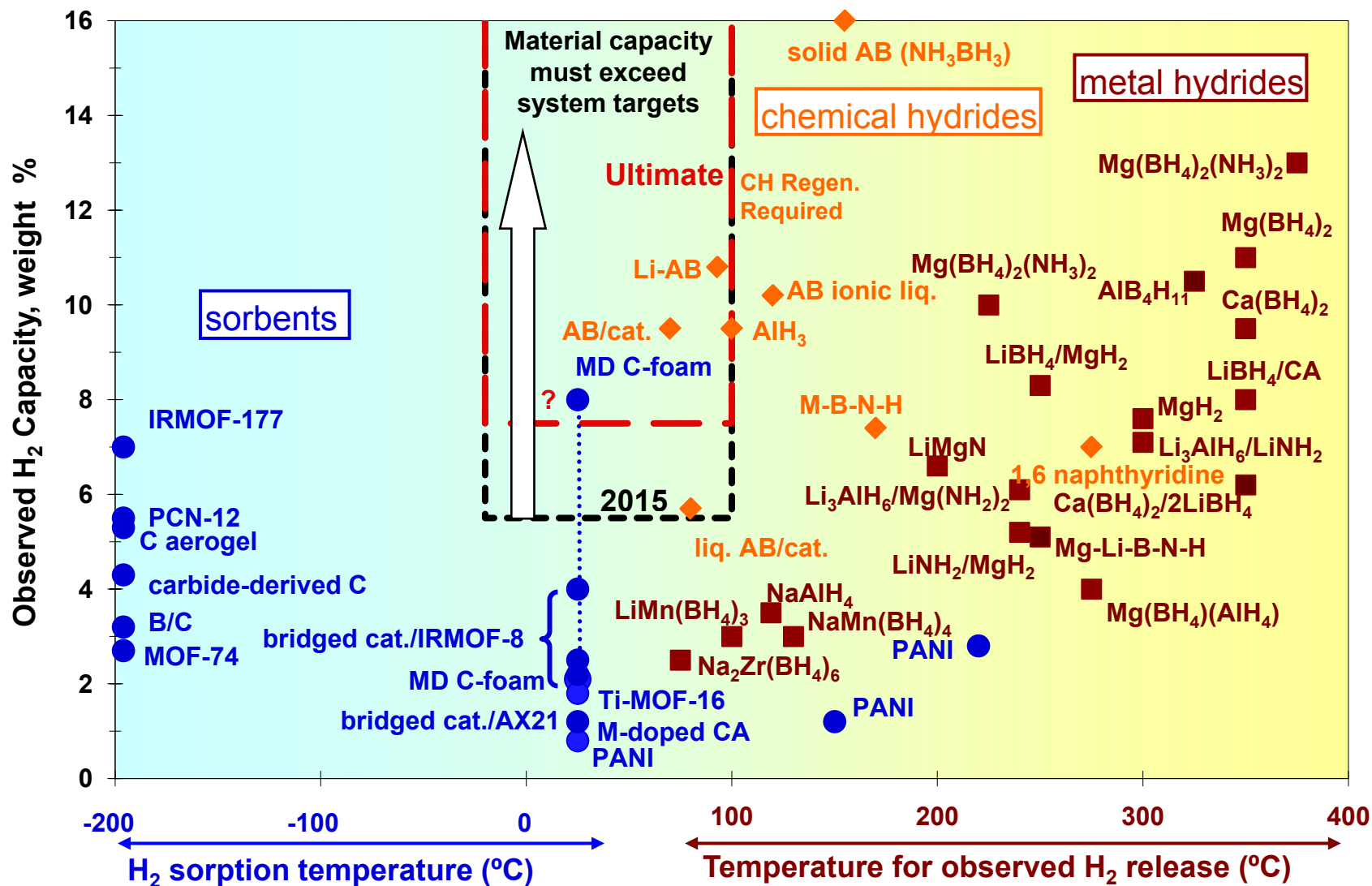
- Database is designed to capture materials data from all projects
- Database deployed for data input by Material Centers April 2010
- Public website will be launched first quarter of fiscal year 2011
  - Site will be searchable by materials properties
  - Data can be exported in various forms
  - New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

The screenshot displays the 'Hydrogen Materials Database' interface. At the top, there is a header for the 'U.S. DEPARTMENT OF ENERGY | Fuel Cell Technologies Program' and the title 'Hydrogen Materials Database'. Below the header, there are navigation links: 'Show Adsorbents', 'Show Chemical Hydrides', 'Show Reversible Hydrides', and 'Hydrogen Materials Reference'. The main content area is titled 'CHEMICAL HYDRIDES' and features a search bar with a 'Go' button. Below the search bar are filters for 'Development Status Code' (set to 'All'), 'Variant Type Code' (set to 'All'), and 'Archived' (set to 'All'). A toolbar shows '15 Items' and '10' items per page. The data is presented in a table with the following columns: Material Name, Chemical Formula, Variant Type Code, Development Status Code, Synthesis Method, Synthesis Conditions, Precursors, Activation, Entered By User, Entry Date, and Institution. Three rows of data are visible, all with a 'Continuing Development' status and 'University Of Pennsylvania' as the institution.

	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	<a href="#">Continuing Development</a>	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	<a href="#">University Of Pennsylvania</a>
	AB/bmimCl (20wt%)-1	H3NBH3/bmimCl (20wt%)-1	Mixture	<a href="#">Continuing Development</a>	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	<a href="#">University Of Pennsylvania</a>
	AB/bmimCl (20wt%)-2	H3NBH3/bmimCl (20wt%)-2	Mixture	<a href="#">Continuing Development</a>	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	<a href="#">University Of Pennsylvania</a>



## Status at 2009 AMR Review

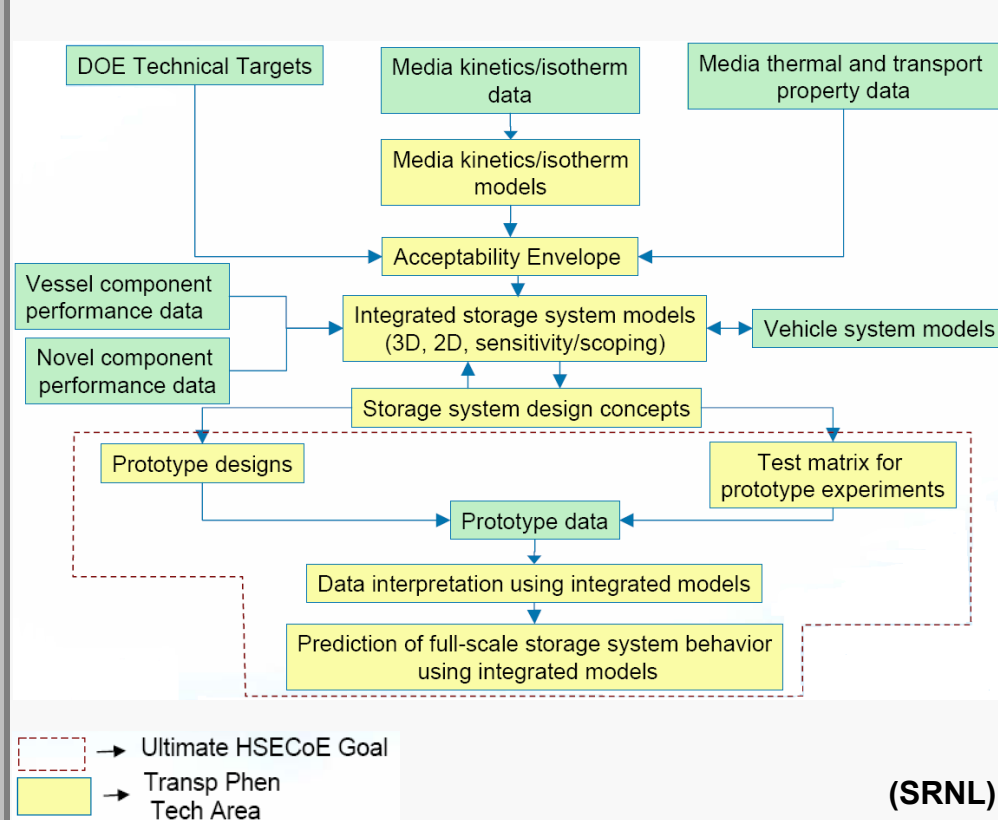






## Focus on model development and material evaluation

### Modeling of Storage Systems

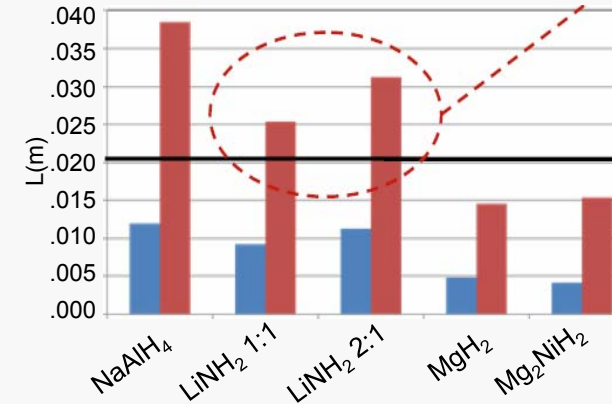
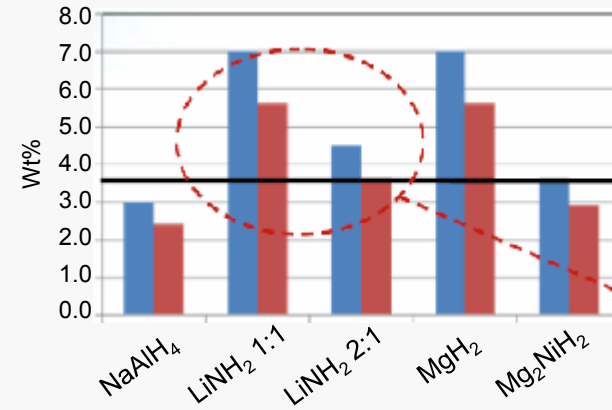


### Acceptability Envelope

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

■ Pure Material ■ Graphite Enhanced Material

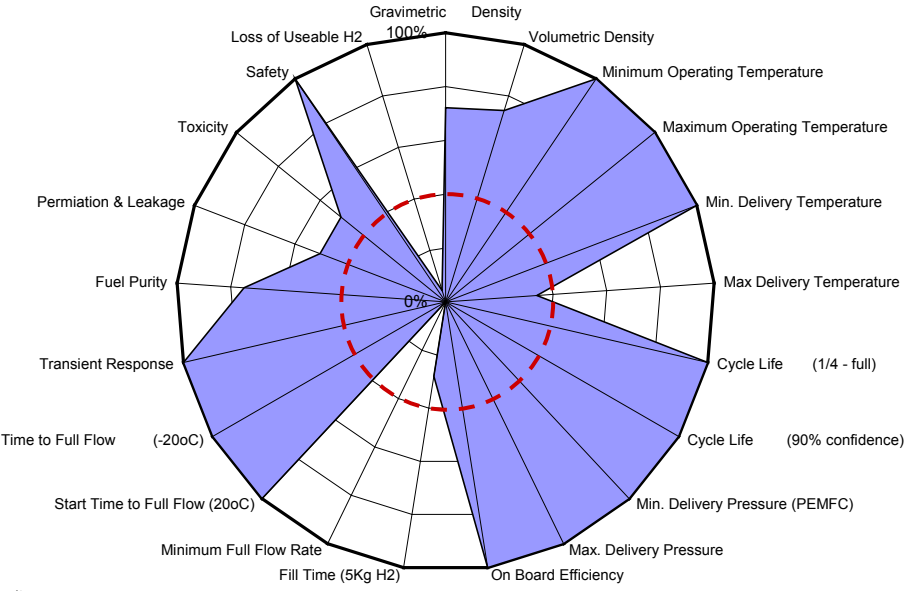
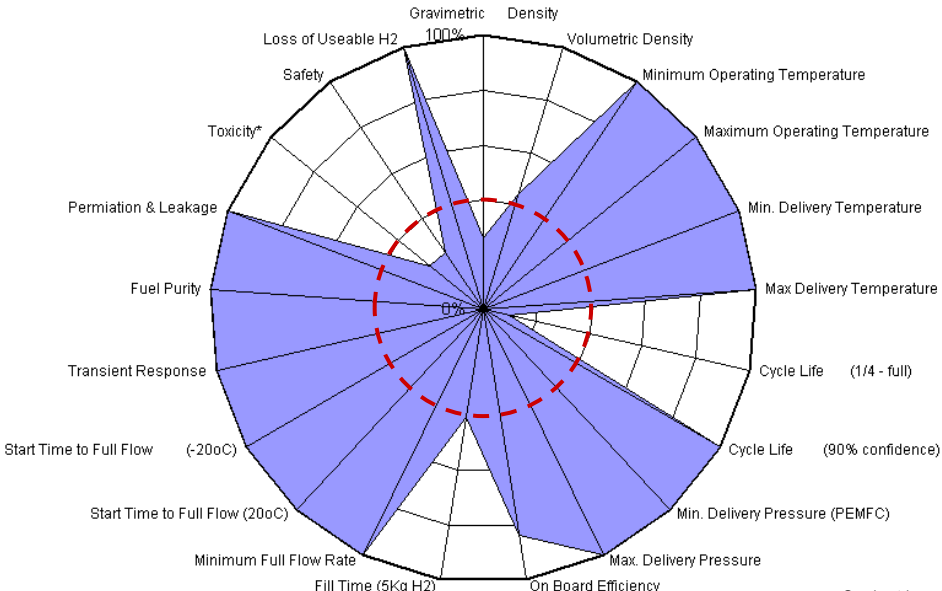


Suggests that Li-Mg-N materials may be the most promising metal hydrides for further consideration

(SRNL)

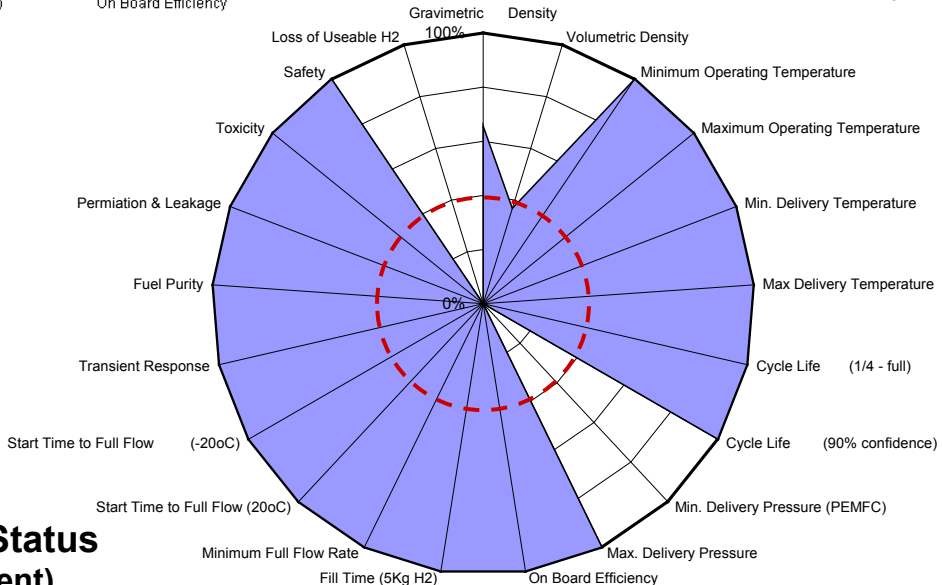
L(m) is the distance between heat transfer elements in meters

## Systems evaluated against complete set of performance targets



**Metal Hydrides (NaAlH<sub>4</sub>)**

**Chemical Hydride System (Solid Ammonia-Borane Bed)**



**Adsorbent System Status (AX-21 Cryo-Adsorbent)**

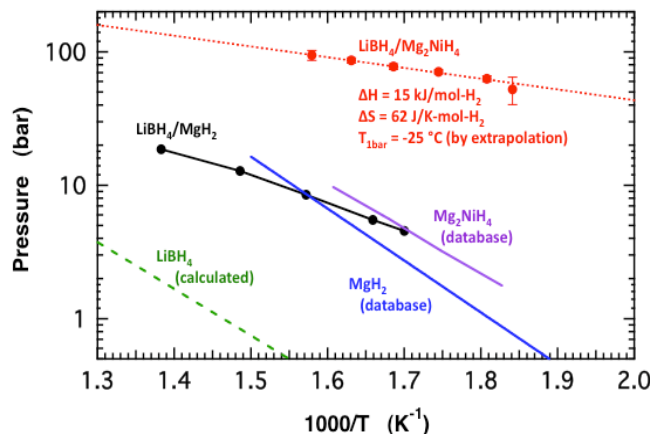
## Progress being made in reversible metal hydride material discovery

### Hydride Destabilization

- Destabilization results in lower  $\Delta H$  and  $T_{1\text{ bar}}$

#### LiBH<sub>4</sub>/Mg<sub>2</sub>NiH<sub>4</sub> system

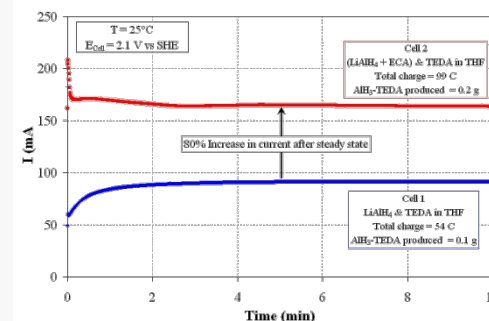
- $\Delta H$  (= 15 kJ/mol-H<sub>2</sub>) and  $\Delta S$  (= 62 J/K-mol-H<sub>2</sub>) are the lowest reported so far for a reversible system



(HRL)

### AlH<sub>3</sub> Generated Electrochemically

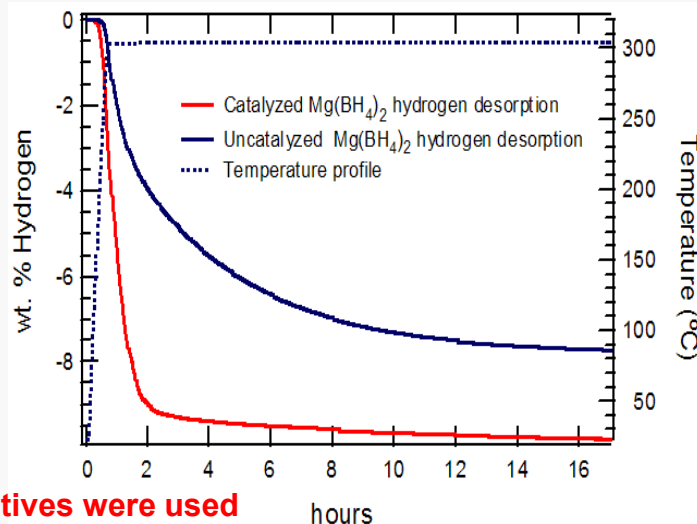
- ElectroCatalytic Additive found to increase steady-state current by 80%
- Dramatic increase in production rates.



(SRNL)

### Role of Additives on H<sub>2</sub> release from Mg(BH<sub>4</sub>)<sub>2</sub>

- 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



List what additives were used

### AlH<sub>3</sub> Regeneration

- Five pathways identified to form AlH<sub>3</sub> adducts from H<sub>2</sub> and Al
- Transamination demonstrated with high yields for DMEA and TMA.
- TEA-AlH<sub>3</sub> separated with ~70% recovered AlH<sub>3</sub>

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<sub>2</sub> with Al

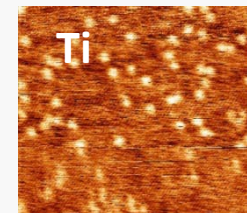
- Ti on clean Al surface critical for dissociating molecular hydrogen.
- Enables formation of mobile AlH<sub>x</sub> entities on the surface



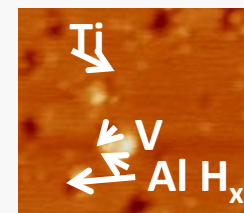
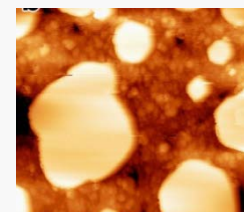
Aluminum on Silicon with no Ti



Aluminum on Silicon with Ti



With Hydrogen exposure

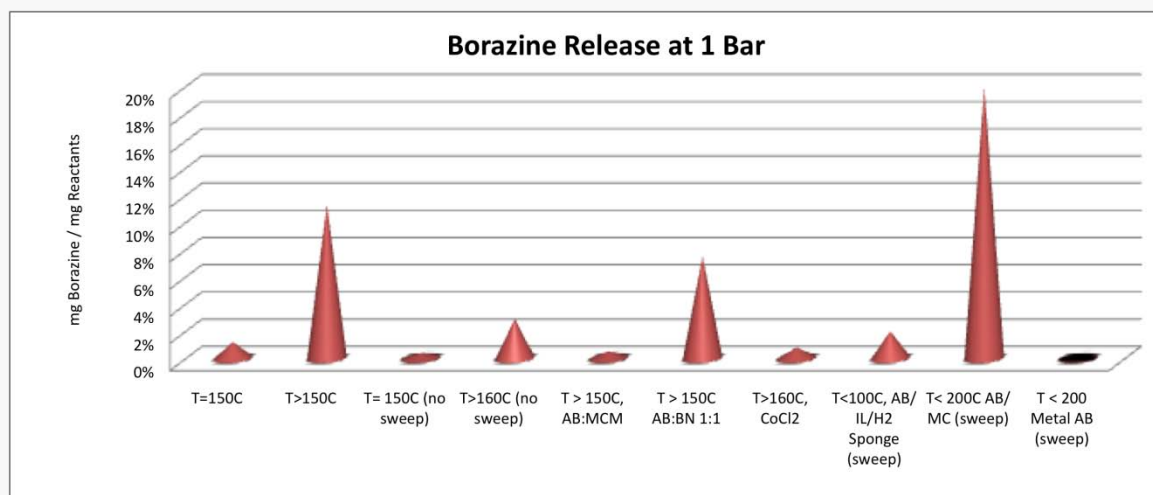


## Chemical Hydrogen Storage Material

### Impurities

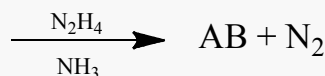
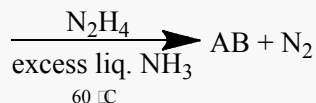
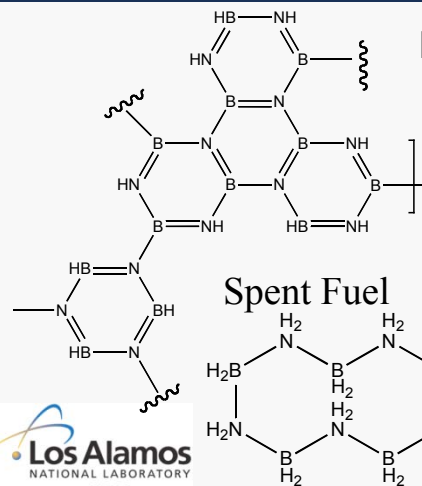
PNNL and LANL developed methods for quantification and strategies for mitigation of impurities released during hydrogen release from ammonia borane.

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

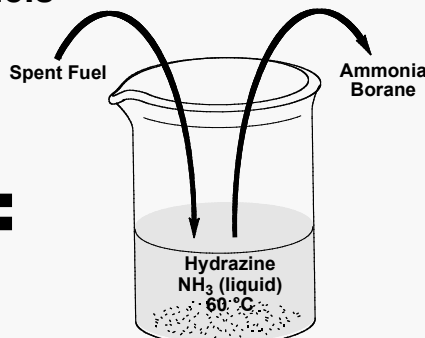


## Chemical Hydrogen Storage Material

### Regeneration of Spent Fuels



=



“one-pot” regen  
Quantitative conversion by NMR

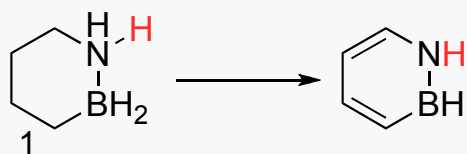
- Method gives ammonia borane for multiple spent fuel forms.
- Improvements in process efficiency and capital cost should result from the lower mass throughput (relative to previous process)

### New Materials from University of Oregon:

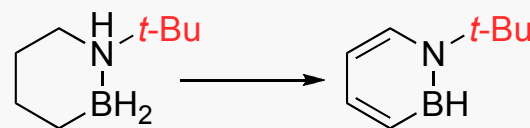
Coupling exothermic BHNH release with endothermic H-C-C-H in the same molecule is a successful approach

Material (1)

more readily available model of (1)

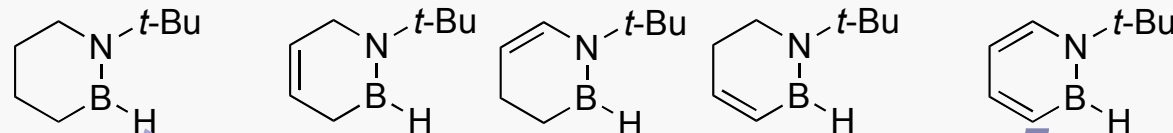


vs.



G at 298K = -2.3  
(kcal/mol)

G at 298K = -0.4  
(kcal/mol)



Rehydrogenates under mild conditions

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



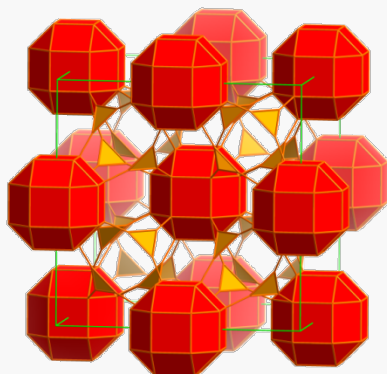
THE UNIVERSITY OF  
**ALABAMA**

UNIVERSITY OF  
**WASHINGTON**



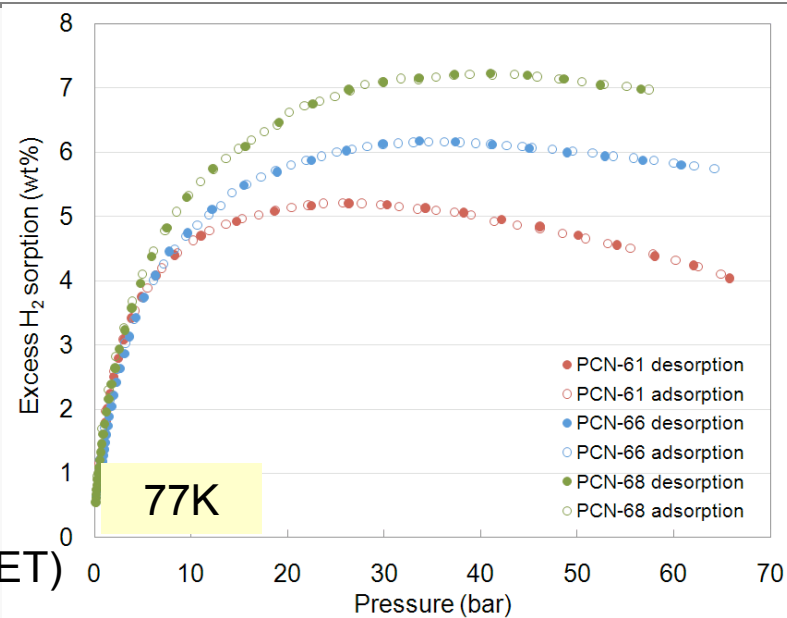
## Accomplishments: Cryosorbents

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



PCN-61    PCN-66    PCN-68

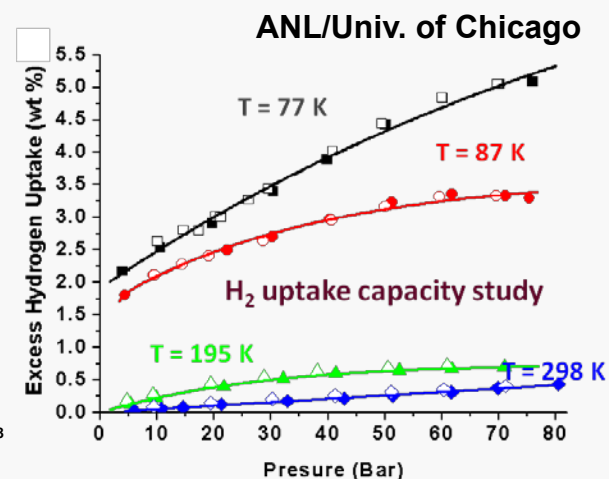
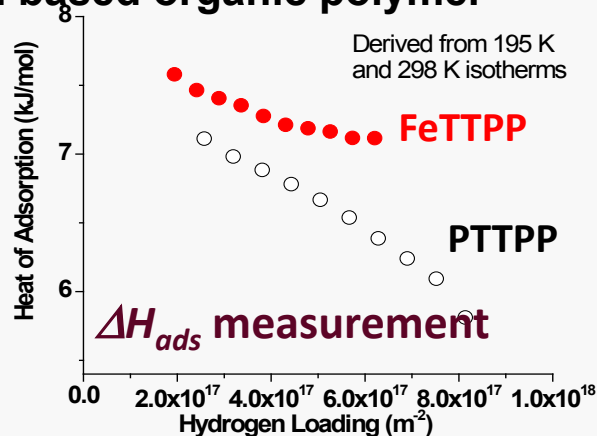
PCN-68: 6033 m<sup>2</sup>/g Langmuir (5109 m<sup>2</sup>/g BET) and ~ 7.2 wt% excess H<sub>2</sub> capacity



TAMU; Data by GM

## Nanostructured polyporphyrin based organic polymer

- Achieved H<sub>2</sub> uptake of 5.1w% at 77K and 0.6w% at RT
- Observed H<sub>2</sub> 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



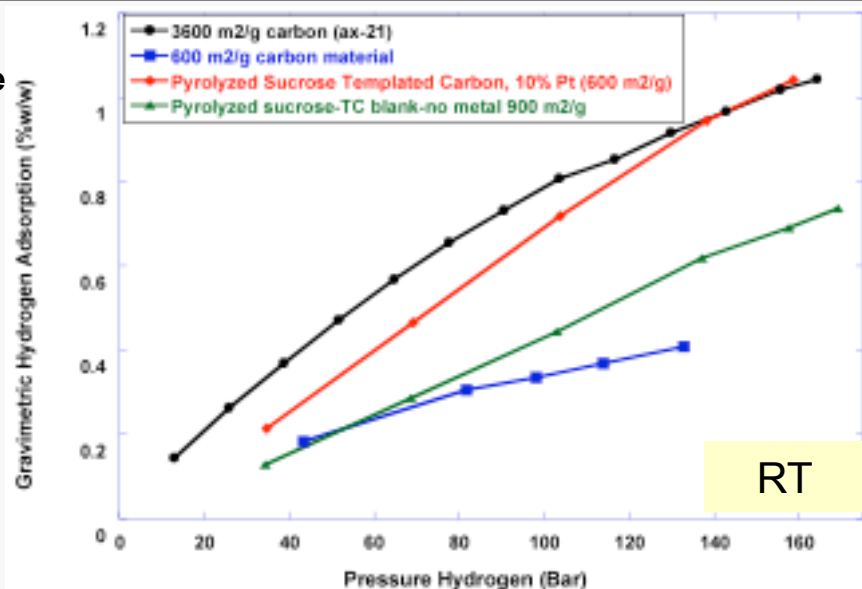


## Accomplishments: Towards Room Temperature & Moderate Pressure Conditions

### Weak Chemisorption Materials

Pt/ Carbon from Pyrolyzed Sucrose on Silica Sphere Template

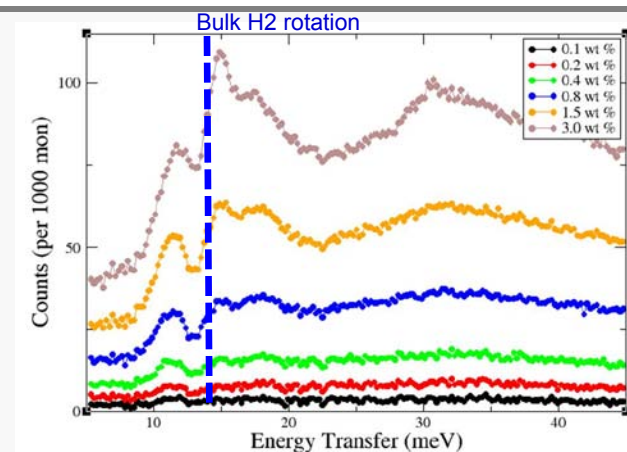
- **Excellent Kinetics: < 5 min to saturation**
- Adsorption of hydrogen still increasing at 150 bar
- Minimal irreversibility. Multiple cycles with no loss of sorption capacity or water formation.
- Demonstrates unique features of pyrolyzed sucrose that is used for “bridging” to MOFs
- Unexpected capacity on “small” surface area, 600 m<sup>2</sup>/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<sub>2</sub> interactions in a substituted carbon
  - DRIFTS observes reversible H interaction in B-C materials
- Experimental results confirm calculations that B-C increases  $\Delta H$  values



NIST and Penn State INS: H<sub>2</sub> rotational spectra

# 2010 Status: Compressed Gas

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

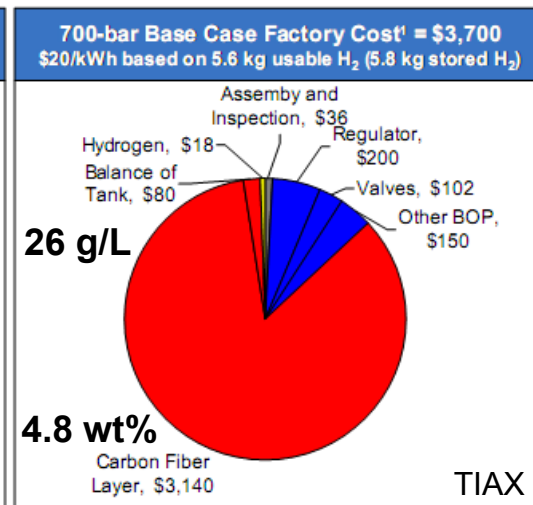
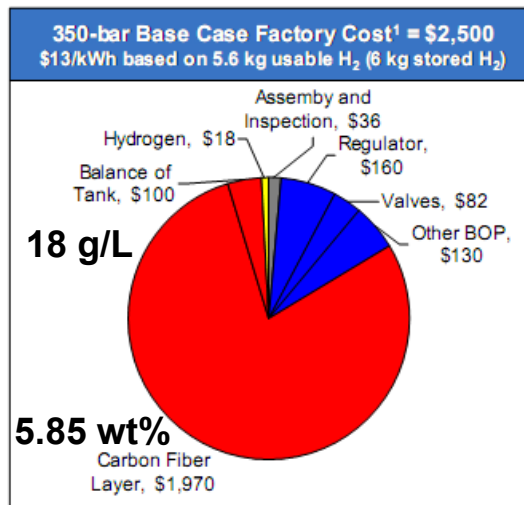
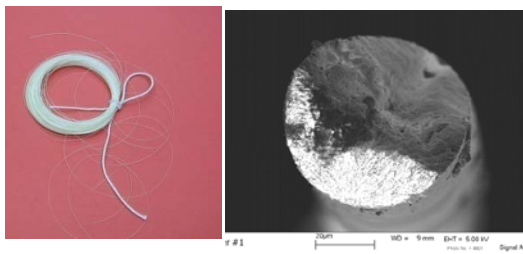


With conventional processing using a carbon fiber-grade (CF) PAN, precursor is over **50%** of the carbon fiber cost

#### 4 Elements of Cost Reduction

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

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



<sup>1</sup> Cost estimate in 2005 USD. Includes processing costs.

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

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.

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

# 2010 Progress: Analysis

## Cryogenic pressure vessels offer potential to exceed 2015 H<sub>2</sub> storage goals

3<sup>rd</sup> generation cryogenic pressure vessel prototype



2<sup>nd</sup> generation cryogenic pressure vessel prototype

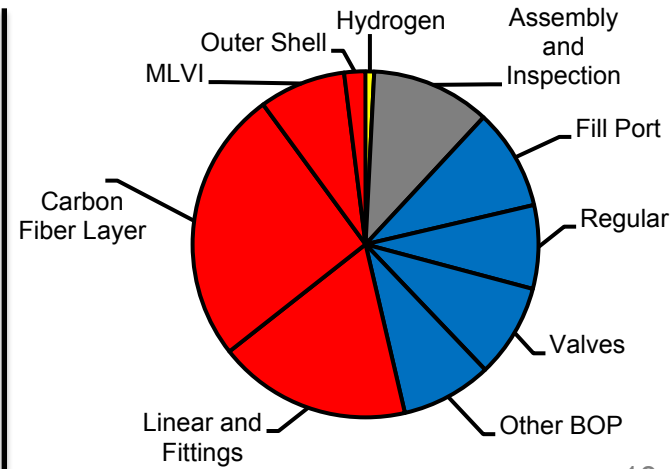
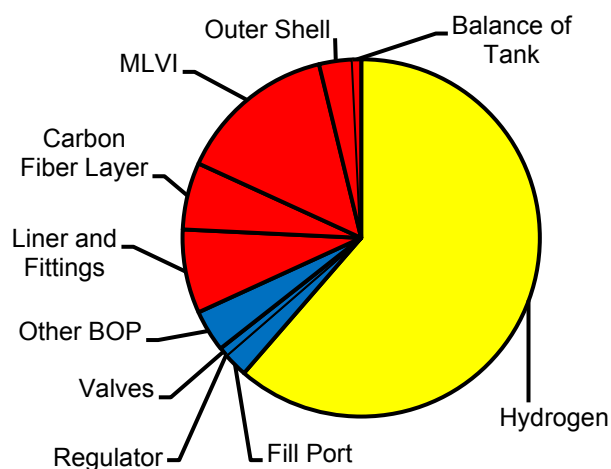
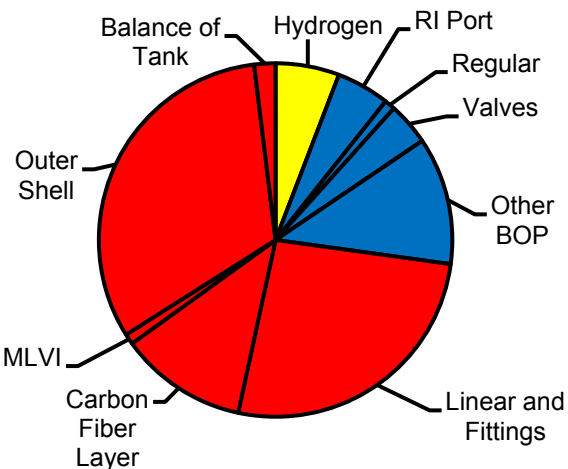
The 3<sup>rd</sup> generation cryogenic pressure vessel prototype saves 25 kg and 70 L compared to the previous 2<sup>nd</sup> generation prototype for storing 10.7 kg H<sub>2</sub> at 7.1 wt% H<sub>2</sub> and 44.5 kg H<sub>2</sub>/L (LLNL)

ANL/TIAX analyses indicate that scaling vessel size to store 5.6 kg H<sub>2</sub> for a passenger vehicle reduces capacities to 5.5 wt% H<sub>2</sub> at 42 g H<sub>2</sub>/L at lower cost than a 700-bar Compressed gas tank.

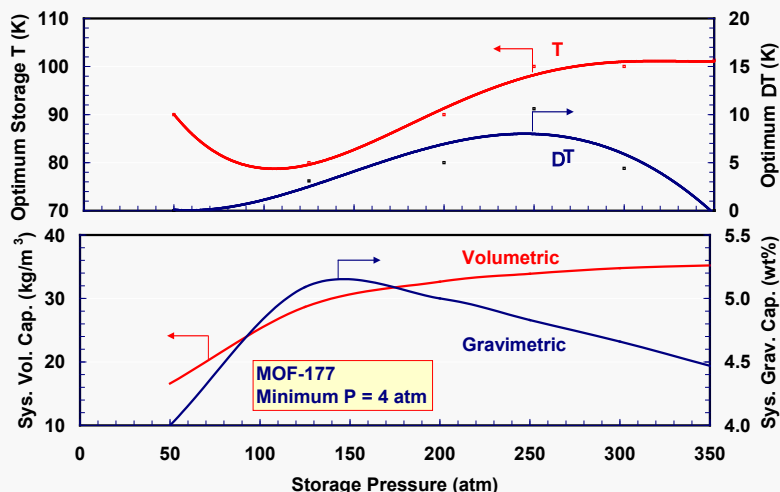
**5.8 kg Base Case Weight = 102 kg**  
5.5 wt% based on 5.6 kg usage LH<sub>2</sub>

**5.8 kg Base Case Volume = 131 L**  
43 g H<sub>2</sub>/L based on 5.6 kg usable LH<sub>2</sub>

**5.8 kg Base Case Factory Cost<sup>1</sup> = \$2,200**  
\$12/kWh based on 5.6 kg useable LH<sub>2</sub>



## Metal Organic Frameworks Adiabatic Liquid H<sub>2</sub> 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<sub>2</sub> discharged), 1.9 kW
- Variable Q, heat supplied only if tank P < 4 atm, 6.3-kW peak Q

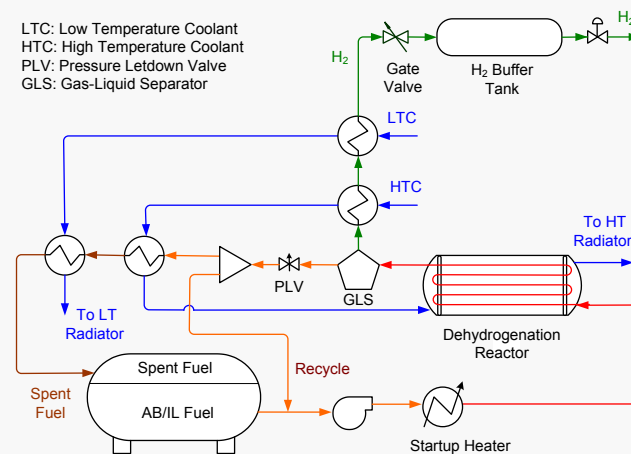
Performance & Cost Metric	MOF-177	Units
System Gravimetric Capacity	4.1	Wt%
System Volumetric Capacity	34.1	Kg-H <sub>2</sub> /m <sup>3</sup>
Storage System Cost	18	\$/kWh
Fuel Cost	4.6	\$/gge
Cycle Life (1/4 full tank)	5500	Cycles
Min Delivery Pressure	4	atm
System Fill Rate	1.5 – 2	Kg-H <sub>2</sub>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





## 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



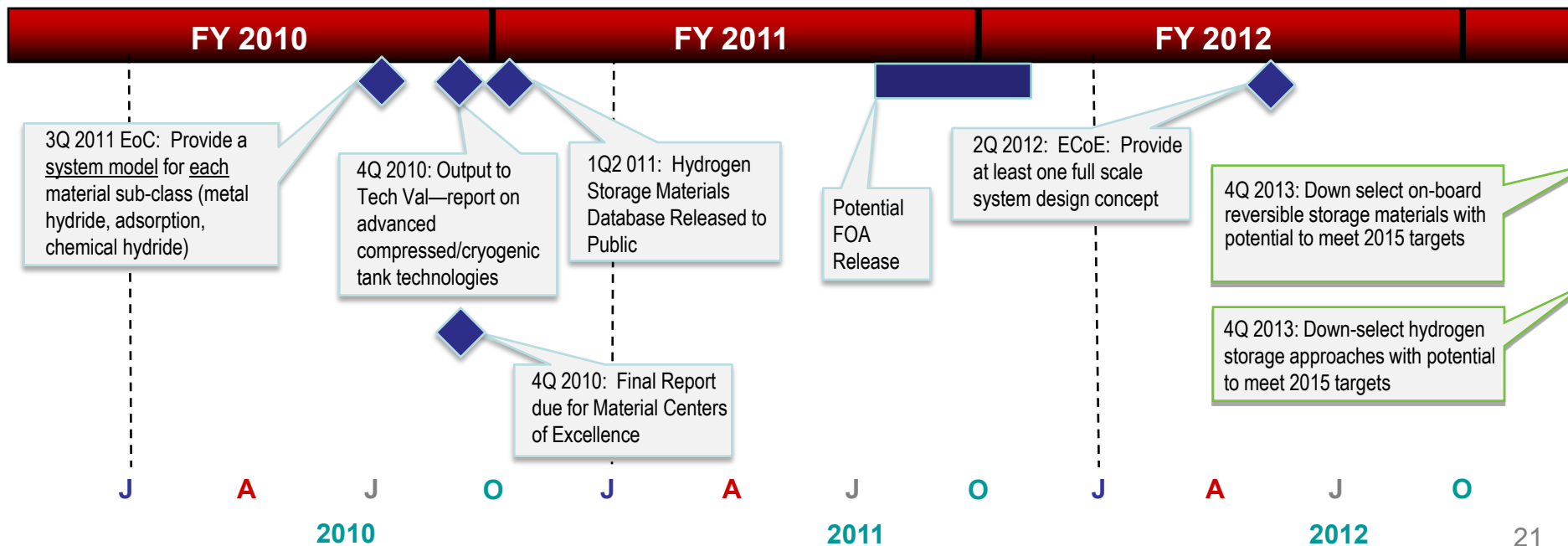
## Major Upcoming Milestones

### 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.



- 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.



- 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.**

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