U.S. DEPARTMENT OF ENERGY

Hydrogen Storage

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2007 DOE Hydrogen Program
Merit Review and Peer Evaluation Meeting

May 15, 2007

[1] Sandia- Retired, on assignment to DOE, Washington DC

Outline

- Goals and Objectives
  - Targets & challenges
- Budget
- Progress
  - Results in the last year
  - R&D examples
- Future Plans

Hydrogen Storage: The "Grand Challenge"

Goal: On-board hydrogen storage for > 300 mile driving range and meet all performance (wt, vol, kinetics, etc.) , safety and cost requirements.

These Are System Targets

↓

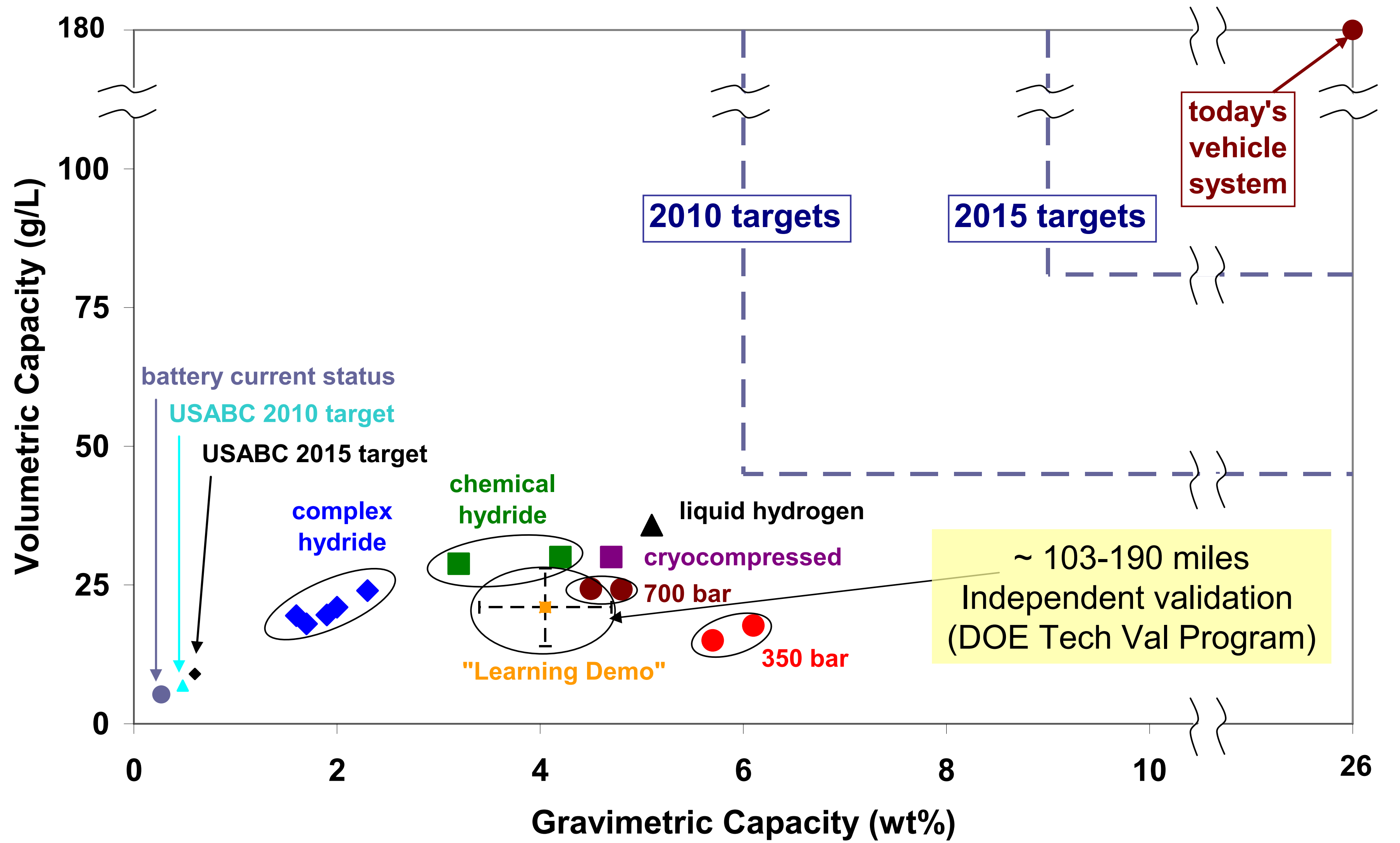
Material capacities must be higher!

Examples of Targets	2010	2015
System Gravimetric Capacity (net)	6 wt.% (2.0 kWh/kg)	9 wt.% (3.0 kWh/kg)
System Volumetric Capacity (net)	1.5 kWh/L (45 g/L)	2.7 kWh/L (81 g/L)
Storage System Cost	$4/kWh (~$133/kg H_2)	$2/kWh ($67/kg H_2)
Min. Full Flow Rate	0.02 g/s/kW	0.02 g/s/kW
Refueling Time (for 5 kg)	3 min	2.5 min
Cycle Life (Durability)	1000 cycles	1500 cycles

More targets and explanations at www.eere.energy.gov/hydrogenandfuelcells/

Current Status vs. Targets

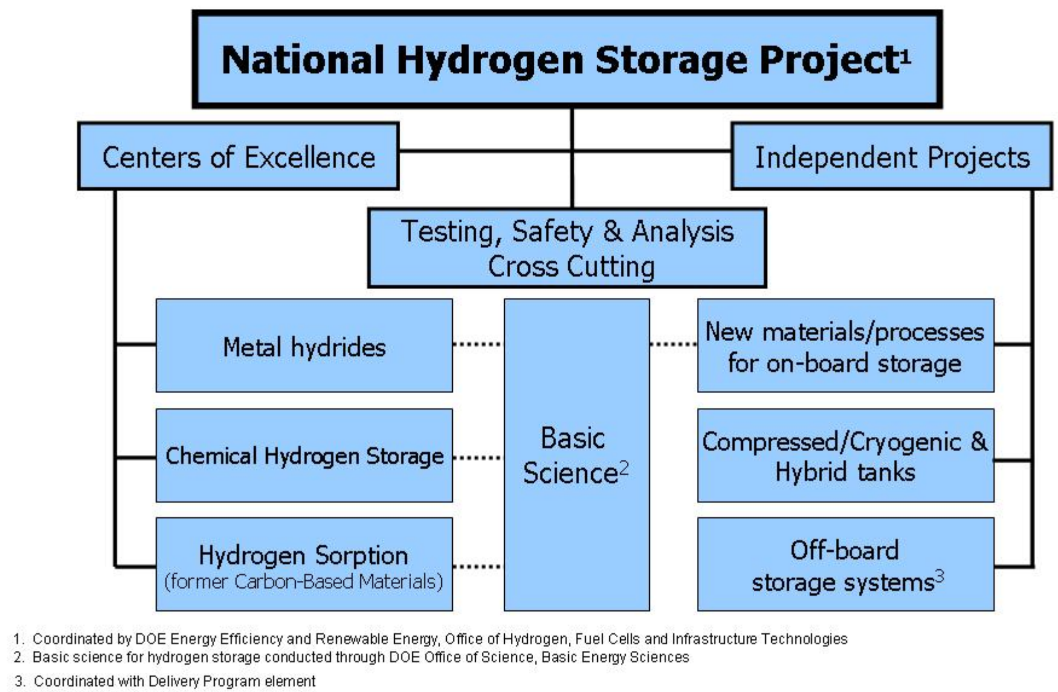
No technology meets targets- results include data from vehicle validation



Estimates from developers & analysis results; periodically updated by DOE. "Learning Demo" data is for 63 vehicles.

Strategy: Diverse Portfolio with Materials Focus

"…DOE should continue to elicit new concepts and ideas, because success in overcoming the major stumbling block of on-board storage is critical for the future of transportation use of fuel cells."[1]

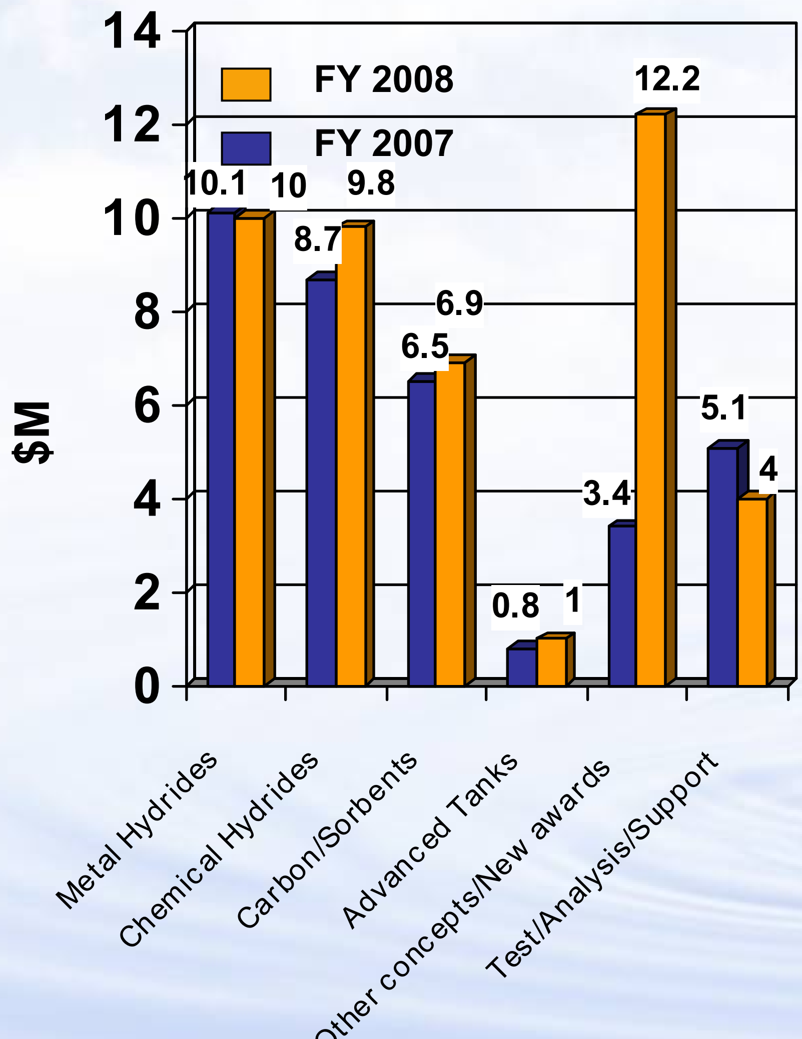


- Balanced portfolio
- ~ 40 universities, 15 companies, 10 federal labs
- Aims to address NAS & other peer review recommendations
- Annual solicitation for increased flexibility
- Close coordination with basic science
- Coordination with industry, other agencies & globally

1. NRC H_2 Economy Report (2004) p.44

Applied R&D Hydrogen Storage Budget

FY2008 Budget Request = $43.9M
FY2007 Appropriation = $34.6M
(FY2006 Appropriation = $26.0M)



- **Emphasis:** Ramp up materials R&D through CoE & independent projects
- Tailor materials to focus on T, P, kinetics (as well as capacity)
- New Center of Excellence planned- Engineering Sciences*

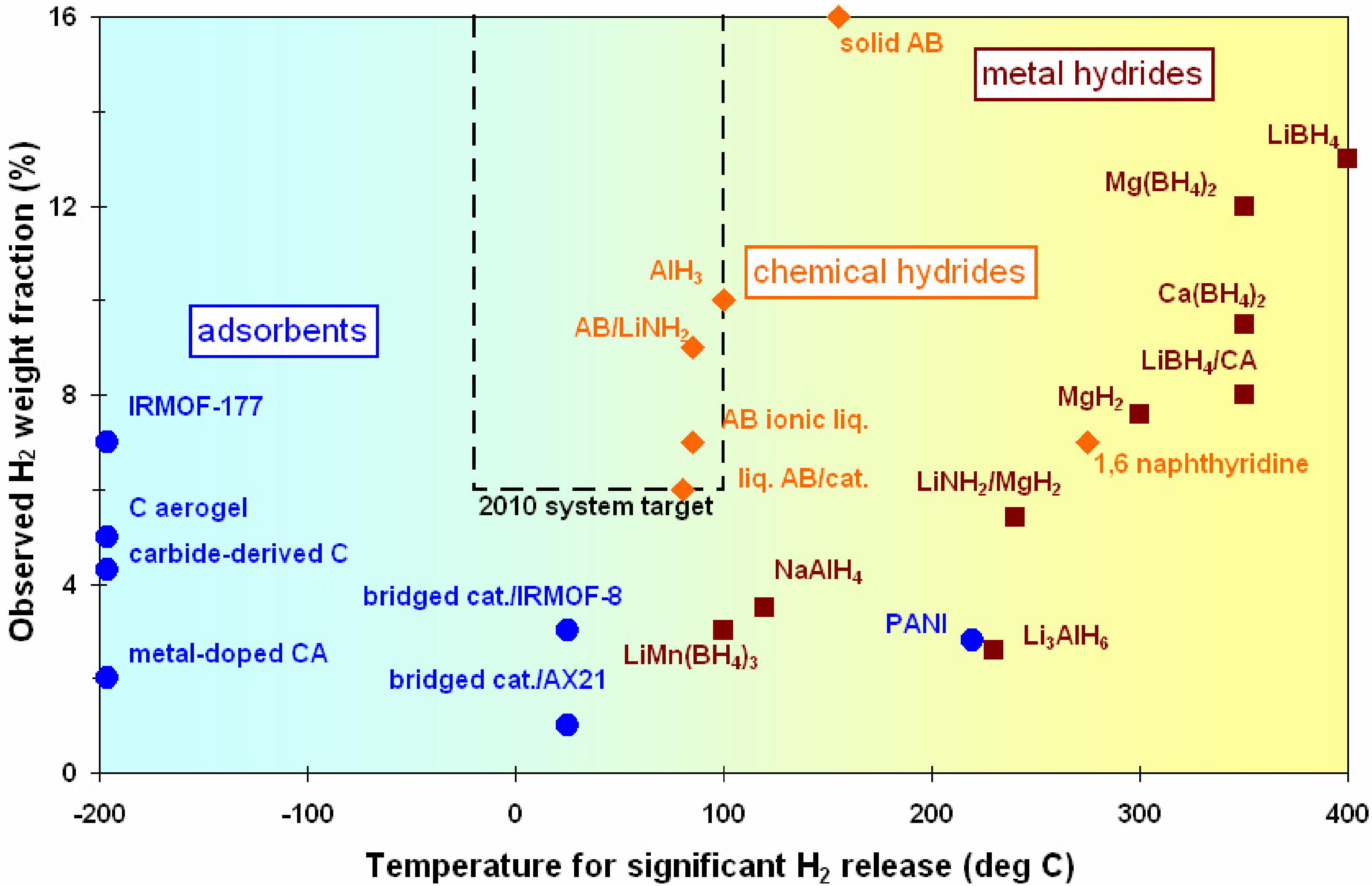
Close coordination with Basic Science
$36.4M (FY07)
$59.5M (FY08)
Includes basic science for hydrogen storage, production and use (e.g., catalysis, membranes, etc.)

*subject to appropriations

Selected Examples of Progress: High capacity materials also focused on improving thermodynamics, kinetics, regeneration

	Metal Hydrides	Chemical H_2 Storage	Adsorbents/Carbon
2006	Alane ~8-10 wt%,~150 g/L (<150 C) Borohydrides >9 wt%,~100 g/L (~250 - 350 C) Destabilized Binary hydrides ~5-7wt%,~60-90 g/L (~250 C) Li Mg Amides ~5.5wt%,~80 g/L (>200 C)	4,7 Phenanthroline (organic liquids) ~7 wt%, ~65 g/L(<225 C) Seeded Ammonia Borane ~9 wt%,~90 g/L(>120 C) Ammonia Borane/Li amide ~7 wt%, ~54 g/L(~85 C)	Metal-Organic Frameworks IRMOF-177 ~7 wt%,~30 g/L(77K) Bridged catalysts/IRMOF-8 ~1.8 wt.%,~10 g/L (room temperature) Metal/carbon hybrids, MetCars (*theory) ~6-8wt%*,~39 g/L*
2007	Alane (AlH_3) regeneration Chemical, electrochemical, supercritical fluids $LiBH_4$/C aerogels 6-8 wt.%, ~55-75 g/L (~300 C) Reversible $Ca(BH_4)_2$ ~9.6 wt.%, ~105 g/L (~350 C) $Mn(BH_4)_2$ 9-13 wt.% (>100 C) $Mg(BH_4)_2$ 9-12 wt.%, ~110 g/L (~350 C) Destabilized hydrides DFT identified new reactions $LiBH_4/MgH_2$, $CaH_2/LiBH_4$, $LiNH_2$/LiH/Si	1,6-Naphthyridine ~7 wt.%, ~70 g/L (275 C) Surface supported catalyst Amine boranes Ionic liquids ~7 wt.%, 39 g/L (85 C) AB/$LiNH_2$, AB/LiH ~9 wt.%, ~70 g/L (85 C) Solid AB >16 wt.%, >199 g/L (155 C) (>3g/s/kgAB) Liquid AB/catalyst ~ 6 wt.% (~ 80 C) Regeneration 2 step process, est.>50% eff.	Bridged cat./IRMOF-8 >3 wt.%, 100 bar (25 C) ~20 kJ/mol Bridged cat./AX-21 >1 wt.%, 100 bar (25 C) C aerogels ~5 wt.%, ~30 g/L (77 K) Metal-doped C aerogels ~2 wt.% (77 K) ~7-7.5 kJ/mol PANI 2.8 wt.%, 25 bar (25 C) Release at ~100-220 C

Progress: Material Capacity vs. Temperature

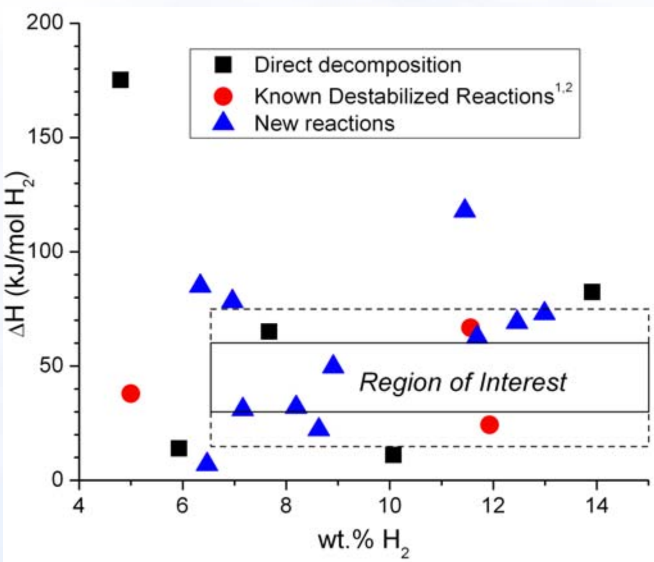


G. Thomas, et al., DOE (April 2007)

Results: Theory Guided Materials Discovery

Theory for rapid screening

- >160 compounds
- >300 reactions
- Energetically favored systems identified



Alapati, Johnson and Sholl,
J. Phys. Chem. B 110 (2006) 8769

Example: Experimental progress

Theory predicted promising properties

$$3Ca(BH_4)_2 \longrightarrow CaB_6 + 2CaH_2 + 10H_2$$

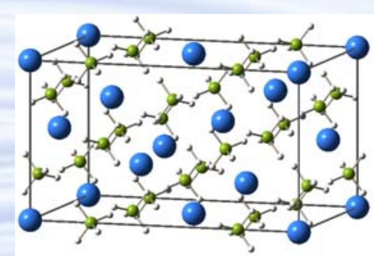
9.6 wt. % ΔH = 53 kJ/mole

Theory guides experiment ↓ ↑ *Experiment refines theory*

Developed synthesis route (75-80% yield)
Reversibility demonstrated

$$CaB_6 + 2CaH_2 \xrightarrow[390\ ^\circ C]{100\ bar\ H_2} 1\%\ \text{rehydrided}$$

$$CaB_6 + 2CaH_2 \xrightarrow[400\ ^\circ C]{700\ bar\ H_2} \text{fully rehydrided}$$

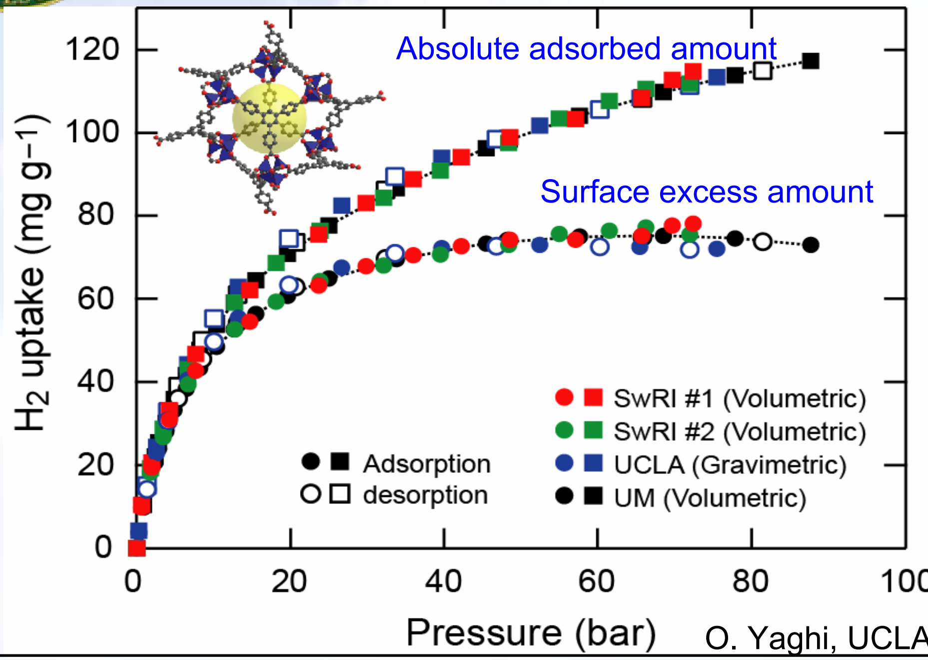


E. Ronnebro, E. Majzoub et al. Sandia

Majzoub, D. Johnson, Bowman et al., MHCoE

Phys Rev B 74, 155122 (2006)

Results: Sorbent Materials

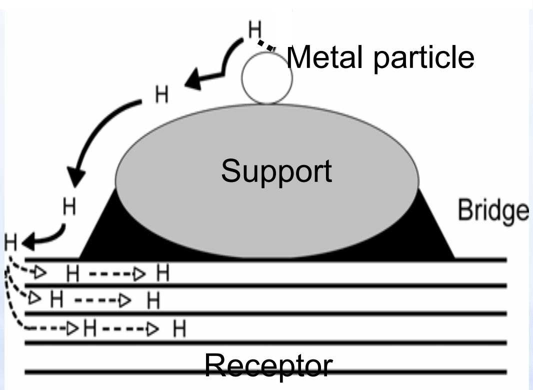


O. Yaghi, UCLA

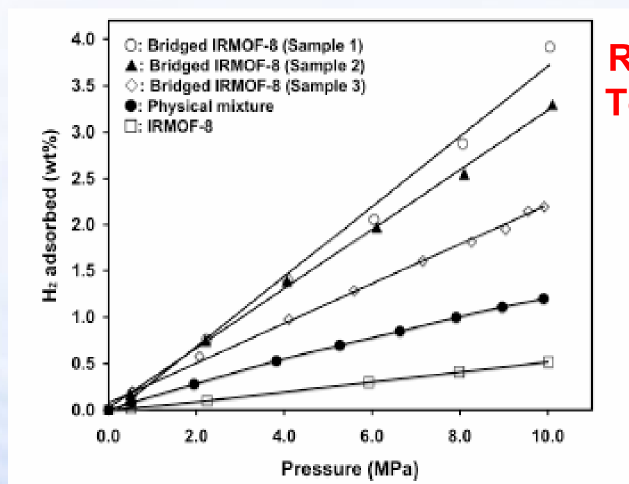
Independent verification of MOF-177 (O. Yaghi et al.- highest capacity to date worldwide; > 7 wt.%, 77 K)

Independent verification of > 2x increase in capacity due to spillover (R. Yang et al.)

Spillover by Yang, U Michigan

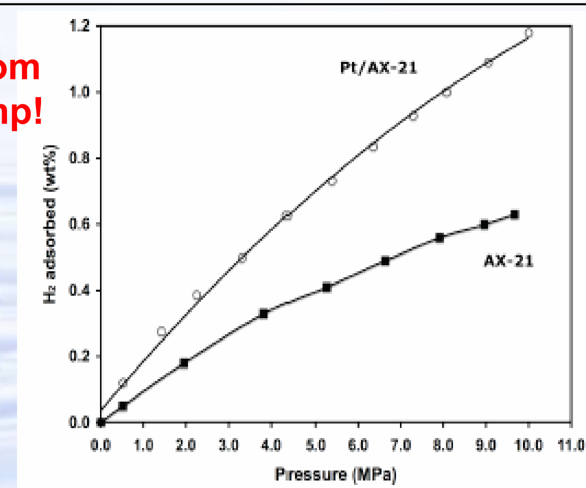


R. Yang, U. MI



Room Temp!

R. Yang, U. MI

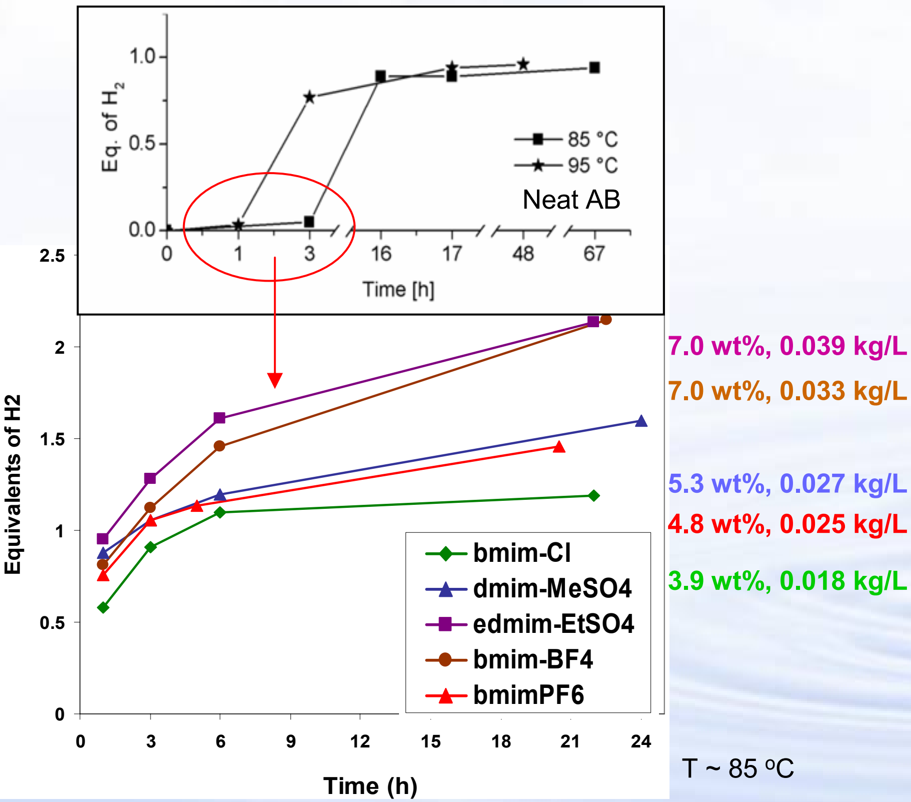


R. Yang, U MI, P. Parilla, et al., NREL & HS Center

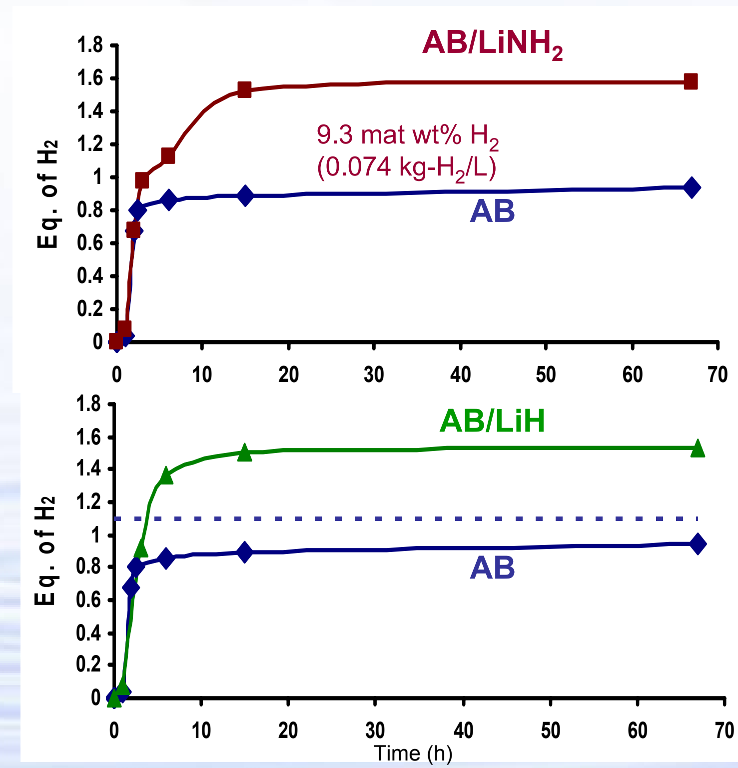
Results: AmineBoranes- Hydrogen Release

$NH_3BH_3 \rightarrow BNH_x + 3H_2$ **19.4 wt.%, 160 g/L** (theoretical material capacity)

New ionic liquids enhance H release; eliminate induction time



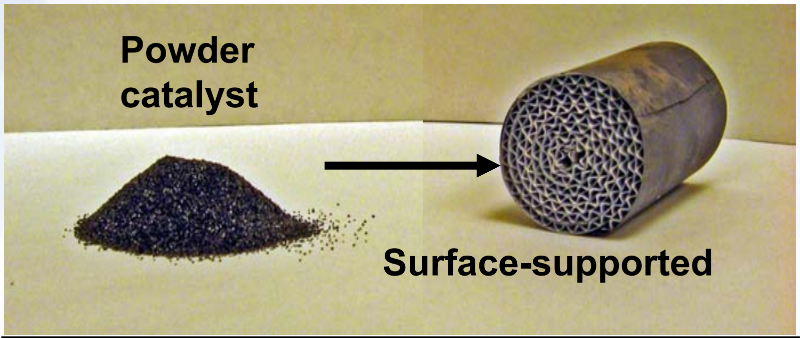
Chemical promoters enhance H release in ammonia borane (AB)

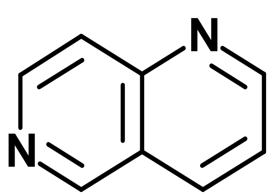


Sneddon, et al, U. Penn and CH Center

Results: Liquid Carriers and Systems Analysis

Organic liquid carriers & catalysts





1,6-Naphthyridine

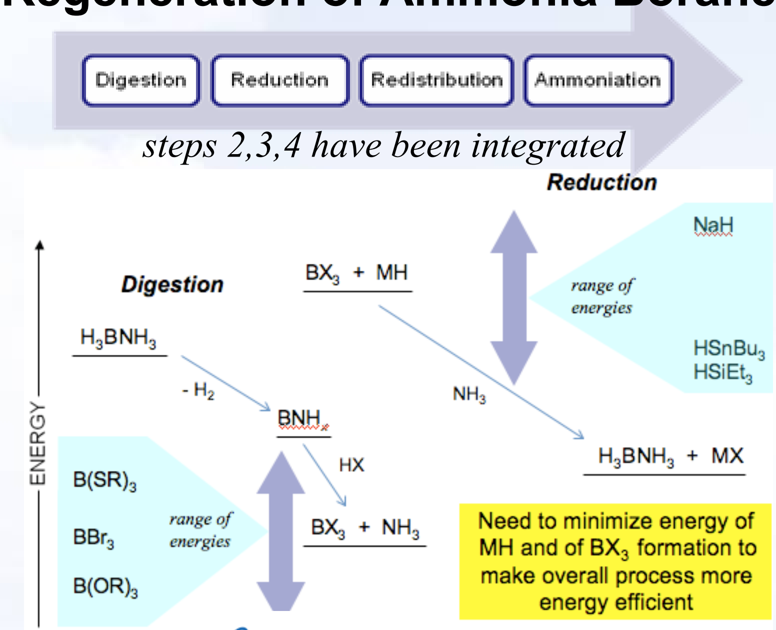
Liquid at room temp.

7.2 wt. % H_2, ~70 g H_2/l

release temp. ~275 C

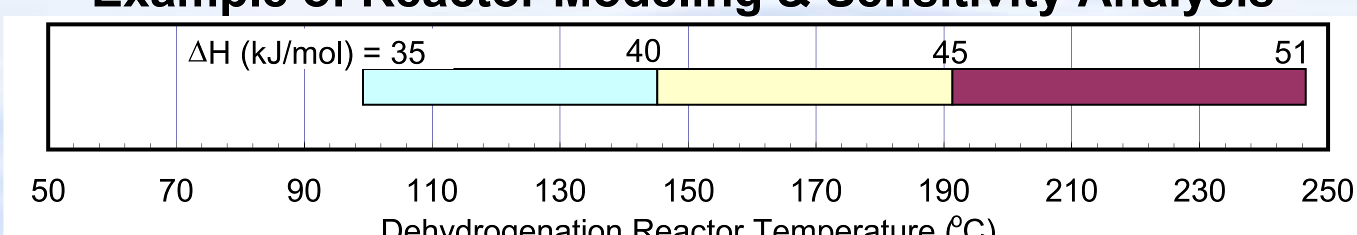
A. Cooper, et al., Air Products

Regeneration of Ammonia Borane



THE UNIVERSITY OF ALABAMA · Los Alamos NATIONAL LABORATORY EST.1943 · Penn UNIVERSITY of PENNSYLVANIA · Pacific Northwest

Example of Reactor Modeling & Sensitivity Analysis



R. Ahluwalia, et al. ANL

Results: Regeneration Option Assessments

Example of systematic approach to down-selects

Option Criterion	Weighting	Schlesinger	Metal Reduction							Echem			Borane			
			Mg	Al	Ti	Si	Zn	Carbothermal	Elemental	1-stop	2-step	HT melts	BCl3	TMB	M + B2O3	Metathesis
Chemistry demonstrated	**Pref**	**Yes**	**Yes**	**Yes**	**No**	**Yes**	**No**	**No**	**Yes**	**Yes**	**Yes**	**No**	**Yes**	**Yes**	**Yes**	**Yes**
Cost/per unit H2 (NaBH4)																
Energy consump (theor efficiency)	**25**	1	5	7	7	7										8
Raw material consump - high conv /yields	**25**	3	8	7	7	7										7
Low operating severity	**5**	7	8	8	8	8										7
Few chemical reactions	**5**	5	8	8	8	8										5
Few separation/processing steps	**5**	5	8	8	8	8										5
Capital cost, $ per unit H2 (NaBH4)																
Low complexity	**10**	6	8	8	8	8										5
Low technical risk	**5**	10	7	7	7	7										7
EHS (environmental / health / safety)																
Emissions, wastes, CO2	**10**	10	8	8	8	8										6
toxicity, safety, flammability, H2O-reactive	**5**	8	7	6	7	7										6
other ecological components?																
Logistics (supply / distribution)																
Abundant raw materials	**5**	10	7	10	7	8	6	10	8	10	10	10	10	10	8	10
Total Score		**485**	**710**	**745**	**735**	**740**	**780**	**725**	**700**	**675**	**680**	**645**	**560**	**565**	**535**	**560**

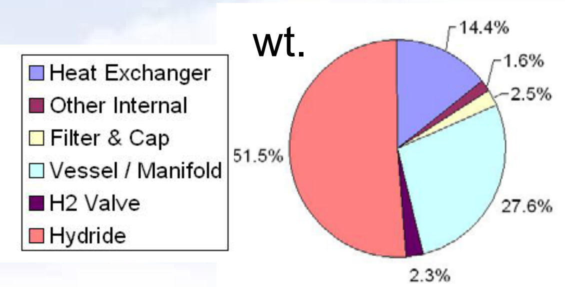
- Assess efficiency potential & other factors for viable chemical carriers
- Develop & demonstrate chemistry & processes to improve regeneration efficiency

Different weighting factors can be analyzed

Linehan, Lipiecki, Chin, Rohm & Haas and CH Center

Results: Systems, Safety, Testing & Analyses

2nd Gen Prototype Built (Ti-NaAlH4)



Estimated 2.0 wt% & 21 g/L (Projected 2.3 wt.% and 24 g/L)

Mosher, et al, UTRC

Cryo-Compressed Tank Concept Demonstrated w/ DOE Tech Val.

4.7 wt. %

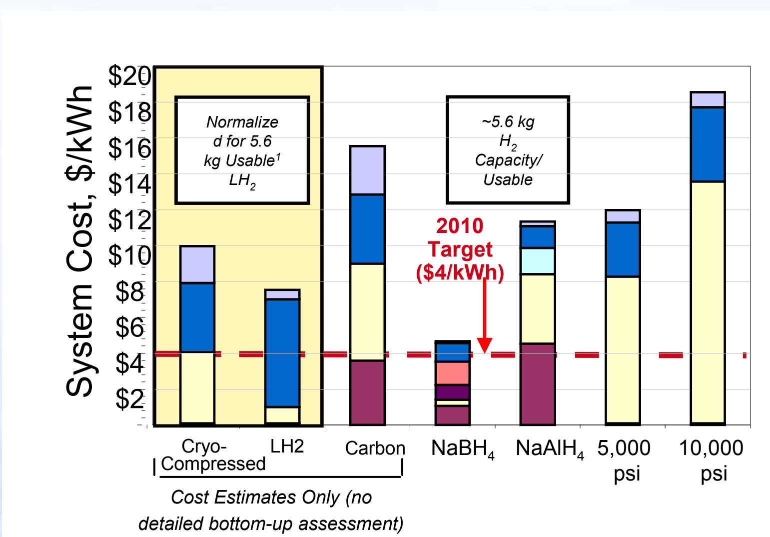
30 g/L

(ANL estimate)

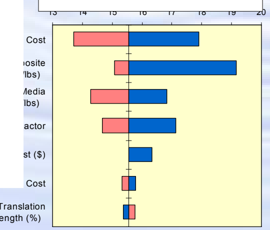
Aceves, Berry, et al, LLNL

Examples of Storage System Cost Analyses

Sensitivity analysis shows key cost drivers



Cost Estimates Only (no detailed bottom-up assessment)



Lasher, et al. TIAX LLC

SwRI- Independent testing underway

New: Storage Materials & Systems Safety (U.S., Japan, Germany, Canada)

Examples of Hydrogen Storage Collaboration

IEA – HIA TASK 22

A total of 43 projects have been proposed for Task 22. This includes participation by 15 countries, 43 organizations, and 46 official experts.

Project Types:

- Experimental
- Engineering
- Theoretical Modeling (scientific or engineering)
- Safety Aspects of Hydrogen Storage Materials

Classes of Storage Media

- Reversible Metal Hydrides
- Regenerative Hydrogen Storage Materials
- Nanoporous Materials
- Rechargeable Organic Liquids and Solids

IPHE

- **Reversible Solid State Hydrogen Storage for Fuel Cell Power supply system** *(Russian Academy of Sciences)*
- **NESSHY – Novel Efficient Solid Storage for Hydrogen** *(National Center for Scientific Research "Demokritos," EU)*
- **Hydrodes & Nanocomposites in Hydrogen Ball Mills** *(University of Waterloo, Canada)*
- **Combination of Amine Boranes with MgH_2 & $LiNH_2$** *(Los Alamos & Pacific Northwest National Labs, USA)*
- **Fundamental Safety Testing & Analysis** *(Savannah River National Lab, USA)*

DoD: DEFENSE LOGISTICS AGENCY

New Storage Awards (4/07):

- **High throughput - Combinatorial Screening:** U of Central Florida, UC Berkeley & Symyx, Miami U (Ohio) & NREL
- **Reversible System Dev't & Demonstration:** Energy Conversion Devices, U of Missouri (phase 1 design)

Interagency Hydrogen R&D Task Force (OSTP)

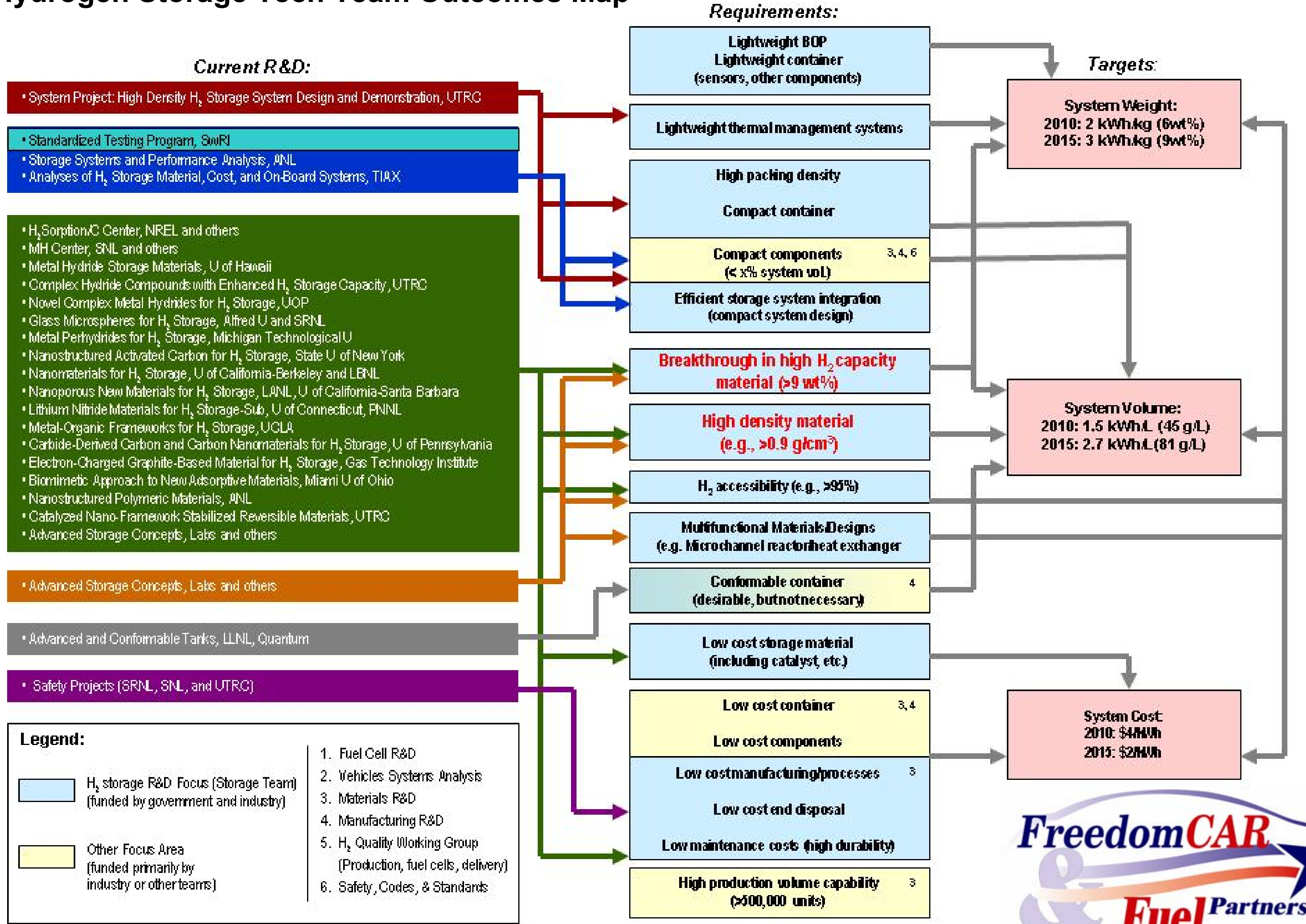
NSF- proposal review in process (5/07)

NIST- neutron scattering

Strategy & Execution

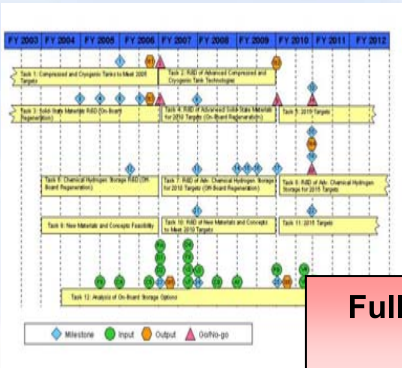
Example- maps portfolio & requirements to meet targets

Hydrogen Storage Tech Team Outcomes Map



FreedomCAR & Fuel Partnership

Key Milestones & Future Plans



2006 | 2007 | 2008

Mar | Jun | Sep | Dec | Mar | Jun | Sep | Dec | Mar

- Theory Focus Session
- Test Facility Validation
- Full Proposals Due
- Assessment of Center Approach
- No-Go on pure Single walled Nanotubes
- Cryo-compressed Tank Assessment
- 2nd System Prototype Complete
- RD&D Plan Updates online
- New Awards Announced
- RFI on New Center of Excellence
- Annual Solicitation *
- Go/No Go $NaBH_4$
- Downselect Reversible Metal Hydrides
- Assess & update targets if required
- New CoE Solicitation *
- Downselect Chemical H_2 Storage Mat'ls

Keep up the sustained effort and high technical quality work & be flexible!

Address volumetric capacity, T, P, kinetics, etc. (not just wt. %!)

*Subject to appropriations and direction

For More Information

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Acknowledgements

DOE Researchers
Global Hydrogen Storage R&D Community
FreedomCAR & Fuel Partnership Technical Team
Reviewers

In Memoriam
Professor Alan MacDiarmid*
1927-2007

*2000 Nobel Prize in Chemistry (conducting polymers)

Thank you

Additional Information

Applied R&D Hydrogen Storage "Grand Challenge" Partners:
Diverse Portfolio with University, Industry and National Lab Participation

Centers of Excellence

Metal Hydride Center

National Laboratory:
Sandia-Livermore

Industrial partners:
General Electric
HRL Laboratories
Intematix Corp.

Universities:
CalTech
Stanford
Pitt/CMU
Hawaii
Illinois
Nevada-Reno
Utah

Federal Lab Partners:
Brookhaven
JPL, NIST
Oak Ridge
Savannah River

Hydrogen Sorption Center

National Laboratory:
NREL

Industrial partners:
Air Products & Chemicals

Universities:
CalTech
Duke
Penn State
Rice
Michigan
North Carolina
Pennsylvania

Federal Lab Partners:
Lawrence Livermore
NIST
Oak Ridge

Chemical Hydrogen Storage Center

National Laboratories:
Los Alamos
Pacific Northwest

Industrial partners:
Intematix Corp.
Millennium Cell
Rohm & Haas
US Borax

Universities:
Northern Arizona
Penn State
Alabama
California-Davis
Univ. of Missouri
Pennsylvania
Washington

Independent Projects

Advanced Metal Hydrides
UTRC, UOP
Savannah River Nat'l Lab
Univ. of Connecticut

Sorbent/Carbon-based Materials
UCLA
State University of New York
Gas Technology Institute
UPenn & Drexel Univ.
Miami Univ. of Ohio

Chemical Hydrogen Storage
Air Products & Chemicals
RTI
Millennium Cell
Safe Hydrogen LLC
Univ. of Hawaii

Other New Materials & Concepts
Alfred University
Michigan Technological University
UC-Berkeley/LBL
UC-Santa Barbara
Argonne Nat'l Lab

Tanks, Safety, Analysis & Testing
Lawrence Livermore Nat'l Lab
Quantum
Argonne Nat'l Lab, TIAX LLC
SwRI, UTRC, Sandia Nat'l Lab
Savannah River Nat'l Lab

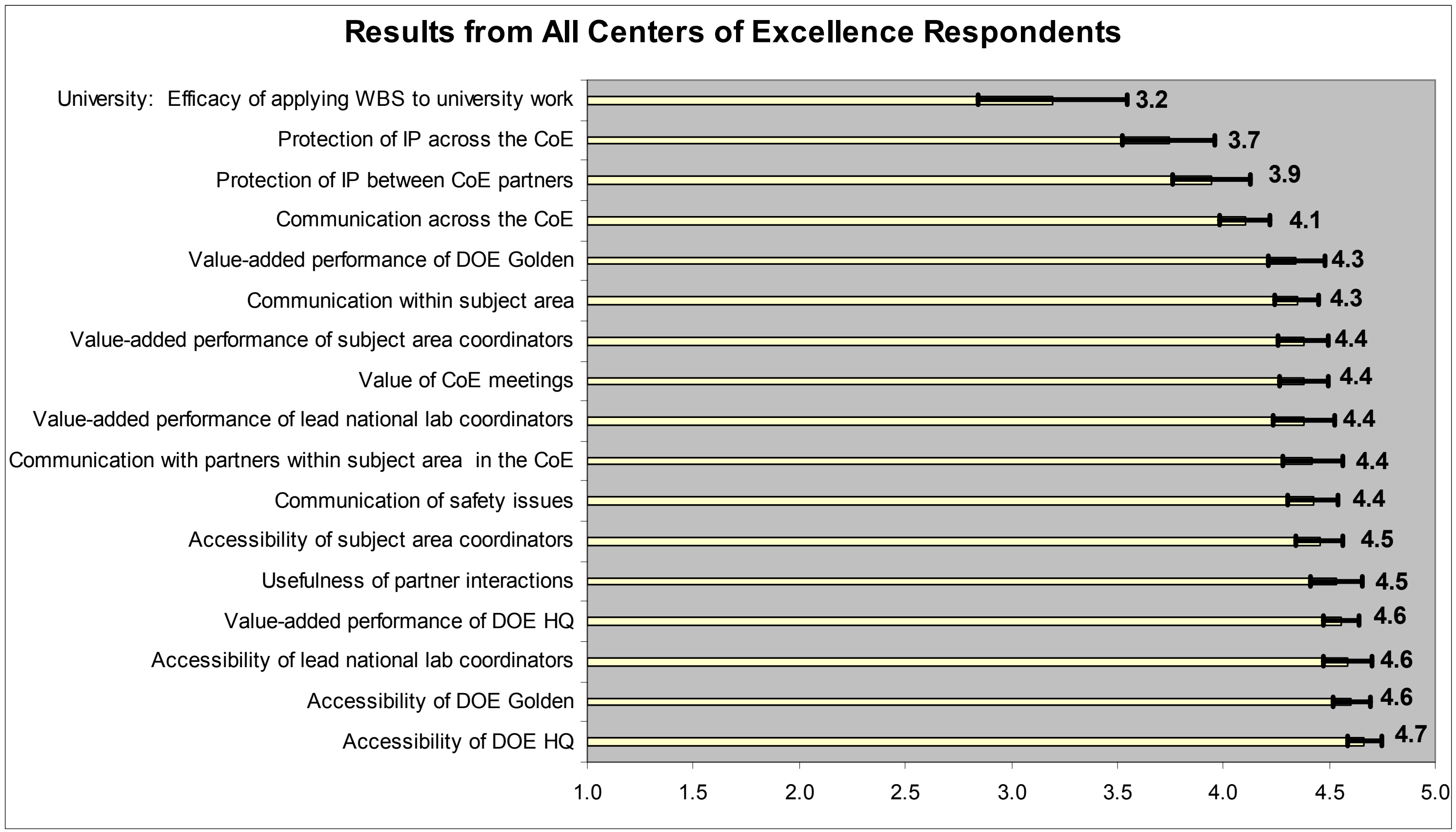
Coordination with: Basic Science (Office of Science, BES)

MIT, U.WA, U. Penn., CO School of Mines, Georgia Tech, Louisiana Tech, Georgia, Missouri-Rolla, Tulane, Southern Illinois; Labs: Ames, BNL, LBNL, ORNL, PNNL, SRNL

Programmatic Results: Focus on strategy & execution

Assessment of CoE model:

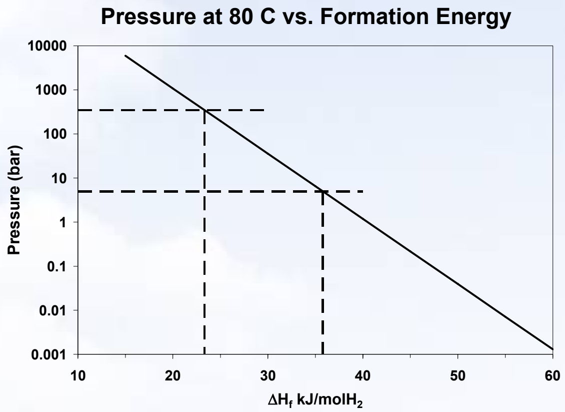
Multi-institutional critical mass applied R&D is proving to be effective



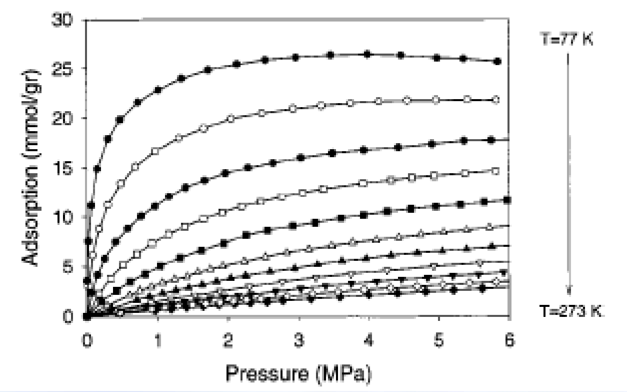
- Annual Solicitation (6 new projects complement portfolio)
- No-go (FY06) on *pure* SWNTs (doped C/basic science still go)
- Assessment of Cryo-compressed tanks complete
- Outcomes maps done & targets revisited through FreedomCAR

It's not just about capacity- much research is focused on tailoring kinetics & thermodynamics…

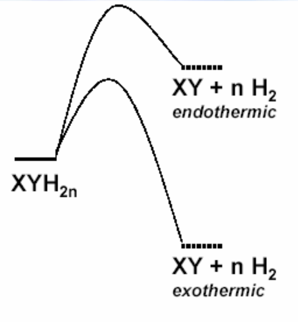
- Hydride heat of formation
  - pressure limits (~20-35 kJ/molH_2)
  - refueling (<20 kJ/molH_2)



- Surface heat of adsorption
  - operating temperature
  - release temperature



- Activation barrier for regeneration
  - energy efficiency
  - near thermo-neutral

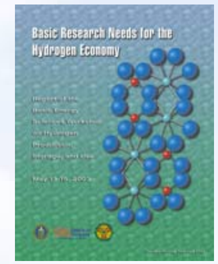


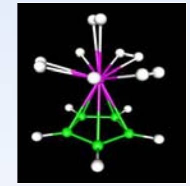
Synergy between Basic Science and Applied Research, Development and Demonstration

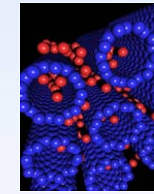
Basic Research

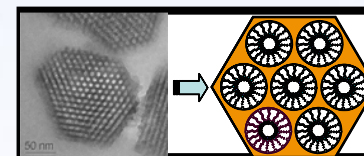
Develop and use theoretical models & fundamental experimentation to generate knowledge:

- Fundamental property & transport phenomena
- Novel material structures, characterization
- Theory, modeling, understand reaction mechanisms





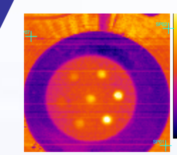


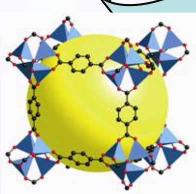


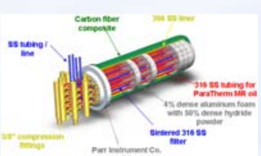
Applied Research & Development

Apply theory & experimentation to design & develop novel, high-performance materials to meet specific performance targets:

- Develop new materials, leverage knowledge from basic research
- Optimize materials and testing to improve performance
- Design, develop and demonstrate materials, components and prototype systems to meet milestones







Technology Validation & Demonstration

Test Systems under Real World Conditions

- Demonstrate and validate performance against targets
- Gain knowledge (e.g. fueling time, driving range, durability, cost, etc.) and apply lessons learned to R&D

Summary

- New Materials & Concepts are critical- address volumetric capacity, T, P, kinetics, etc. (not just wt. %!)
- Basic science is valuable to develop fundamental understanding & complements applied research & development
- Engineering issues need to be considered
  - System issues, thermal mgmt, safety, refueling, testing, etc
- Examples of Essential Capabilities:
  - Modeling & Analysis
  - Combinatorial/high throughput methods
  - Material properties measurements
  - Standardized & accurate testing