Hydrogen Storage

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2007 DOE Hydrogen Program
Merit Review and Peer Evaluation Meeting

May 15, 2007

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[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

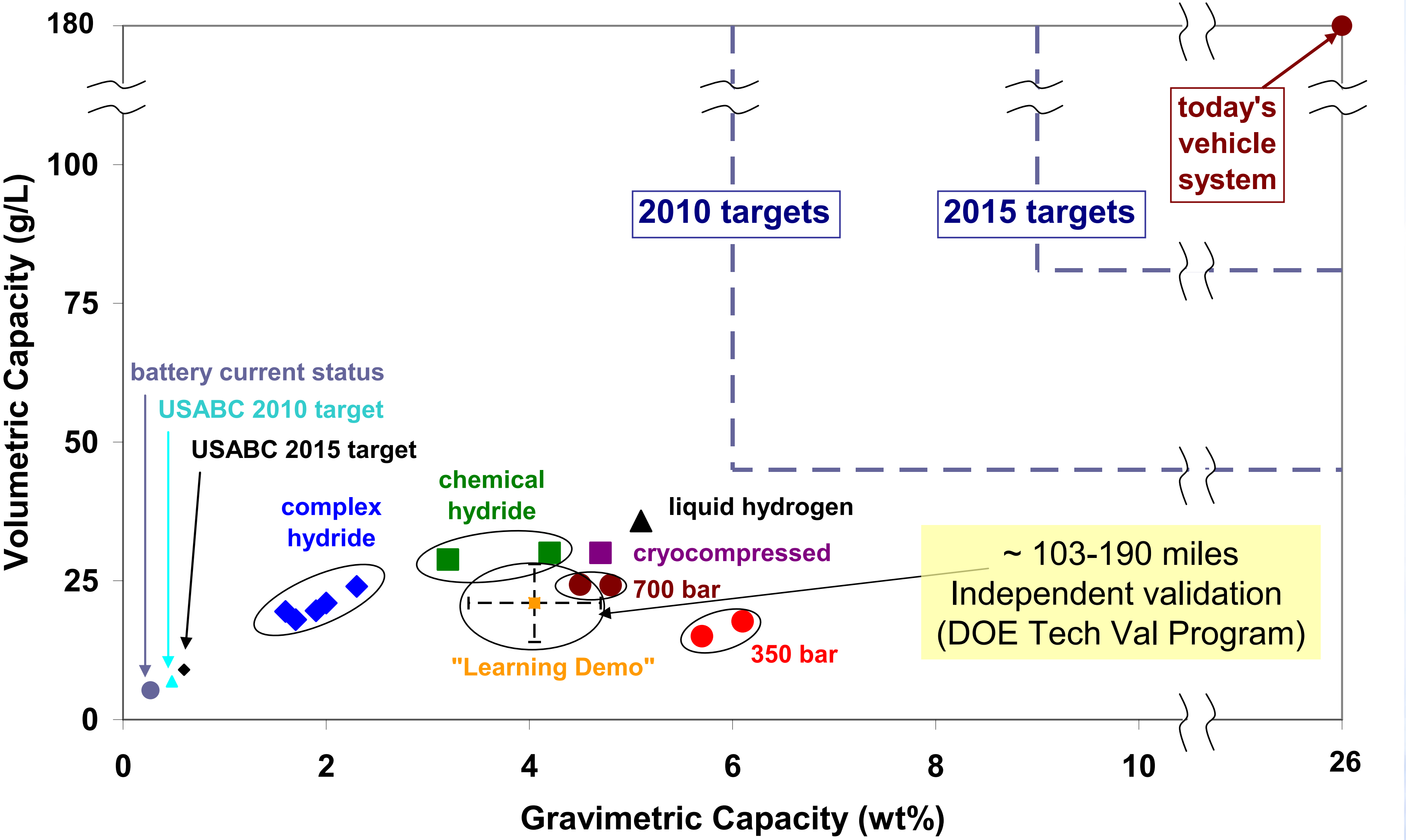
Material capacities must be higher!

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

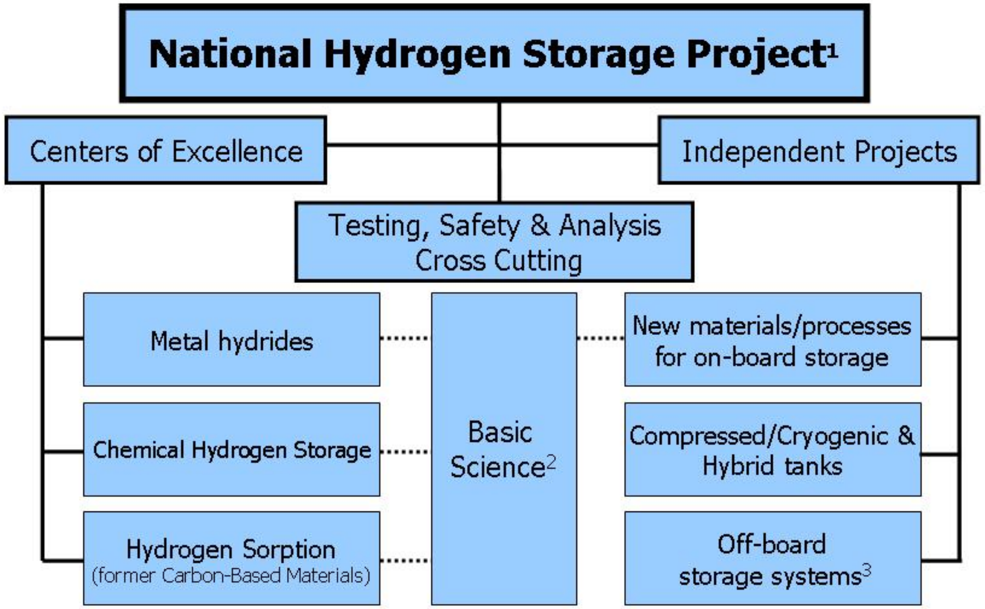


~ 103-190 miles
Independent validation
(DOE Tech Val Program)

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]**



National Hydrogen Storage Project[1]

Centers of Excellence

Independent Projects

Testing, Safety & Analysis
Cross Cutting

Metal hydrides

Chemical Hydrogen Storage

Hydrogen Sorption
(former Carbon-Based Materials)

Basic Science[2]

New materials/processes for on-board storage

Compressed/Cryogenic & Hybrid tanks

Off-board storage systems[3]

1. Coordinated by DOE Energy Efficiency and Renewable Energy, Office of Hydrogen, Fuel Cells and Infrastructure Technologies
2. Basic science for hydrogen storage conducted through DOE Office of Science, Basic Energy Sciences
3. Coordinated with Delivery Program element

- **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**

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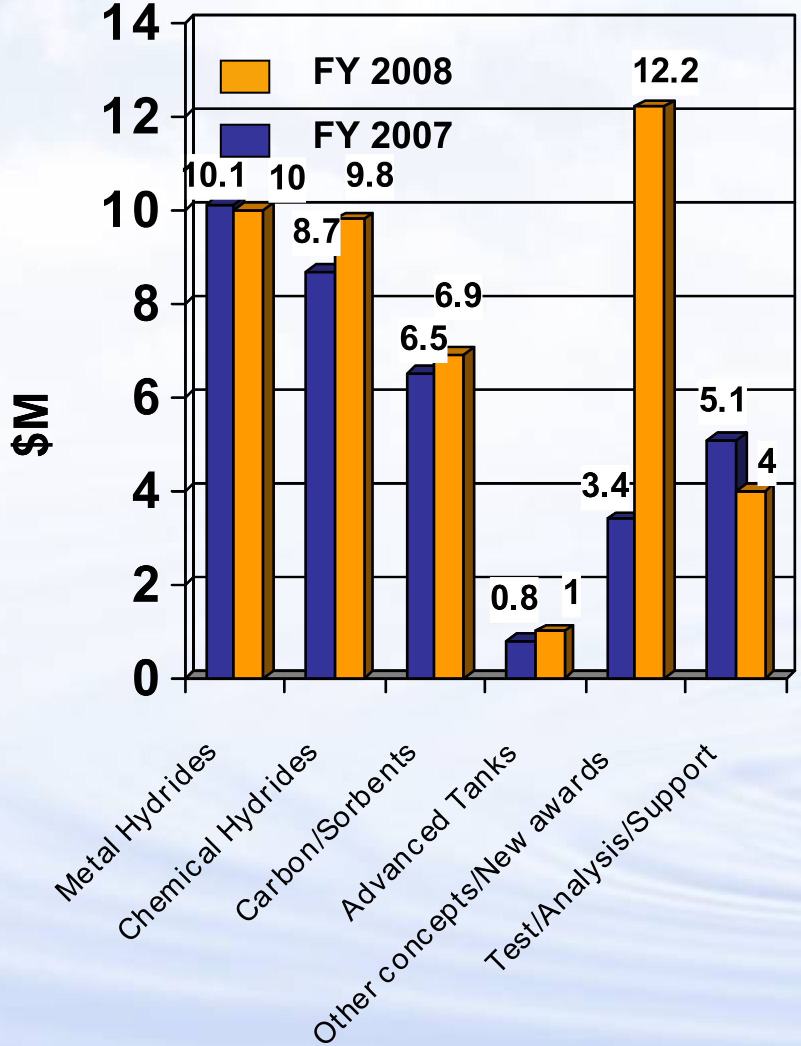
[1] NRC H_2 Economy Report (2004) p.44

DEPARTMENT OF ENERGY UNITED STATES OF AMERICA

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*

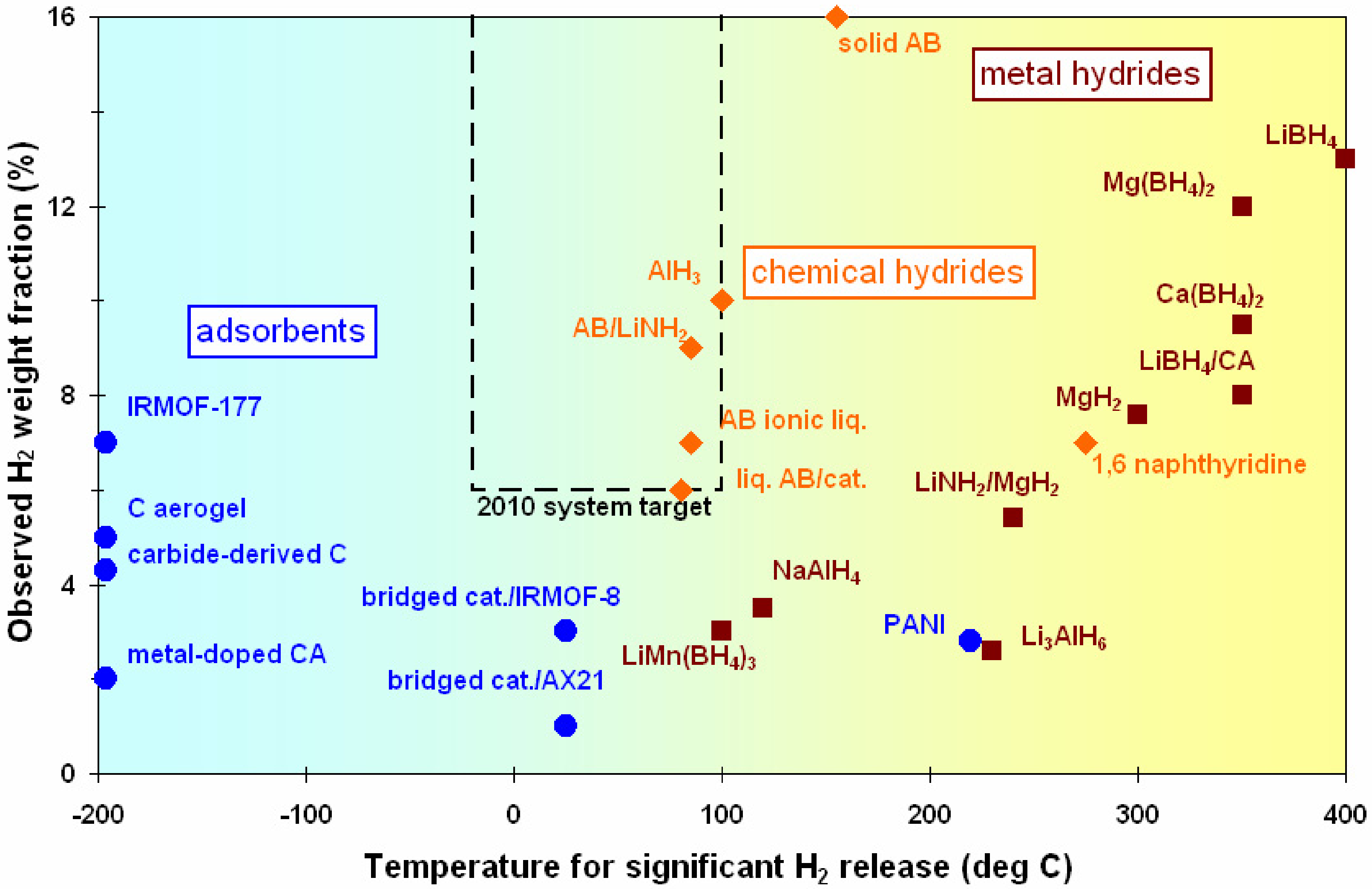
Close coordination with Basic Science
$36.4M (FY07)
$59.5M (FY08)
Includes basic science for hydrogen storage, production and use (e.g., catalysis, membranes, etc.)

*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

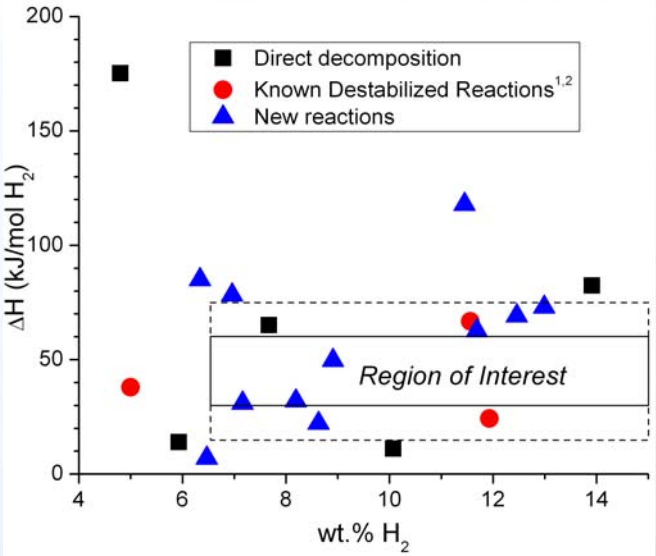


G. Thomas, et al., DOE (April 2007)

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

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

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

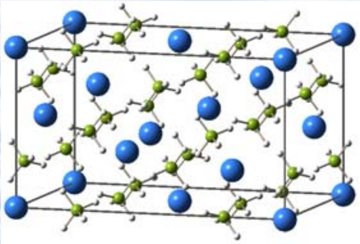
Theory guides experiment

Experiment refines theory

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

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

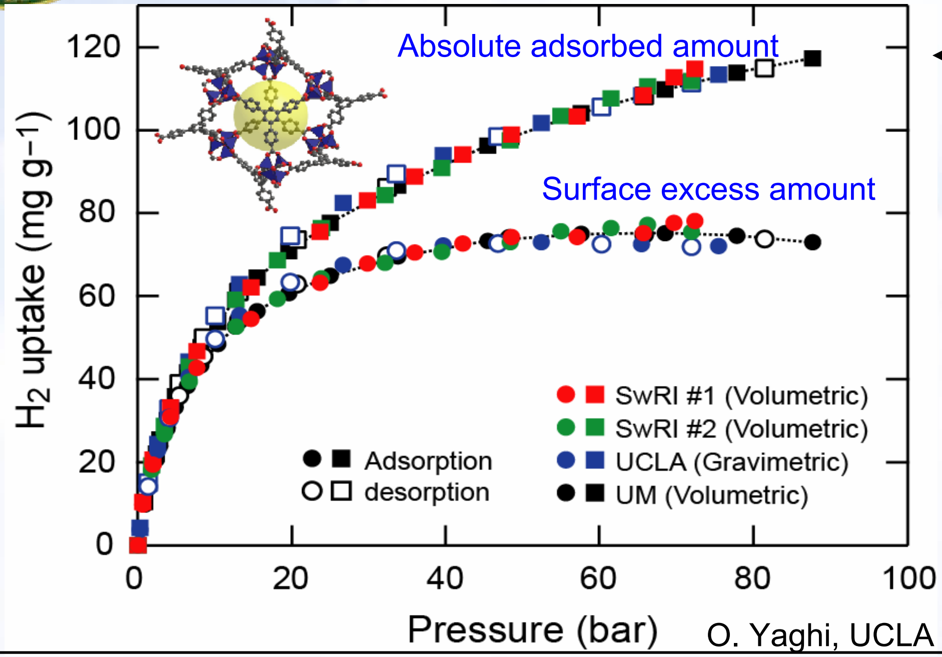
$$CaB_6 + 2CaH_2 \xrightarrow[400\ ^\circ C]{700\ bar\ H_2} \text{fully rehydrided}$$



E. Ronnebro, E. Majzoub et al. Sandia

Phys Rev B 74, 155122 (2006)

Results: Sorbent Materials

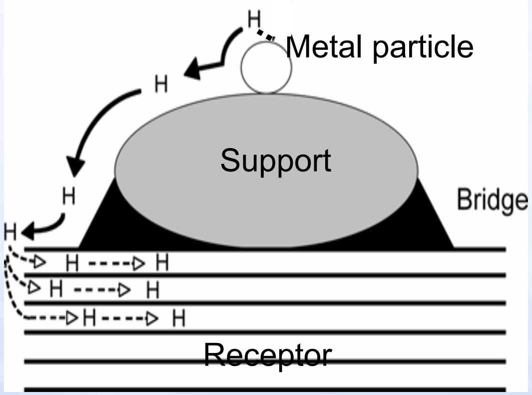


O. Yaghi, UCLA

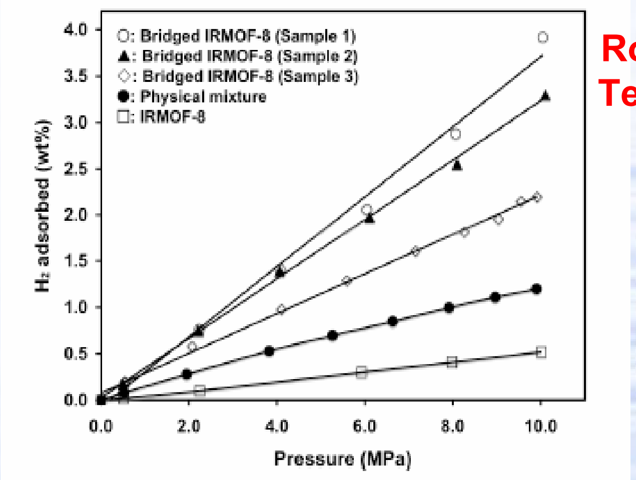
Independent verification of MOF-177 (O. Yaghi et al.- highest capacity to date worldwide; > 7 wt.%, 77 K)

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

Spillover by Yang, U Michigan

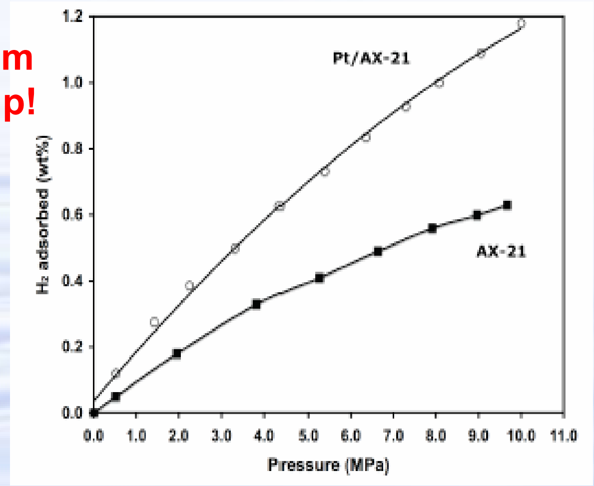


R. Yang, U. MI



R. Yang, U. MI

Room Temp!

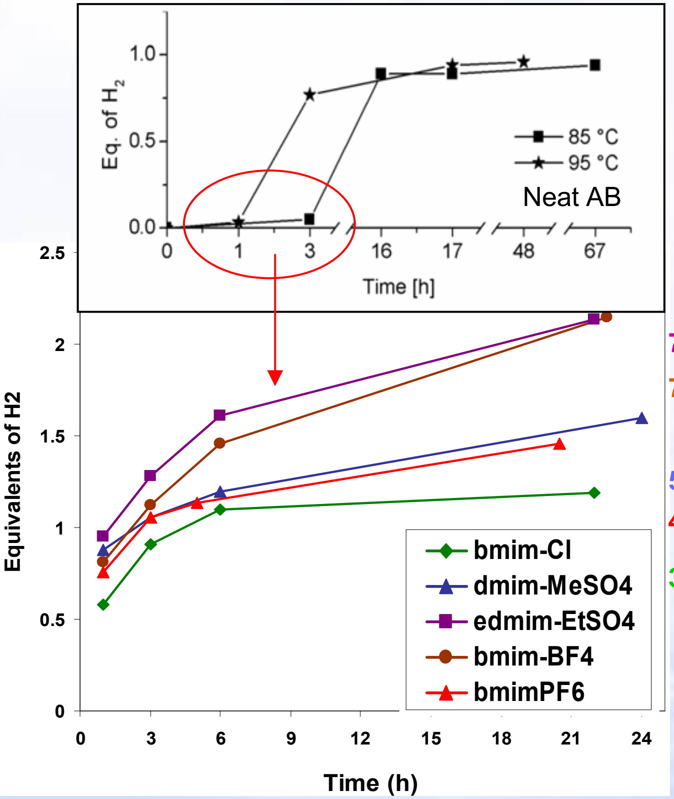


R. Yang, U MI, P. Parilla, et al., NREL & HS Center

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



7.0 wt%, 0.039 kg/L

7.0 wt%, 0.033 kg/L

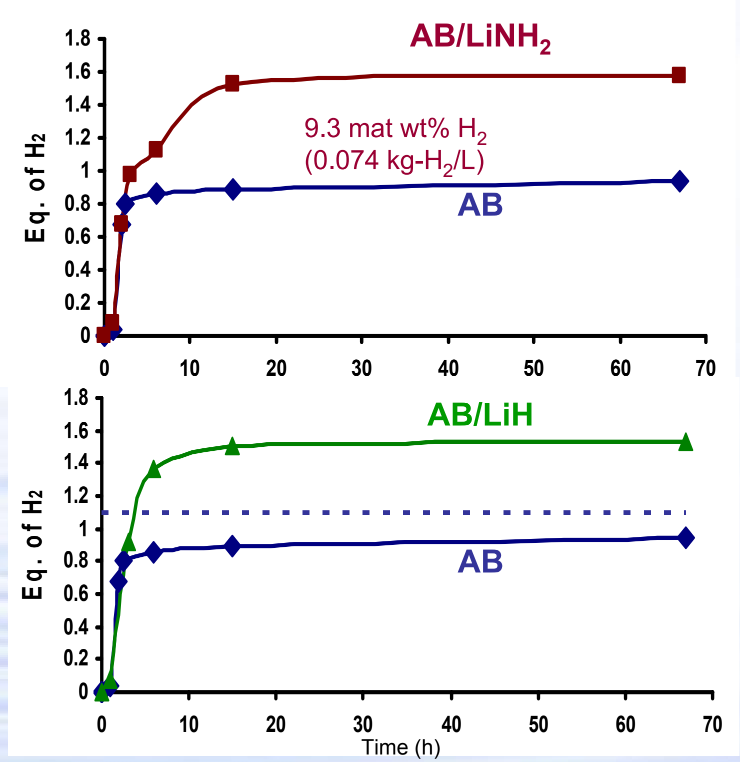
5.3 wt%, 0.027 kg/L

4.8 wt%, 0.025 kg/L

3.9 wt%, 0.018 kg/L

T ~ 85 °C

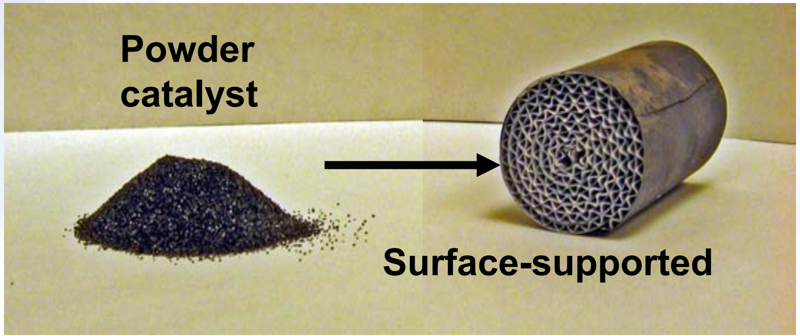
Chemical promoters enhance H release in ammonia borane (AB)

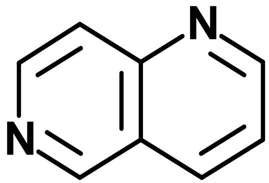


Sneddon, et al, U. Penn and CH Center

Results: Liquid Carriers and Systems Analysis

Organic liquid carriers & catalysts





1,6-Naphthyridine

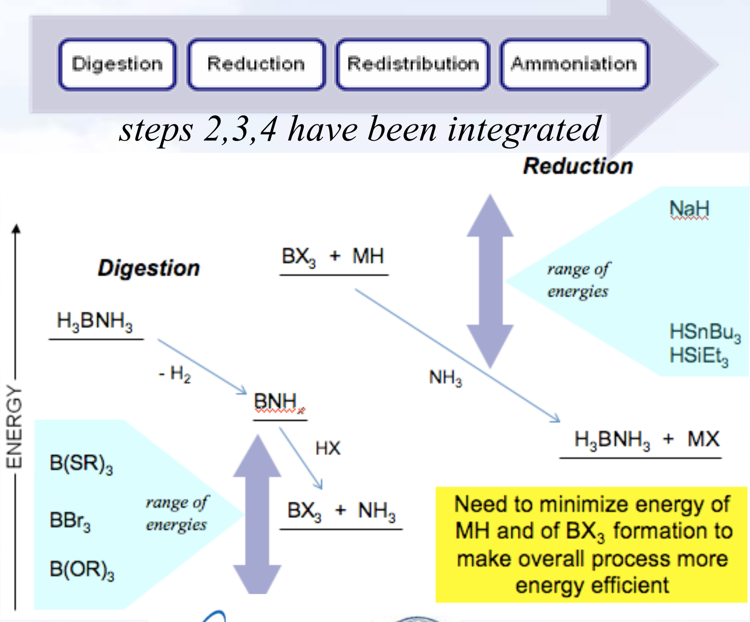
Liquid at room temp.

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

release temp. ~275 C

A. Cooper, et al., Air Products

Regeneration of Ammonia Borane

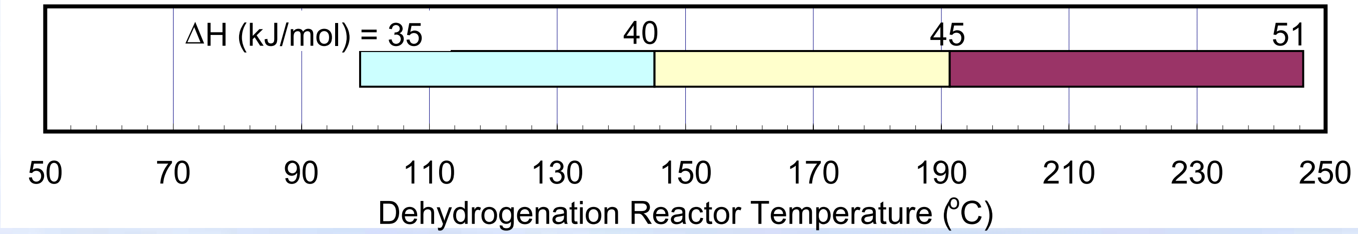


steps 2,3,4 have been integrated

Need to minimize energy of MH and of BX_3 formation to make overall process more energy efficient

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					Carbothermal	Elemental	Echem			Borane			Metathesis
			Mg	Al	Ti	Si	Zn			1-stop	2-step	HT melts	BCl3	TMB	M + B2O3	
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										
Raw material consump - high conv /yields	**25**	3	8	7	7	7										
Low operating severity	**5**	7	8	8	8	8										
Few chemical reactions	**5**	5	8	8	8	8										
Few separation/processing steps	**5**	5	8	8	8	8										
Capital cost, $ per unit H2 (NaBH4)																
Low complexity	**10**	6	8	8	8	8										
Low technical risk	**5**	10	7	7	7	7										
EHS (environmental / health / safety)																
Emissions, wastes, CO2	**10**	10	8	8	8	8										
toxicity, safety, flammability, H2O-reactive	**5**	8	7	6	7	7										
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**

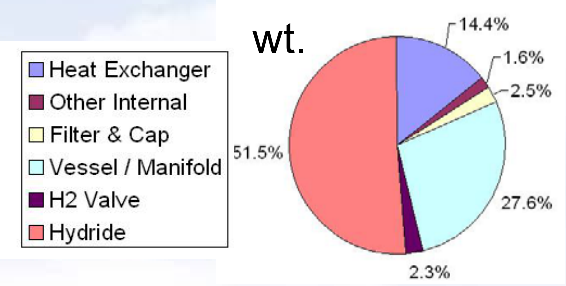
- Assess efficiency potential & other factors for viable chemical carriers
- Develop & demonstrate chemistry & processes to improve regeneration efficiency

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. %

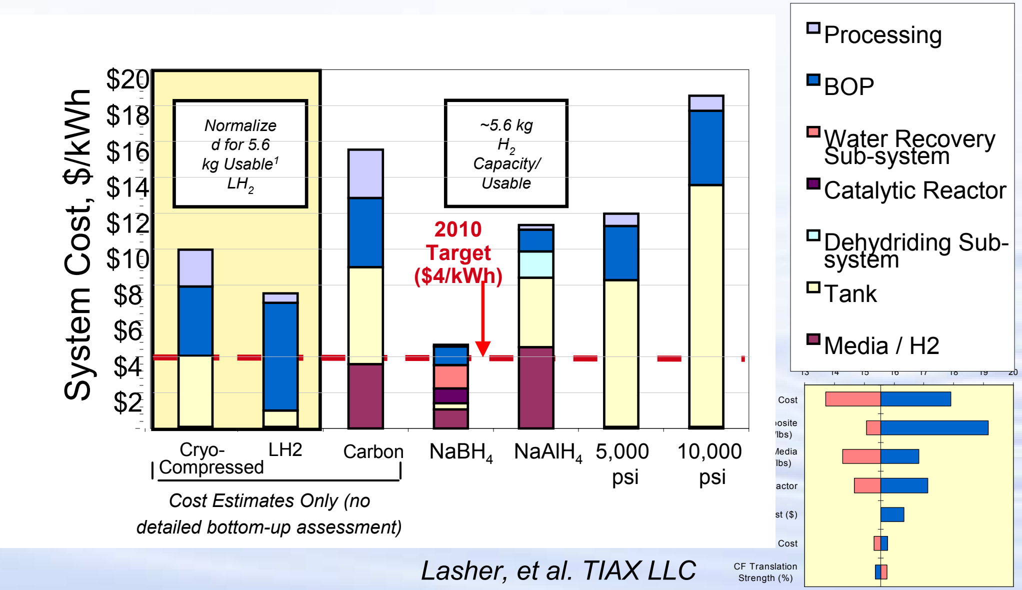
30 g/L

(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)

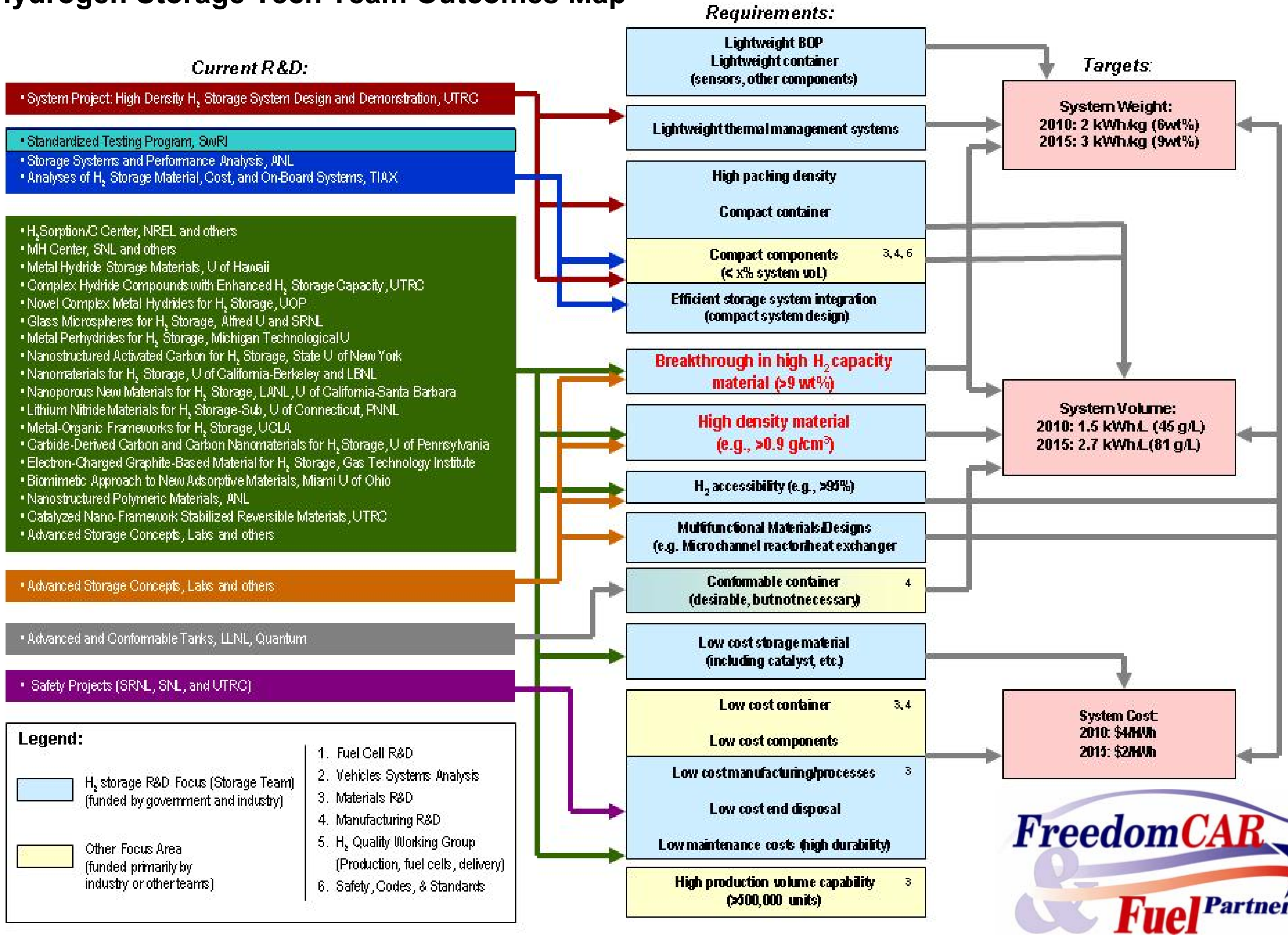
NSF- proposal review in process (5/07)

NIST- neutron scattering

Strategy & Execution

Example- maps portfolio & requirements to meet targets

Hydrogen Storage Tech Team Outcomes Map



Current R&D:

- System Project: High Density H_2 Storage System Design and Demonstration, UTRC

- Standardized Testing Program, SwRI
- Storage Systems and Performance Analysis, ANL
- Analyses of H_2 Storage Material, Cost, and On-Board Systems, TIAX

- H_2 Sorption/C Center, NREL and others
- MH Center, SNL and others
- Metal Hydride Storage Materials, U of Hawaii
- Complex Hydride Compounds with Enhanced H_2 Storage Capacity, UTRC
- Novel Complex Metal Hydrides for H_2 Storage, UOP
- Glass Microspheres for H_2 Storage, Alfred U and SRNL
- Metal Perhydrides for H_2 Storage, Michigan Technological U
- Nanostructured Activated Carbon for H_2 Storage, State U of New York
- Nanomaterials for H_2 Storage, U of California-Berkeley and LBNL
- Nanoporous New Materials for H_2 Storage, LANL, U of California-Santa Barbara
- Lithium Nitride Materials for H_2 Storage-Sub, U of Connecticut, PNNL
- Metal-Organic Frameworks for H_2 Storage, UCLA
- Carbide-Derived Carbon and Carbon Nanomaterials for H_2 Storage, U of Pennsylvania
- Electron-Charged Graphite-Based Material for H_2 Storage, Gas Technology Institute
- Biomimetic Approach to New Adsorptive Materials, Miami U of Ohio
- Nanostructured Polymeric Materials, ANL
- Catalyzed Nano-Framework Stabilized Reversible Materials, UTRC
- Advanced Storage Concepts, Labs and others

- Advanced Storage Concepts, Labs and others

- Advanced and Conformable Tanks, LLNL, Quantum

- Safety Projects (SRNL, SNL, and UTRC)

Requirements:

Lightweight BOP
Lightweight container
(sensors, other components)

Lightweight thermal management systems

High packing density

Compact container

Compact components 3, 4, 6
(< x% system vol.)

Efficient storage system integration
(compact system design)

Breakthrough in high H_2 capacity material (>9 wt%)

High density material
(e.g., >0.9 g/cm^3)

H_2 accessibility (e.g., >95%)

Multifunctional Materials/Designs
(e.g. Microchannel reactor/heat exchanger

Conformable container 4
(desirable, but not necessary)

Low cost storage material
(including catalyst, etc.)

Low cost container 3, 4

Low cost components

Low cost manufacturing/processes 3

Low cost end disposal

Low maintenance costs (high durability)

High production volume capability 3
(>500,000 units)

Targets:

System Weight:
2010: 2 kWh/kg (6wt%)
2015: 3 kWh/kg (9wt%)

System Volume:
2010: 1.5 kWh/L (45 g/L)
2015: 2.7 kWh/L (81 g/L)

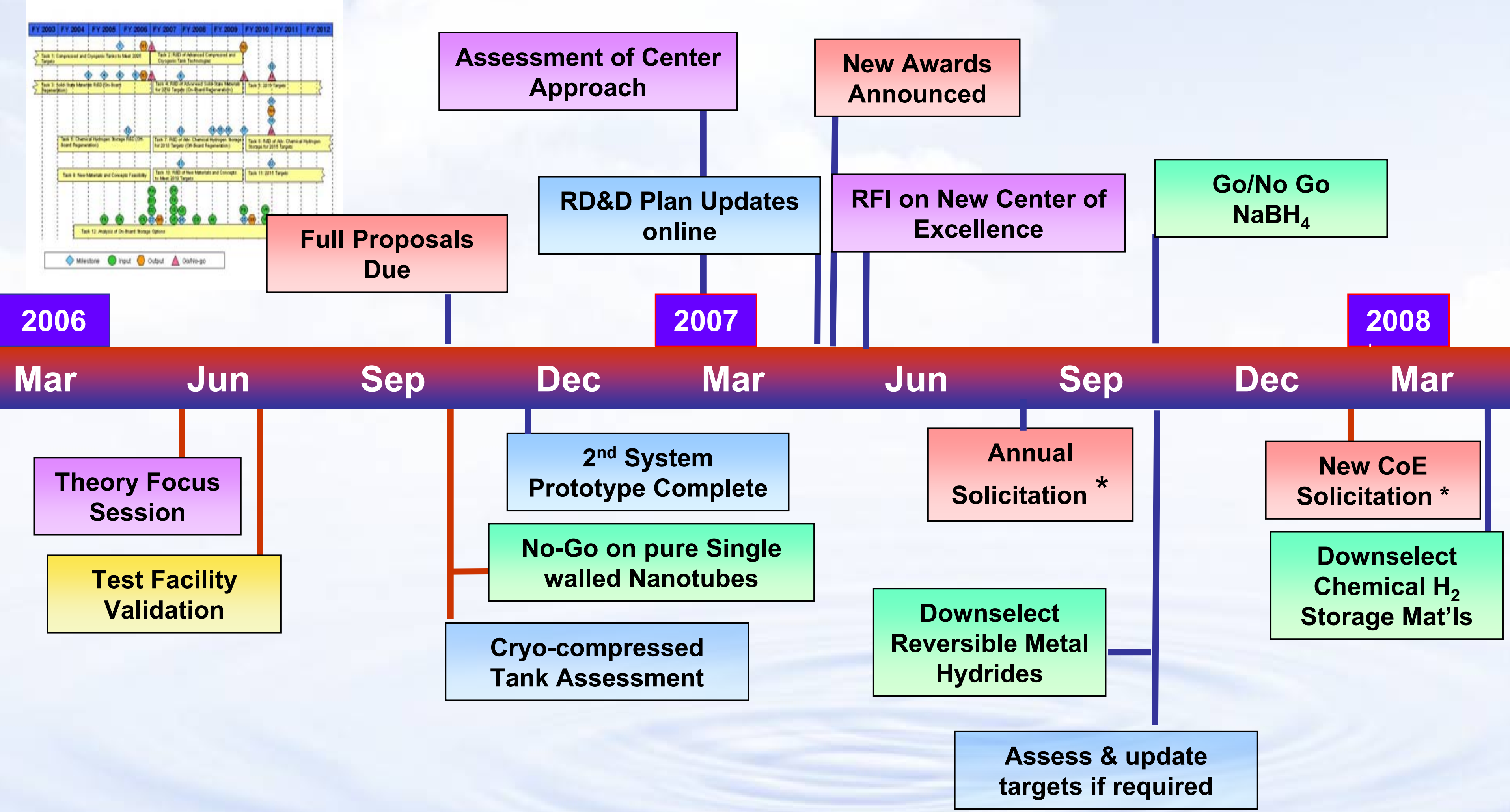
System Cost:
2010: \$4/kWh
2015: \$2/kWh

Legend:

🟦	H_2 storage R&D Focus (Storage Team) (funded by government and industry)
🟨	Other Focus Area (funded primarily by industry or other teams)

1. Fuel Cell R&D
2. Vehicles Systems Analysis
3. Materials R&D
4. Manufacturing R&D
5. H_2 Quality Working Group (Production, fuel cells, delivery)
6. Safety, Codes, & Standards

Key Milestones & Future Plans



2006

2007

2008

Mar

Jun

Sep

Dec

Mar

Jun

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Mar

Theory Focus Session

Test Facility Validation

Full Proposals Due

No-Go on pure Single walled Nanotubes

Cryo-compressed Tank Assessment

2nd System Prototype Complete

Assessment of Center Approach

RD&D Plan Updates online

New Awards Announced

RFI on New Center of Excellence

Annual Solicitation *

Downselect Reversible Metal Hydrides

Go/No Go NaBH$_4$

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

In Memoriam
Professor Alan MacDiarmid*
1927-2007

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*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

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

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

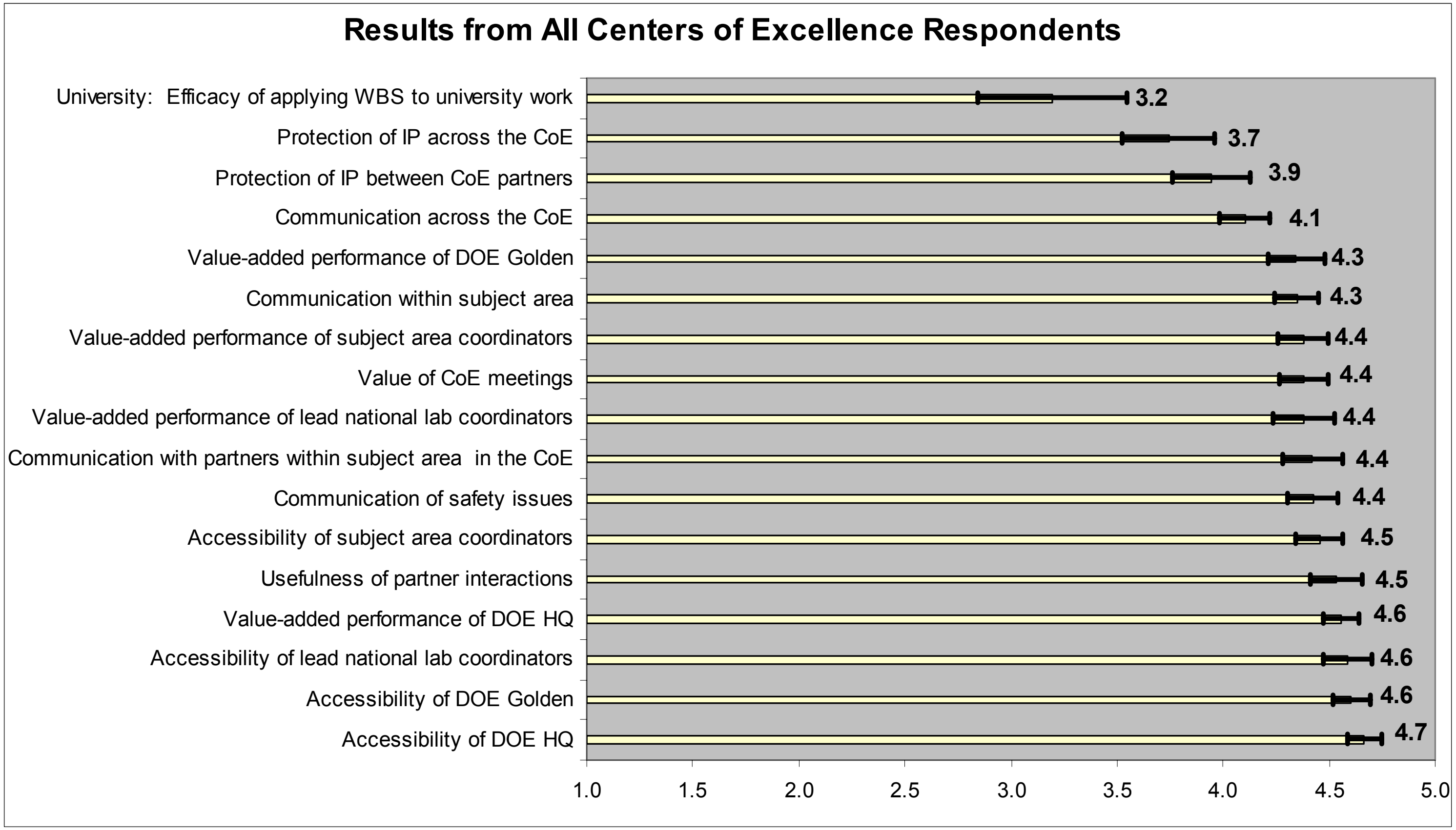
Other New Materials & Concepts
- Alfred University
- Michigan Technological University
- UC-Berkeley/LBL
- UC-Santa Barbara
- Argonne Nat'l Lab

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

Programmatic Results: Focus on strategy & execution

Assessment of CoE model:

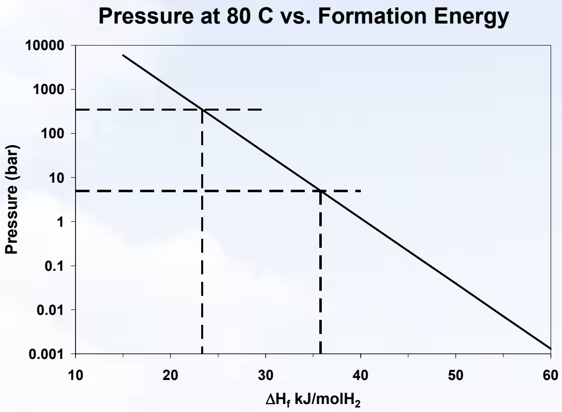
Multi-institutional critical mass applied R&D is proving to be effective


Results from All Centers of Excellence Respondents

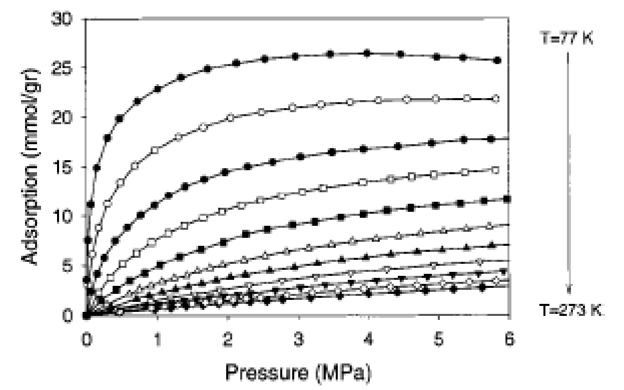
- Annual Solicitation (6 new projects complement portfolio)
- No-go (FY06) on *pure* SWNTs (doped C/basic science still go)
- Assessment of Cryo-compressed tanks complete
- Outcomes maps done & targets revisited through FreedomCAR

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

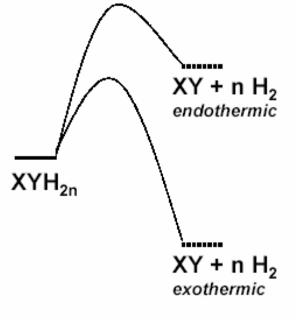
- Hydride heat of formation
  - pressure limits (~20-35 kJ/molH_2)
  - refueling (<20 kJ/molH_2)



- Surface heat of adsorption
  - operating temperature
  - release temperature



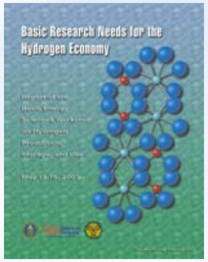
- Activation barrier for regeneration
  - energy efficiency
  - near thermo-neutral

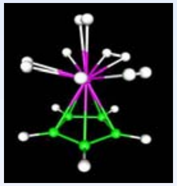


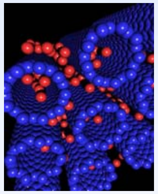
Synergy between Basic Science and Applied Research, Development and Demonstration

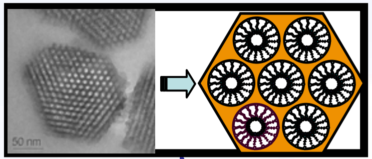
Basic Research

Develop and use theoretical models & fundamental experimentation to generate knowledge:
- Fundamental property & transport phenomena
- Novel material structures, characterization
- Theory, modeling, understand reaction mechanisms


Basic Research Needs for the Hydrogen Economy

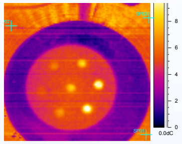


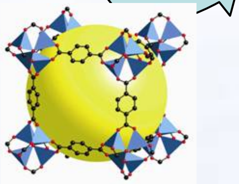


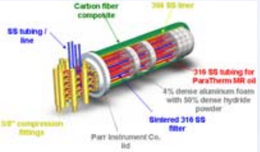


Applied Research & Development

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