U.S. DEPARTMENT OF ENERGY

Hydrogen Program

Materials Issues in Hydrogen R&D: Recent Developments in the DOE's Portfolio

ICMR Symposium on Materials Issues in Hydrogen Production & Storage

University of California, Santa Barbara
August 22, 2006

C. Read, G. Ordaz, G. Thomas[1], and S. Satyapal

Office of Hydrogen, Fuel Cells and Infrastructure Technologies
Office of Energy Efficiency and Renewable Energy

1. Sandia National Laboratory, retired, on assignment to DOE

Program Goal/Challenges

Goal: Technology readiness to enable fuel cell vehicles & hydrogen fuel from diverse domestic resources

Challenges:

Critical Path Technology

- Hydrogen Storage (target: >300-mile range)
- Fuel Cell Cost and Durability (targets: $30 per kW, 5000 hours)
- Hydrogen Cost (target: $2.00 - 3.00 per gallon gasoline equivalent*)

Economic/Institutional

- Codes and Standards (Safety, and Global Competitiveness)
- Hydrogen Delivery (Investment for new Distribution Infrastructure)
- Education (safety and code officials, local communities, state and local governments, students)

*One kilogram of hydrogen contains nearly the same energy as a gallon of gasoline.

Producing Hydrogen

Goal: Hydrogen produced domestically, reducing our dependence on foreign energy sources and providing clean, carbon-free fuel.

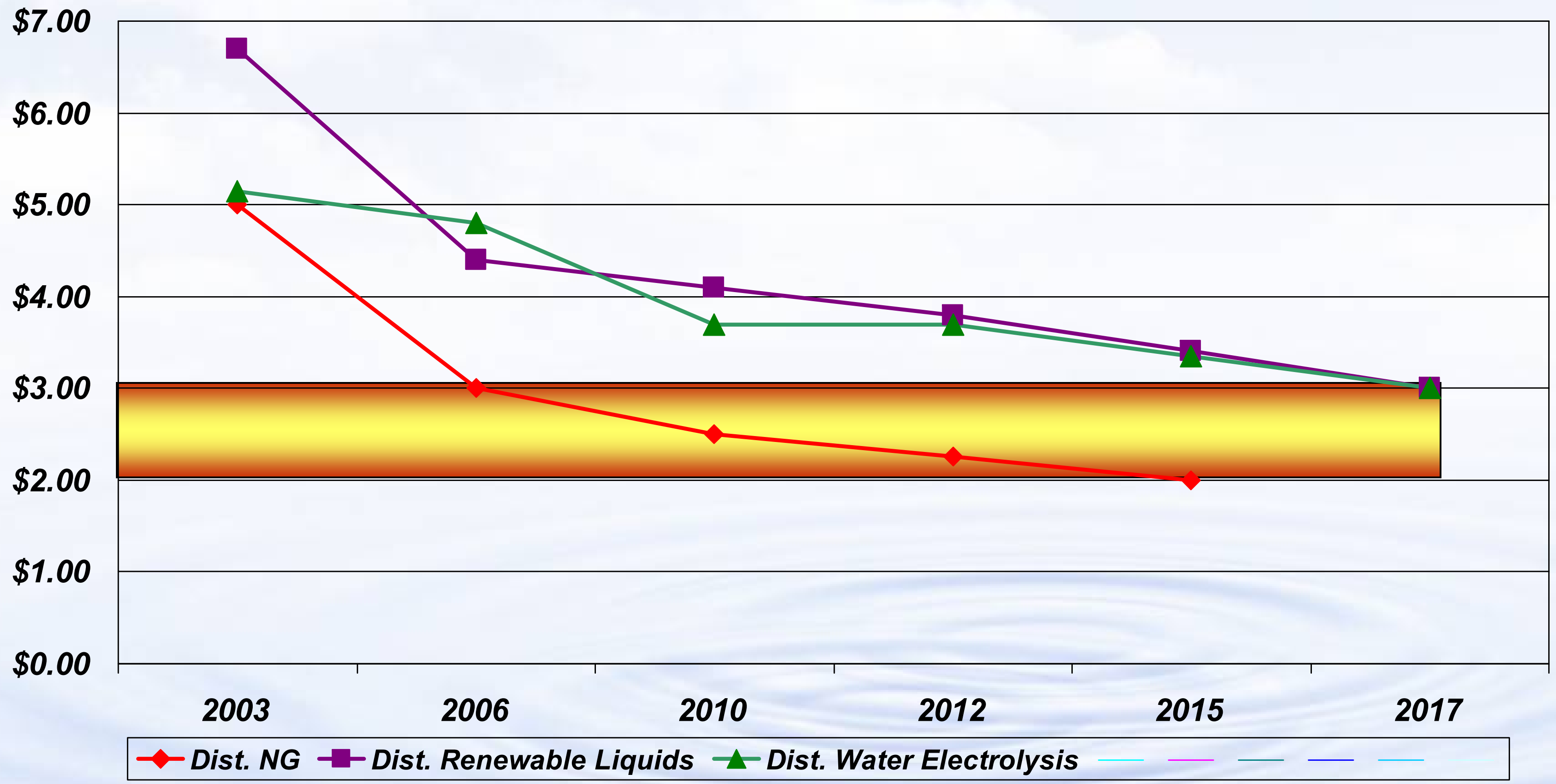
Production Pathways: Hydrogen can be produced from renewable, nuclear, and fossil energy resources using a variety of process technologies, including:

- Renewable electrolysis (using wind, solar, or geothermal energy)
- Biomass and renewable liquids
- High temperature thermochemical
  - ✓ Nuclear energy
  - ✓ High temperature solar
- Biological and photoelectrochemical technologies
- Coal (with carbon sequestration)
- Natural gas

Quick Fact:

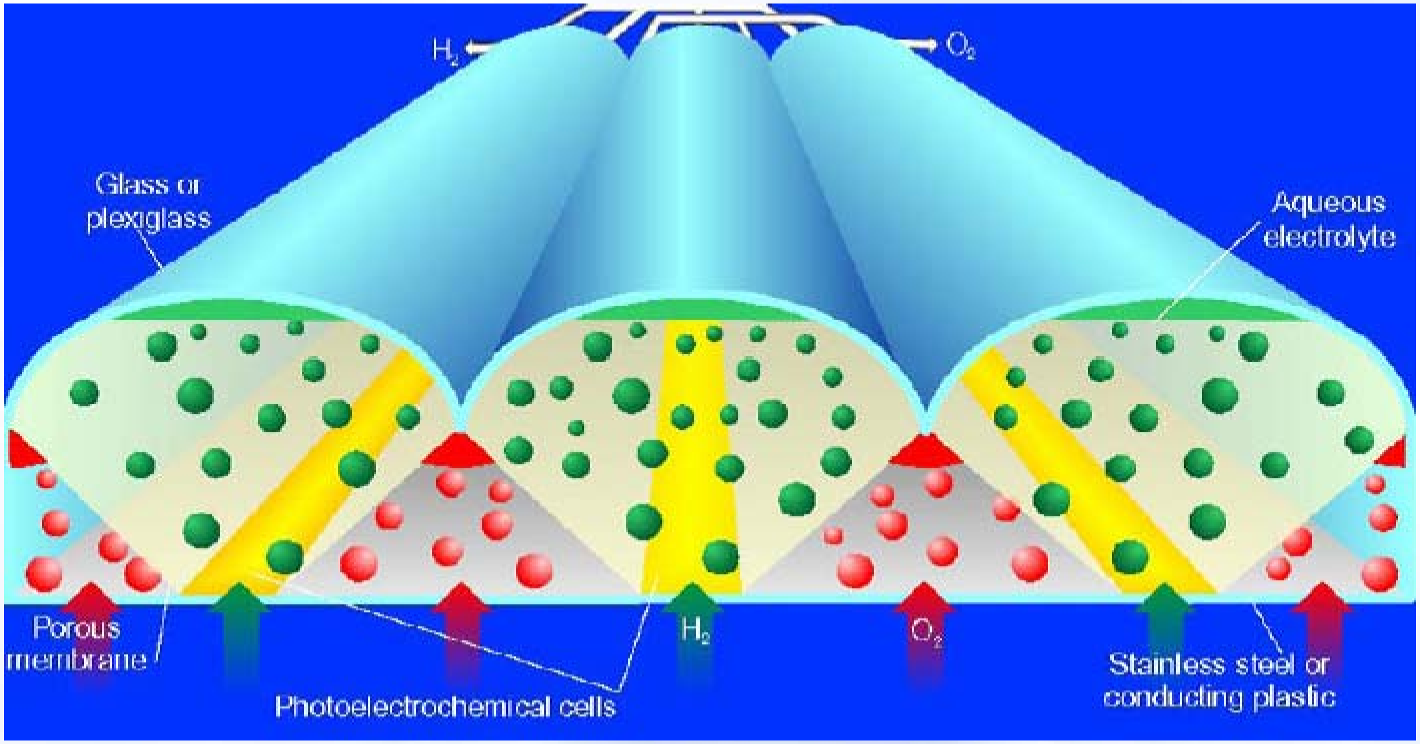
The U.S. hydrogen industry currently produces ~9 million tons of hydrogen a year – that's enough to power about 34 million vehicles.

Distributed Hydrogen Production
Status vs Goal



NREL is focusing on single material applications that will split water using sunlight as the only energy input.

Goal: Stable III-V nitride material for tandem H_2O splitting



Synthesize the semiconductor structure with the necessary properties

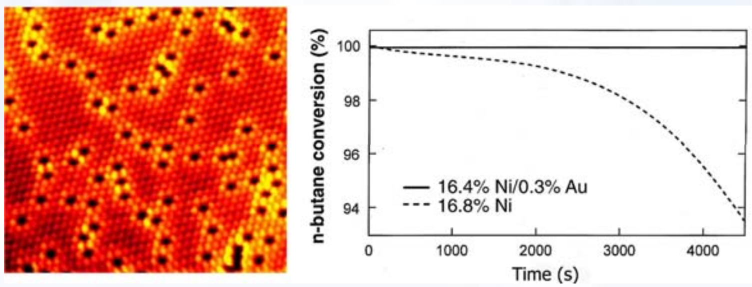
- ✓ GaPN-NREL (high efficiency, stability)
- ✓ CuInGa(Se,S)2 UNAM (Mexico), NREL (Low cost)
- ✓ Silicon Nitride –NREL (protective coating and new material)

J. Turner

BES Priority Research Areas in Hydrogen Production

Fossil Fuel Reforming

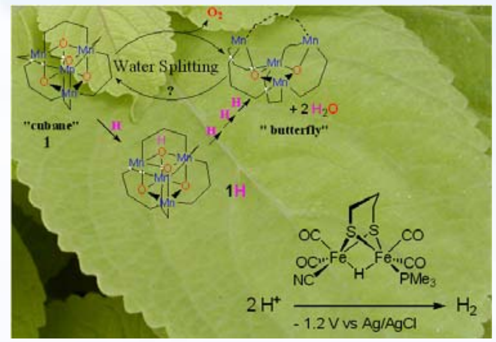
Catalysis; membranes; theory and modeling; nanoscience



Ni surface-alloyed with Au to reduce carbon poisoning

Bio- and Bio-inspired H_2 Production

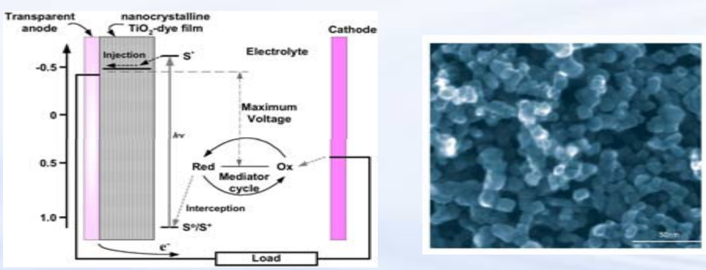
Biological enzyme catalysis; nanoassemblies; bio-inspired materials and processes



Synthetic catalysts for water oxidation and hydrogen activation

Solar Photoelectrochemistry/Photocatalysis

Understanding physical mechanisms; novel materials; theory and modeling; stability of materials

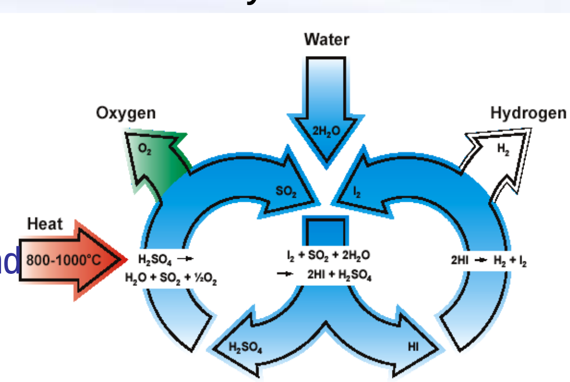


Dye-Sensitized solar cells

Nuclear and Solar Thermal Hydrogen

Thermodynamic data and modeling; novel materials; membranes and catalysts

High T operation places severe demands on reactor design and on materials



Source: BES Hydrogen Workshop Report

Hydrogen Storage: The "Grand Challenge"

On-board hydrogen storage to meet all performance (wt, vol, kinetics, etc.) , safety and cost requirements and enable a more than 300 mile driving range.

Targets	2010	2015
System Gravimetric Capacity (net)= "specific energy"	6 wt.% (7.2 MJ/kg) (2.0 kWh/kg)	9 wt.% (10.8 MJ/kg) (3.0 kWh/kg)
System Volumetric Capacity (net)= "energy density"	1.5 kWh/L (5.4 MJ/L) (45 g/L)	2.7 kWh/L (9.7 MJ/L) (81 g/L)
Storage system cost	\$4/kWh (~\$133/kg H_2)	\$2/kWh (\$67/kg H_2)

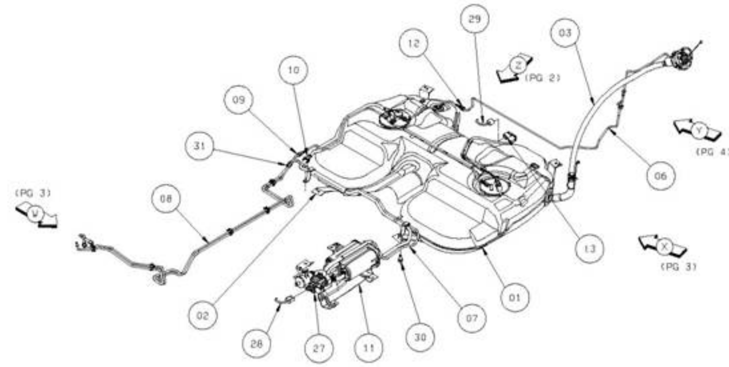
More targets and explanations at www.eere.energy.gov/hydrogenandfuelcells/

FreedomCAR & Fuel Partnership

Targets are for Storage System

Reminder:
<u>System</u>
Targets

Today's gasoline tank system:

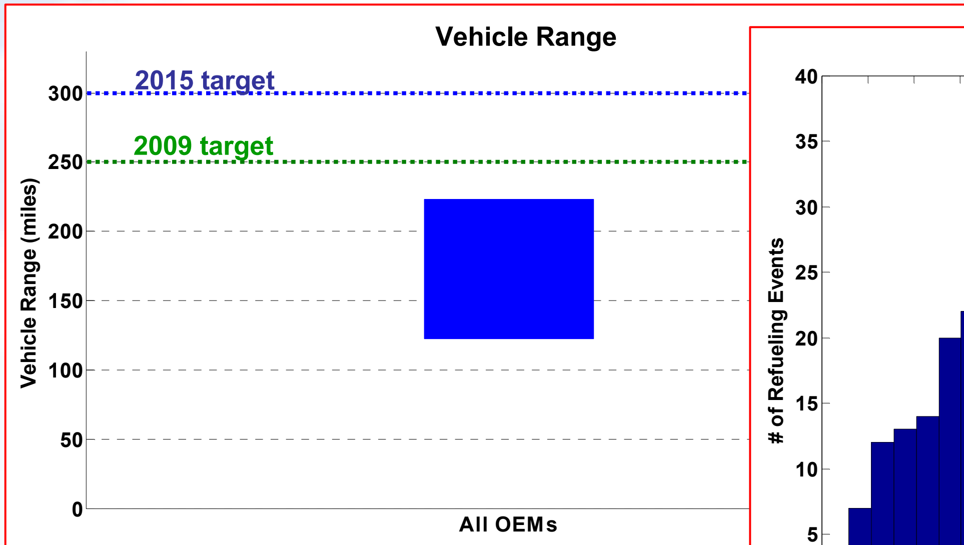


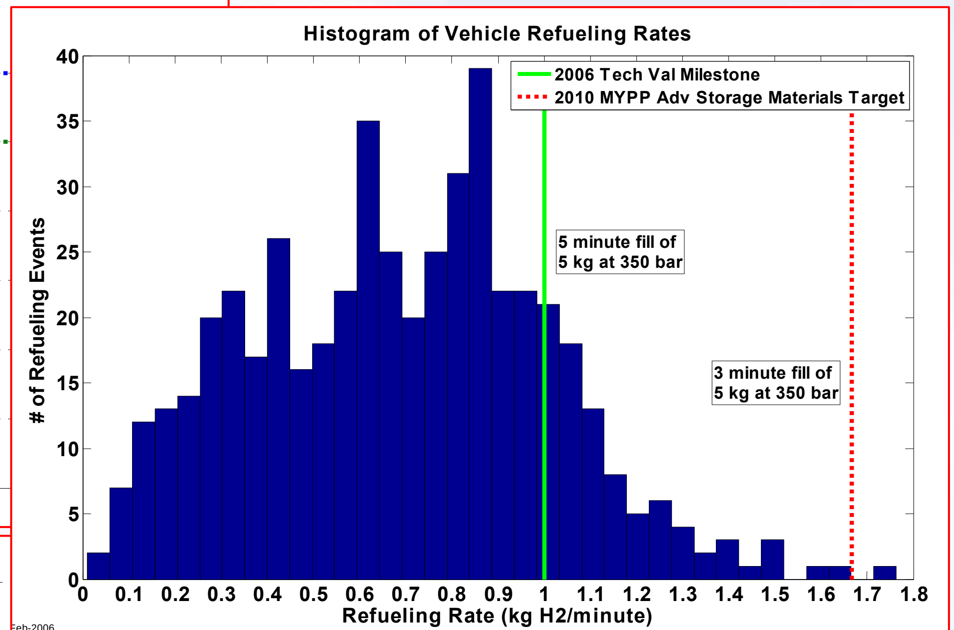
System includes material, tank, and balance of plant- e.g. insulation, sensors, regulators, first charge, any byproducts/reactants, etc.

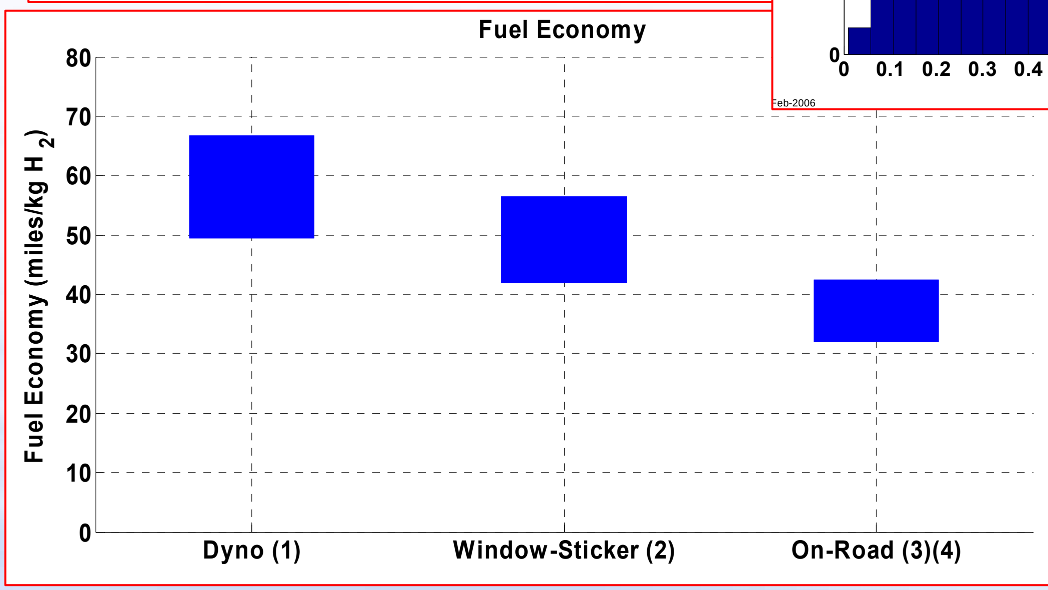
Material capacities must be higher!

Real World Composite Data (58 vehicles)

Improved hydrogen storage technologies that can be packaged in a vehicle are necessary to meet range targets

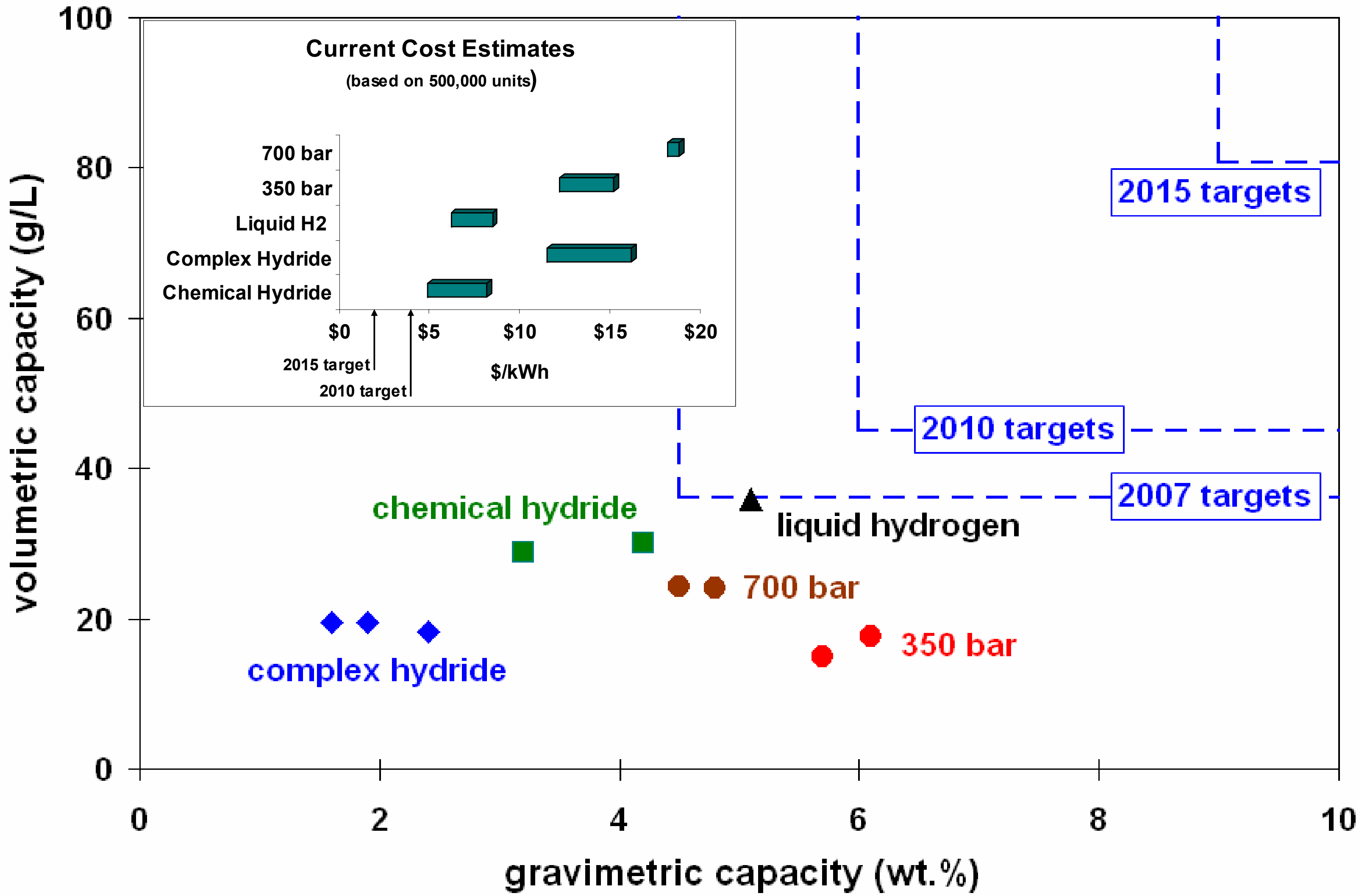






DaimlerChrysler bp
ChevronTexaco Hyundai UTC Fuel Cells
Air Products ConocoPhillips Toyota Honda Nissan BMW UTC Fuel Cells
Ford bp
GM Shell

Current Status
No storage technology meets 2010 or 2015 targets



Note: Estimates from developers. To be periodically updated.
Costs exclude regeneration/processing. Complex hydride system data projected. Data points include analysis results.

Many other requirements requires optimization and possibly trade-offs.

Not just weight %!

- Weight
- Volume & conformability
- System cost (& fuel cost)
- Durability/ Operability
- Charging/ Discharging Rates
- Efficiency
- Fuel Purity
- Environmental Health & Safety

Commercially viable & efficient H2 Storage Systems

Strategy & Results
Broad Portfolio Focused on Materials Technologies

Challenges are technology specific: Pros and Cons for each

Tanks (to 10,000 psi), Chemical hydrides (CH), Metal Hydrides (MH), Carbon/Sorbents (S)

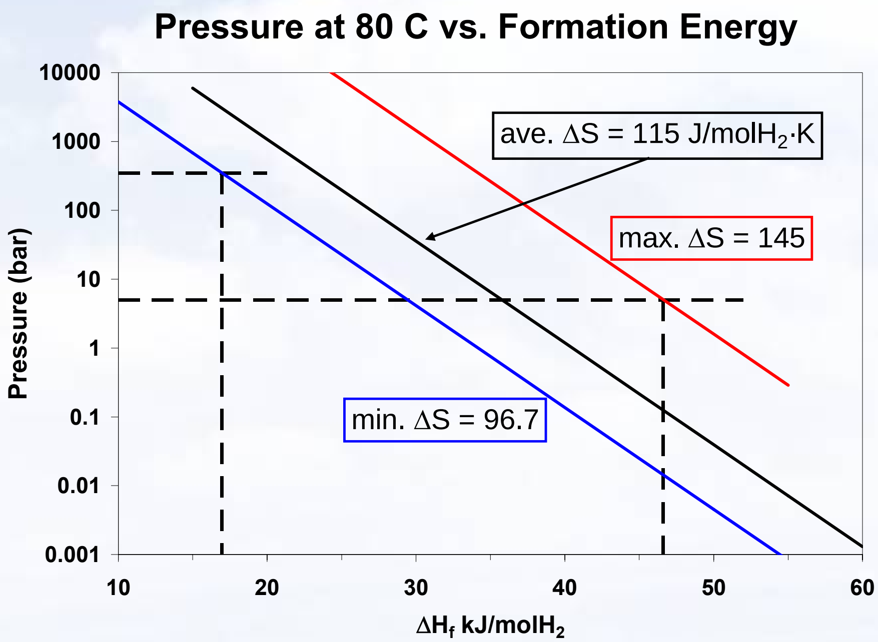
Key 2010 Targets:	Tanks	CH	MH	S
Volume (1.5 kWh/L)	H	M	M	M/H
Weight (2.0 kWh/kg)	M	M	M/H	M
Cost ($4/kWh)	M/H	M/H*	M/H	M/H
Refueling Time (3 min, for 5 kg)	L	L	M/H	M
Discharge Kinetics (0.02 g/s/kW)	L	M	M	M
Durability (1000 cycles)	L	M	M	M

Thermal Mgmt: Key Issues for MH (CH, C) (refers to Refueling Time and Discharge Kinetics)

H = High (Significant challenge) M/H = Medium/High M = Medium L = Low (minimal challenge)

For CH, MH and S- assessment based on potential to meet targets, though systems not yet demonstrated in most cases.
*For CH: Storage system may meet cost but fuel cost of $2-$3/kg is challenge for CH regeneration.

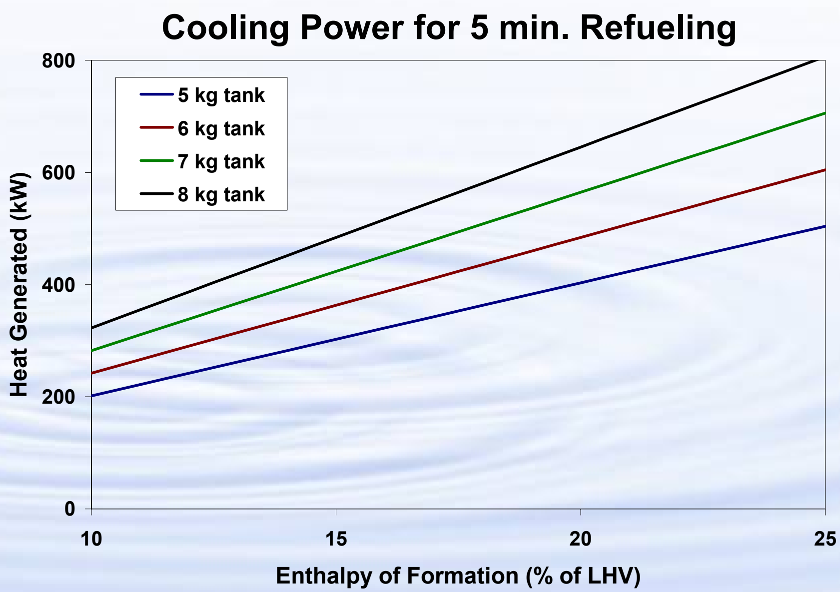
An example trade-off for on-board reversible methods is among ΔH, pressure and re-fill time.



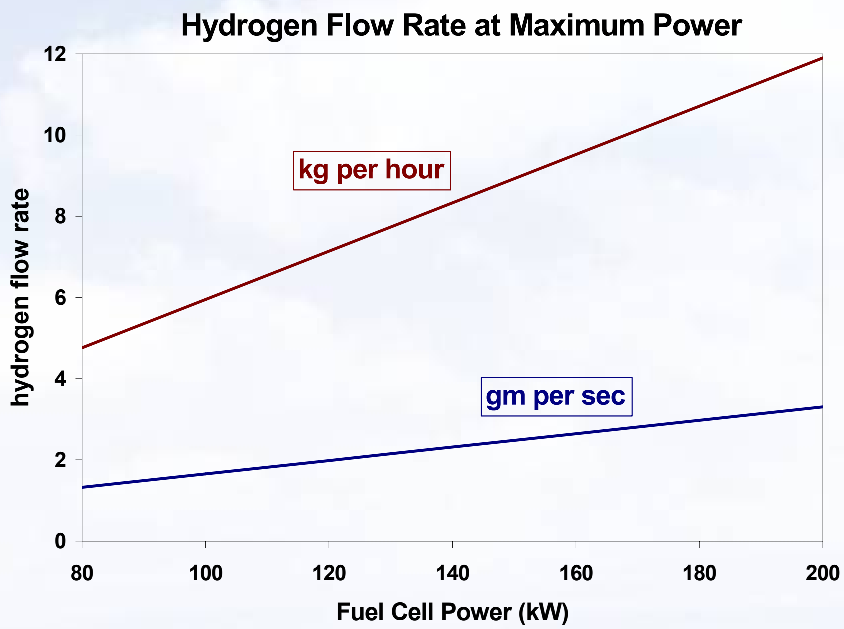
higher ΔH_f results in lower equilibrium pressure:

ΔH_f ~ 17 kJ/molH_2 45 kJ/molH_2
P_{eq} ~ 350 bar 5 bar

lower ΔH_f reduces cooling power needs for refueling:
e.g., for ΔH_f ~ 30 kJ/molH_2
need 800 kW for 8 kg H_2
and 5 minute fill time



Examples of other important targets to keep in mind….

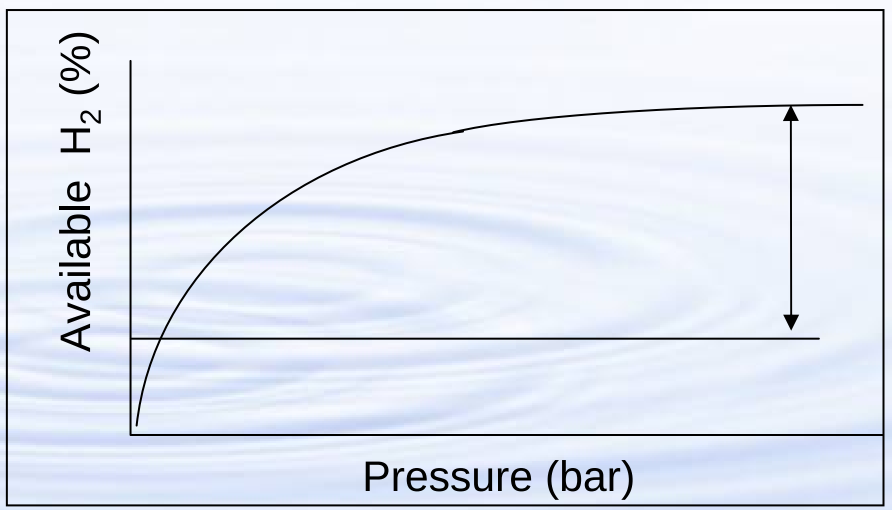


Discharge Kinetics

0.02 g/s/kW

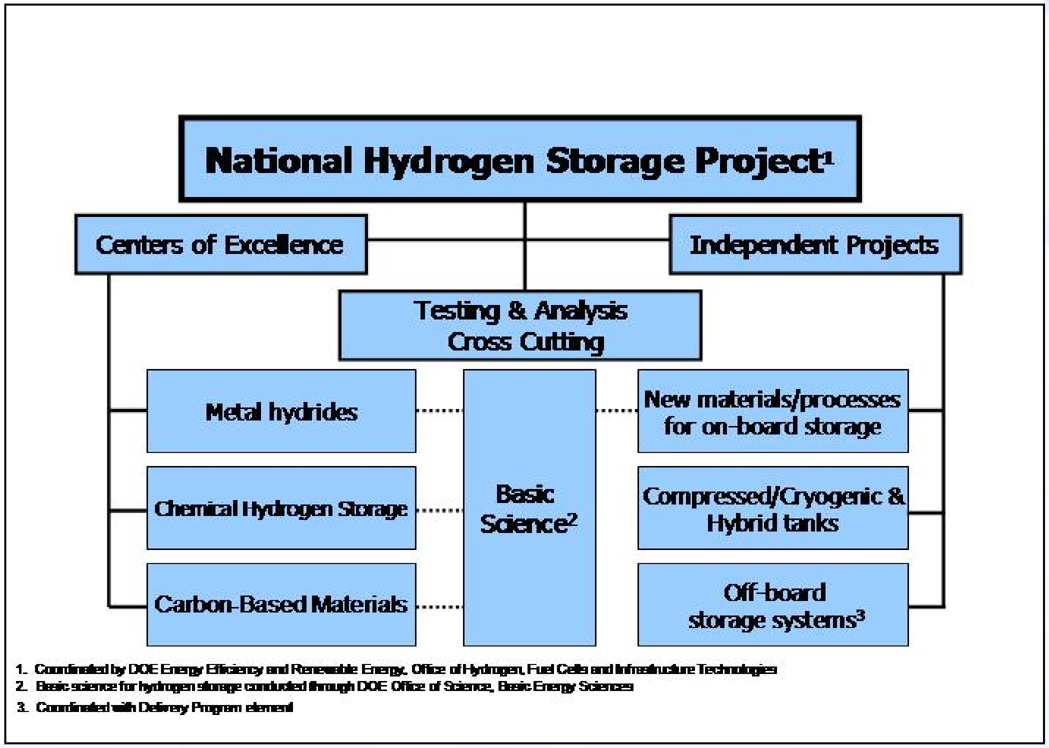
For 100 kW fuel cell, need > 2 g/s flow rate

Desorption rate must be available over the entire hydrogen content range of the material

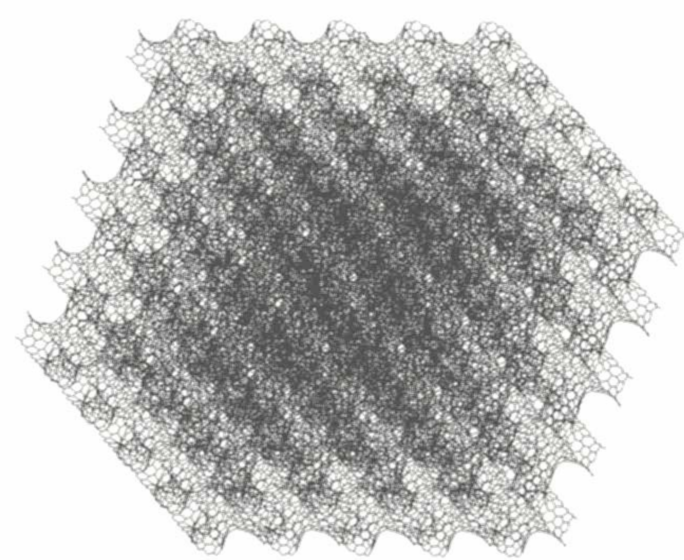


Ref: G. Thomas

Strategy and Program Plans



- **Focus is materials-based technologies**
  - **Systematic approach**
  - **Robust theory/simulation and rapid screening**
  - **Tailor properties**



Yakobson, Rice U.

- **Centers of Excellence** ($5-6M/yr) plus independent projects, launched at $150 M over 5 years (plan- subject to appropriations)
- **~ 40 universities, 15 companies, 10 federal labs** (including 17 new BES awards)
- **Diverse portfolio addresses NAS recommendations**

"…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." (NRC Report,p.44)

Results: Examples of Progress (2005-2006)
New materials with higher capacities being found

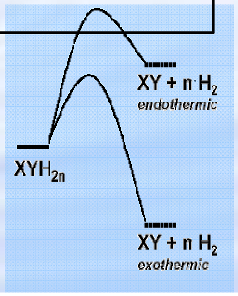
Material Capacities for Hydrogen Storage

Advanced Metal Hydrides	Chemical H_2 Storage	Carbon/ Sorbents & New Materials
Li Mg Amides ~5.5wt%, ~2.8 kWh/L (>200 C) Alane ~7-10 wt%, ~5 kWh/L (<150 C) Li borohydrides >9 wt%, ~3.5 kWh/l (~350 C) Destabilized Binary hydrides ~5-7wt%, ~2-3 kWh/L (250 C) LiMgAlane, M-B-N-H ~ 7-8.8 wt%, > 1.3 kWh/L (~150-340 C)	Phenanthrolene/ organic liquids ~7 wt%,~1.8 kWh/L (>150 C) Ammonia Borane/Scaffolds ~6 wt%,~2-4 kWh/L (<100 C)	Metal/carbon hybrids, MetCars 6 to > 8wt%*, ~1.3* kWh/l (*theory) Bridged catalysts IRMOF-8 ~1.8 wt.%,~0.3 kWh/L (room T) Metal-Organic Frameworks IRMOF-177 ~7 wt%, ~1 kWh/L (77K)

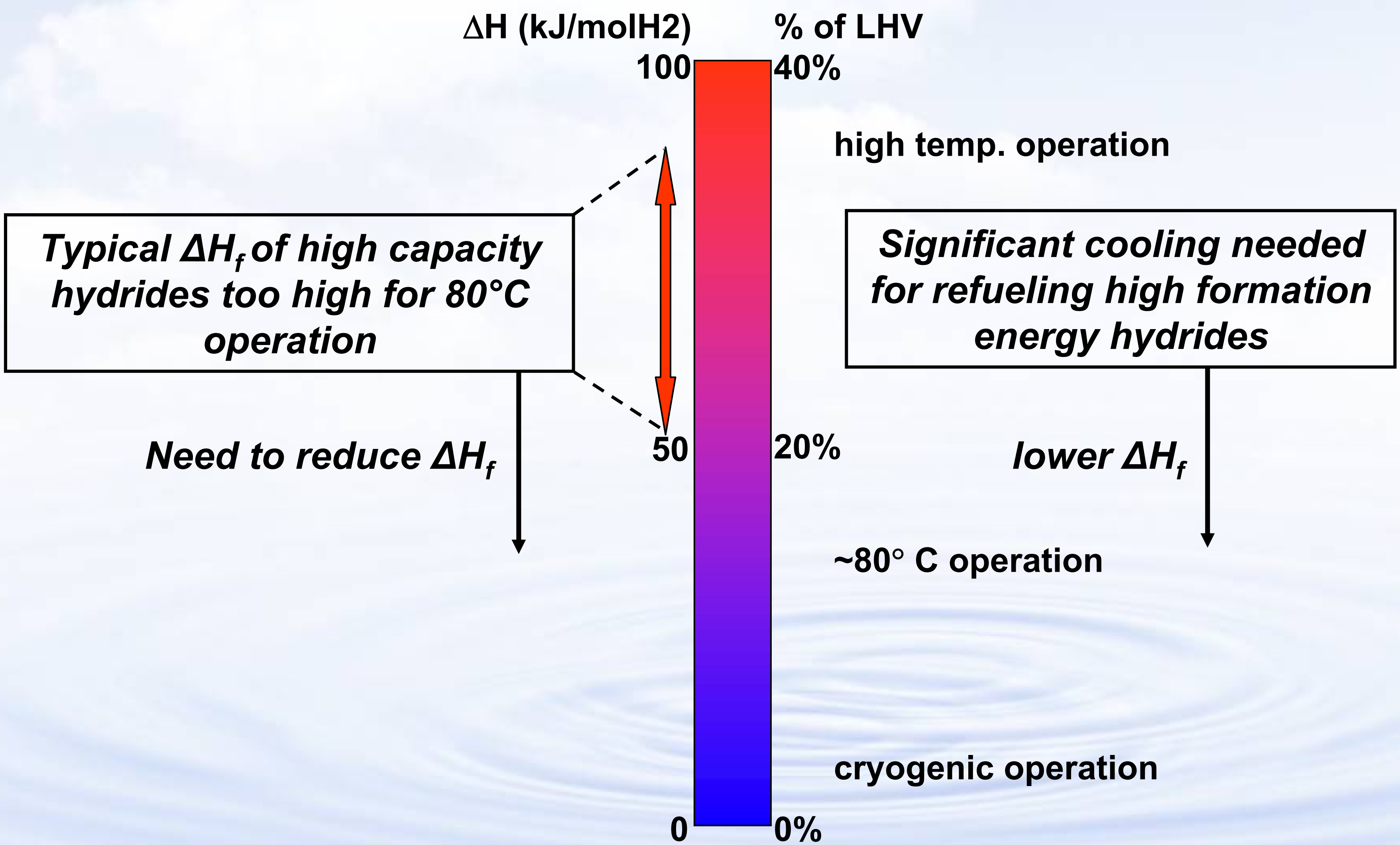
Note: Material capacities only. No balance of plant. Estimates for volumetric capacities.

We are excited by these results but there are still issues…

Next steps: Operability (Temperature, pressure, kinetics, etc.)

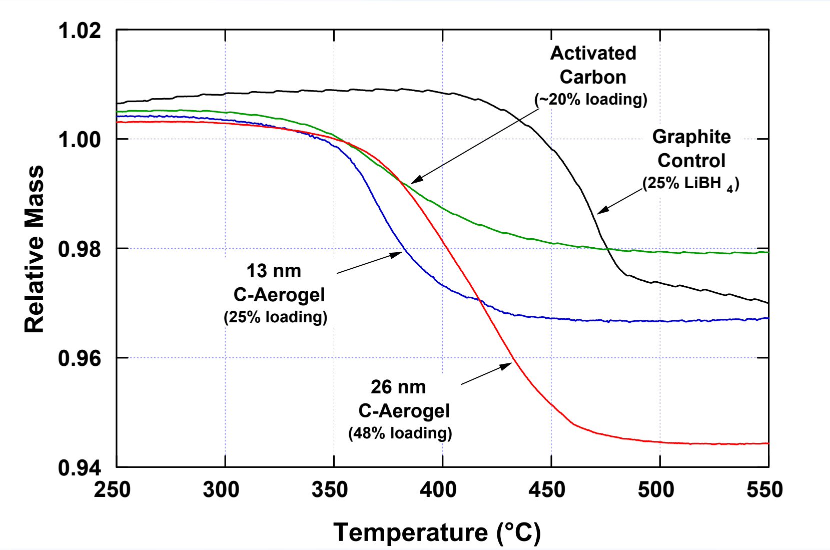


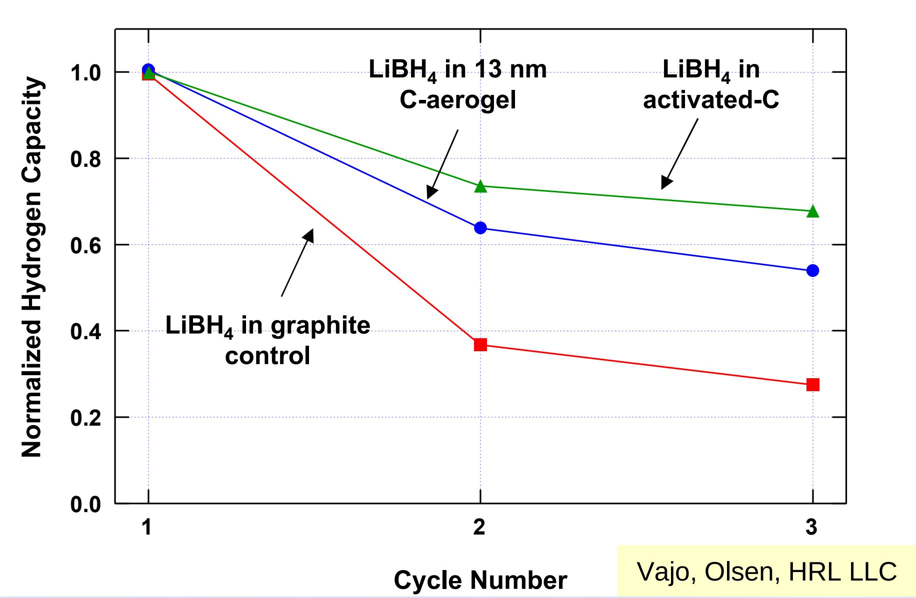
Heat of formation of reversible hydride impacts both operation and refueling



Results: MH researchers are finding new materials with favorable thermodynamics but have kinetic limitations.

- TGA for H_2 desorption from $LiBH_4$ incorporated into nanoporous scaffolds & non-porous graphite control. Lower T_d in carbon aerogels and activated carbon compared to graphite control
- Improved cycling capacity for $LiBH_4$ in scaffold structures. Capacity determined from dehydrogenation after hydrogenation (100 bar H_2, 400°C, 2 hr).





Vajo, Olsen, HRL LLC

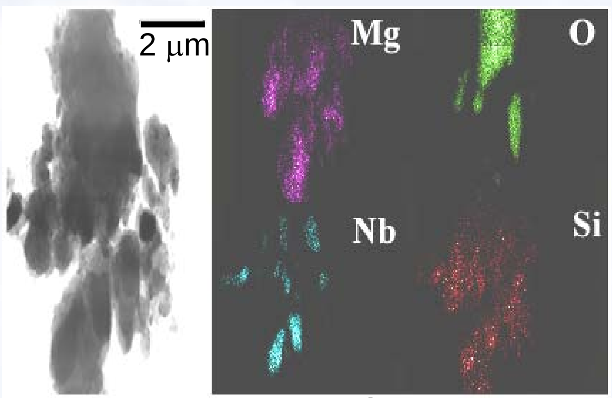
METAL HYDRIDE CENTER OF EXCELLENCE
HRL LABORATORIES

MH researchers are also combining advanced characterization with theoretical modeling to predict promising structures.

Structural/chemical information

TEM structure
And crystallography

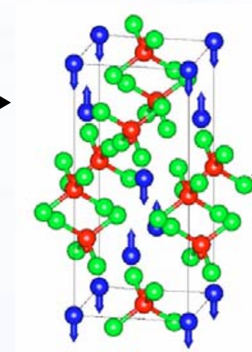
EDS and EELS
Chemical and bonding
information



Provides Needed information

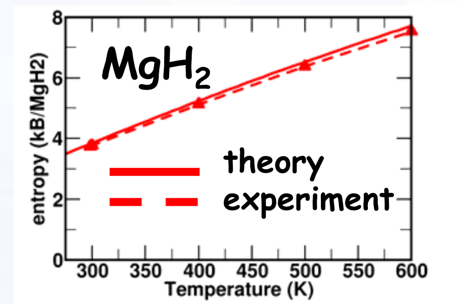
Aids interpretation

First principles calculations of thermodynamic properties



Vienna Ab-initio Simulation Package

+ **PHONON code**



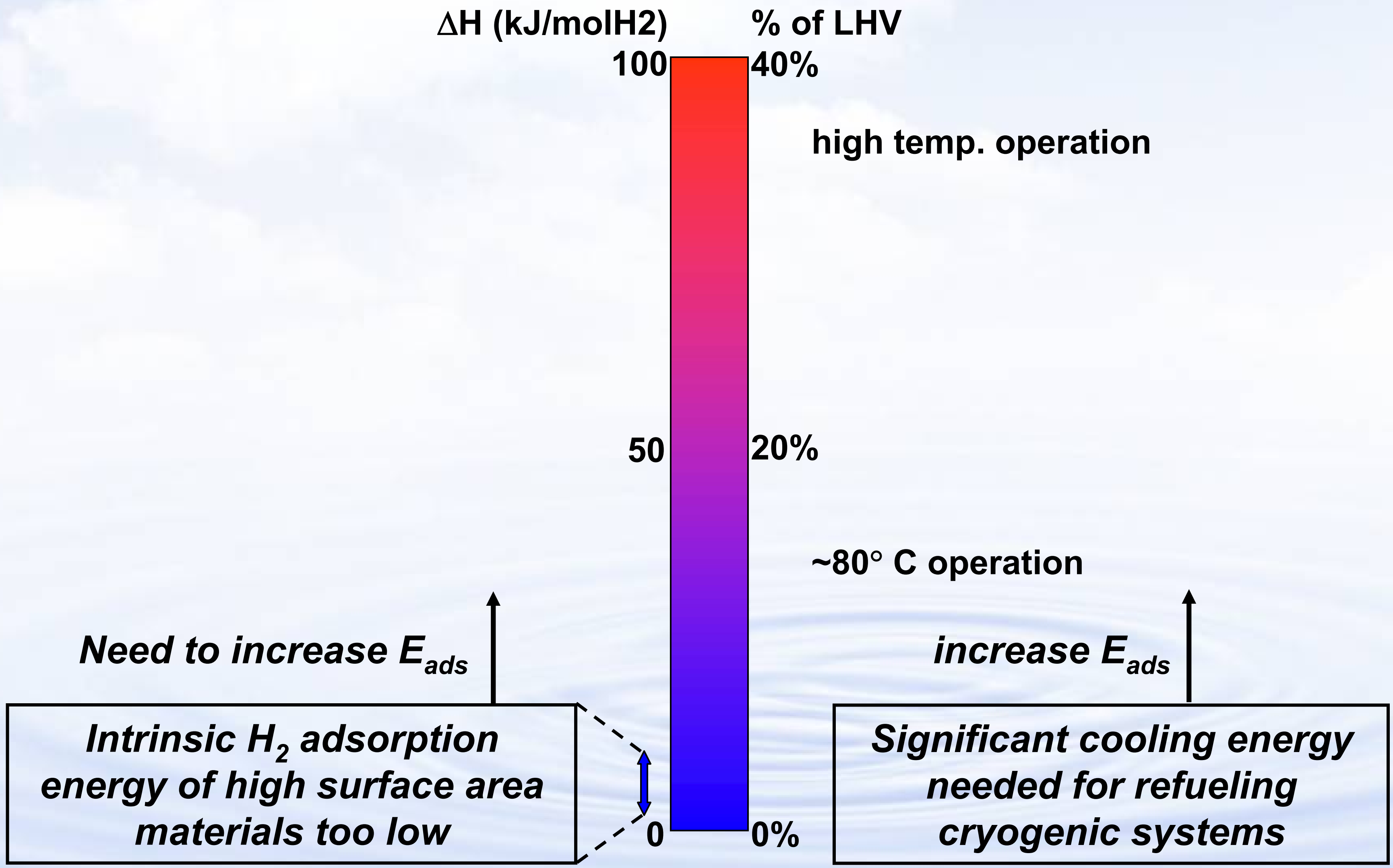
X-ray diffraction – B. Clemens, Stanford
Neutron diffraction – T. Udovic, NIST

DFT ----------- K. Johnson, U. Pitt.
Monte Carlo E. Majzoub – SNL
DFT----- D. Sholl - CMU

Outcome: Provides guidance for new alloys with improved properties

METAL HYDRIDE CENTER OF EXCELLENCE · MSE Illinois · NIST · Sandia National Laboratories · Carnegie Mellon · University of Pittsburgh · STANFORD MATERIALS SCIENCE AND ENGINEERING

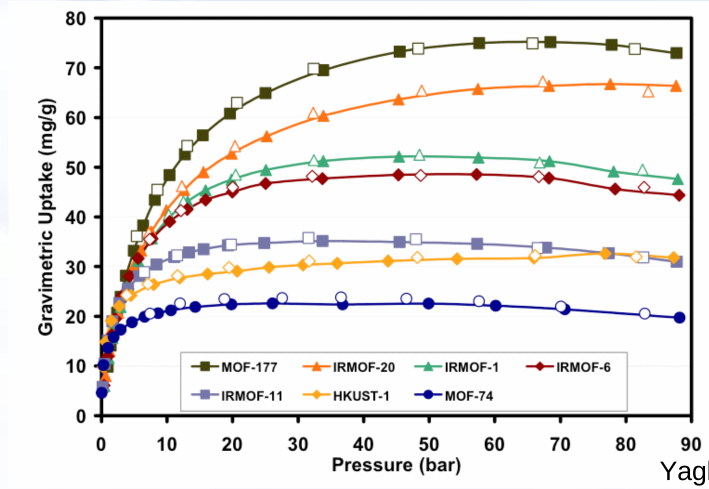
Adsorbent materials generally have too low a binding energy for hydrogen.



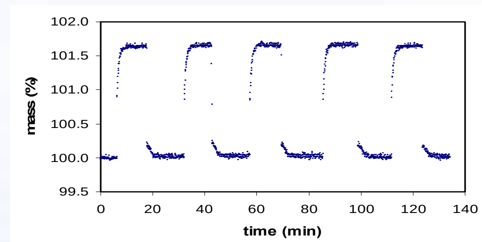
Results: Carbon and Sorbents are looking at increasing capacity and binding energy.

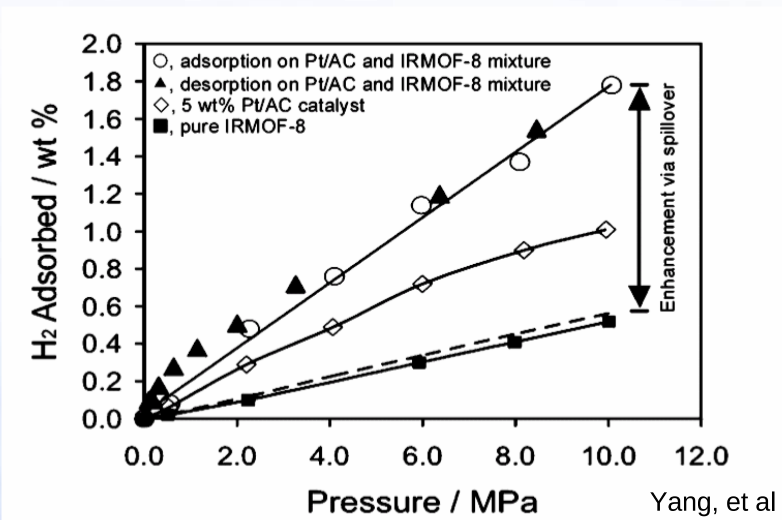
Carbon Center & New Materials:

- **>7 wt.% at 77K shown on MOFs (> 30 g/L)**
- **Several cycles reversibility shown**
- **Four-fold enhancement in H_2 storage via "spillover"**



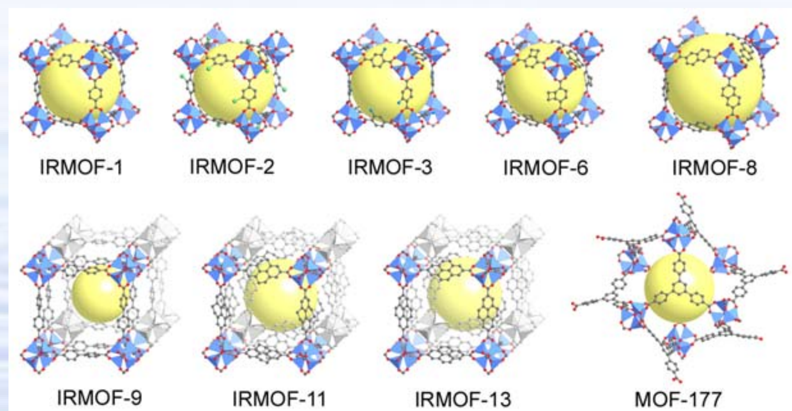
Yaghi, Matzger (UCLA, U MI)





Yang, et al (U MI)

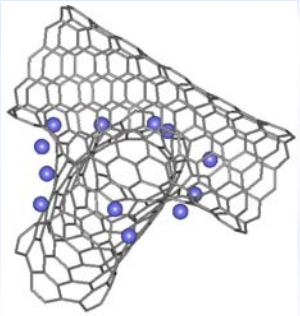
Y. Li and R.T. Yang, *JACS (2006)*

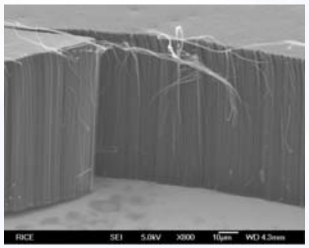


Yaghi, et al

A.G. Wong-Foy, A.J. Matzger, O.M. Yaghi, *JACS* (2006)

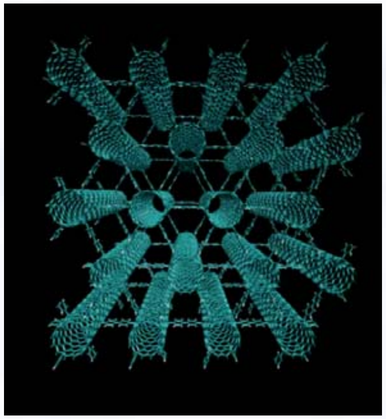
Results: The Carbon CoE is also using theory to design tailored nanostructures.





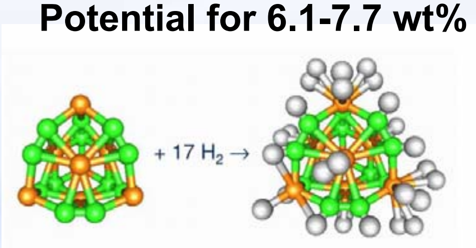
CNT “Carpet”
Tour, et al, Rice U.

Yakobson, Ding, Lin
Rice University
Carbon Center

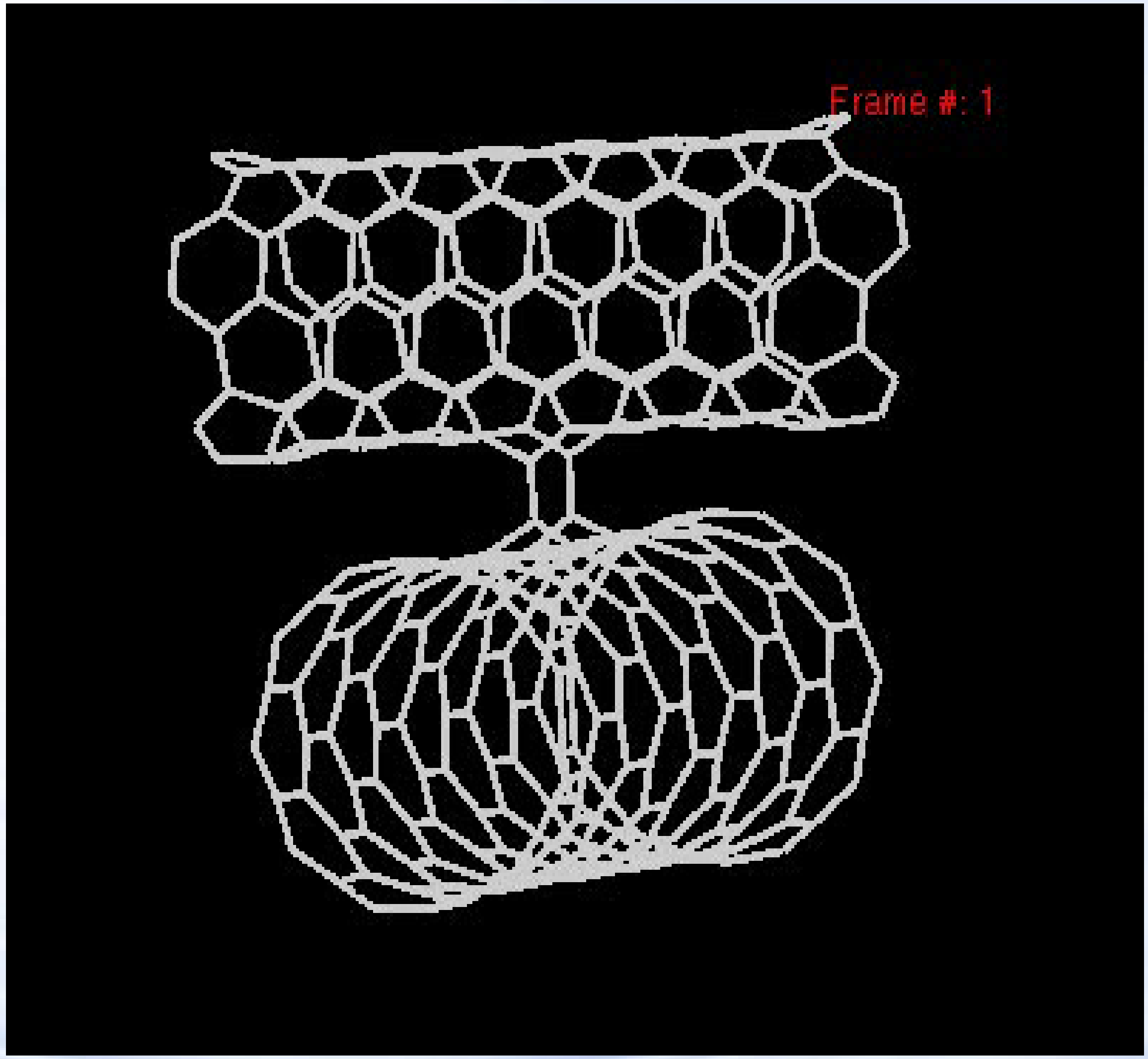


NREL-Carbon Center

Potential for 6.1-7.7 wt%



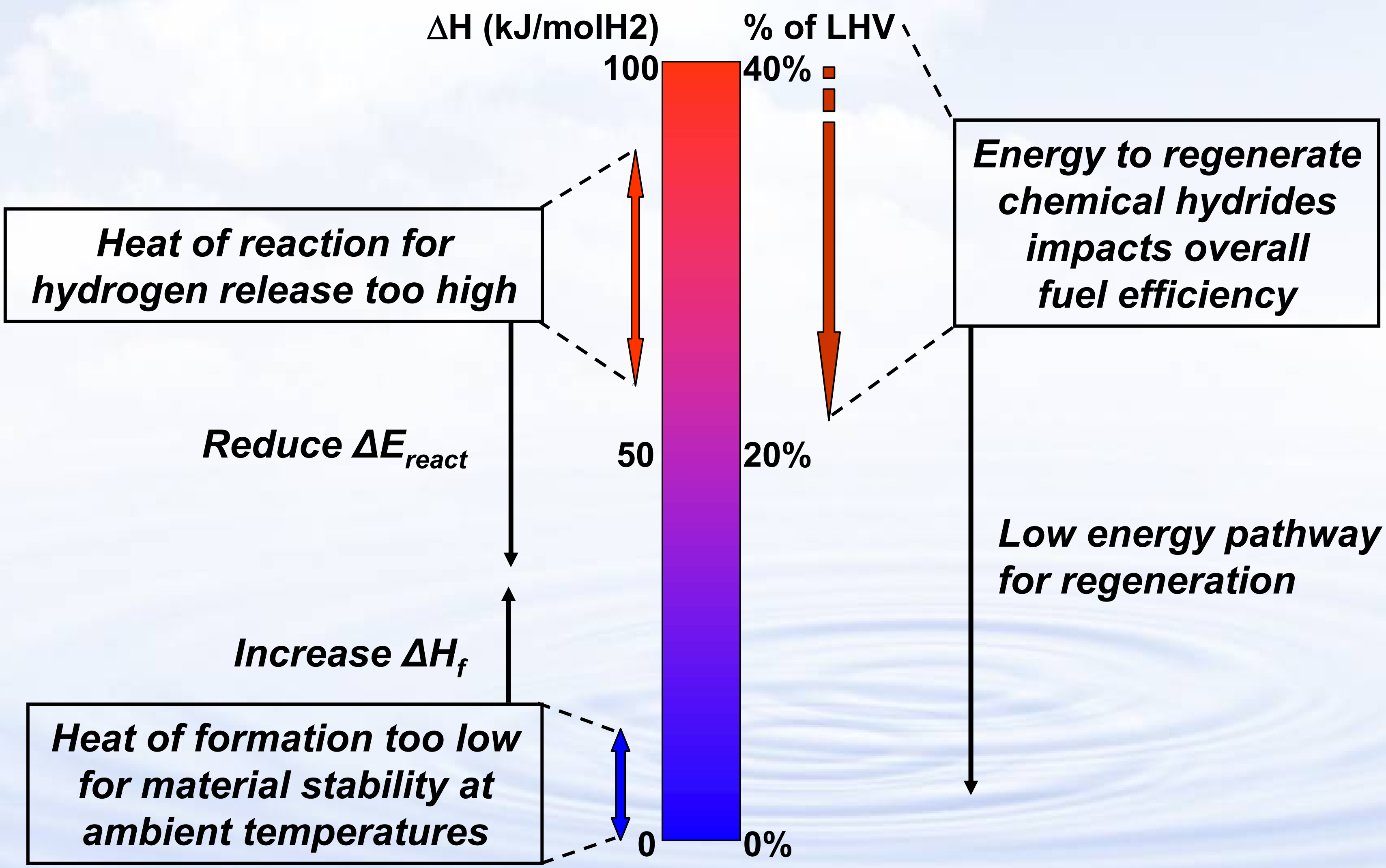
MetCars
Y. Zhao, A.C. Dillon, Y.-H. Kim, M.J. Heben, S.B. Zhang, in prep



Yakobson, et al

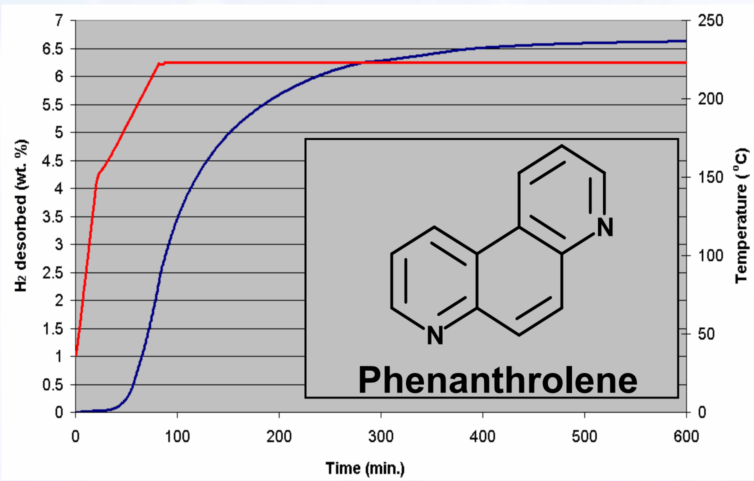
Theoretical modeling conducted to predict optimum structures and storage capacities

Thermodynamics of chemical (non-reversible) hydrides must also be tailored.



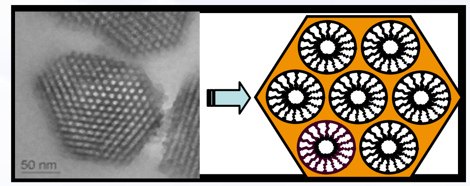
Results: Chemical carrier research is addressing both on-board kinetics and regeneration chemistry.

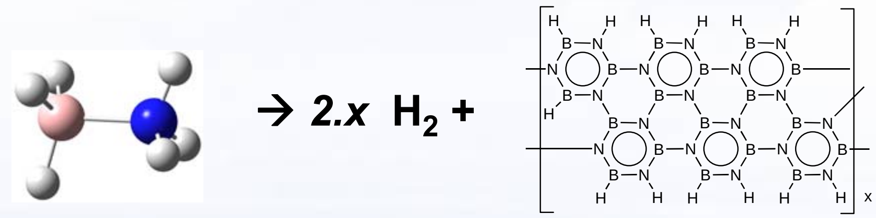
- **Organic liquids: >7 wt.%, 69 g/L**
  - 1.5 wt% more than FY05
  - > 100 catalysts screened
  - > Dehydrogenation with 10x less Pt in catalysts



Cooper, Pez, et al, Air Products

- **NH_3BH_3 in mesoporous scaffolds:**
  - >6 wt% material capacity
  - H_2 release at < 80 C
  - Reduced borazine formation



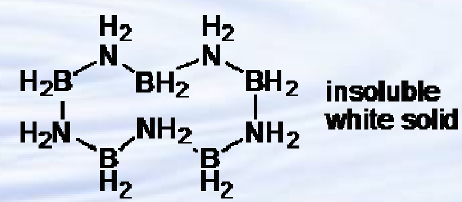


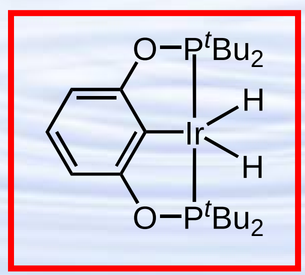
Autrey, Gutowski, et al, PNNL Chemical CoE

Rapid dehydrogenation catalysts demonstrated

U. of Washington, Chemical CoE

$$H_3NBH_3 \xrightarrow[\text{THF, rt}]{\text{Ir cat.}} 1/5\,[H_2NBH_2]_5 + H_2$$





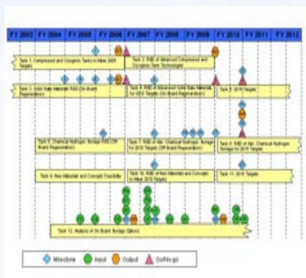
Original catalyst development- Jensen, et al (U HI)

Hydrogen Storage – Future Plans

International Partnership for the Hydrogen Economy

IPHE Hydrogen Storage Conference Lucca, Italy

Centers of Excellence Launched



Solicitation Released

Ammonia Paper Released for Comment

Full Proposals Due Oct 4 06

Pre-Proposals Due

FY07 Go/No-go $NaBH_4$

2005 | Mar | Jun | Sep | Dec | 2006 | Mar | Jun | Sep | 2007 | Dec

Mar

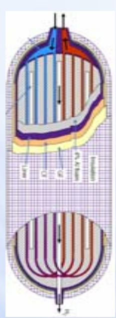
Testing Workshop

Updated Roadmap

Theory Focus Session

Release Solicitation *

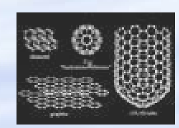
Storage Systems Analysis Working Group Launched



Test Facility Validation

Go/No Go Single - walled Nanotubes

Cryo-compressed Tank Assessment

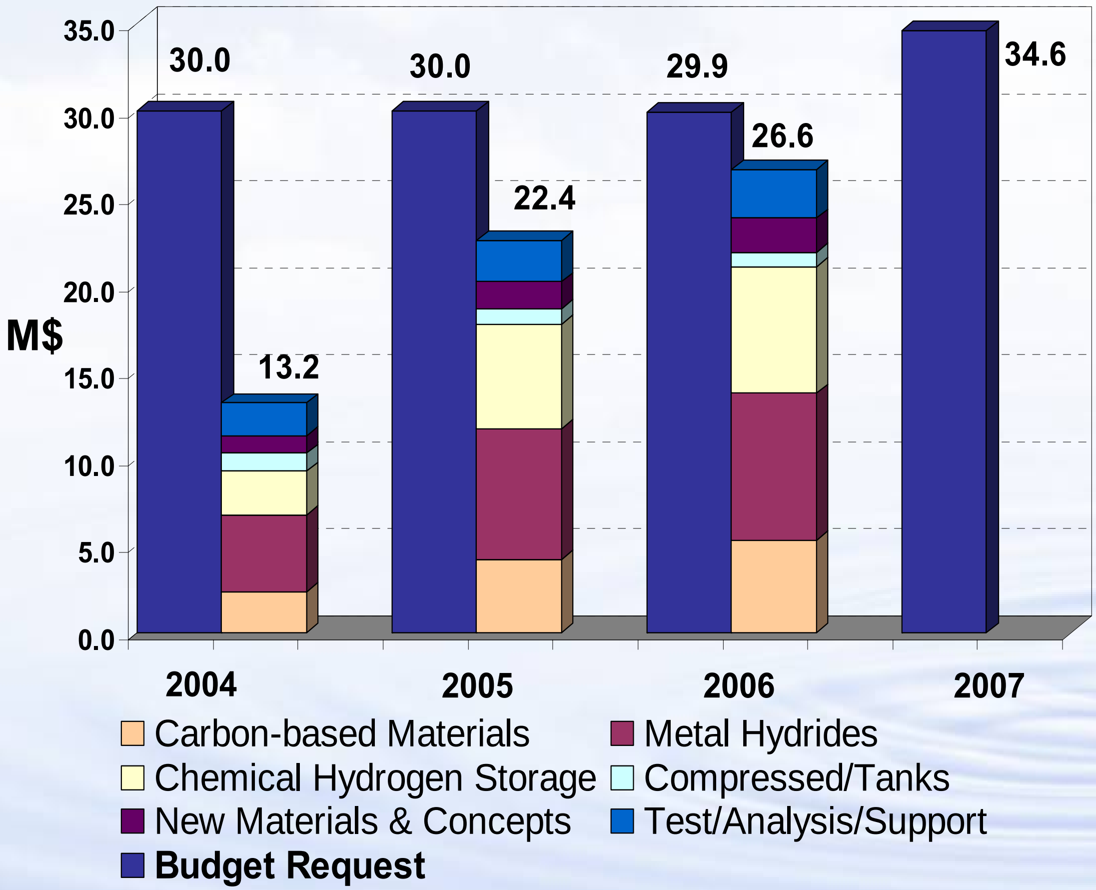


*Subject to appropriations

DOE Hydrogen Storage Budget

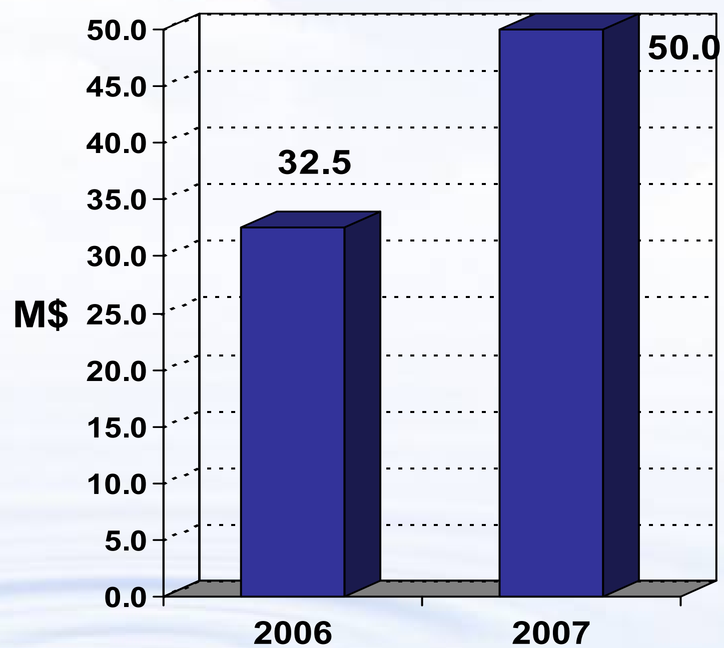
DOE- EERE

FY2007 Budget Request = $34.6M
FY2006 Funding = $26.6M



DOE- Office of Science

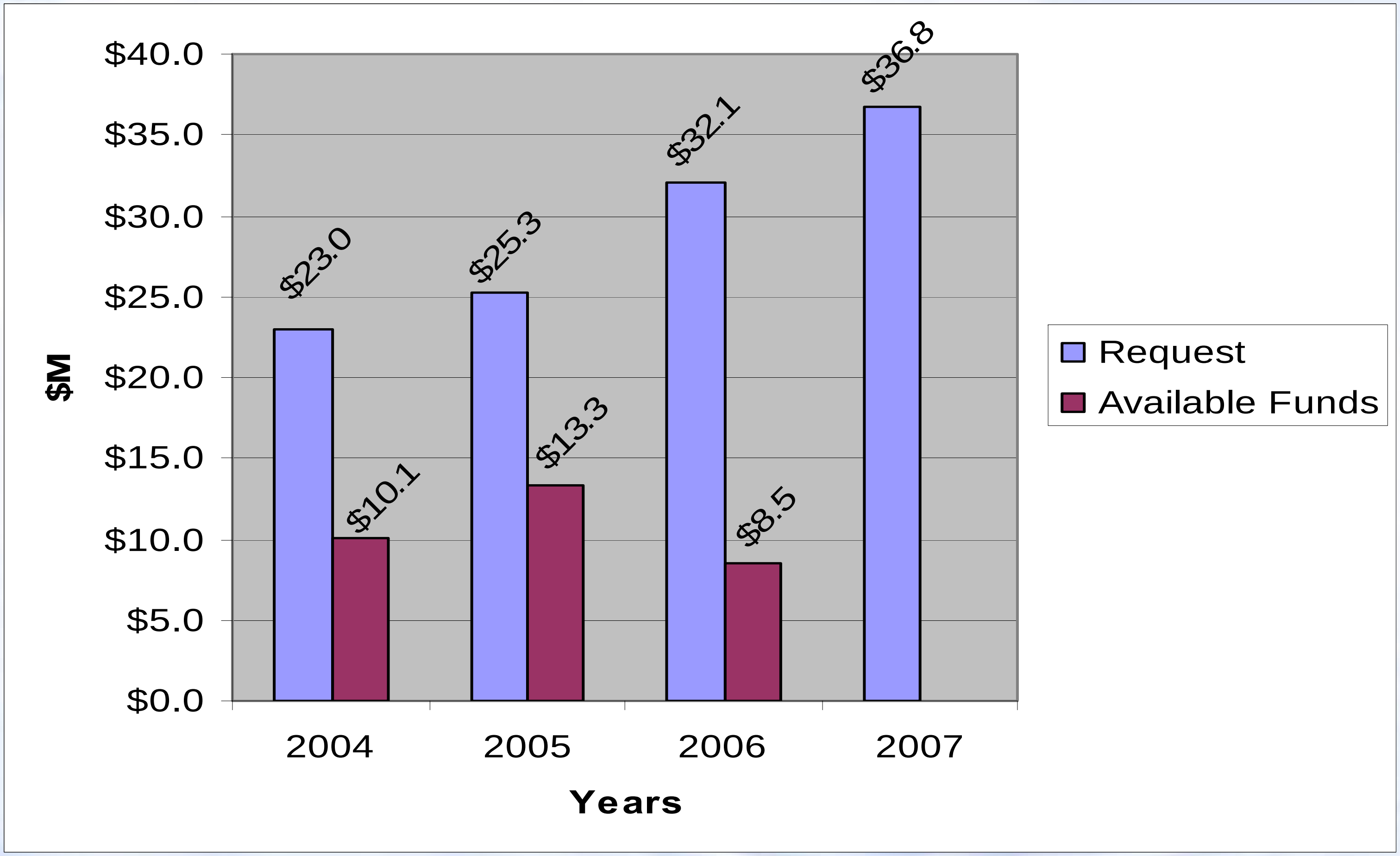
FY2007 Budget Request = $50.0M*
FY2006 Funding = $32.5M*



* For Basic Science within the Hydrogen Fuel Initiative, including hydrogen storage, membranes, catalysts, etc.

Planned funding for Basic Science in Hydrogen Storage in FY06: $7.13M

EERE Hydrogen Production and Delivery R&D Budget



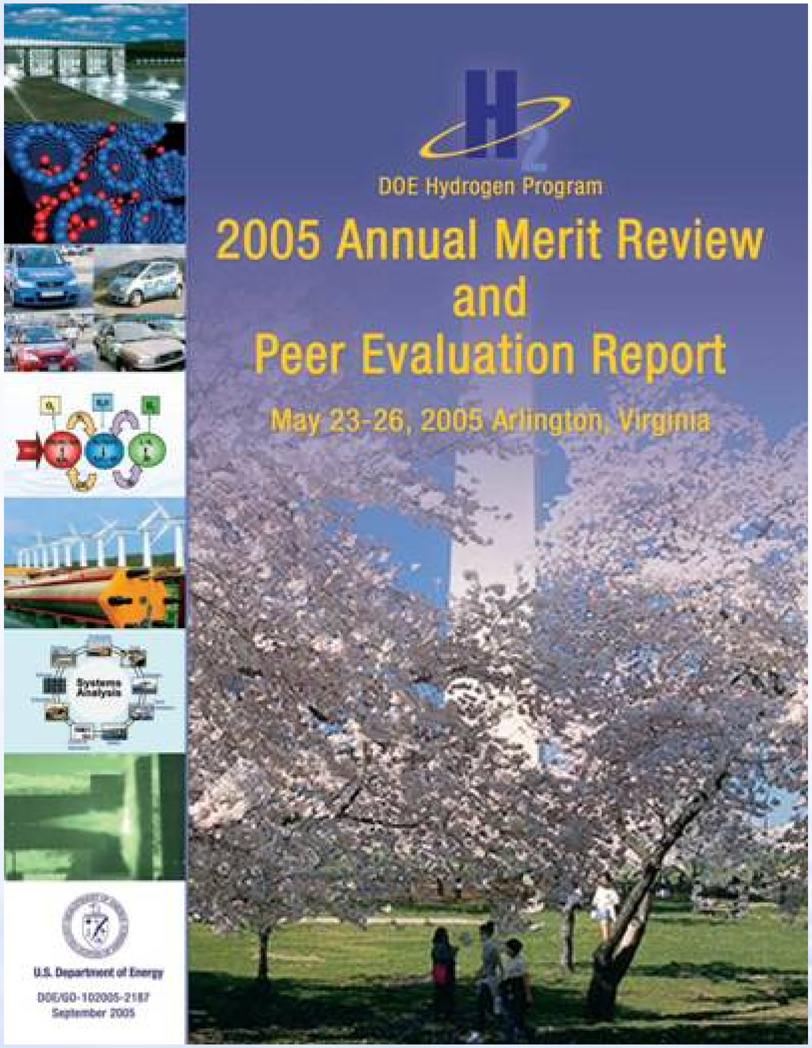
- Difference between the total 04-07 request and available funds is $48.5M

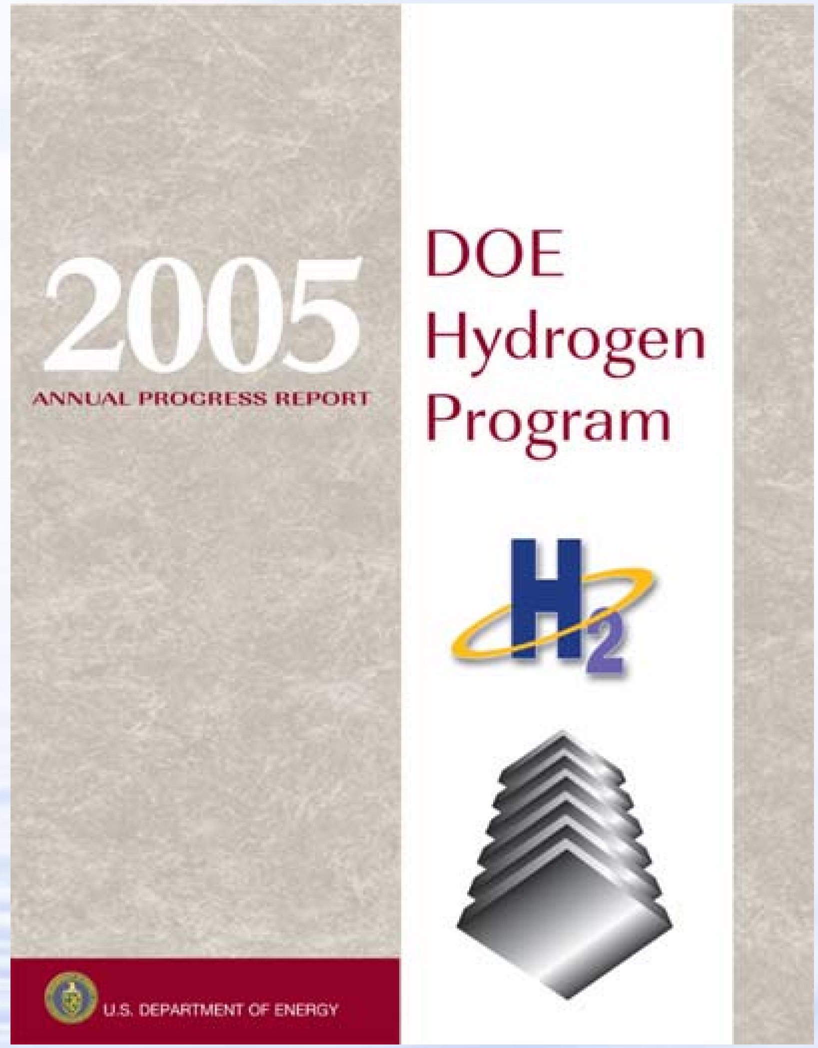
* Budget numbers do not include earmarks

Summary: We need you to solve the Storage "Grand Challenge"!

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

2007 Annual DOE Hydrogen Program
Merit Review and Peer Evaluation Meeting
Arlington, VA May 14-18, 2007





www.hydrogen.energy.gov

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Relevant Web Sites for DOE-SC-BES Programs:

Core Research Program

http://www.science.doe.gov/bes (Office of Basic Energy Sciences)
http://www.science.doe.gov/bes/dms/DMSE.htm (Division of Materials Sciences & Engineering)
http://www.science.doe.gov/grants/ (Sponsored research details)
http://www.science.doe.gov/bes/dms/Submit_Proposals/submit_proposals.htm
http://www.grants.gov/

http://www.science.doe.gov/bes/dms/Submit_Proposals/1pager.pdf
(1 page information flyer)

Major Research Facilities

http://www.sc.doe.gov/bes/BESfacilities.htm
http://www.science.doe.gov/bes/User_Facilities/dsuf/DSUF.htm

SBIR/STTR

http://sbir.er.doe.gov/sbir