Hydrogen Production and Storage R&D Activities at the U.S. Department of Energy

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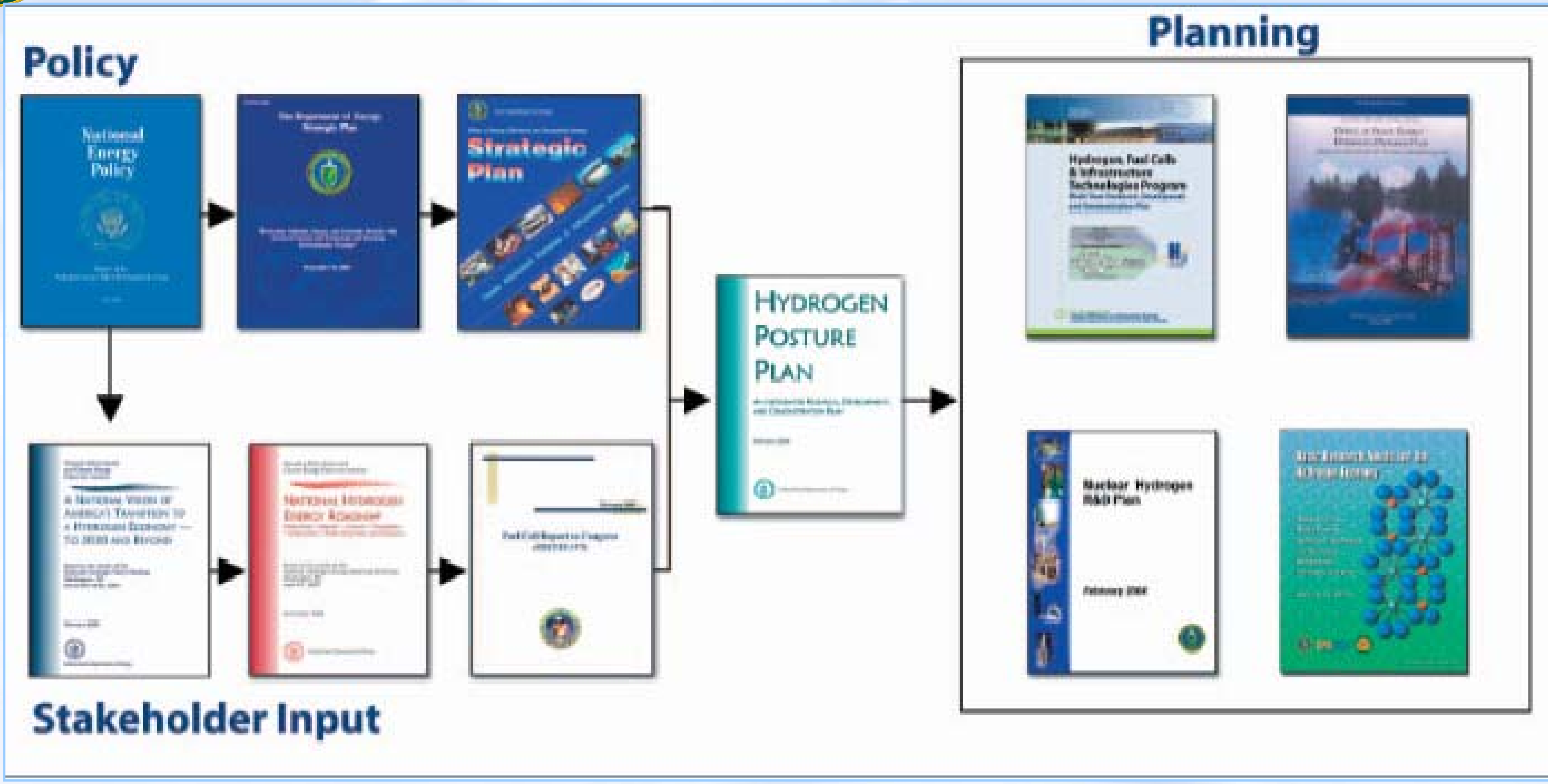
DOE Hydrogen Program

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

Overview

- President’s Hydrogen Fuel Initiative
- Why Hydrogen?
- General overview of hydrogen production
- Focus: The “Grand Challenge” of hydrogen storage
  - Targets & current state-of-the-art
  - U.S. “National Hydrogen Storage Project”
  - What’s needed?
- Summary & Contacts

Strategic and RD&D Planning



Drivers: Energy security, Reduced criteria & greenhouse gas emissions

President's Hydrogen Fuel Initiative $1.2 B over 5 years (launched FY 04

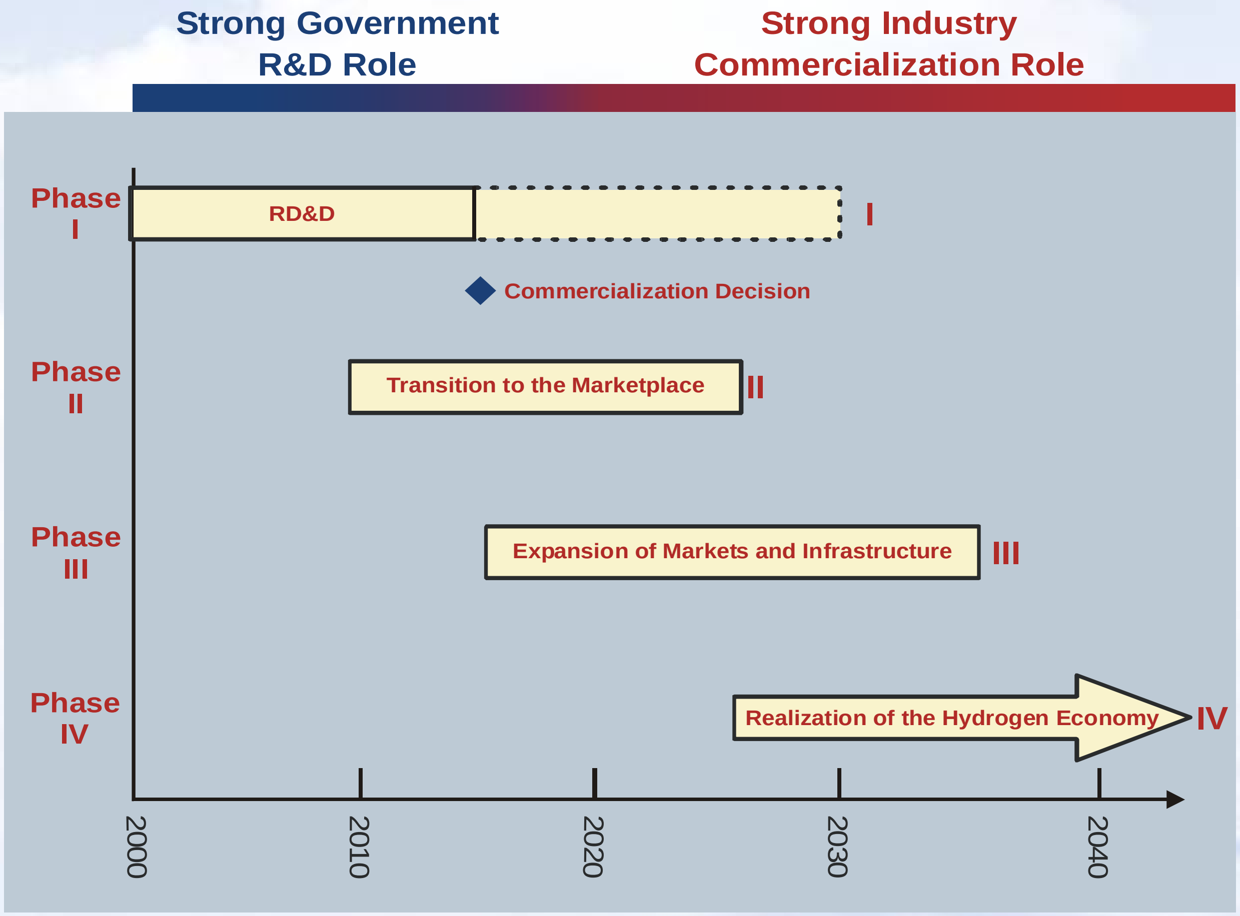
Partnerships- OSTP (NSF, NIST, DOE, DOT, USDA, EPA, NASA, etc.)

FreedomCAR & Fuel Partnership

IPHE International Partnership for the Hydrogen Economy

www.hydrogen.gov or www.hydrogen.energy.gov

Hydrogen Economy Timeline



Transitional Phases

I. Technology Development Phase

II. Initial Market Penetration Phase

III. Infrastructure Investment Phase

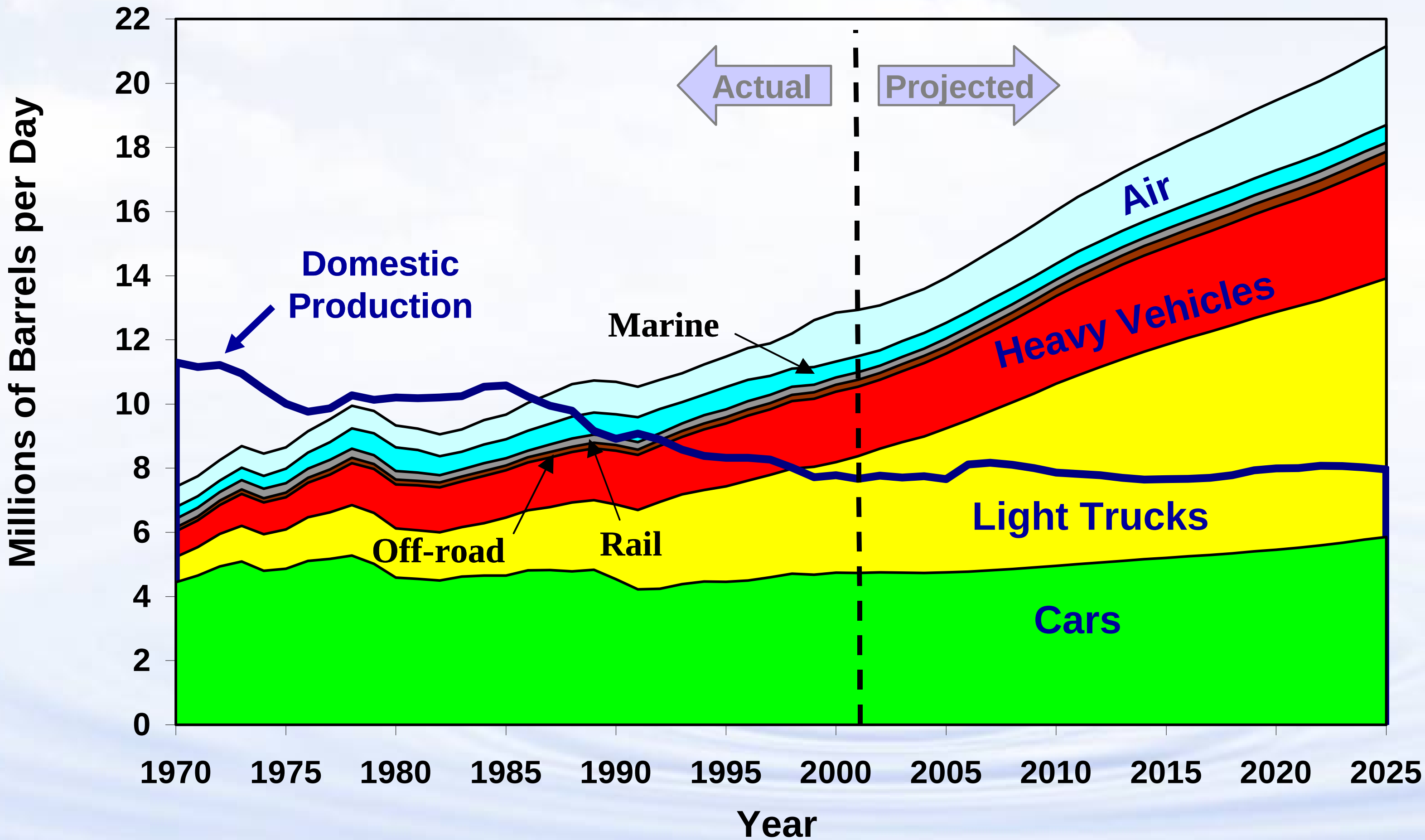
IV. Fully Developed Market and Infrastructure Phase

Focus now: critical path barriers for commercialization decision in 2015.

- **Production ($2-$3/gge)**
- **Storage (3 kWh/kg, 2.7 kWh/l,$2/kWh)**
- **Fuel cells ($30/kW, 5000 hrs)**

U.S. Energy Dependence

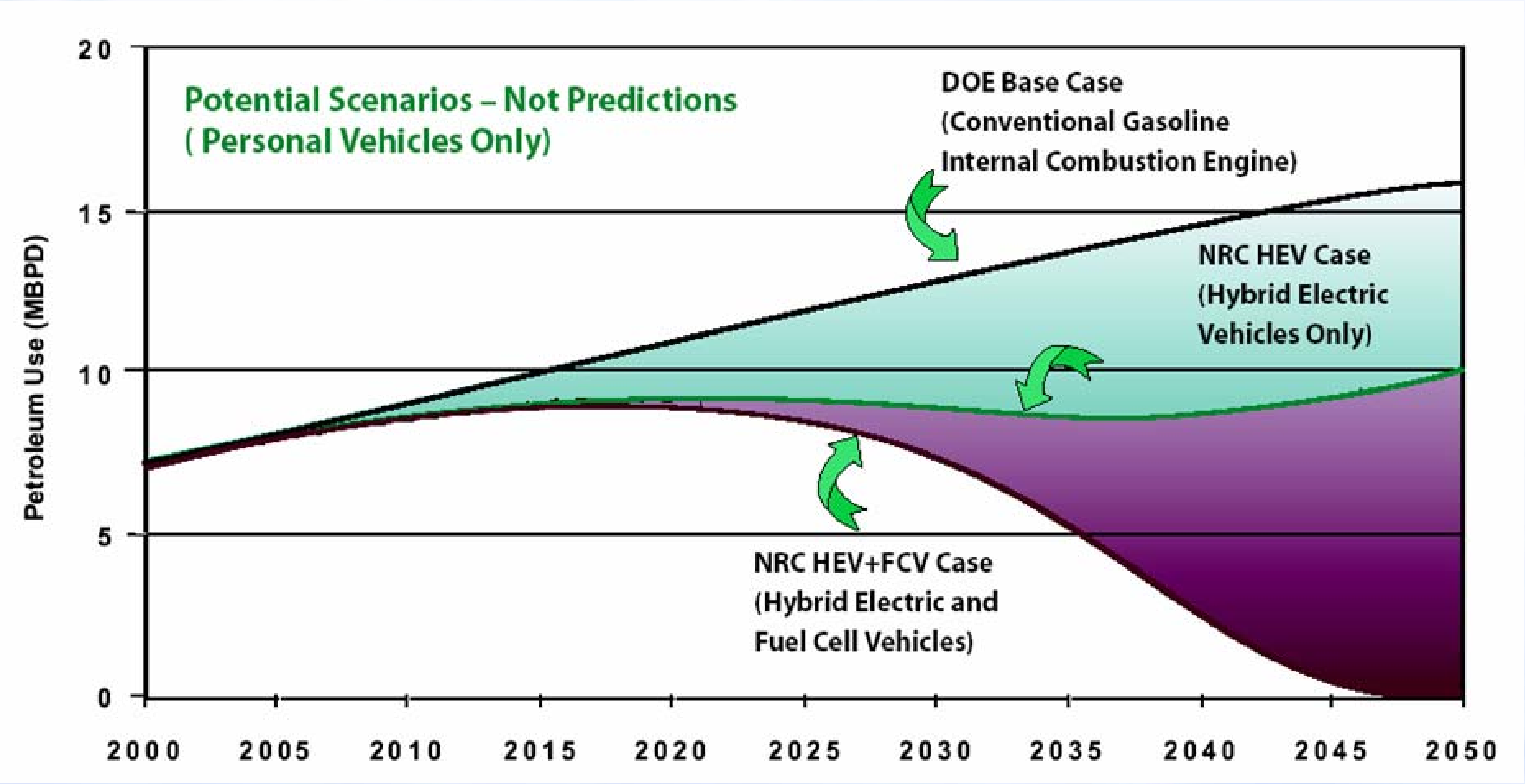
Petroleum dependence is driven by transportation



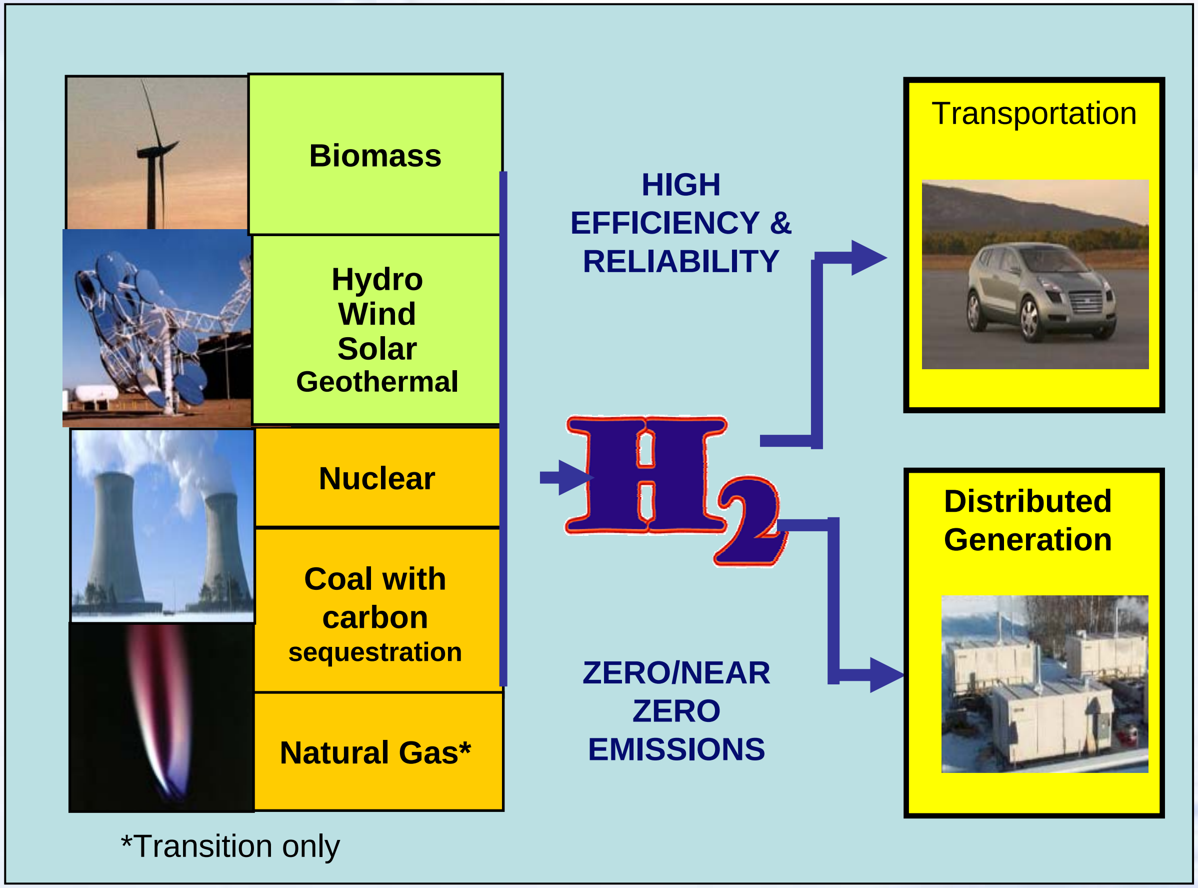
Source: Transportation Energy Data Book: Edition 22, September 2002, and EIA Annual Energy Outlook 2003, January 2003

U.S. Energy Dependence

Fuel substitution needed to complement hybrid strategy



Why Hydrogen?



Source: DOE Hydrogen Program, S. Chalk et al

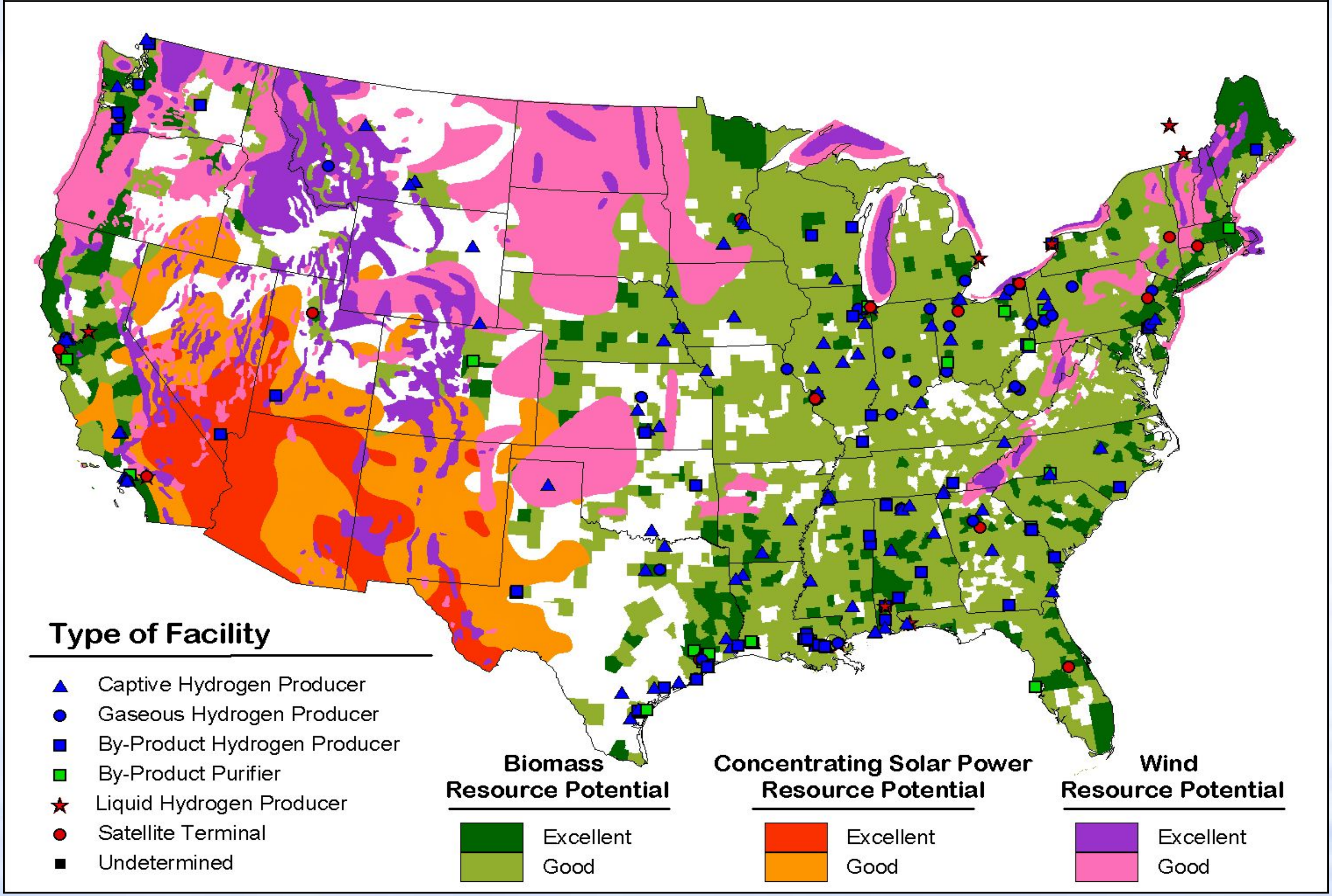
- Multiple domestic resources
- Non toxic
- Water vapor emissions
- Decouple carbon emissions from tailpipe
- Flexibility (transportation, stationary, portable)
- Efficiency of fuel cells
- Highest energy density by wt of all known fuels
- Alternatives?

Nothing's perfect. Issues:

- Energy carrier, not source
- Production, storage, delivery, safety, etc.

Renewable resources are available in most regions of the U.S.

Source: National Renewable Energy Laboratory



Where will the hydrogen come from?

Approximate amounts needed for 20% demand of 64 M tons/yr (2040)

Carbon Neutral Resource	Needed for H_2[a, g]	Availability	Current Consumption	Consumption with H_2 Production (factor times current)
Reforming and/or Partial Oxidation[b] (million metric tons per year)				
Biomass	140-280	800 (biomass residue and waste) + 300 (dedicated crops[c])	200 (3 quads for heat, power & electricity)	**1.7-2.4**
***Coal** (with sequestration)*	110	115,000 (recoverable bituminous coal)	1000 million (all grades)	**1.1**
Water Electrolysis[d] (gigawatts of electricity)				
Wind	200	3250	4	**51**
Solar	260	Southwest US: 2,300 kWh/m^2-year	<1	**>260 times current**
Nuclear	80	345,000 metric tons[e]	100	**1.8**
Thermo-Chemical (gigawatts thermal energy)				
Nuclear	110	345,000 metric tons[e]	310[f]	**1.3**

Current H_2 production (M tons/yr): ~ 9 (U.S.) and ~ 50 (global)

From Hydrogen Posture Plan (www.hydrogen.energy.gov)

Hydrogen Storage "Grand Challenge":

How to store H_2 on-board a vehicle to meet performance (wt, vol, kinetics, etc.), safety and cost requirements and enable > 300 mile range, without compromising passenger/cargo space??

- **Energy content of Hydrogen:**
  - **Weight Basis:**
    - **~ 3x gasoline**
    - **120 MJ/kg (liquid H_2) vs. ~ 44 MJ/kg (gasoline)**
- **Problem is volumetric capacity:**
  - **3 MJ/L (5000 psi H_2)**
  - **8 MJ/L (LH_2) vs. ~ 32 MJ/L (gasoline)**

Hydrogen Storage Targets

Targets: Developed through FreedomCAR & Fuel Partnership

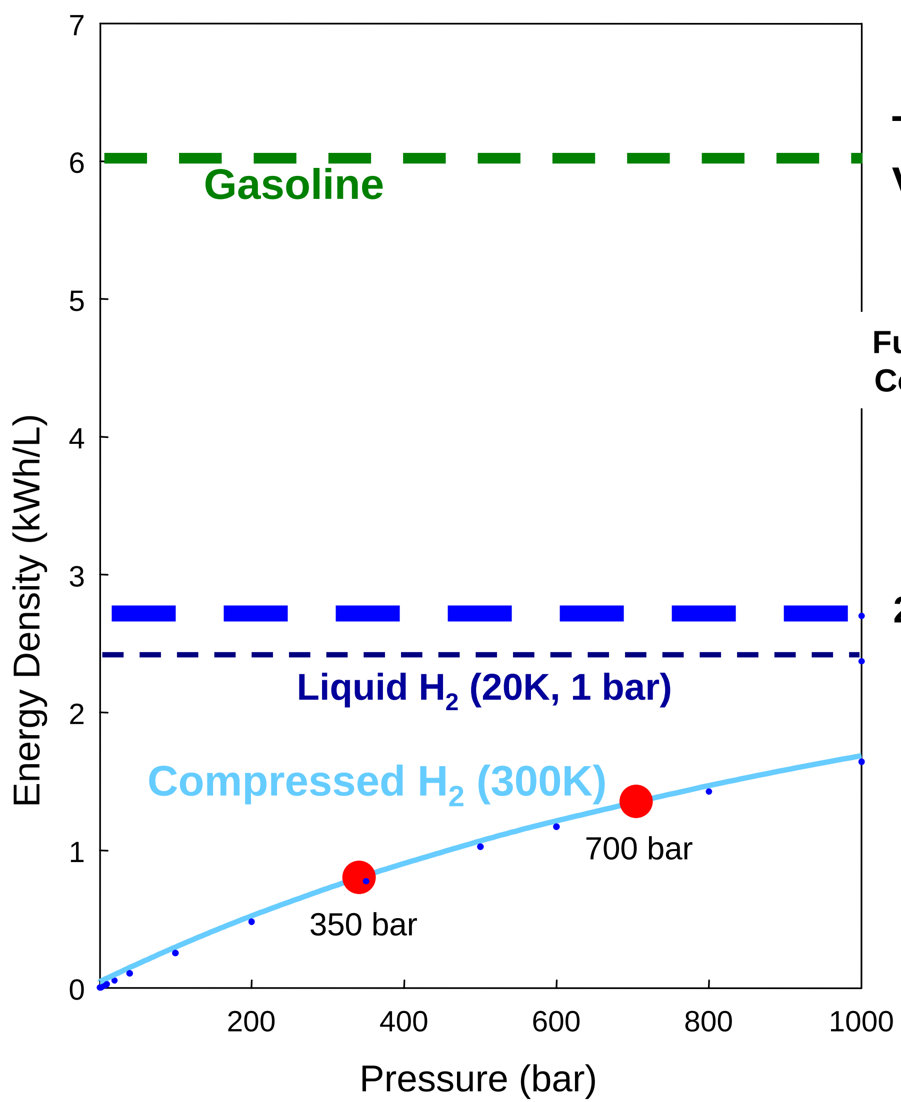
These Are System Targets

Material capacities must be higher!

	2010	2015
System Gravimetric Capacity= Specific Energy (net)	2.0 kWh/kg (7.2 MJ/kg) (6 wt%)	3.0 kWh/kg (10.8 MJ/kg) (9 wt%)
System Volumetric Capacity=Energy Density (net)	1.5 kWh/L (5.4 MJ/L) (0.045 kg/L)	2.7 kWh/L (9.7 MJ/L) (0.081 kg/L)
Storage system cost	\$4/kWh (~\$133/kg H_2)	\$2/kWh (\$67/kg H_2)

Explanations at www.eere.energy.gov/hydrogenandfuelcells/

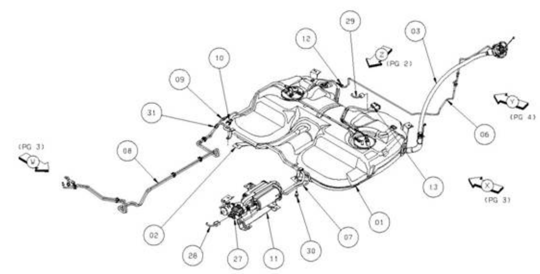
Energy Density is Critical



Today's Vehicles

Fuel Cell Efficiency, Conformable Tanks

2015 Target



Today's gasoline "tank": fuel tank, hoses, fuel lines , fuel pump, fuel filter, carbon vapor canister, leak detection device, etc.

For Hydrogen Systems: Also include insulation, sensors, regulators, first charge, any byproducts/reactants, etc.

Options for vehicular hydrogen storage

Hydrogen Storage Options

Reversible On-Board

High Pressure Tanks

- High Pressure Hydrogen
- Glass Microspheres

Cryogenic Tanks

- Liquid Hydrogen
- Low temp
- Liq/gas mix

Adsorbents (Physisorption based)

- MOFs
- Carbon Nanotubes
- Nanostructures

Metal Hydrides

- Alanates
- Alanes
- Lithium Amides
- Destabilized metal hydrides

Regenerable Off-Board

Chemical Hydrides

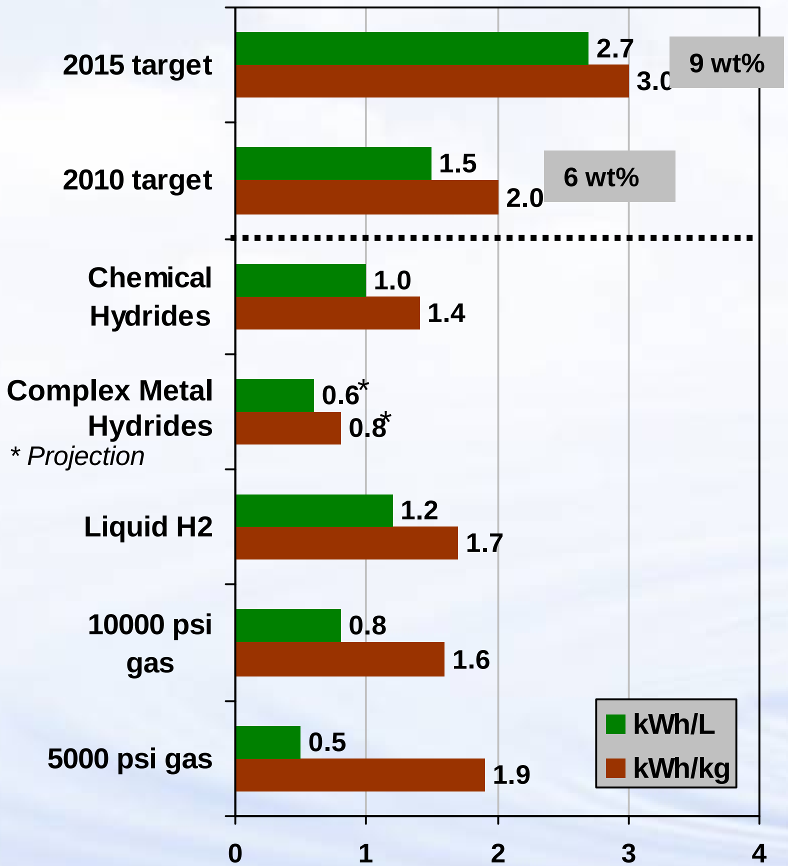
- Sodium Borohydride
- Organic Liquids
- Magnesium Hydride Slurries
- Ammonia Borane

S. Satyapal, DOE Hydrogen Storage Program

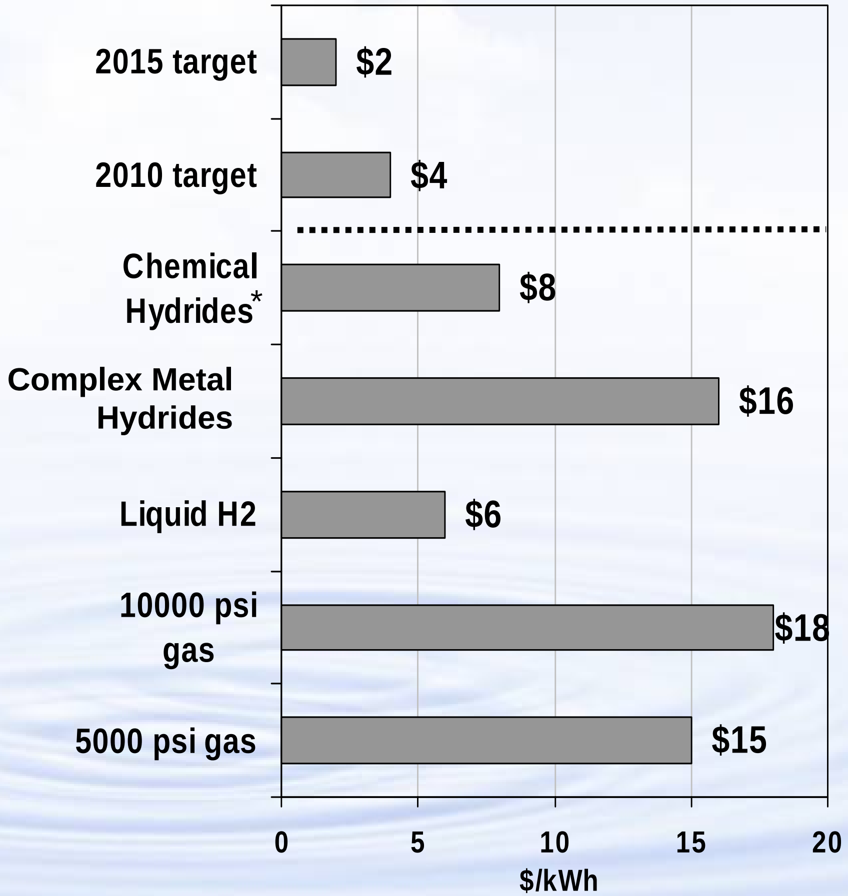
Status Relative to Targets

No current hydrogen storage technology meets the targets.

Volumetric & Gravimetric Energy Capacity



System Cost, $/kWh

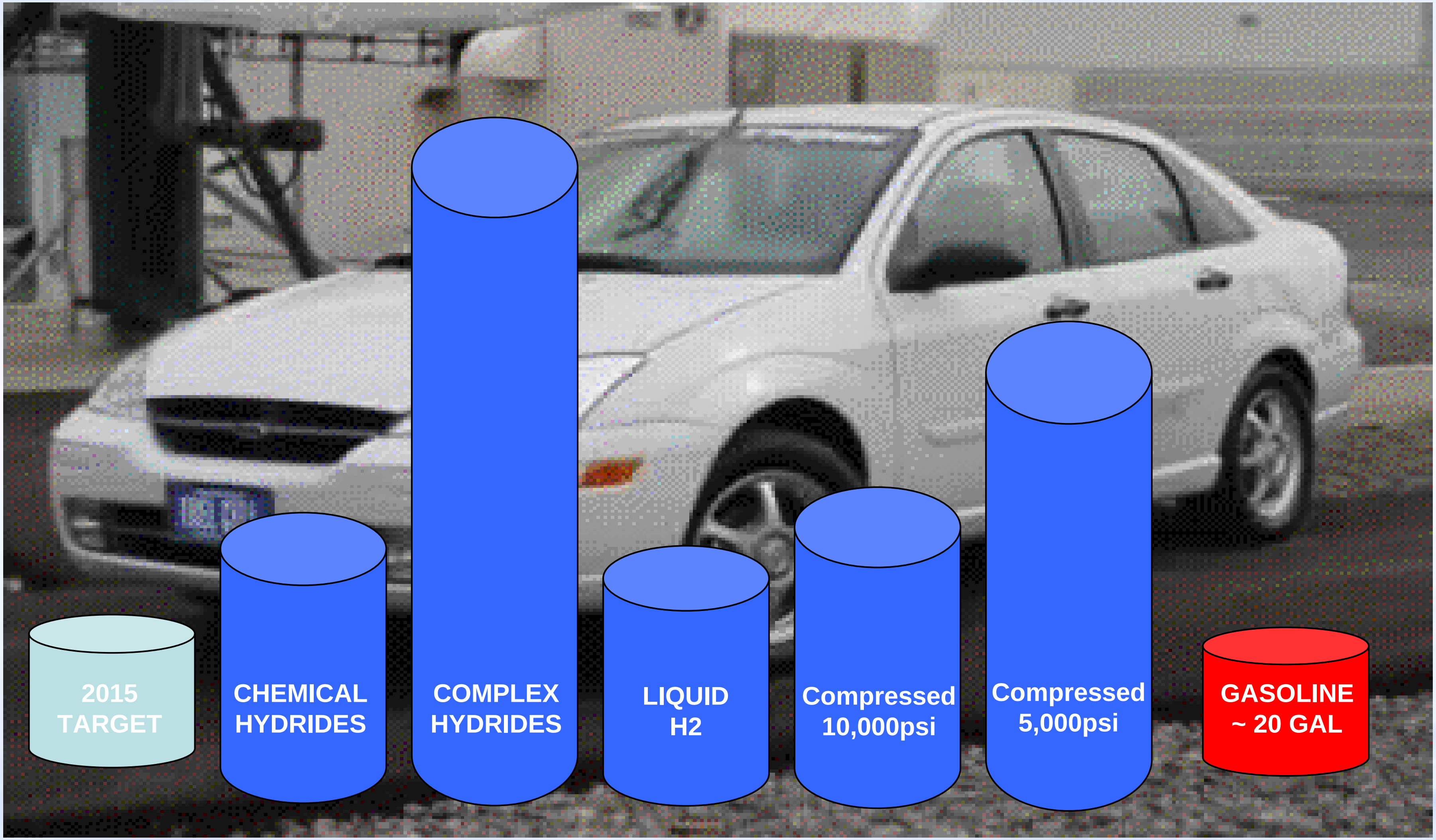


Estimates from developers- to be continuously updated

* *Regeneration costs excluded*

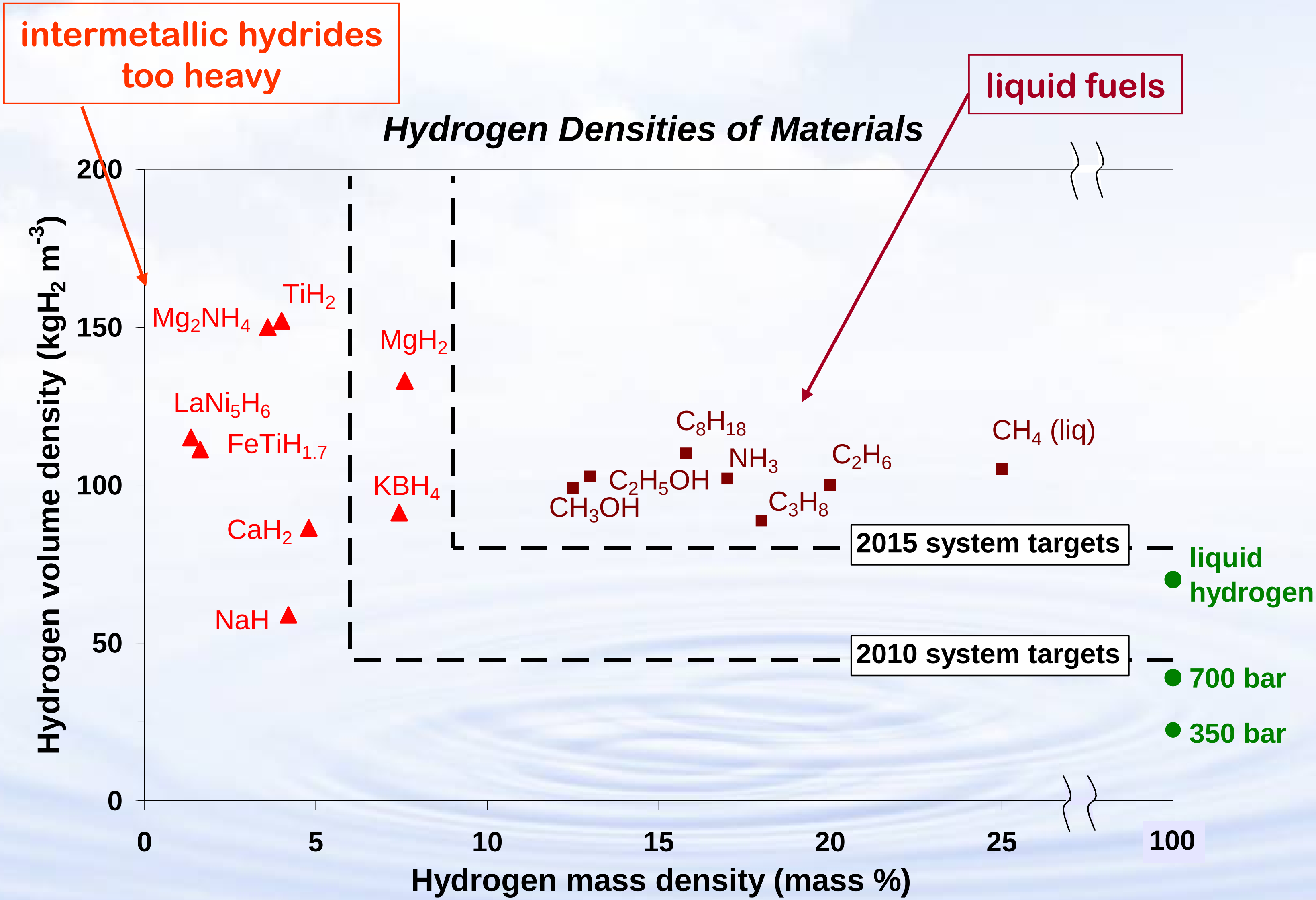
Storage System Volume Comparison…
Where we are, where we need to be

System Volume Estimates- Based on 5 kg hydrogen



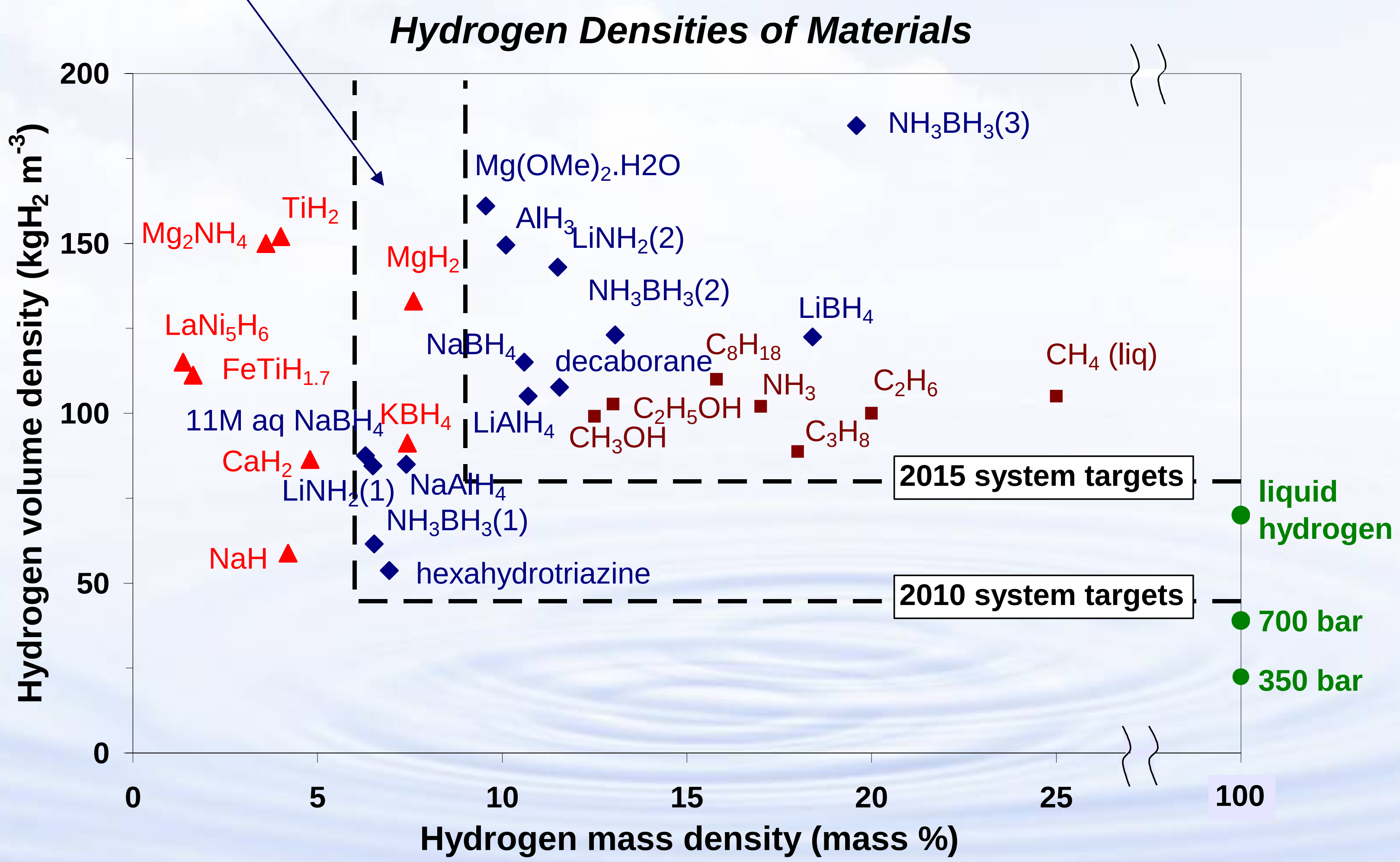
Fuel Cell Vehicle- Photo from www.cafcp.org

Hydrogen Storage Materials-Based Capacities

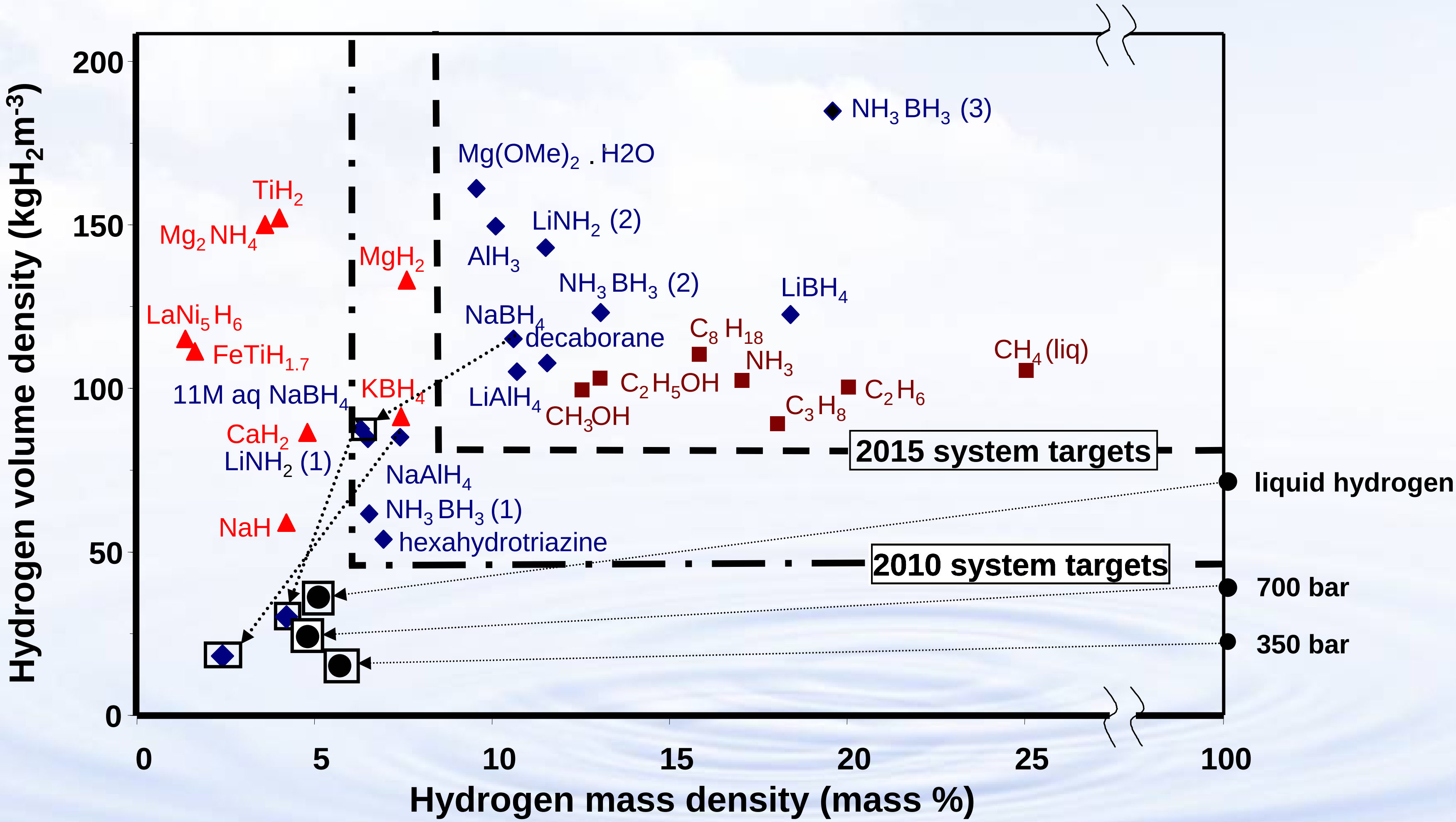


Program focus is on high energy density materials

Some of the materials under study as state-of-the-art



No current material meets system requirements



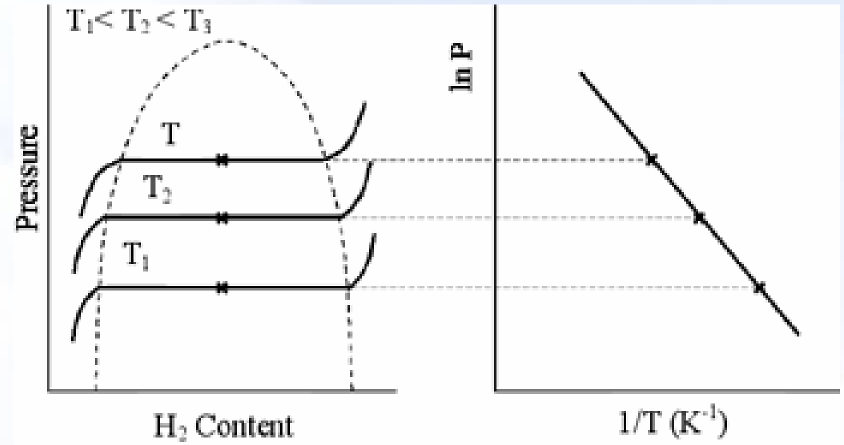
Fundamentals of materials-based technologies

Equilibrium between gas and solid:

$$P = \exp(-\Delta H/RT + \Delta S/R)$$

or $\ln P = -\Delta H/RT + \ln P$

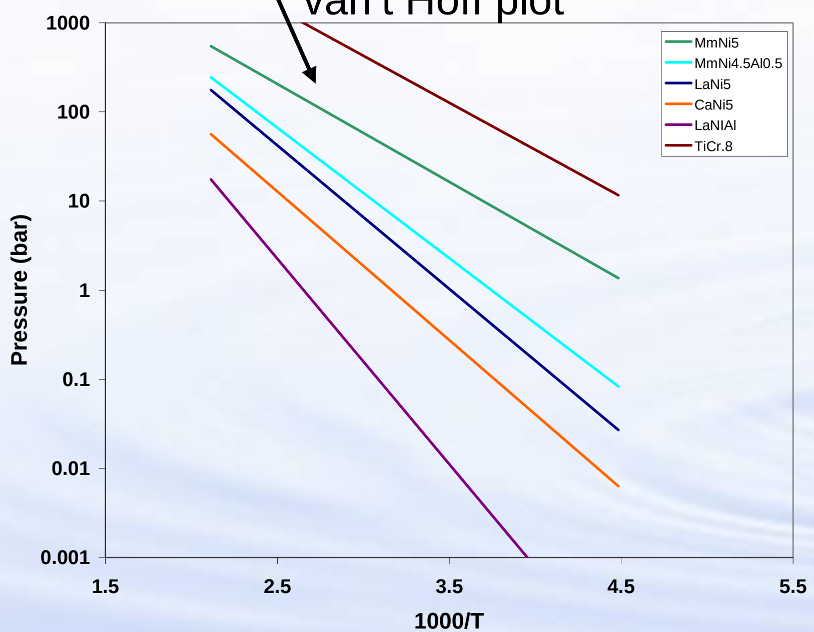
ΔH=enthalpy (kJ/mol H_2)

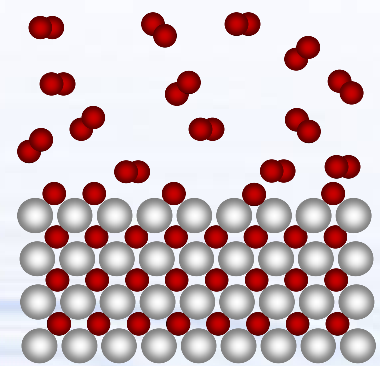


Idealized PCT curves and van't Hoff plot

$\boxed{d(\ln P)/d(1/T) = \Delta H/R}$

van't Hoff plot

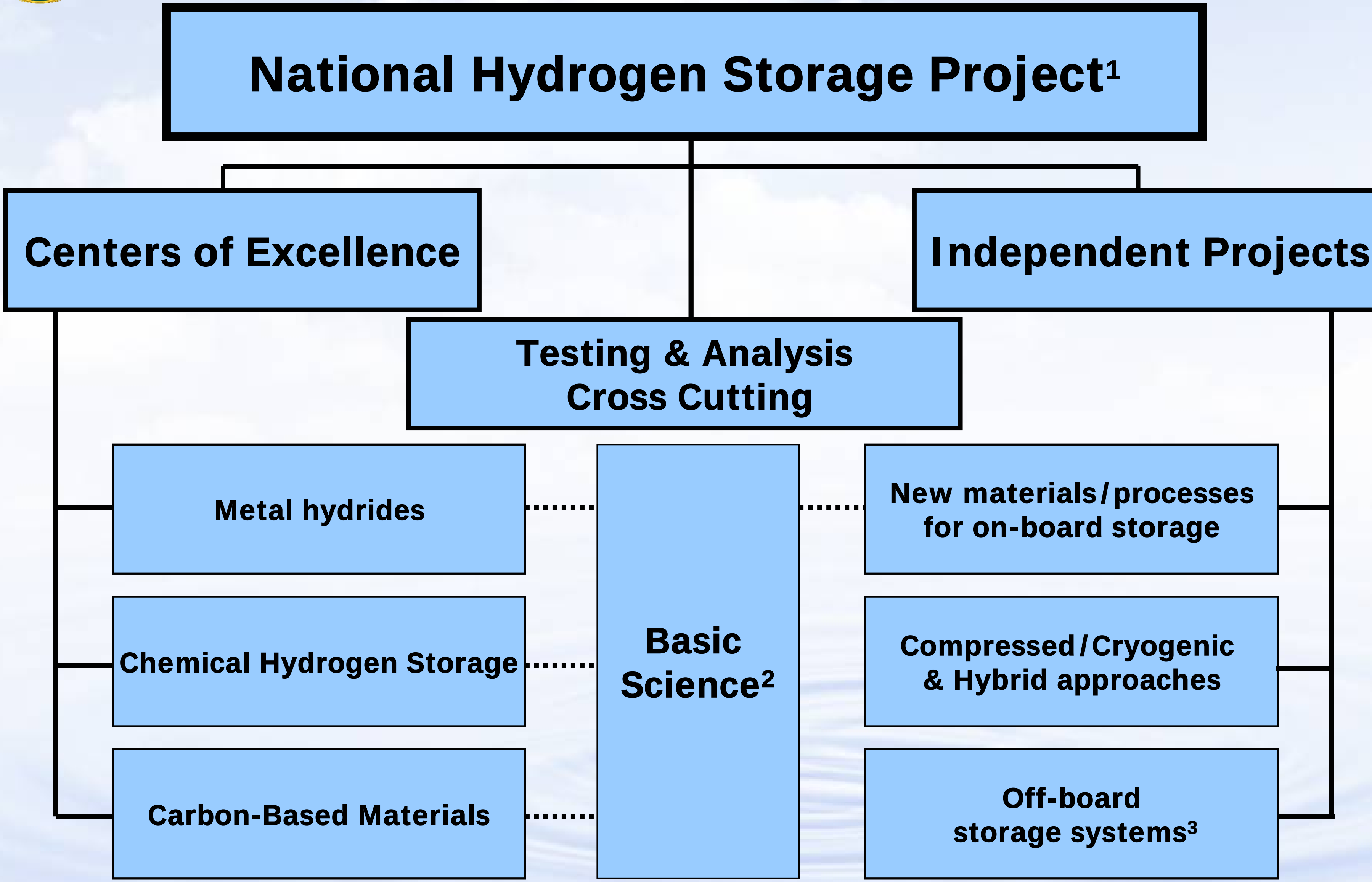




Intermetallic hydrides

For ΔH of ~ 30-40 kJ/mol, need to reject ~ 500 kW of heat when refueling!

Examples of Major R&D in the Field of Storage



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

Hydrogen Storage
“Grand Challenge” Partners

Centers of Excellence

Metal Hydride Center

National Laboratory:
Sandia-Livermore

Industrial partners:
General Electric
HRL Laboratories
Intematix Corp.

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

Federal Lab Partners:
Brookhaven
JPL
NIST
Oak Ridge
Savannah River

Carbon Materials Center

National Laboratory:
NREL

Industrial partners:
Air Products &
Chemicals

Universities:
CalTech
Duke
Penn State
Rice
Michigan
North Carolina
Pennsylvania

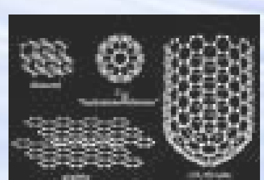
Federal Lab Partners:
Lawrence Livermore
NIST
Oak Ridge

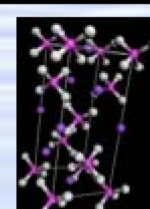
Chemical Hydrogen Center

National Laboratories:
Los Alamos
Pacific Northwest

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

Universities:
Northern Arizona
Penn State
Alabama
California-Davis
UCLA
Pennsylvania
Washington





Independent Projects

New Materials & Concepts
Alfred University
Carnegie Institute of Washington
Cleveland State University
Michigan Technological University
TOFTEC
UC-Berkeley
UC-Santa Barbara
University of Connecticut
University of Michigan
University of Missouri

High-Capacity Hydrides
UTRC
UOP
Savannah River NL

Carbon-based Materials
State University of New York
Gas Technology Institute
UPenn & Drexel Univ.

Chemical Hydrogen Storage
Air Products & Chemicals
RTI
Millennium Cell
Safe Hydrogen LLC

OffBoard, Tanks, Analysis & Testing
Gas Technology Institute
Lawrence Livermore
Quantum
Argonne Nat’l Lab & TIAX LLC
SwRI

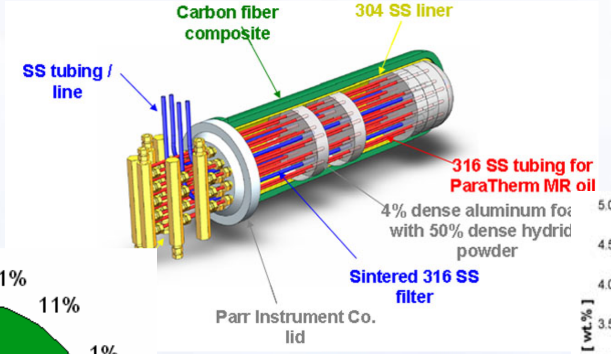
Recent Progress- Metal Hydrides

System Engineering:

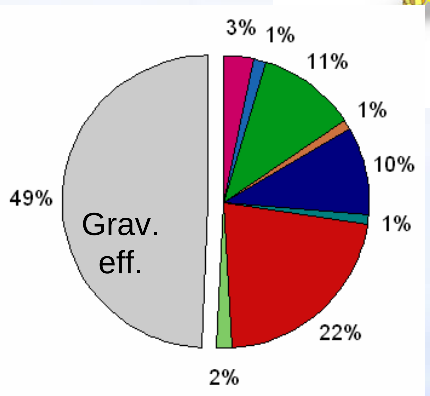
- 1-kg H_2 prototype ***(Anton, et al, UTRC)***
- ~50% is balance of plant

Materials Development:

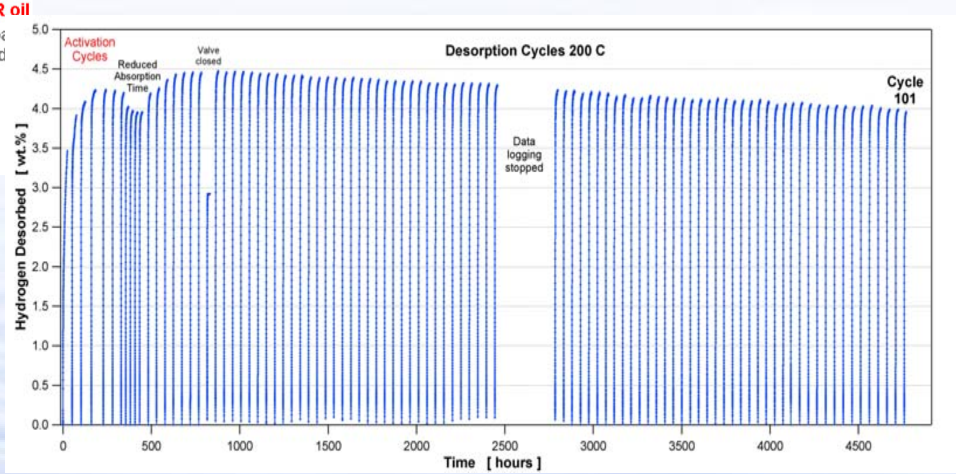
- Mg Li-amides > 5 wt% materials-based capacity ***(Luo, Wang, et al, SNL),***
- >100 cycles



UTRC



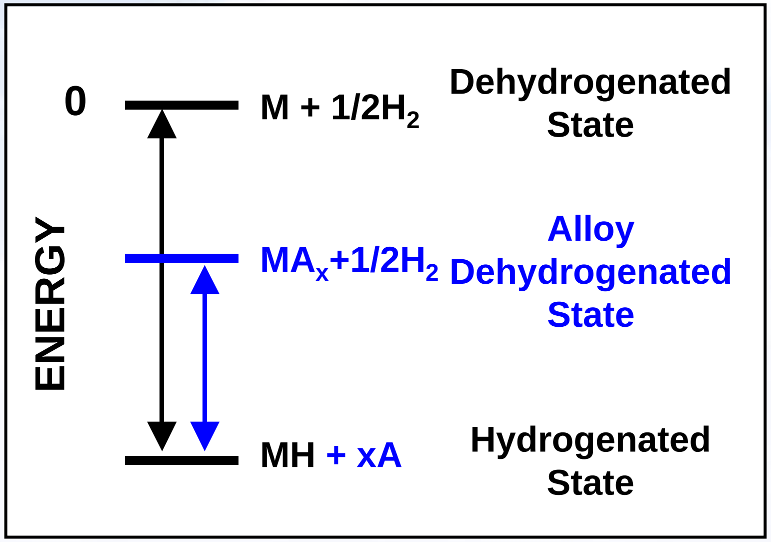
660 Wh / kg **530 Wh / L**

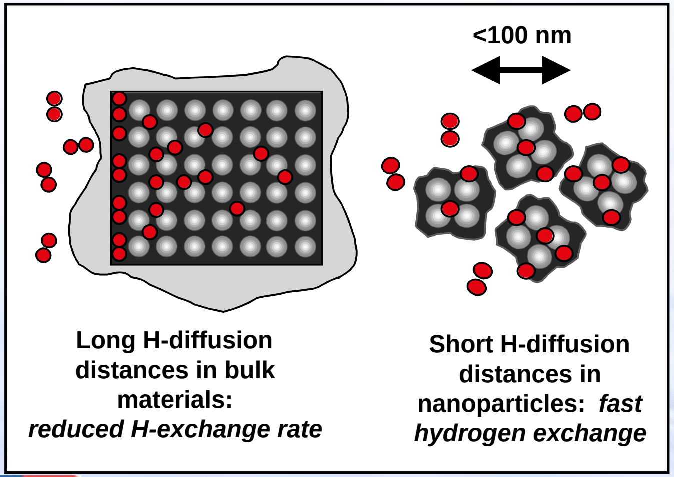


Sandia

Exciting Possibilities- Destabilized hydrides and nano-engineering

E.g., New system (11.4 wt. % and 0.095 kg/L) – $LiBH_4$ / MgH_2





Strategies:

- Alter Thermodynamics by Hydride Destabilization
- Enhance Kinetics by Nano-engineering

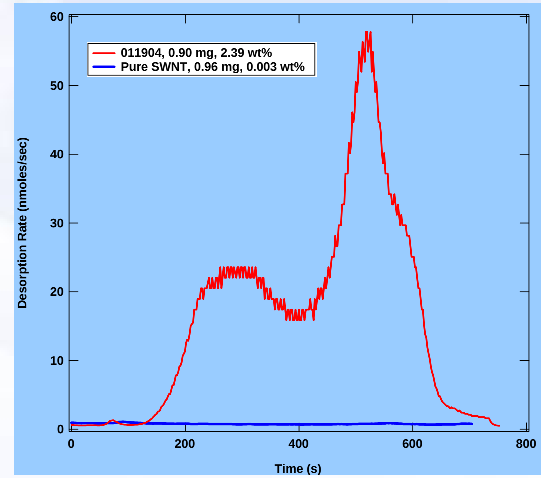
- Reversibility: 9 to 10 wt. %
- But T still high (~375°C); kinetics slow

J.J. Vajo, *et al.*, J. Phys. Chem. B, 108, 13977-13983 (2004).

J. Vajo, S. Skeith, and F. Mertens, J. Phys. Chem. B, 109, 3719-3722 (2005).

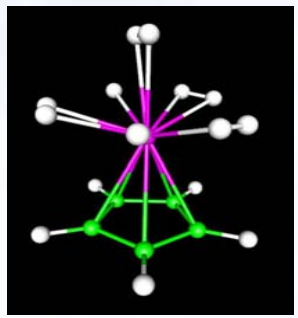
Recent Progress- Carbon and New Materials

Doped nanotubes ~2.5 - 3 wt.%

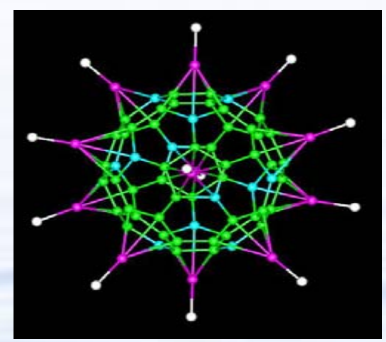


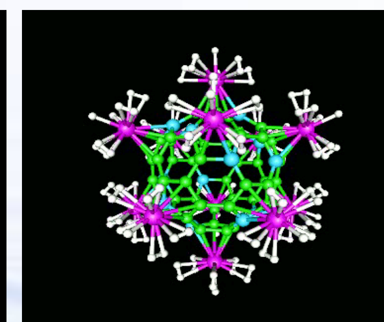
H_2 Desorption

- Binding energies calculated
- Theoretically predicted materials



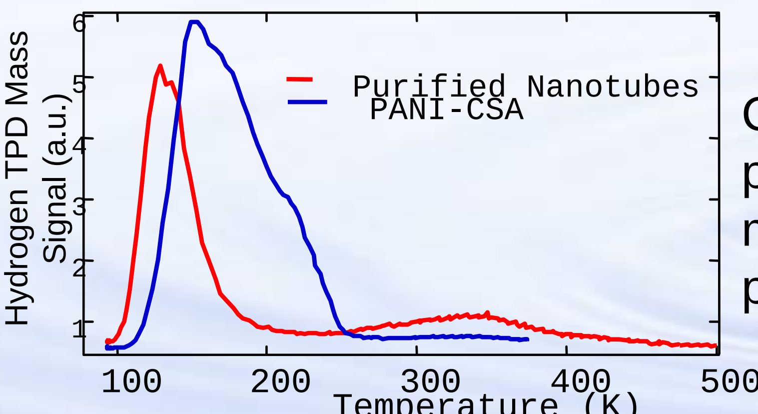
$Cp[ScH_2(H_2)_4]$





$$C_{48}B_{12}[ScH]_{12} \overset{60H_2}{\rightleftarrows} C_{48}B_{12}[ScH(H_2)_5]_{12}$$

Potential for 8.8 wt%

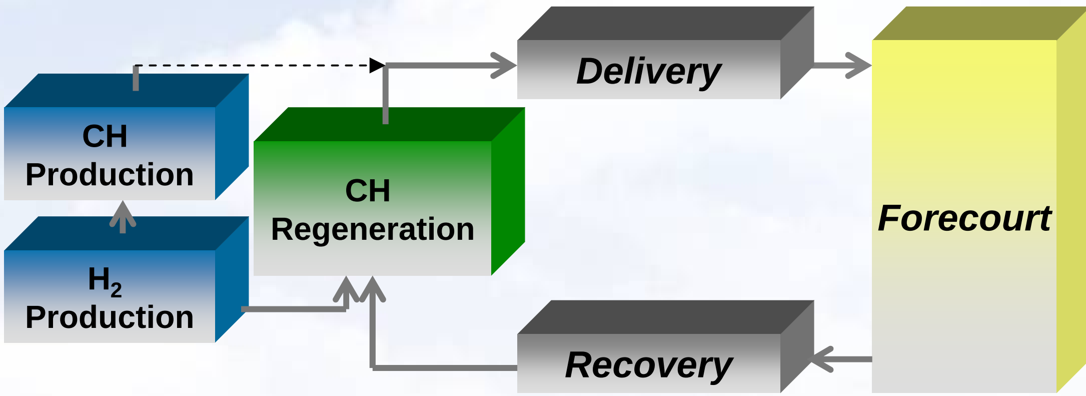


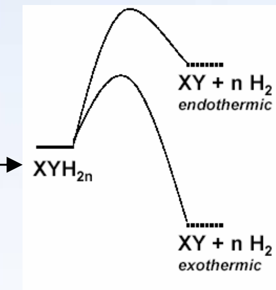
Conducting polymers may show promise

MacDiarmid, et al, U.Penn, Heben et al, NREL

Zhao, Dillon, Zhang, Heben, NREL

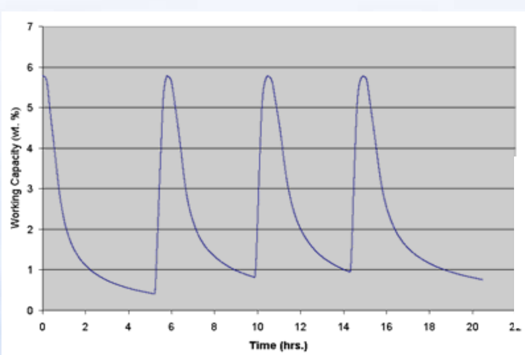
Recent Progress- Chemical Hydrogen Storage



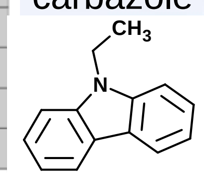


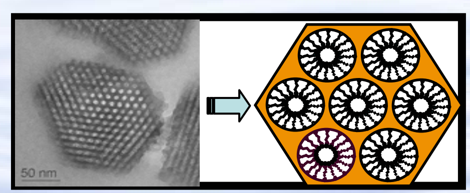
- Promising chemical hydrides with 5.5 to 7 wt% and 50-65 g/L materials-based H_2 storage capacity

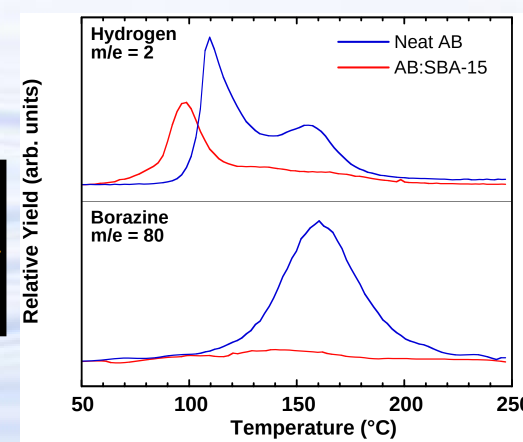
- Mesoporous scaffolds internally coated with ammonia borane show >6 wt% capacity, hydrogen release at < 80 C and reduced borazine formation



N-ethyl-carbazole







Cooper, Pez, et al, Air Products

Autrey, Gutowski, et al, PNNL

Key Message:

- Need ideas, new materials, catalysts, processes
- Need fundamental understanding, characterization tools, modeling, material properties
- Need applied materials development, optimization, system engineering, safety understanding/analysis
- Multidisciplinary skills critical

References and Contacts:

- **Steve Chalk**: DOE Hydrogen Program Manager
- **Sunita Satyapal**: Hydrogen Storage Team Leader, *sunita.satyapal@ee.doe.gov*
- **Pete Devlin:** Hydrogen Production Team Leader *peter.devlin@ee.doe.gov*

For Basic Science in Hydrogen/Fuel Cells: Harriet Kung, harriet.kung@science.doe.gov

www.hydrogen.gov or www.hydrogen.energy.gov

Examples of Funding Opportunities

- **Web sites: www.hydrogen.gov, www.hydrogen.energy.gov, www.eere.energy.gov/hydrogenandfuelcells**
- **SBIR/STTR opportunities**
  - SBIR/STTR opportunities with DOE solicited yearly
  - Solicitation released beginning of FY (e.g.,October); proposals due early calendar year (e.g., January)
  - ***http://sbir.er.doe.gov/sbir/ and www.zyn.com/sbir/***
- **Inventions & Innovations opportunities**
  - I&I opportunities with DOE solicited 1 to 2 times per year
  - Topics supporting program areas in renewable energy and energy efficiency solicited
  - ***www.eere.energy.gov/inventions***

- **International Partnership for the Hydrogen Economy (NOT for funding but for collaborations on existing projects)**
  - ***www.iphe.net***

Additional Slides

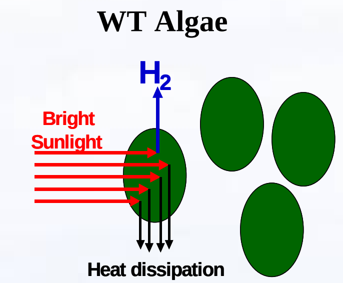
One example of long-term research: Photobiological H_2 Production

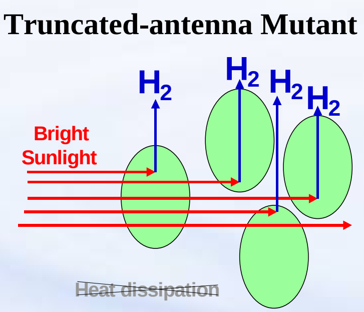
Issues Limiting Algal H_2 Photoproduction

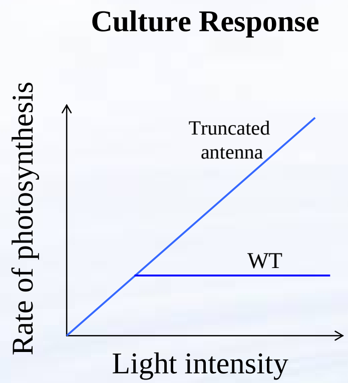
- Hydrogenase enzyme sensitive to O_2
- e^- transport from H_2O to enzyme down-regulated by proton gradient
- Large chlorophyll arrays can reduce solar efficiency

Potential Solutions

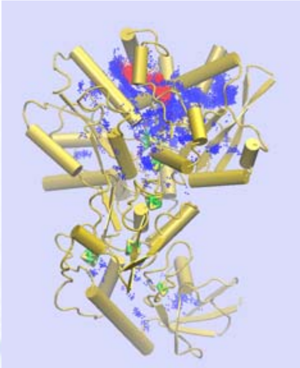
- Molecular-engineer enzyme to work in O_2 (e.g., Ghirardi, NREL)
- Create proton channel under H_2-producing conditions (e.g., Lee, ORNL)
- Truncate chlorophyll antenna size by insertional mutagenesis (eg,Melis, Berkeley)







H_2 and O_2 trajectory simulations



Cover fig., Biochem. Soc. Trans., vol. 33, 2005

Ref: Ghirardi et al., Biochem. Soc. Trans., 33, 70 (2004)
Cohen et al., Biochem. Soc. Trans., 33, 80 (2004)
Lee and Greenbaum, Appl. Biochem. Bioeng. 105-108, 303-313 (2003)
Polle et al., Planta 217, 49-59 (2003)

Hydrogen Production and Delivery

Distributed Reforming Using Natural Gas and Renewable Liquids

- Develop intensified, lower capital cost, more efficient NG reformer technology
- Develop improved catalysts and technology for renewable liquids reforming (e.g. ethanol, sugar alcohols, Bio-oil)
- Lead Partners: GE, APCi, H2Gen, Virent, Ohio State Research

Electrolysis

- Develop low cost and high efficiency materials and system designs
- Integrated compression
- Integrated wind power/electrolysis systems
- Lead partners: Teledyne, Giner, Materials and Systems Research

Biomass Gasification

- Developed integrated gasification, reforming, shift and separations technology to reduce capital and improve efficiency.
- Lead Partners: GTI, UTRC, SRI, Ceramatec, Arizona State U.

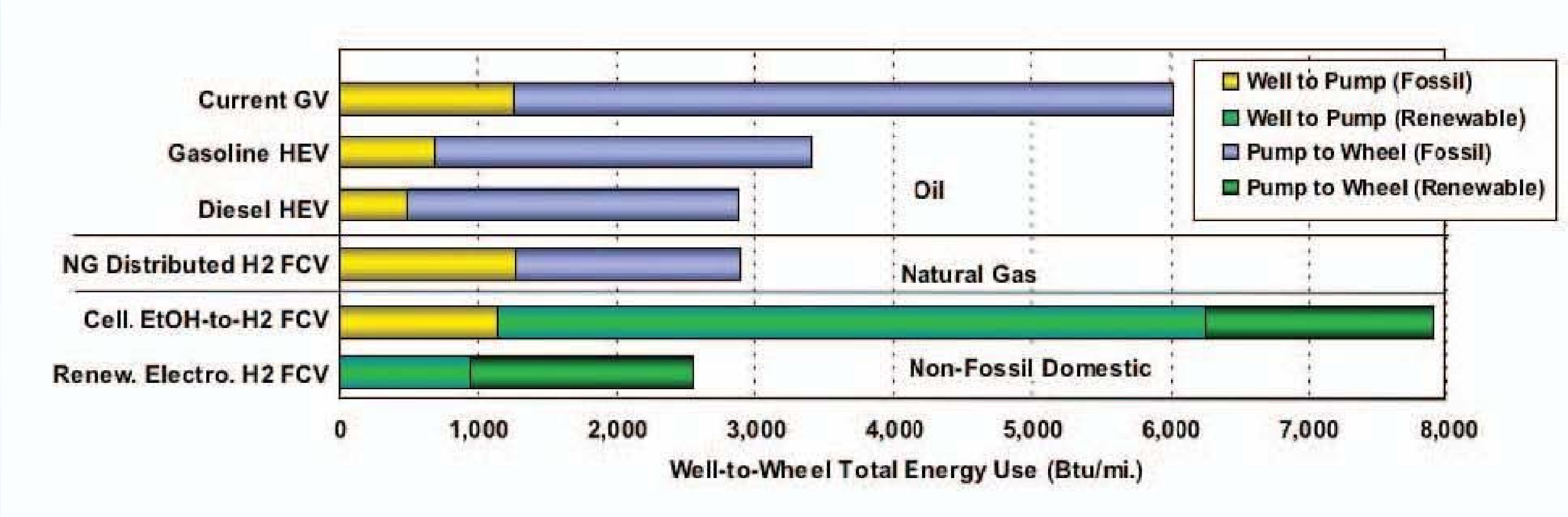
Solar/Photolytic

- Develop durable materials for direct photo-electrochemical solid state water splitting using sunlight
  - Lead Partners: Univ. of California, MV Systems, U, of Hawaii, Midwest Optoelectronics
- Research microorganisms that split water using sunlight
  - Lead Partners: Univ. of California, Craig Venter Inst.
- Research thermochemical cycles that split water using heat (600 – 2100 C) from solar concentrators
- Lead Partners: UNLV, U. of Colorado, SAIC

Delivery

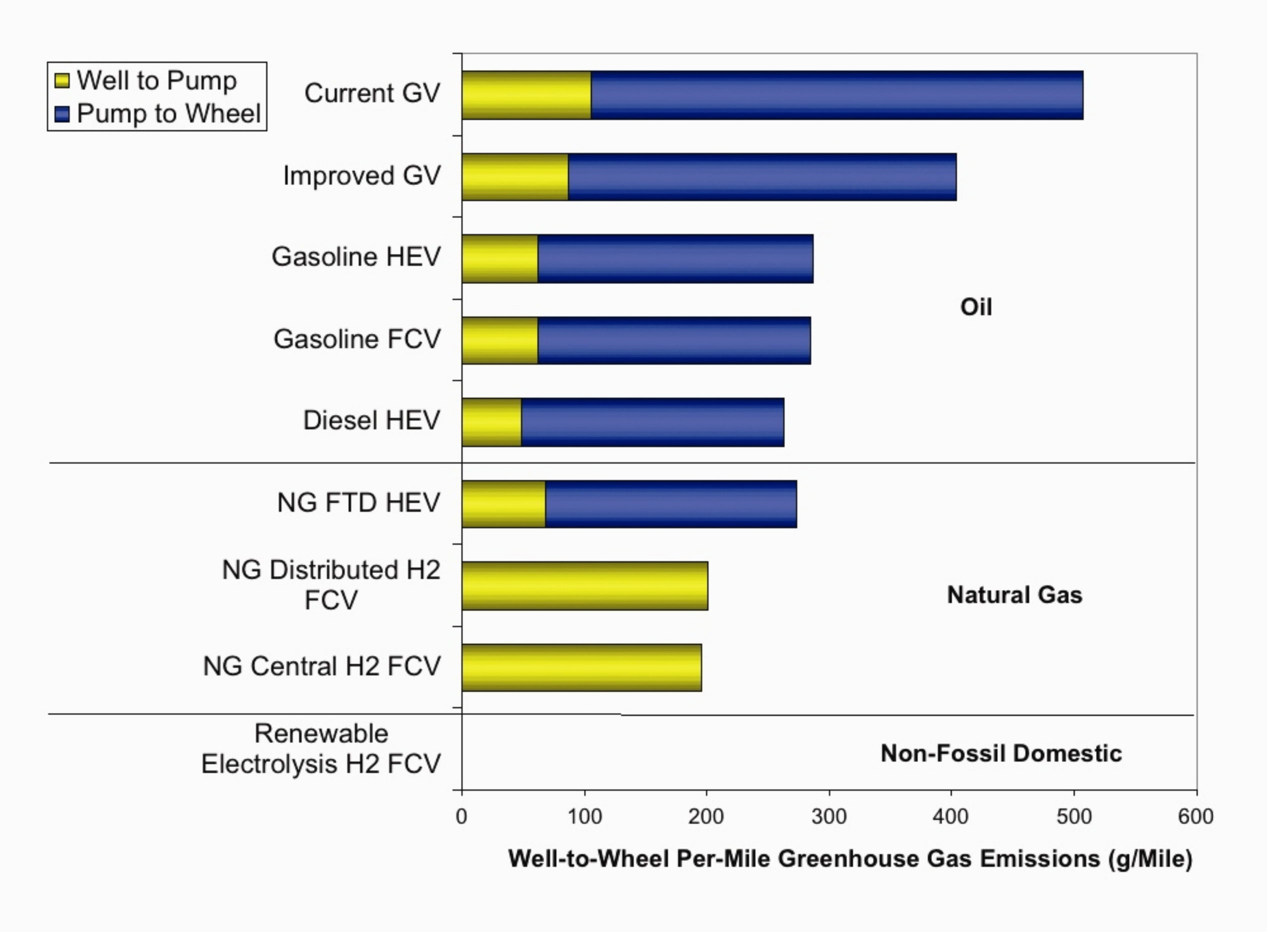
- Infrastructure options and trade-offs analysis
- Develop lower cost and robust technology for pipelines, compression, off-board storage, carriers, and liquefaction
- Lead Partners: Nexant, Gas Equipment Engineering Corp, NCRC Corp., APCI, SECAT, U. of Illinois

Comparative Vehicle Technologies: Well-to-Wheels Energy Use



Even with fuel production factored in, a fuel cell vehicle powered by hydrogen from natural gas offers improved efficiency over conventional gasoline-hybrid options.

Comparative Vehicle Technologies: Well-to-Wheels Greenhouse Gas Emissions



Hydrogen fuel cell vehicles can offer greenhouse gas benefits, even in the case of natural gas without carbon sequestration