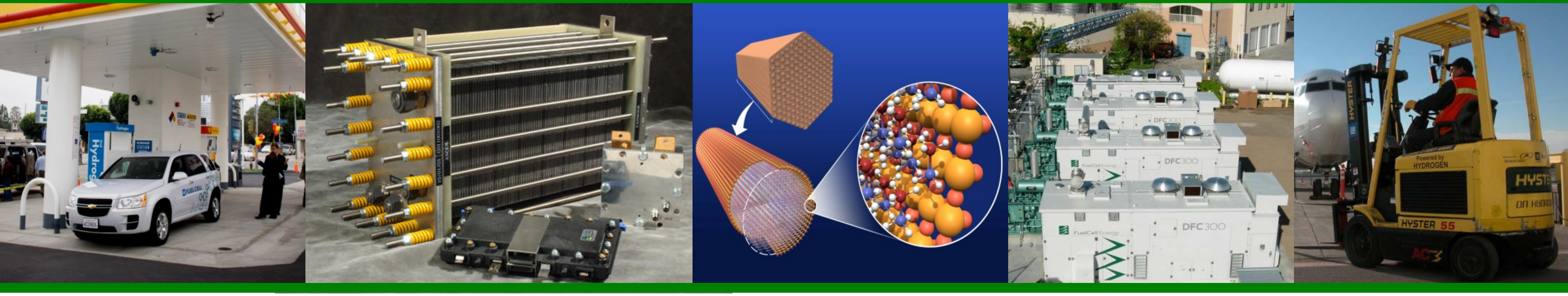
U.S. DEPARTMENT OF ENERGY



Hydrogen Storage

Ned T. Stetson

2012 Annual Merit Review and Peer Evaluation Meeting

May 14, 2012

Goal and Objectives

Goal: ***Develop & demonstrate viable H_2 storage technologies for transportation, stationary, material handling, and portable power applications***

Develop storage systems that meets ***all*** DOE system targets simultaneously.

- **System Engineering / Systems Analysis**
  - Demonstrate the technologies required to achieve the 2017 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
  - Roll-out performance and cost targets for early market applications
  - Initiate projects through SBIR on early market applications
- **R&D on materials for breakthrough storage technologies**
  - Increased focus on carbon fiber to reduce the cost of physical storage systems
  - Continue new hydrogen storage material discovery R&D for advanced storage systems
  - Strengthen coordination between basic & applied research within DOE and across agencies

Challenges: Light-duty Vehicles

To achieve significant market penetration of FCEVs, H_2 storage systems must enable a driving range of greater than 300 miles across all vehicle platforms—while meeting vehicular packaging, cost and performance requirements.

Near-term Option

Compressed gas storage offers a near-term option for initial vehicle commercialization* and early markets

- ***Cost*** **of composite tank is challenging**
- **> 75% of the cost is projected to be due to the carbon fiber layer with 50% of the carbon fiber cost due to the precursor**
- **Other applications are being commercialized now where H_2 storage is a barrier**

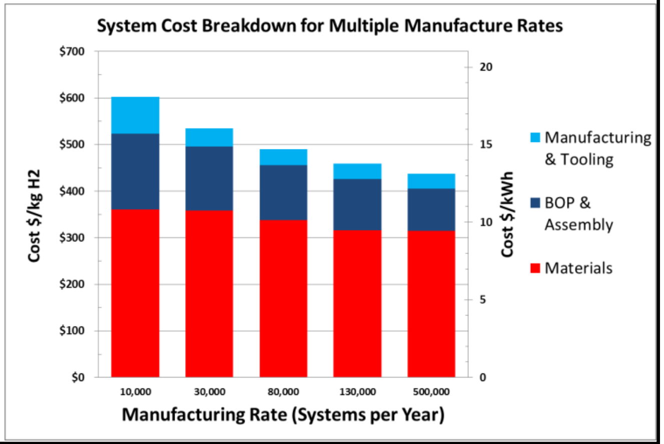
Longer-term Options

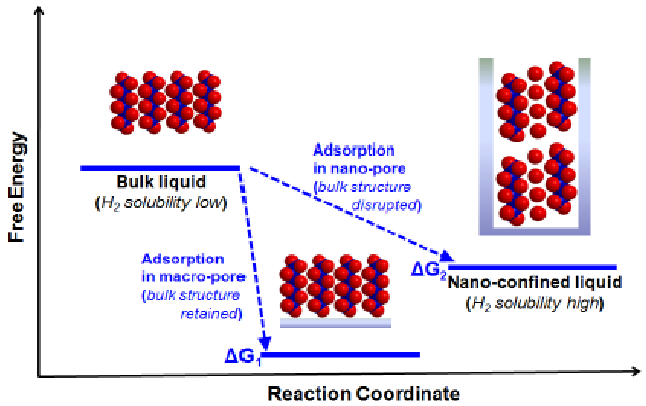
Materials-based solutions targeted to meet all on-board storage targets simultaneously

- **Improving gravimetric and volumetric capacities**
- **Having sufficient kinetics within appropriate temperature and pressure ranges**
- **Lowering cost of overall engineered systems**

Cost is in the CF Matrix!

Type IV 700 bar





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* A driving range of more than 400 miles was independently validated for a Toyota Advanced FCEV with 700-bar Type IV composite cylinders: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/toyota_fchv-adv_range_verification.pdf.

Challenges: Preliminary Targets for Material Handling Equipment

Hydrogen fuel cells are finding acceptance in material handling applications (e.g., forklifts)—but high-pressure H_2 infrastructure limits deployment.

Storage Parameter	Units	2015	2020
System Gravimetric Capacity:	*kWh/kg*	NA	NA
Usable, specific-energy from H_2 (net useful energy/max system mass)	*(kg H_2/kg system)*	NA	NA
System Volumetric Capacity:	*kWh/L*	0.7	1.3
Usable energy density from H_2 (net useful energy/max system volume)	*(kg H_2/L system)*	(0.02)	(0.04)
Storage System Cost *(based on LHV of delivered H_2):*	*\$/kWh* *(\$/kg H_2)*	20 667	15 500
Durability/Operability:			
· *Operational cycle life (1/4 tank to full)*	*Cycles*	5000 (5 yr)	10000 (10 yr)
· *Min delivery pressure from storage system;*	*bar (abs)*	3	3
Charging / Discharging Rates:	H_2 capacity	2 kg	
· *System fill time*	*min* *(kg H_2/min)*	5 0.4	3 0.7
· *Minimum full flow rate*	*(g/s)/kW*	0.02	0.02
Shock and Vibration	g	3	15

Preliminary H_2 storage targets developed for material handling equipment; RFI issued to gather input from stakeholders on appropriateness of targets.

Challenges: Targets for Portable Power

Portable hydrogen fuel cell appliances are coming to market—hydrogen storage is essential for their successful commercialization.

Storage Parameter	Units	2015	2020
System Gravimetric Capacity:	*kWh/kg*	0.3	1.0
Usable, specific-energy from H_2 (net useful energy/max system mass)	*(kg H_2/kg system)*	(0.01)	(0.03)
System Volumetric Capacity:	*kWh/L*	1.0	1.7
Usable energy density from H_2 (net useful energy/max system volume)	*(kg H_2/L system)*	(0.03)	(0.05)
Storage System Cost *(based on LHV of delivered H_2):*	*$/Wh* *($/g H_2)*	2.0 67	1.0 33
Durability/Operability:		Single use / Rechargeable	
· *Operational cycle life (1/4 tank to full)*	*Cycles*	NA / 25	NA / 100
· *Min delivery pressure from storage system;*	*bar (abs)*	1.5	1.5
· *Max delivery pressure from storage system*	*bar (abs)*	3	3
Environmental Health & Safety: · *Permeation & leakage* · *Toxicity* · *Safety*		Meets ISO-16111:2008; IEC 62282; or other applicable standards	

Preliminary H_2 storage targets developed for Portable Power; RFI issued to gather input from stakeholders on appropriateness of targets.

Current Status

Analyses show 2017 onboard vehicle gravimetric and volumetric targets are within reach of some hydrogen storage technologies!

Storage Targets	Gravimetric kWh/kg (kg H_2/kg system)	Volumetric kWh/L (kg H_2/L system)	Costs* \$/kWh net (\$/kg H_2)
2010	1.5 (0.045)	0.9 (0.028)	TBD (TBD)
2017	1.8 (0.055)	1.3 (0.040)	TBD (TBD)
Ultimate	2.5 (0.075)	2.3 (0.070)	TBD (TBD)

Current Status	Gravimetric (kWh/kg sys)	Volumetric (kWh/L sys)	Costs (\$/kWh)
700 bar compressed (Type IV)[a]	1.7	0.9	18.9
350 bar compressed (Type IV)[a]	1.8	0.6	15.5
Cryo-compressed (276 bar)[a]	1.9	1.4	12.0
Metal Hydride ($NaAlH_4$)[b]	0.4	0.4	11.3
Sorbent (MOF-5, 200 bar)[b]	1.7	0.9	18.0
Off-board regenerable (AB)[b]	1.4	1.3	NA

* Cost targets are being finalized and are expected to be released soon.

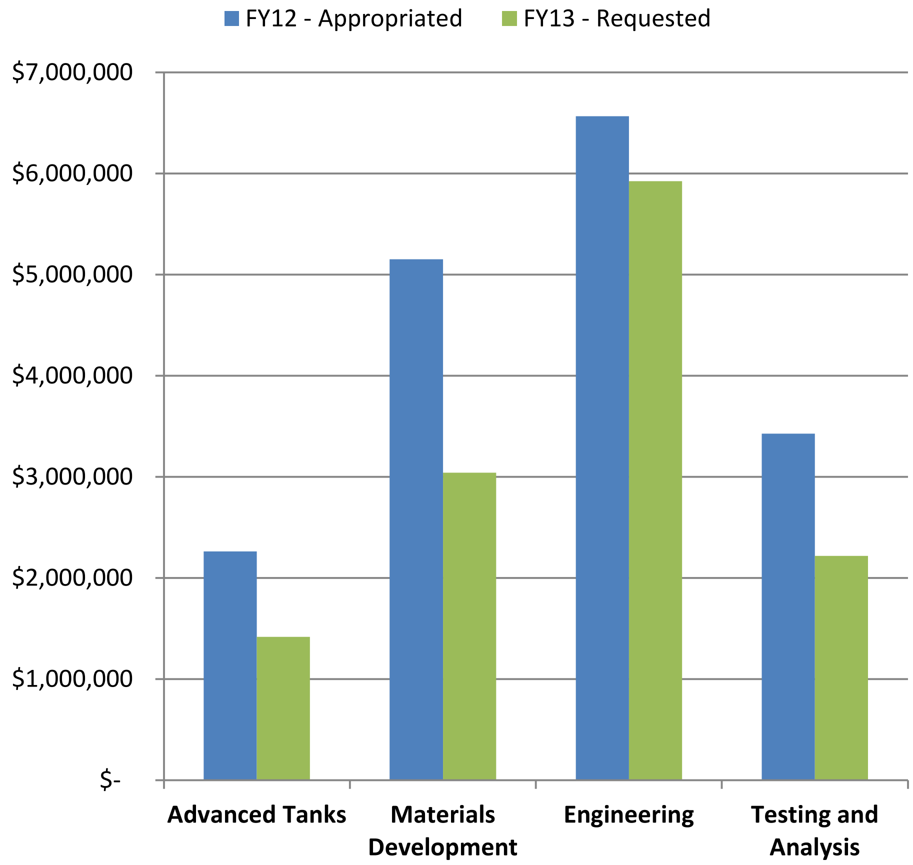
[a] based on TIAX/ANL projections, [b] based on Hydrogen Storage Engineering Center of Excellence projections

Hydrogen Storage Budget

U.S. DEPARTMENT OF ENERGY

FY 2013 Request = $13M

FY 2012 Appropriation = $17.4M



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 2012 & 2013 and improve coordination with National Science Foundation, ARPA-e, and Energy Frontier Research Centers activities
- Focus on cost reduction for high pressure tanks
- Increased analysis efforts for low to high production volumes
- Increased emphasis on early market storage applications

2012 Progress: Output from the Materials CoEs

U.S. DEPARTMENT OF ENERGY

Getting the word out on the progress made in developing and understanding hydrogen storage material properties!

SANDIA REPORT
SAND2012-0786
Unlimited Release
Printed February 2012

Final Report for the DOE Metal Hydride Center of Excellence

Lennie Klebanoff
Director, Metal Hydride Center of Excellence

Jay Keller
Deputy Director, Metal Hydride Center of Excellence

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Approved for public release; further dissemination unlimited.

Sandia National Laboratories

Final Report for the DOE Chemical Hydrogen Storage Center of Excellence

Kevin C. Ott

Final reports and executive summaries from the three Hydrogen Storage Materials CoEs available through the DOE website:

http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage

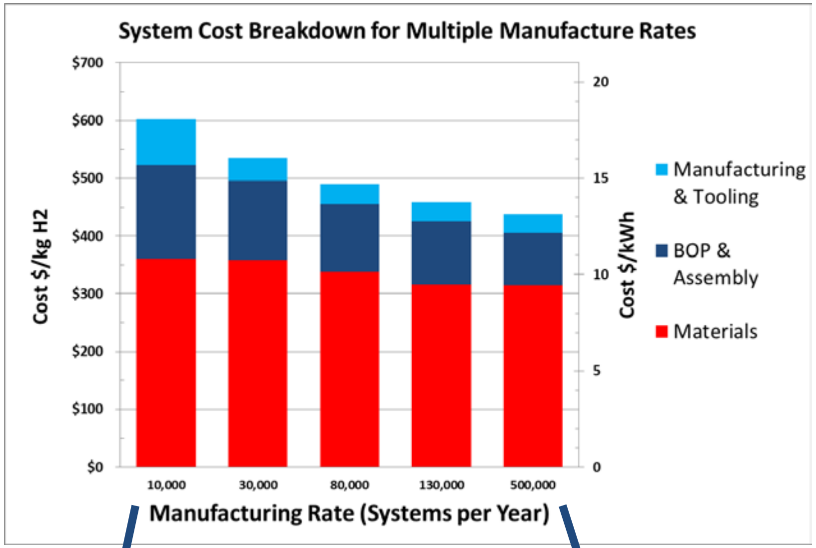
Publicly available, searchable database on Hydrogen Storage Materials Properties launched: http://hydrogenmaterialssearch.govtools.us/

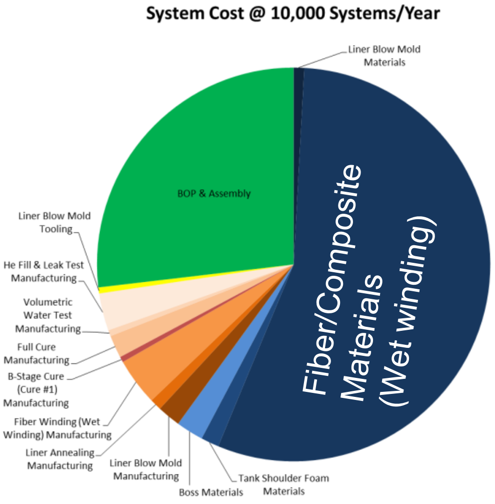
Still looking to populate it with more data!

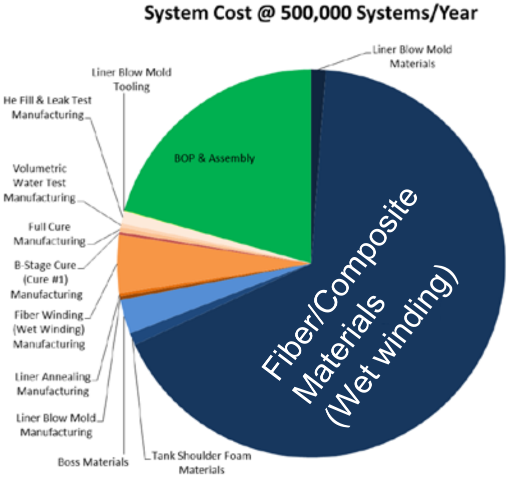
Hydrogen Storage Materials Database

Current Status: *Cost Analysis*

Tank costs come down with volume manufacture, but they remain too high! Carbon fiber composite costs dominate even at low-volume manufacture.

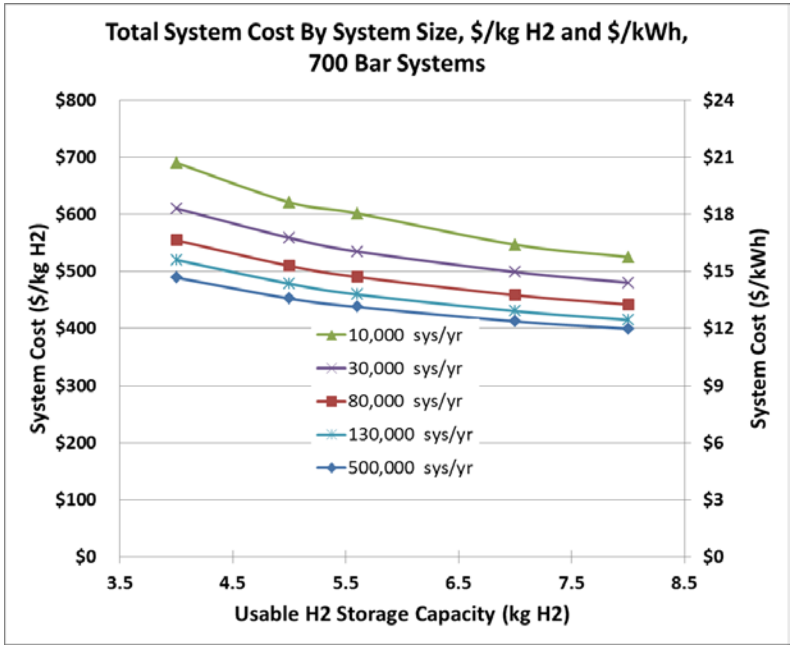

System Cost Breakdown for Multiple Manufacture Rates


System Cost @ 10,000 Systems/Year


System Cost @ 500,000 Systems/Year

***Preliminary** analyses show "wet winding" manufacture is lower cost than using "Prepreg" (precombined fiber and resin).*

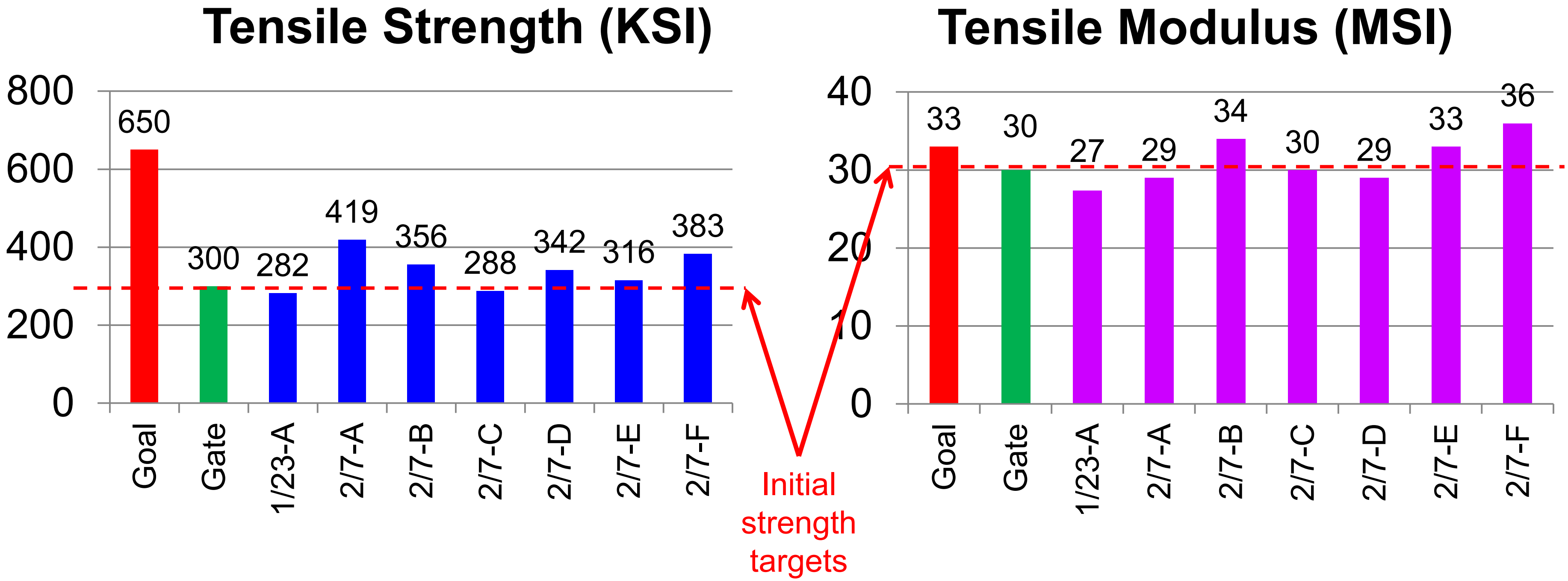
Costs ~ linear with H_2 storage capacity


Total System Cost By System Size, $/kg H2 and $/kWh, 700 Bar Systems

Strategic Analysis, Inc.

2012 Progress: Reducing CF precursor cost

Low-cost PAN precursors offer opportunity to reduce CF costs by up to 30%.*



Initial batch of fiber from first PAN/MA formulation converted to CF:

First trial results: 282 KSI, 27.4 MSI (Processed 1/23/2012)
Second Trial: *6 various conditions* (Processed 2/07/2012)

Initial trial conversions of first batch of textile PAN/MA fibers look very promising–initial strength targets met!

* Kline & Company Report 2007

2012 Progress: *New Advanced Tank Project*

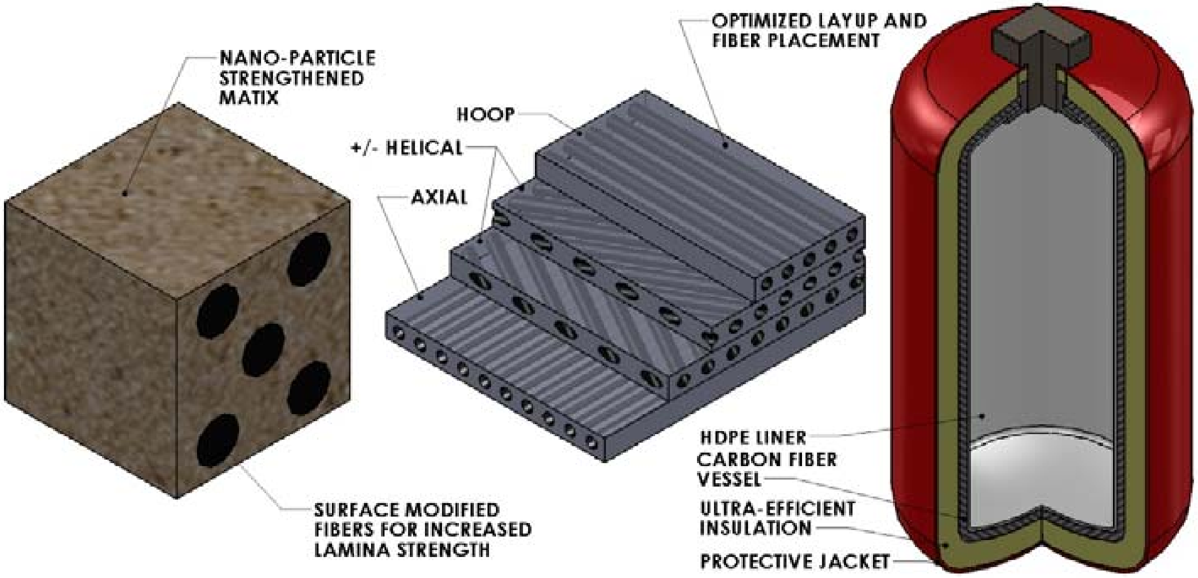
Synergistically enhanced materials and design parameters for reducing the cost of hydrogen storage tanks

Project Lead: **Pacific Northwest National Laboratory** (PI: Kevin Simmons)

Partners: Ford Motor Company, Lincoln Composites, Toray Carbon Fibers America, Inc. and AOC Inc.

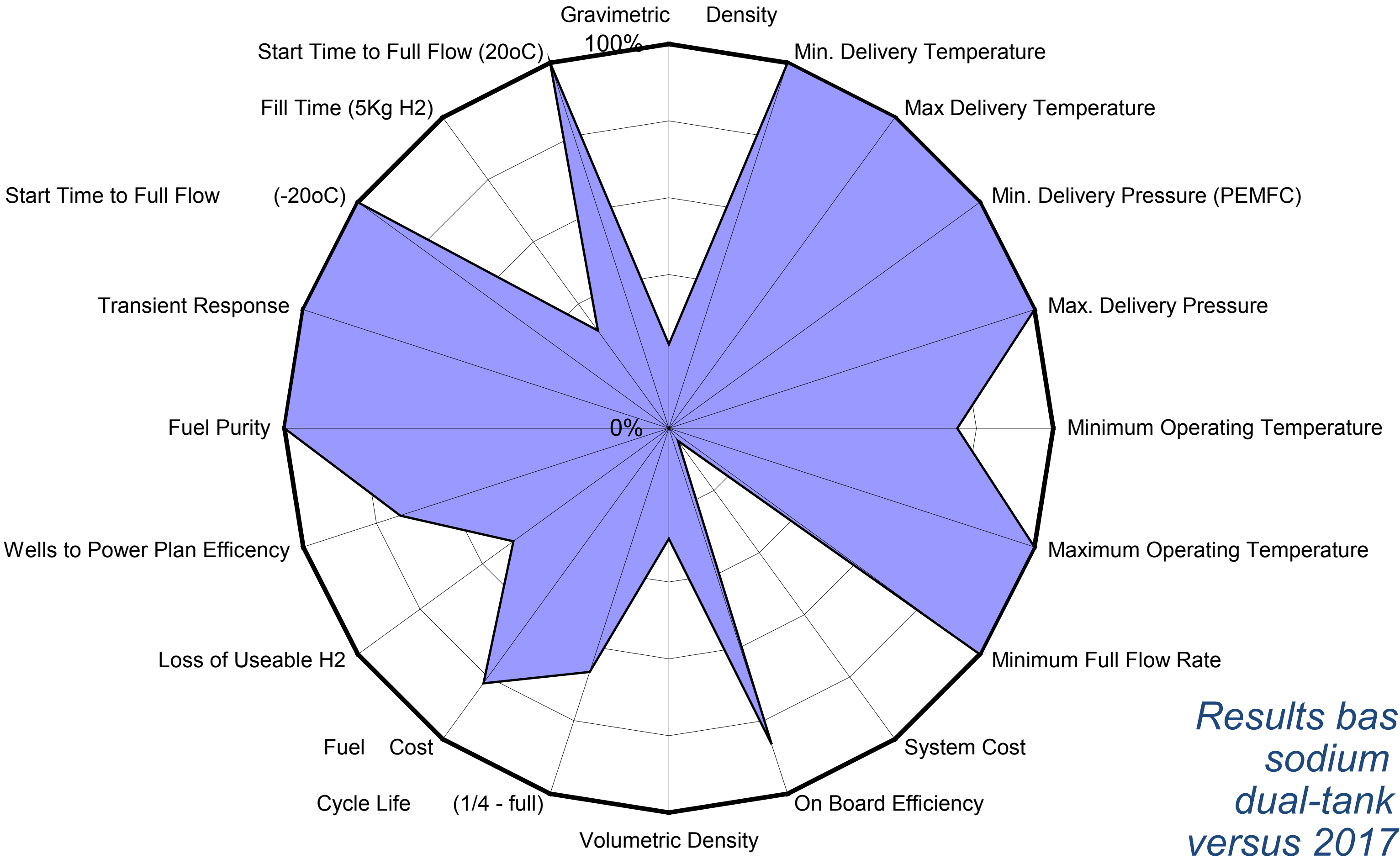
Coordinated approach for compressed H_2 tank cost-reduction focuses on:

- Improved carbon fiber composite materials; design and manufacture of hydrogen storage tanks
- Investigates use of "cold" hydrogen, including impact on the infrastructure
- Targets cost reduction by more than 1/3 compared to current projections



2012 Progress: HSECoE – Status of Metal Hydride Systems

No metal hydride material currently exists that will allow a complete system to meet all key DOE system performance targets for onboard vehicle applications.



Results based on a sodium alanate dual-tank system versus 2017 targets

No-Go decision made for metal hydride system within the HSECoE; this does not preclude further metal hydride materials development.

2012 Progress: Predicting Metal Hydride Requirements — Enthalpy Such That Only Waste Heat is Used

Attributes

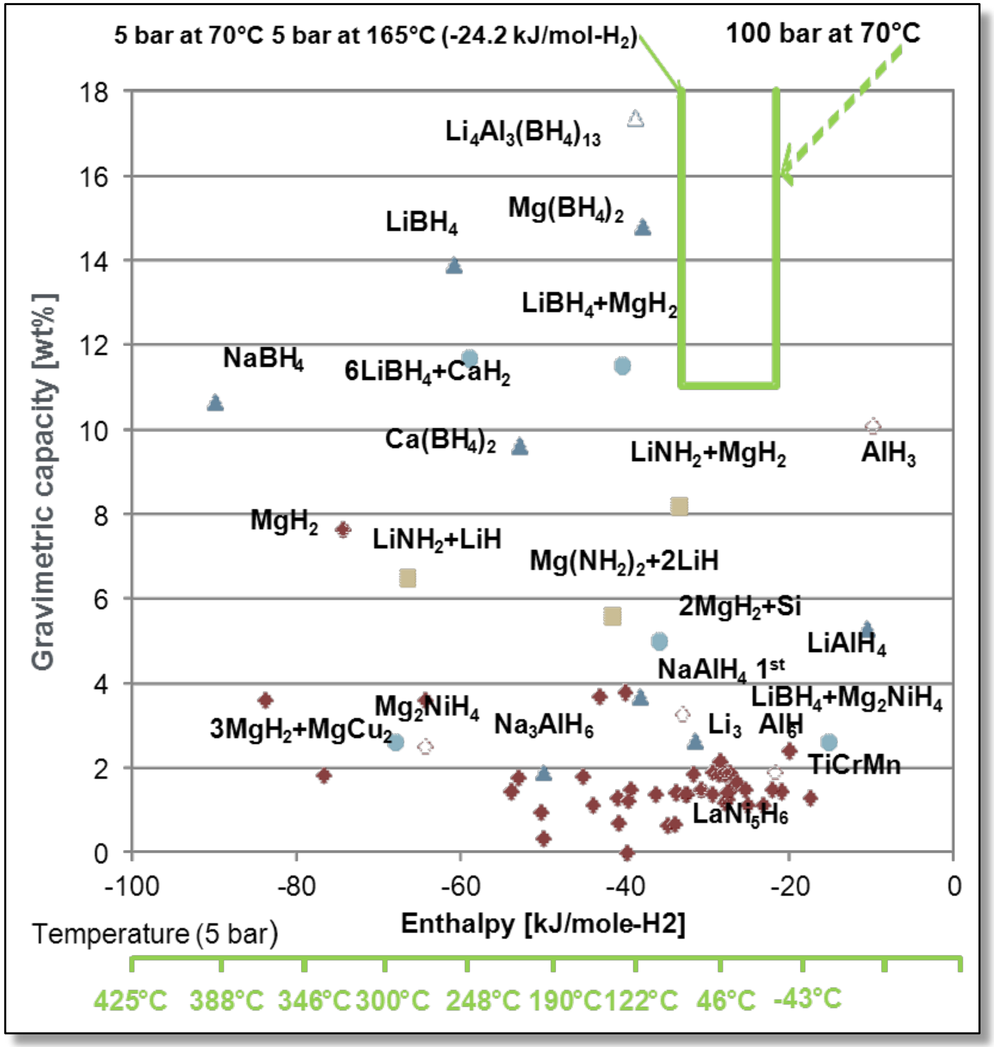
- Very simple system.
- Fuel cell waste heat stream used
- No separate buffer tank: use H_2 in pores.

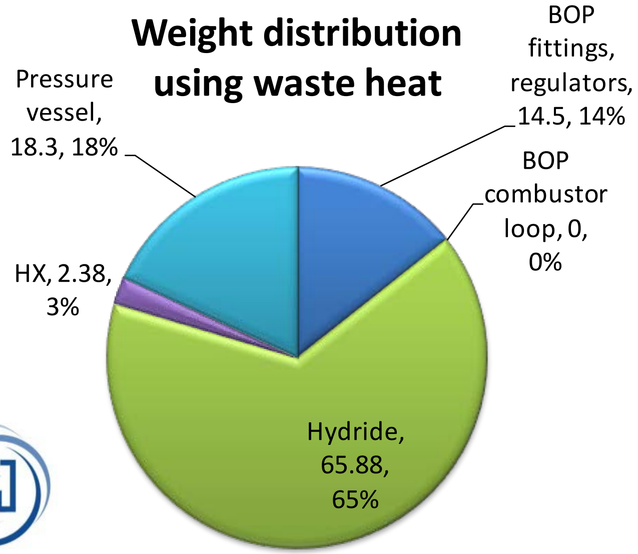
Media Characteristics

- $\Delta H = 27$ kJ/mol-H_2 ($T_{5\ bar} = 20.7\ ^oC$)
- 11 wt.% material capacity

Results

- ***Satisfies all targets.***
- On-board efficiency: ~100%
- System: 101 kg, 124 liters

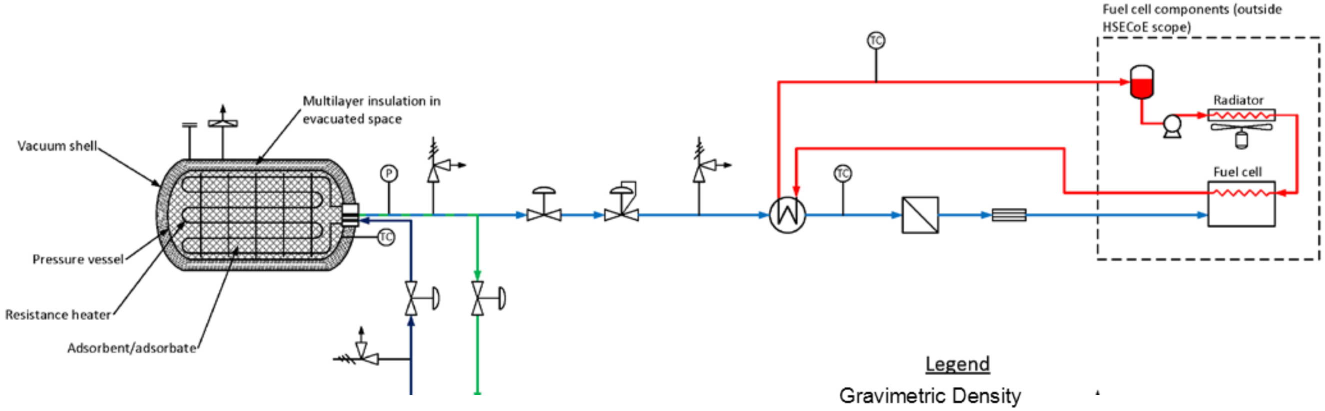


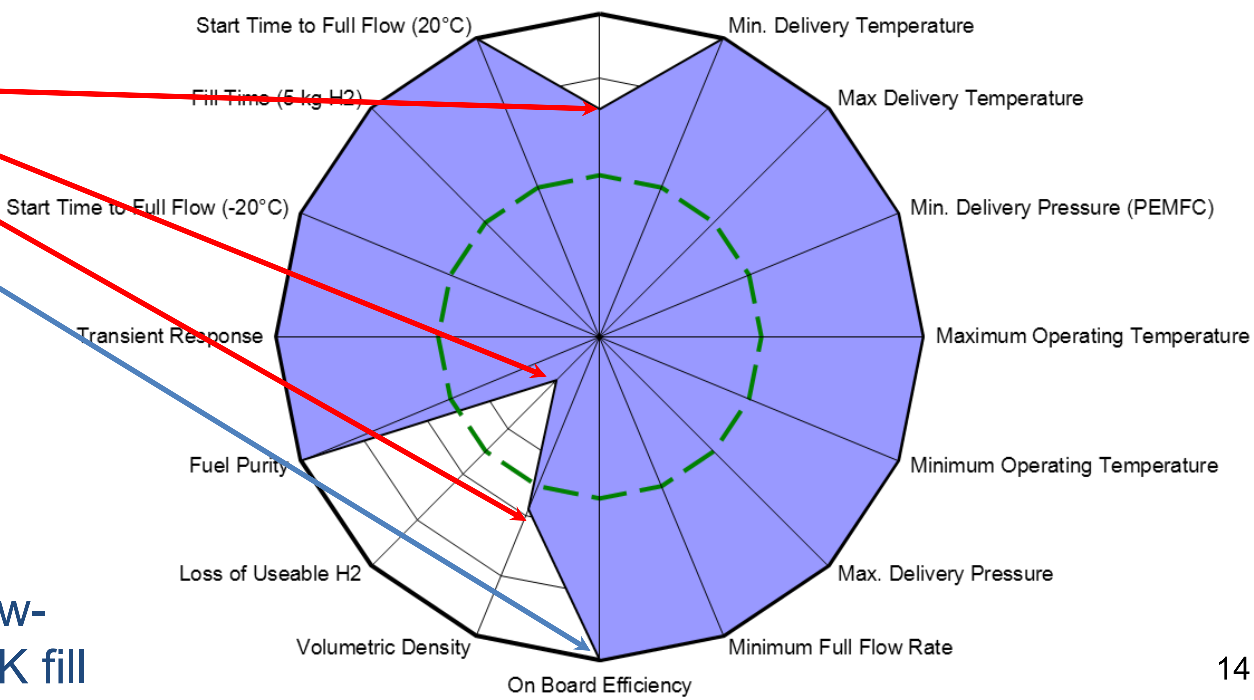


Material property requirements can be determined to focus material discovery efforts

2012 Progress: HSECoE – Cryo-sorbent Systems

Current cryo-sorbent system designs are projected to meet most DOE 2017 performance targets for onboard vehicle applications.



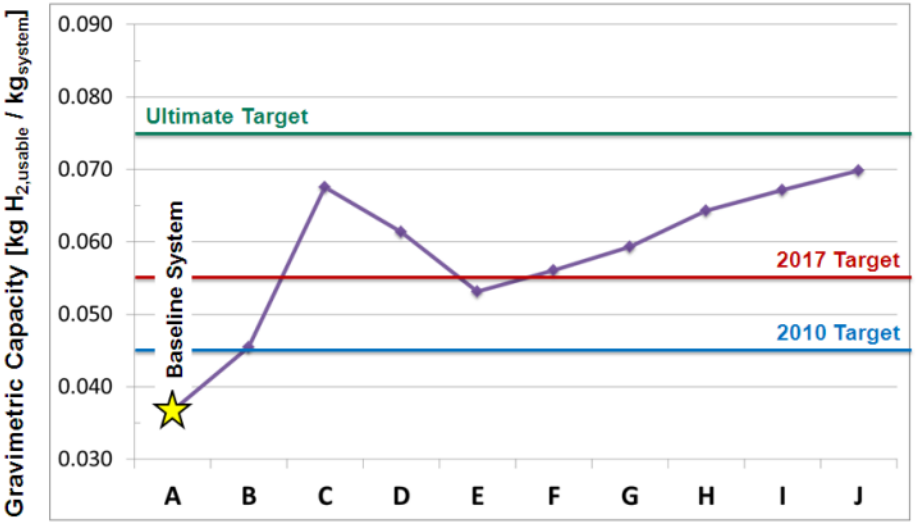


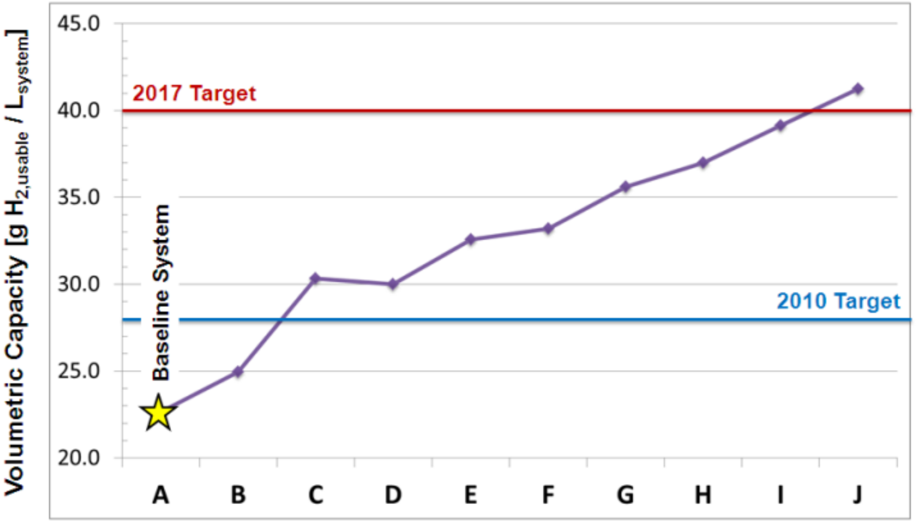
1. Gravimetric Density
2. Loss of Usable H_2
3. Volumetric Density
4. On-Board Efficiency
5. System Cost

AX-21, 200 bar, flow-through design, 80K fill

2012 Progress: HSECoE – Sorbent System Improvement Pathways

Combined system and material improvements show potential path to exceed 2017 onboard performance targets.





Step	Description
A	Phase 1 Baseline – Activated Carbon in a Composite Tank; Flow-Through Cooling with a Resistance Heater; Full Conditions of 80 K, 200 bar
B	Change Material to Powdered MOF-5
C	Change Full Tank Conditions to 40 K, 60 bar
D	Change Tank to Type I Aluminum (lower cost)
E	Change to Compacted MOF-5 (0.32 g/cc)
F	Increase Compacted MOF-5 thermal conductivity by an order of magnitude
G	Change from Flow-Through Cooling with a Resistance Heater to the M.A.T.I.
H	Reduce mass and volume of BOP components by 25%
I	Improve material capacity by 10%
J	Improve material capacity by 20%

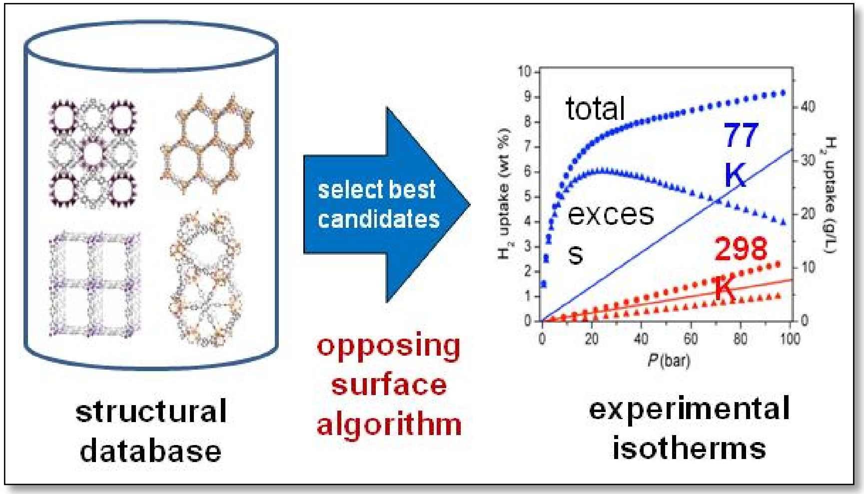
2012 Progress: *Two New Projects – Sorbents*

Hydrogen storage in engineered MOFs and nano-confined liquids optimized for onboard hydrogen storage applications

Lawrence Berkeley National Laboratory (PI: Jeffery Long)

Partners: NIST and GM

A theory-guided approach to synthesize novel materials with high hydrogen adsorption capacities



structural database

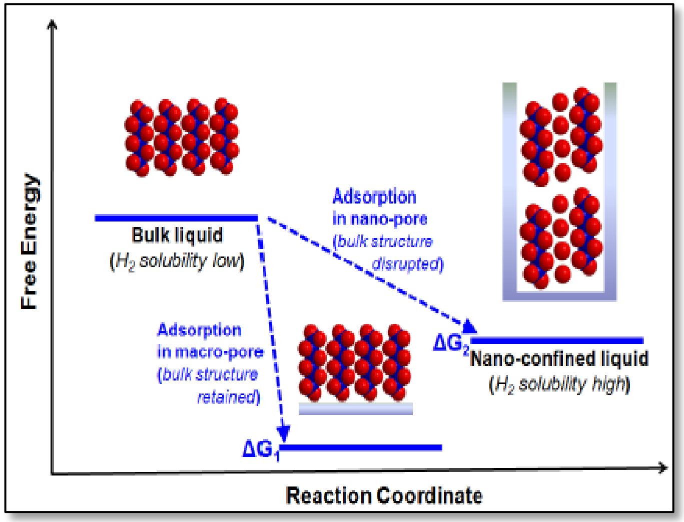
opposing surface algorithm

experimental isotherms

HRL Laboratories, LLC

(PI: John Vajo)

Investigates engineered liquids to efficiently absorb and release hydrogen gas



2012 Progress: *Spillover Taskforce Update*

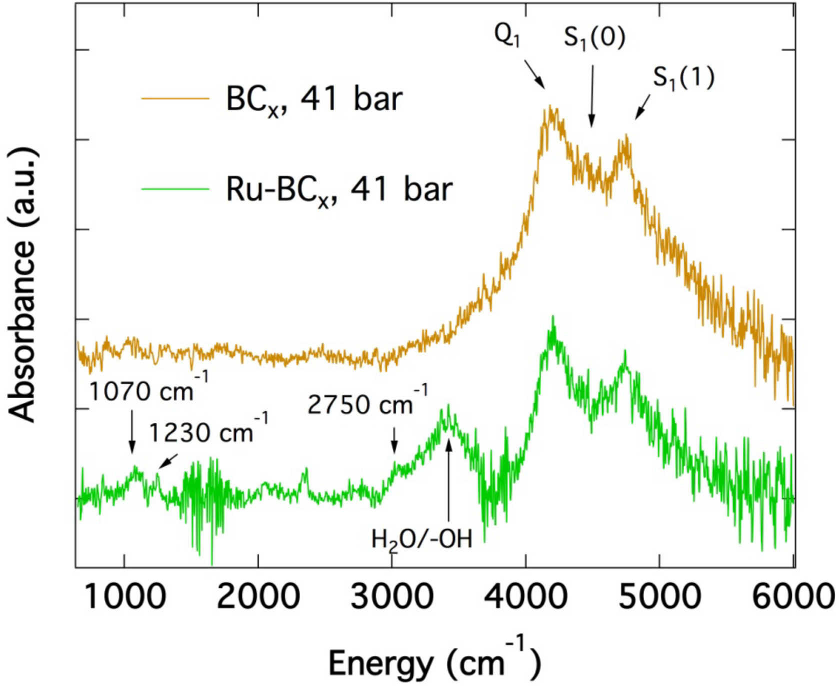
U.S. DEPARTMENT OF ENERGY

International taskforce confirms excess adsorption at room temperature can be increased by spillover effect.

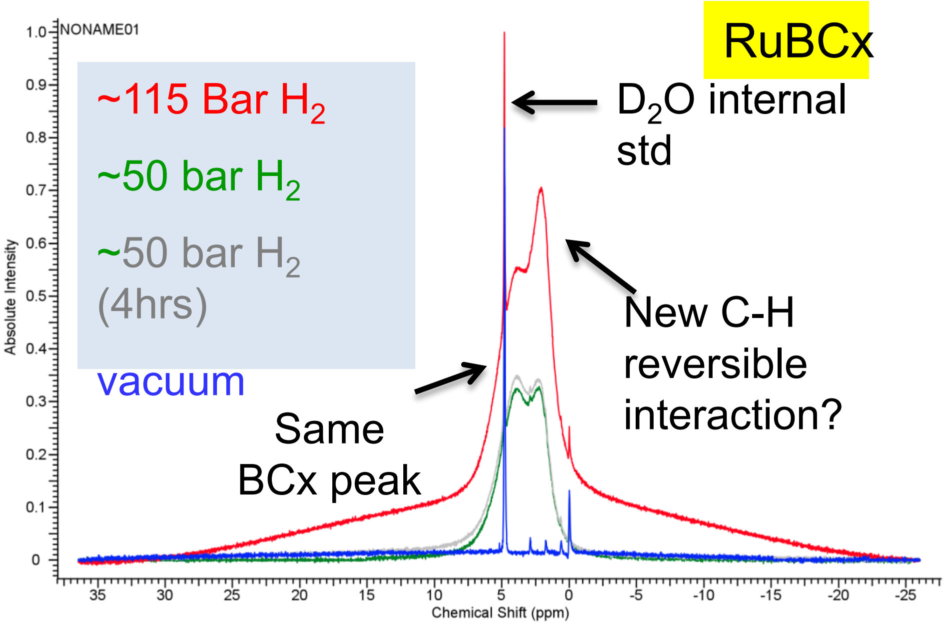
Achievements:

- Demonstrated reproducibility between laboratories – synthesis and measurements
- Demonstrated > 15% enhancement in room-temperature adsorption on metal-doped sorbents – $RuBC_x$ and Pd-TC
- Demonstrated spectroscopic evidence of reversible substrate-hydrogen interactions—DRIFTS, NMR and Inelastic Neutron Scattering

DRIFTS analysis



NMR analysis

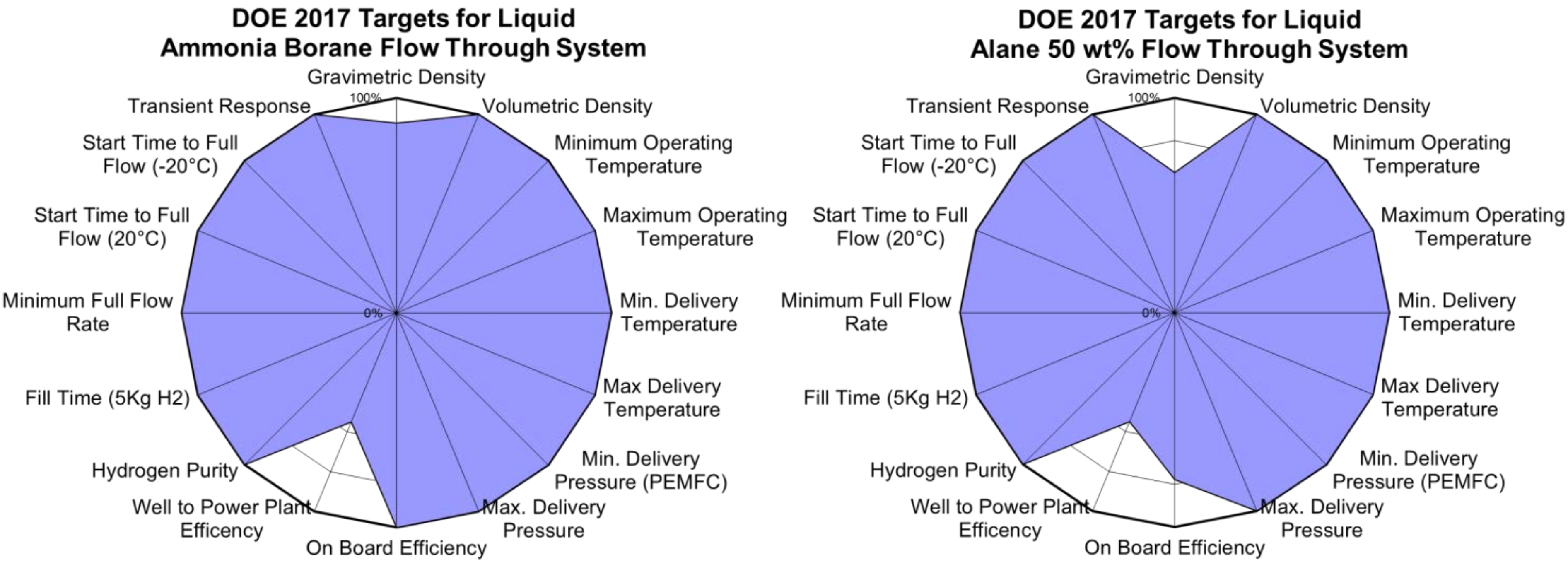


2012 Progress: HSECoE – Status of Chemical Hydrogen Systems

U.S. DEPARTMENT OF ENERGY

Endo- and exothermic release material systems can meet most key DOE system performance targets for onboard vehicle applications.

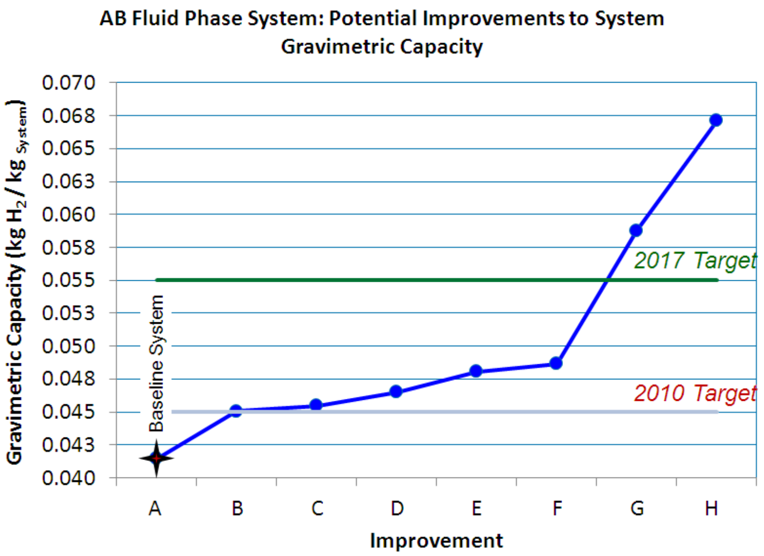
Projections for Exothermic (Ammonia Borane) and Endothermic (Alane) Hydrogen Release Systems – 50% mass loaded fluids

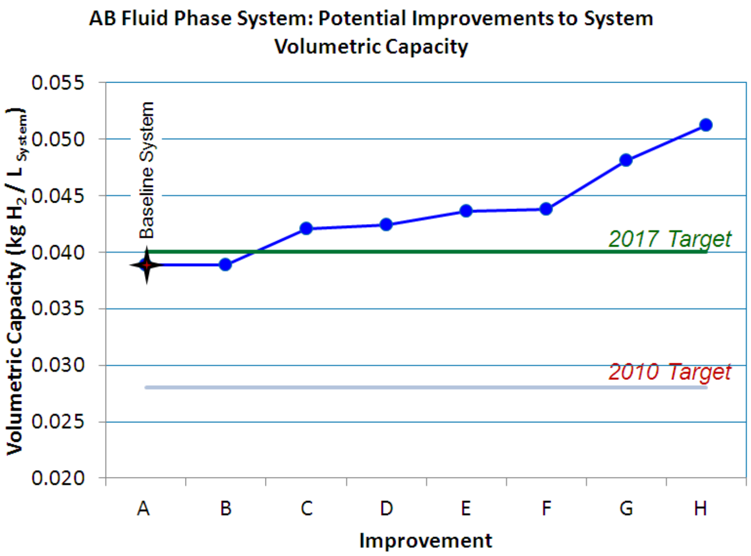


Off-board regeneration efficiency is still an issue.

2012 Progress: HSECoE – Chemical Hydrogen System Improvement Pathways

Combined system and material improvements show potential path to exceed DOE 2017 onboard performance targets.


AB Fluid Phase System: Potential Improvements to System Gravimetric Capacity


AB Fluid Phase System: Potential Improvements to System Volumetric Capacity

Step	Description
A	Phase 1 Baseline: 50:50 Fluid composition
B	Change from steel shell ballast tank to aluminum
C	Reduce HX from 76 kW to 38 kW
D	Reduce H_2 Wetted Tubing
E	Low Mass Borazine Scrubber
F	Low Mass Ammonia Scrubber
G	Increase AB loading from 50 to 65 wt. %
H	Increase AB loading from 65 to 80 wt. %

2012 Progress: *New Project—Liquid Carriers*

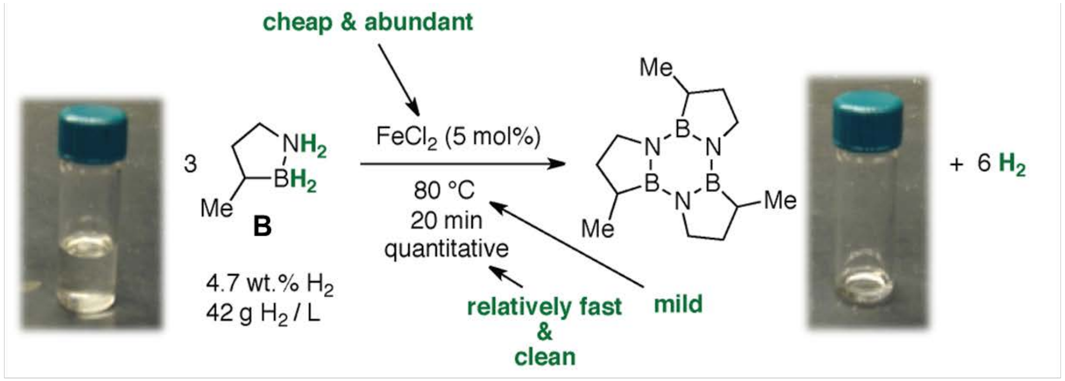
Novel Carbon (C) – Boron (B) – Nitrogen (N) containing hydrogen storage materials as liquid hydrogen carriers

University of Oregon (PI: Shih-Yuan Liu)

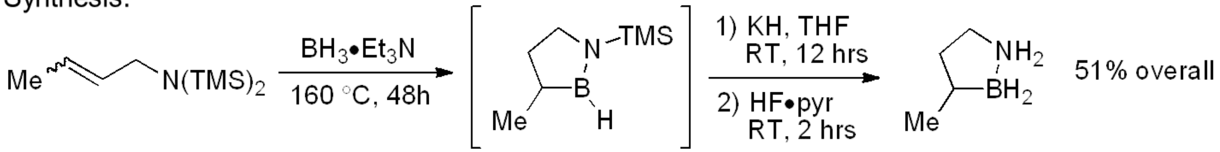
Partners: Pacific Northwest National Laboratory, Univ. of Alabama, Protonex Technology Corp.

Develop novel boron and nitrogen-doped liquid organic materials for chemical hydrogen storage

- Remain liquid throughout all phases of hydrogenation;
- Capable of hydrogen release and regeneration within operational temperature and pressure ranges for target applications
- Enable liquid refueling



Synthesis:



Summary

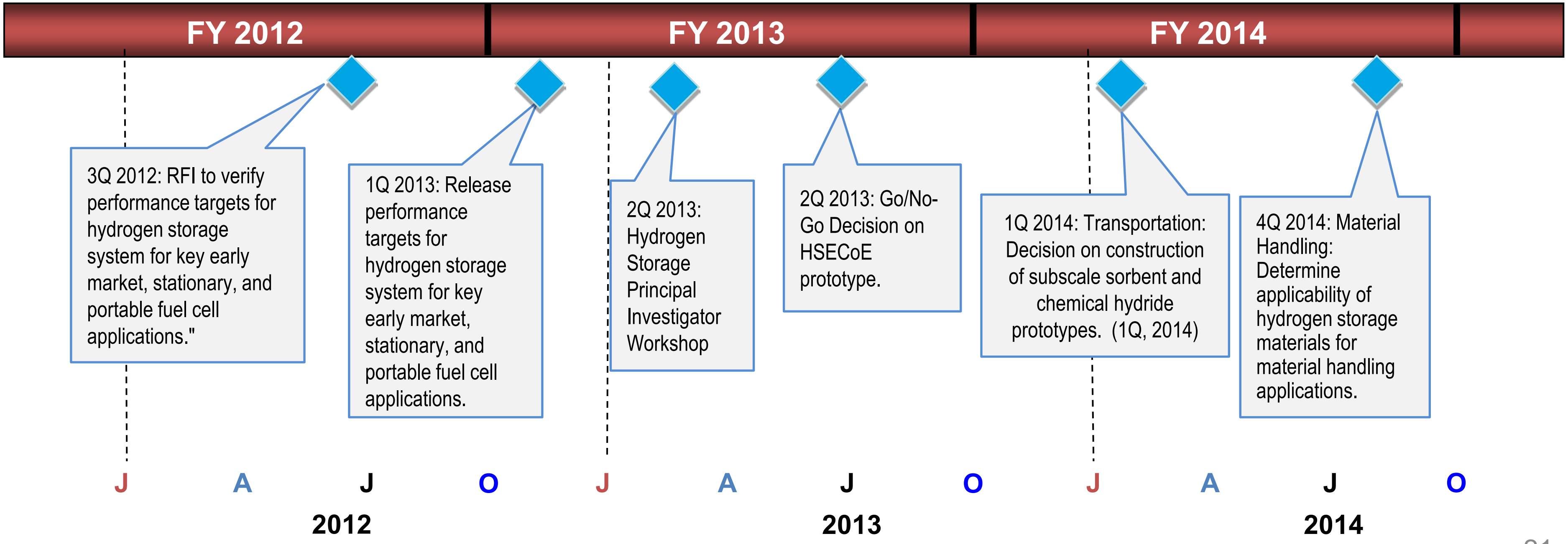
Summary of activities and upcoming milestones

Physical Storage

- Projects underway to reduce the cost of carbon fiber precursors
- Initiated new efforts through SBIR and Funding Opportunity Announcement topics

Material-based Storage

- Hydrogen Storage Engineering Center of Excellence is validating their modeled projections and identifying improvements over the current baseline materials-based systems
- Continued to improve materials-based performance through independent projects
- Finalizing performance targets for material handling equipment and portable power..



3Q 2012: RFI to verify performance targets for hydrogen storage system for key early market, stationary, and portable fuel cell applications."

1Q 2013: Release performance targets for hydrogen storage system for key early market, stationary, and portable fuel cell applications.

2Q 2013: Hydrogen Storage Principal Investigator Workshop

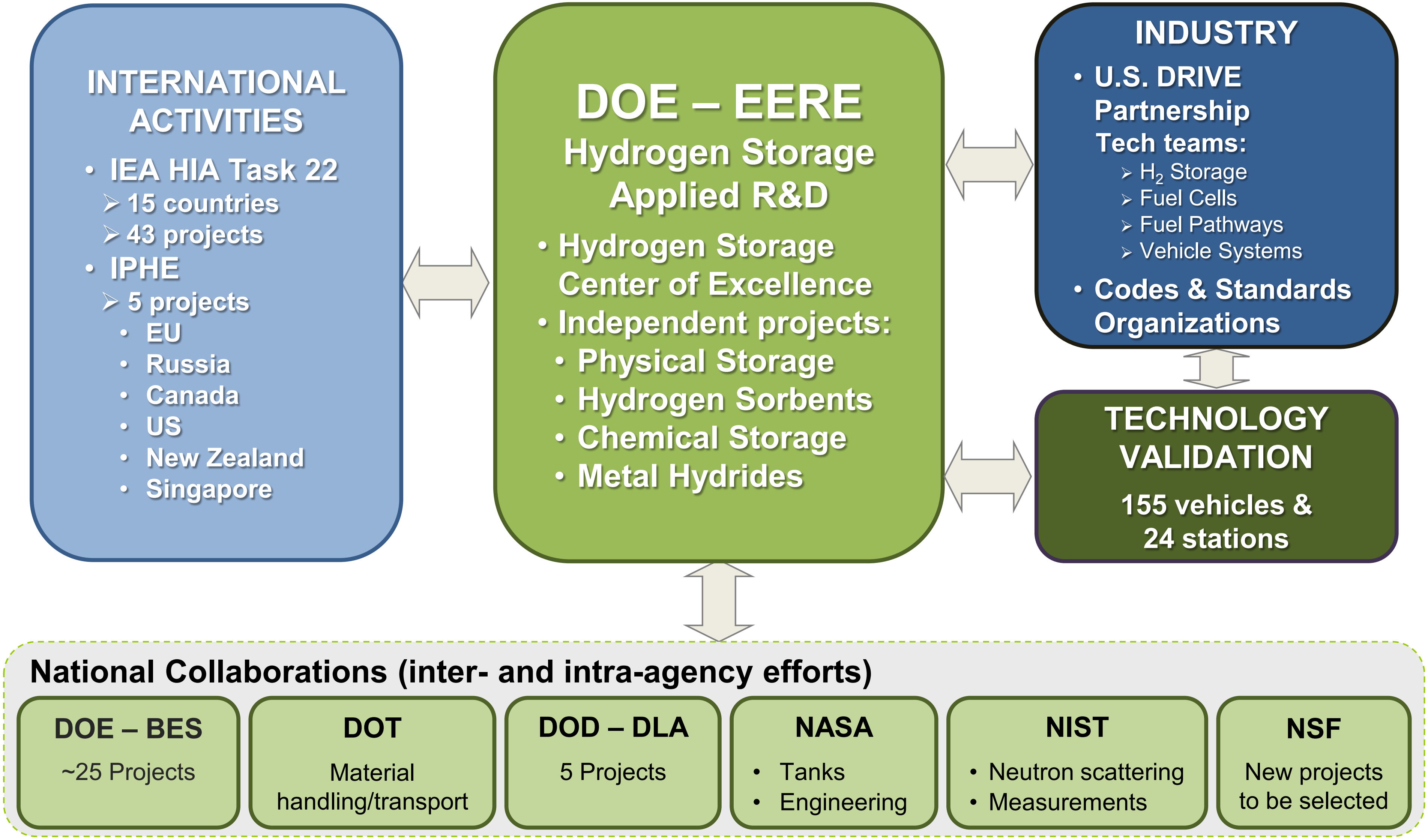
2Q 2013: Go/No-Go Decision on HSECoE prototype.

1Q 2014: Transportation: Decision on construction of subscale sorbent and chemical hydride prototypes. (1Q, 2014)

4Q 2014: Material Handling: Determine applicability of hydrogen storage materials for material handling applications.

Hydrogen Storage Collaborations

Applied R&D is coordinated among national and international organizations



INTERNATIONAL ACTIVITIES

- IEA HIA Task 22
  - 15 countries
  - 43 projects
- IPHE
  - 5 projects
    - EU
    - Russia
    - Canada
    - US
    - New Zealand
    - Singapore

DOE – EERE

Hydrogen Storage Applied R&D

- Hydrogen Storage Center of Excellence
- Independent projects:
  - Physical Storage
  - Hydrogen Sorbents
  - Chemical Storage
  - Metal Hydrides

INDUSTRY

- U.S. DRIVE Partnership Tech teams:
  - H_2 Storage
  - Fuel Cells
  - Fuel Pathways
  - Vehicle Systems
- Codes & Standards Organizations

TECHNOLOGY VALIDATION

155 vehicles & 24 stations

National Collaborations (inter- and intra-agency efforts)

DOE – BES

~25 Projects

DOT

Material handling/transport

DOD – DLA

5 Projects

NASA

- Tanks
- Engineering

NIST

- Neutron scattering
- Measurements

NSF

New projects to be selected

The Hydrogen Storage Team

U.S. DEPARTMENT OF ENERGY

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Scott McWhorter *On Assignment from SRNL* *202-586-7009* *scott.mcwhorter@ee.doe.gov*	***Katie Randolph*** *720-356-1759* *katie.randolph@go.doe.gov*
Kathleen O'Malley *Support contractor* *202-586-4786* *kathleen.o'malley@ee.doe.gov*	***Coming soon on assignment from CalTech — Channing Ahn!***

Additional Information

Challenges: Onboard Automotive Targets

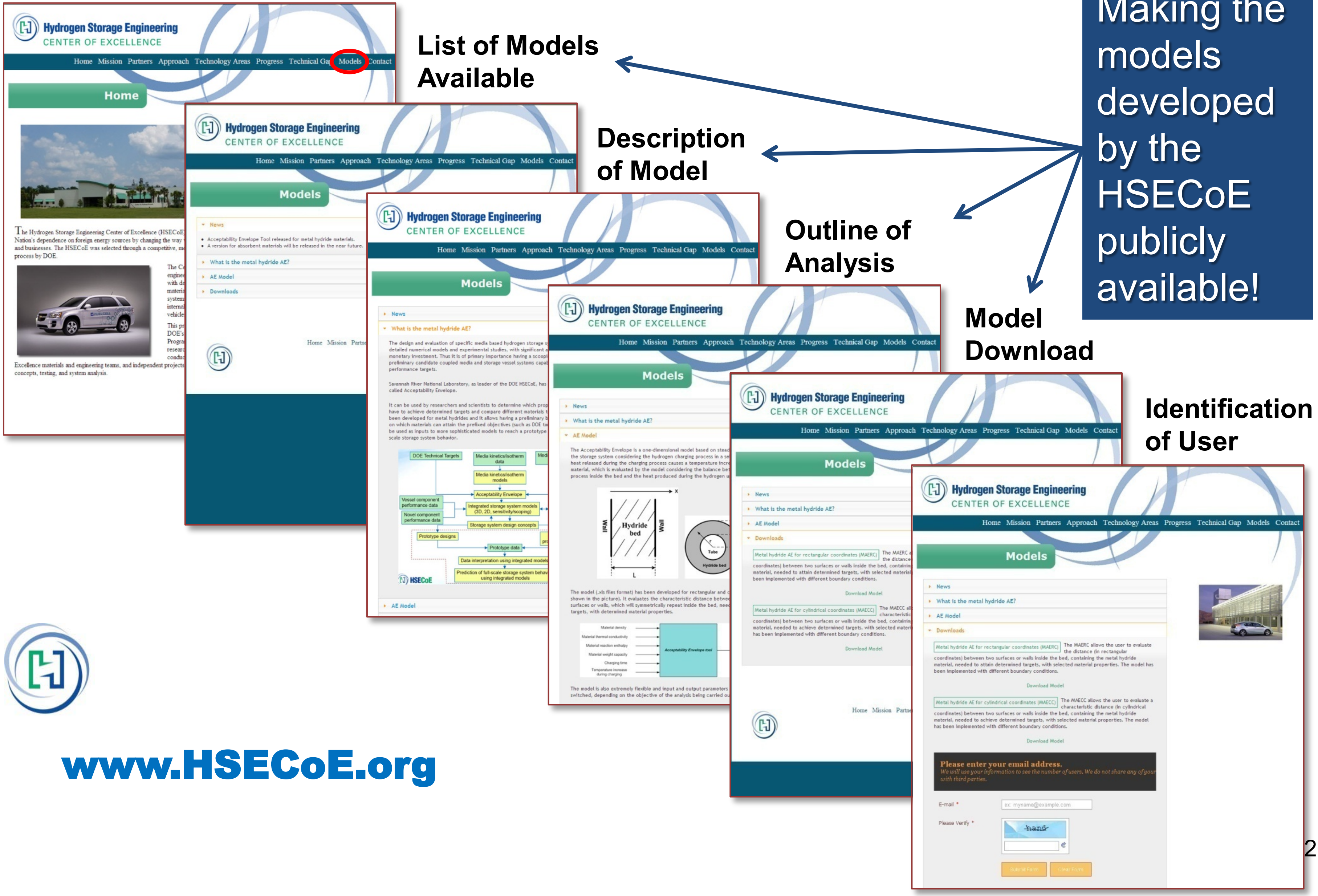
Hydrogen storage onboard light-duty vehicles face significant technical challenges, with meeting acceptable costs being one of the most difficult.

Target	**2017**	**Ultimate**
System Gravimetric Density [wt.%] (kWh/kg)	**[5.5]** **(1.8)**	**[7.5]** **(2.5)**
System Volumetric Density [g/L] (kWh/L)	**[40]** **(1.3)**	**[70]** **(2.3)**
System fill time for 5-kg fill [min] (kgH_2/min)	**[3.3]** **(1.5)**	**[2.5]** **(2.0)**
System cost [\$/kgH_2] (\$/kWh$_{net}$)*	**tbd**	**tbd**

* Cost targets are still being finalized with U.S. DRIVE;
However, progress is being made!

2012 Progress: Getting tools out for public use

Making the models developed by the HSECoE publicly available!



List of Models Available

Description of Model

Outline of Analysis

Model Download

Identification of User

Metal hydride AE for rectangular coordinates (MAERC) The MAERC allows the user to evaluate the distance (in rectangular coordinates) between two surfaces or walls inside the bed, containing the metal hydride material, needed to attain determined targets, with selected material properties. The model has been implemented with different boundary conditions.

Download Model

Metal hydride AE for cylindrical coordinates (MAECC) The MAECC allows the user to evaluate a characteristic distance (in cylindrical coordinates) between two surfaces or walls inside the bed, containing the metal hydride material, needed to achieve determined targets, with selected material properties. The model has been implemented with different boundary conditions.

Download Model

Please enter your email address.
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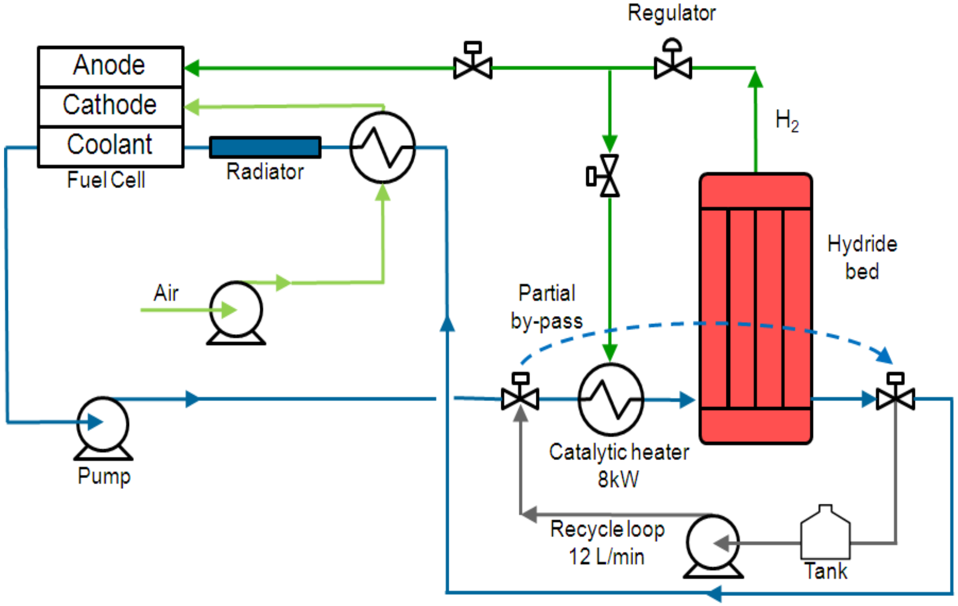
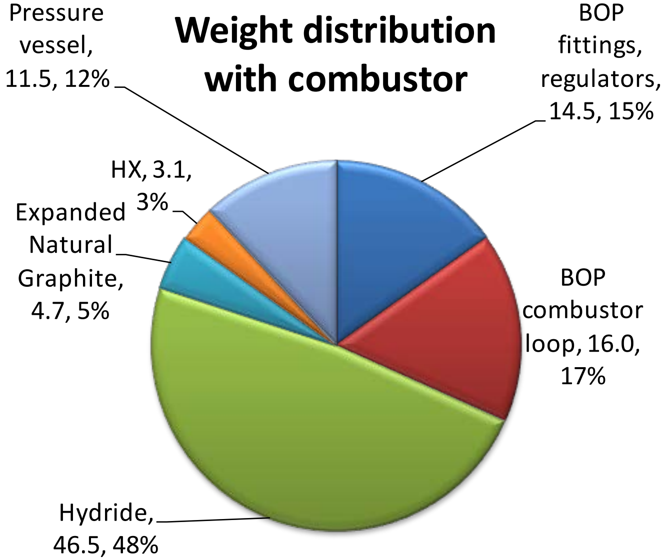
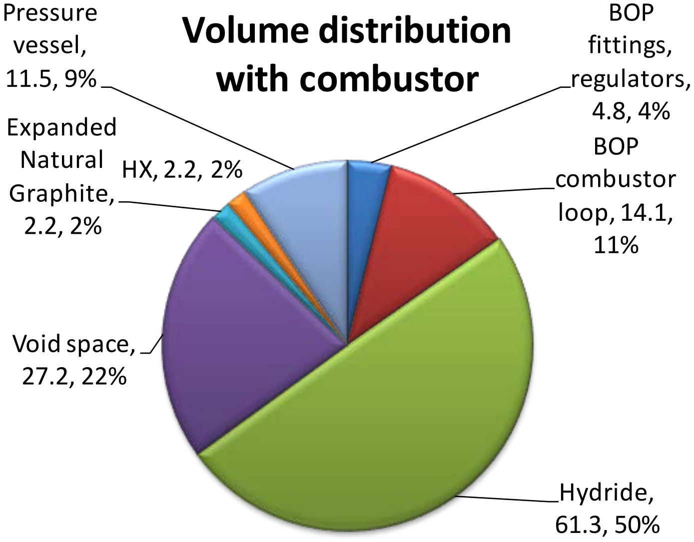
2012 Progress: Predicting Metal Hydride Requirements - Enthalpy such that waste heat is not enough

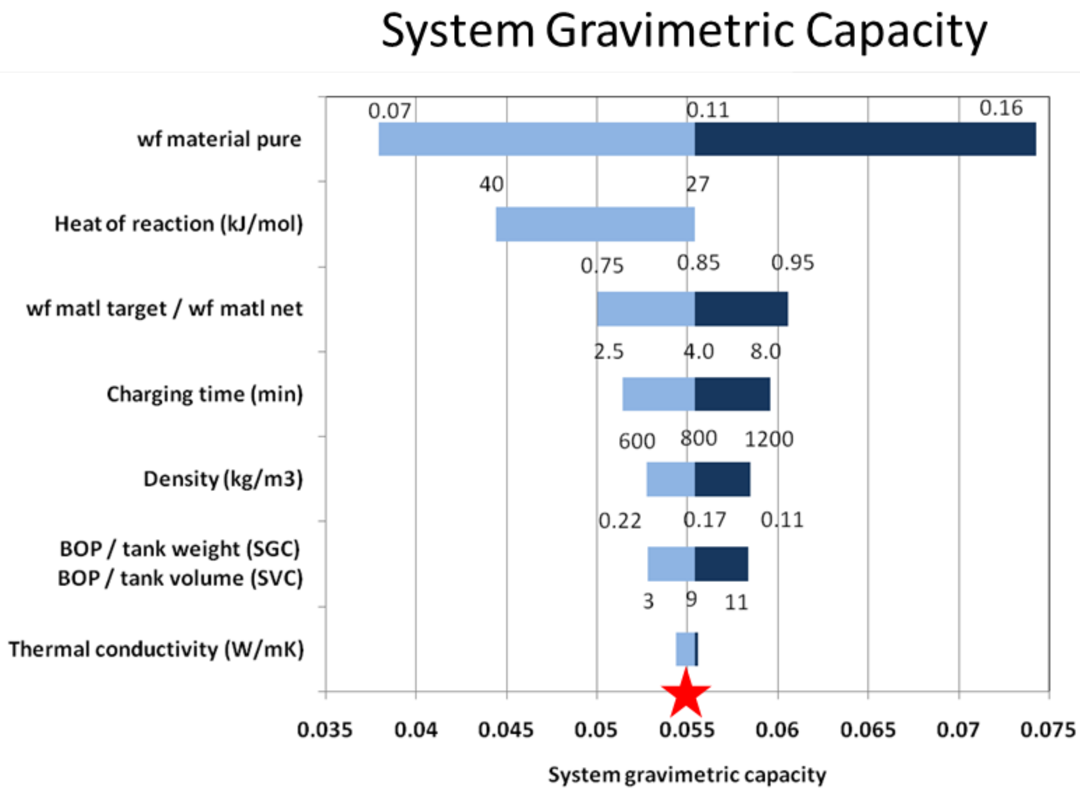
- Attributes
  - Mix of fuel cell coolant and recycled fluid used for warm-up and to maintain T_{tank}.
  - No separate buffer tank: use H_2 in pores.
- **Media Characteristics**
  - **$\Delta H = -40$ kJ/mol-H_2 ($T_{5\ bar} = 122.8$ °C)**
  - **17 wt.% pure material capacity**
- Results
  - Satisfies targets except system efficiency.
  - On-board efficiency: ~81%
  - System: 103 kg, 126 liters
  - Operating at 130°C delivers 5.4 kg-H_2 (delivered + combusted: 6.6 kg-H_2)

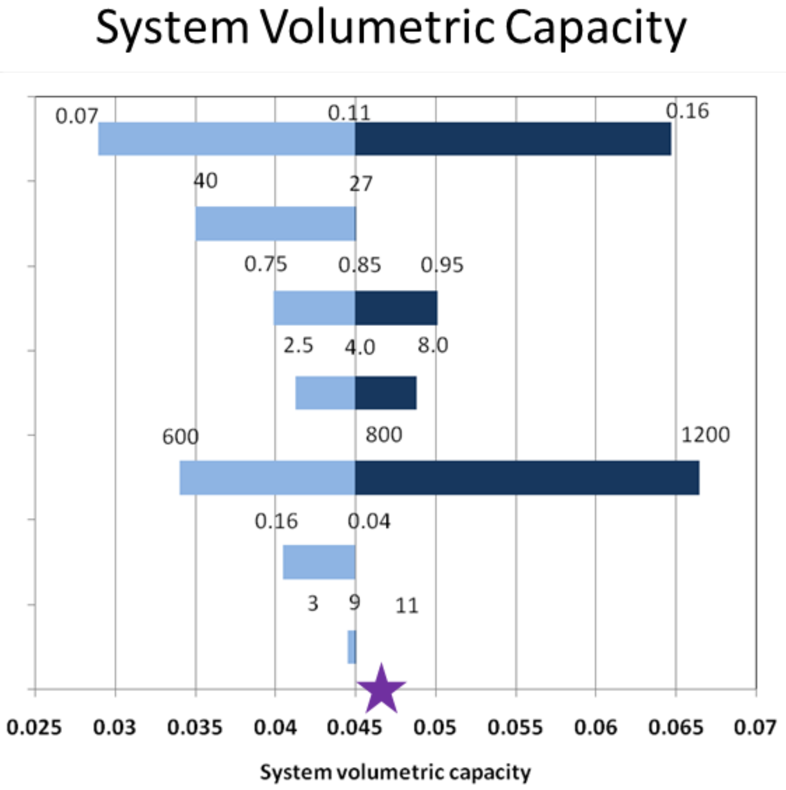



Weight distribution with combustor


Volume distribution with combustor

2012 Progress: MH Sensitivity Analysis: System Gravimetric & Volumetric Capacity


System Gravimetric Capacity


System Volumetric Capacity

★ ★ **DOE 2017 targets, gravimetric and volumetric capacity, respectively**

Sensitivity Parameters (Baseline case)

- Wf matl = 11%
- Heat of reaction = 27 kJ/molH2
- Wf matl target / wf matl net = 85% *
- Charging time = 4 min
- Bulk density = 800 kg/m^3
- BOP weight / tank weight = 17%
  BOP volume / tank volume = 4%
- Thermal conductivity = 9 W/mK *

2012 Progress: *New Project – Sorbents*

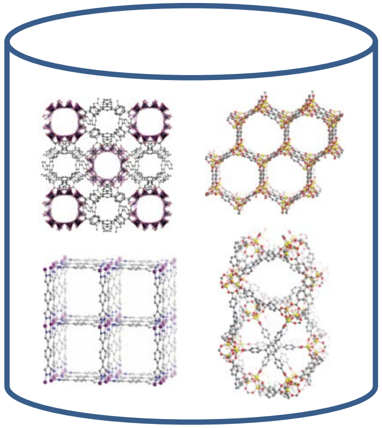
Hydrogen Storage in Metal-Organic Frameworks optimized for onboard hydrogen storage applications

Project Lead: **Lawrence Berkeley National Laboratory** – PI: Jeffery Long

Partners: National Institute of Standards and Technology, GM

Description: a theory-guided approach to synthesize novel materials with high hydrogen adsorption capacities

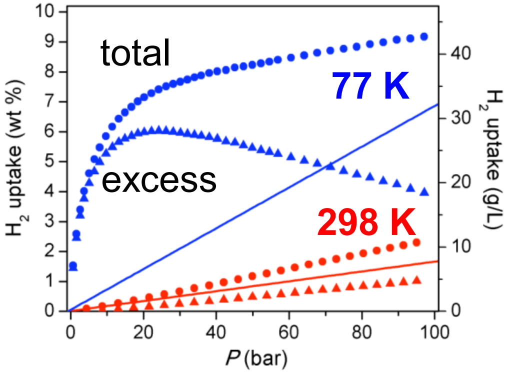
- develop and test “metal-organic framework” materials;
- surfaces allowing high charge density;
- pores engineered to enable hydrogen storage at near-ambient temperatures.



structural database

select best candidates

opposing surface algorithm



experimental isotherms

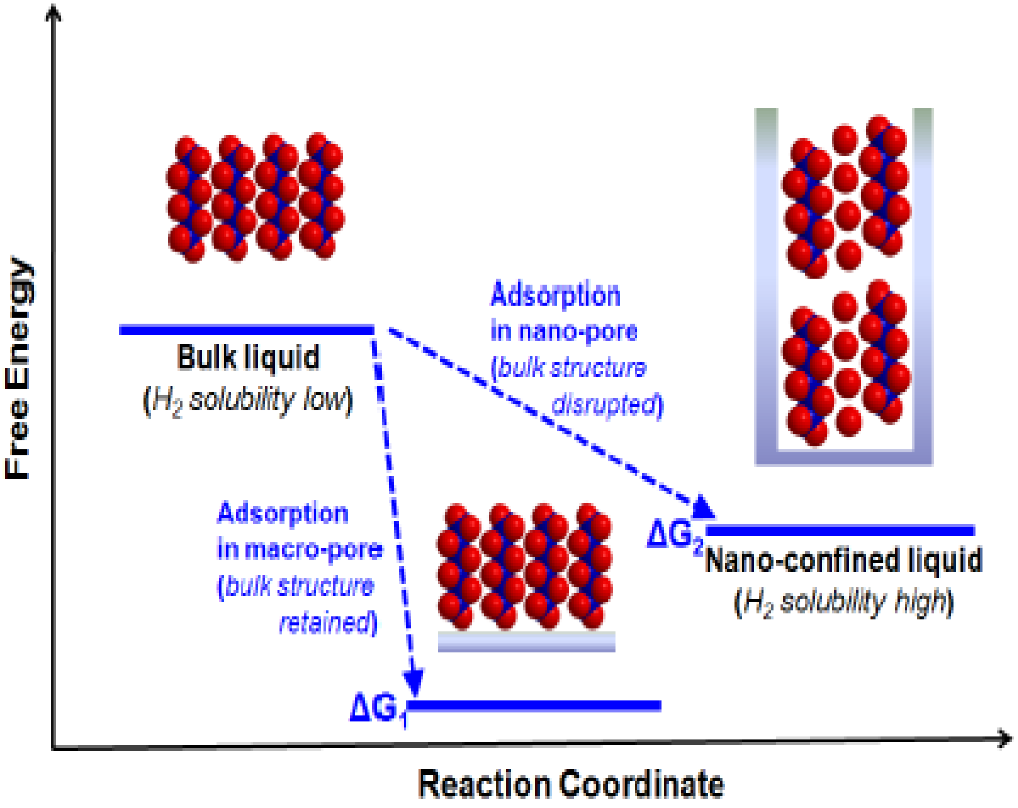
2012 Progress: *New Project – Novel Concept*

Room-Temperature Hydrogen Storage in Nano-confined Liquids - significantly higher dissolution quantities versus bulk liquids

Project Lead: **HRL Laboratories, LLC** – PI: John Vajo

Description: Investigates engineered liquids to efficiently absorb and release hydrogen gas;

- liquids nano-confined in porous structures absorb significantly more gas;
- develop composite materials capable of dissolving up to ***50 times greater*** quantities than bulk liquid;
- enable a high density, ambient temperature, compact hydrogen storage.

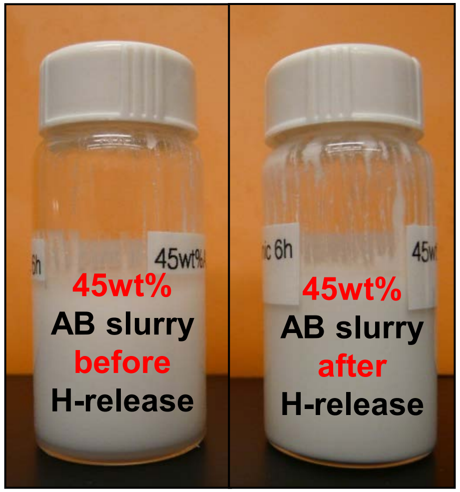


2012 Progress: Development of fluid AB materials

U.S. DEPARTMENT OF ENERGY

Liquid-Slurry Chemical Hydrogen Storage Development (AB Slurry)

Down-select to AB silicone oil slurry
45wt% AB slurry:~7wt% H_2



Pacific Northwest NATIONAL LABORATORY

Source: PNNL

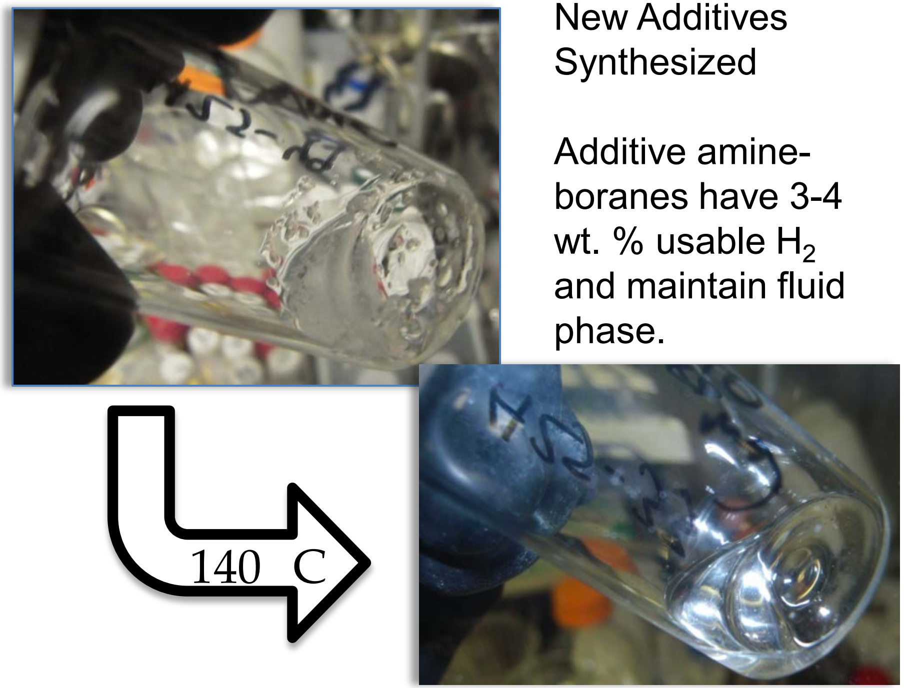
Material remains a liquid-slurry before and after H-release
Fresh slurry no settling/flocculation for 3+ months
Spent slurry settling within several hours

	AB slurry before H-release	AB slurry after H-release	Measured Temp. (ºC)
Plastic viscosity (cP)	~ 617	~ 442	25
Yield stress (Pa)	~ 48	~ 3.7	25

Fluid Phase H_2 Storage Material Development (Liquid AB)

New Additives Synthesized

Additive amine-boranes have 3-4 wt. % usable H_2 and maintain fluid phase.



Picture @ Room Temperature

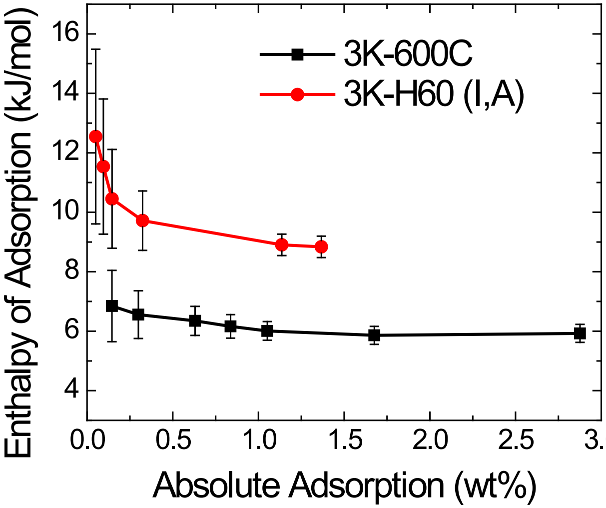
20 wt. %AB in hexylAB (6.0 wt. % H_2) transforms from a slurry to liquid upon dehydrogenation

Source: LANL

Los Alamos NATIONAL LABORATORY

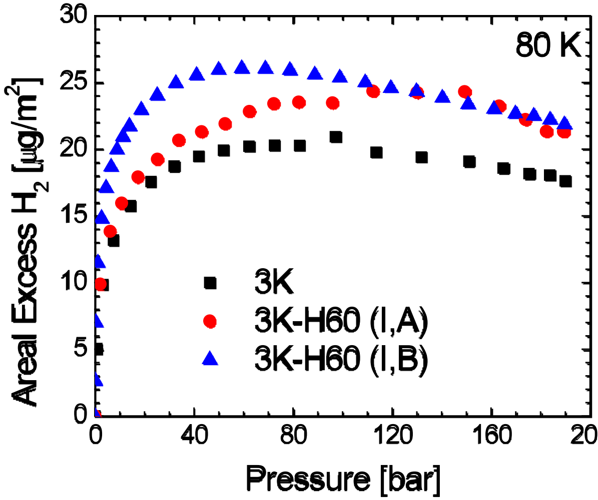
2012 Progress: *Improving Sorbents*

Achieved ~9% Boron Doping with <15% Reduction in Surface Area Leading to Higher Binding Energies and Uptake

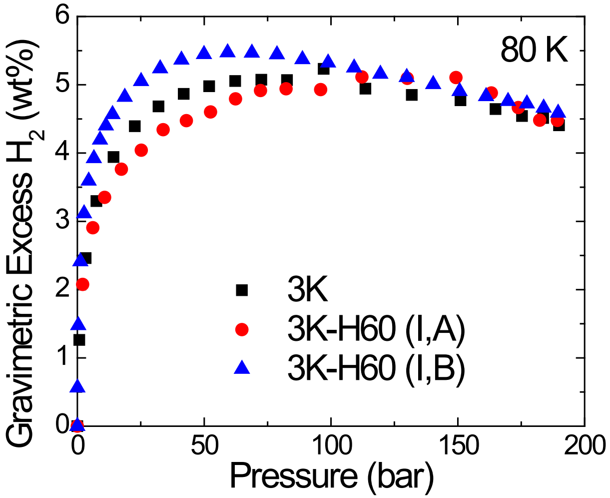


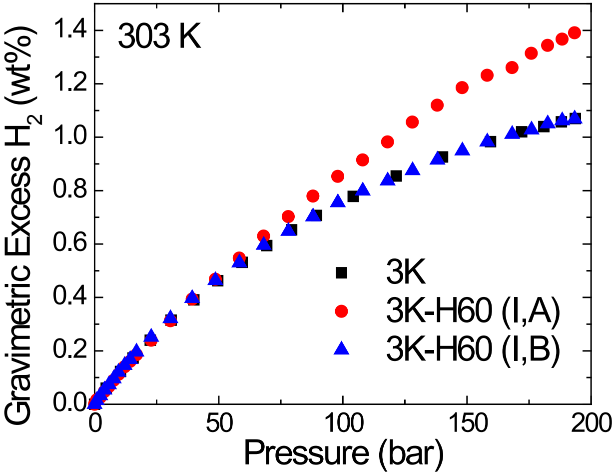
Increases Binding Energy as Predicted by Theory

Leads to Increase in Uptake per Unit Surface Area



Results in Increase in Gravimetric Capacity (80 K and 303 K)





Sample	B:C %	Σ_{N2} (m^2/g)
3K-600C, undoped	0.0	2500
3K-H60 (I,A), 1-step doping, annealed at 600 C	8.6	2100
3K-H60 (I,B), 1-step doping, annealed at 1000 C	6.7	2100