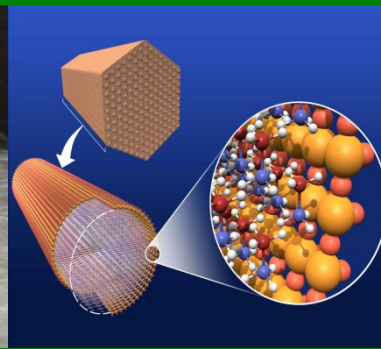




U.S. DEPARTMENT OF
ENERGY



Hydrogen Storage

Ned T. Stetson

*2012 Annual Merit Review and Peer Evaluation Meeting
May 14, 2012*

***Goal:** Develop & demonstrate viable H₂ 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, H₂ storage systems must enable a driving range of greater than 300 miles across all vehicle platforms—while meeting vehicular packaging, cost and performance requirements.

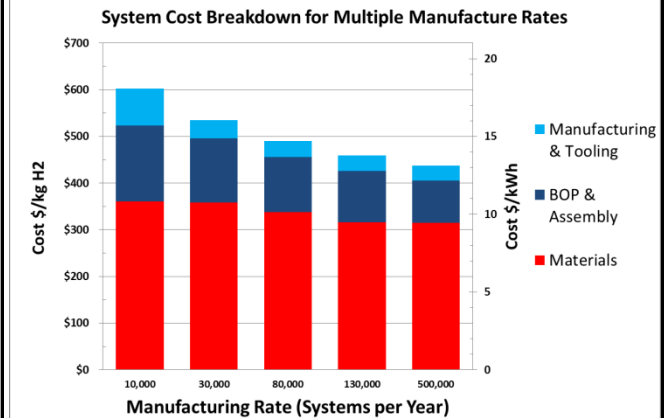
Near-term Option

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 H₂ storage is a barrier

Cost is in the CF Matrix!

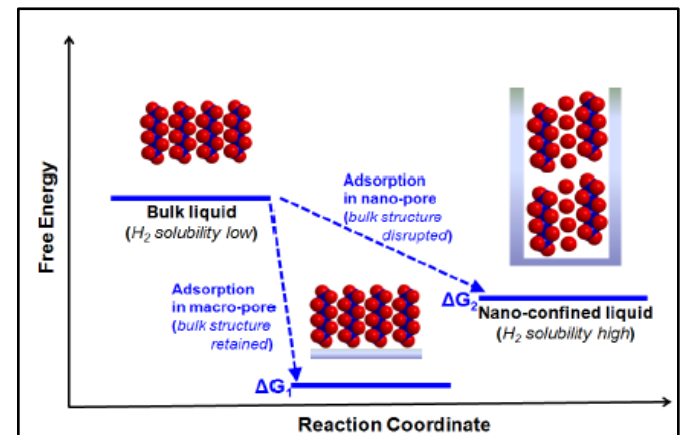
Type IV 700 bar



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



* 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 H₂ infrastructure limits deployment.

Storage Parameter	Units	2015	2020
System Gravimetric Capacity: <i>Usable, specific-energy from H₂ (net useful energy/max system mass)</i>	<i>kWh/kg</i> <i>(kg H₂/kg system)</i>	NA	NA
System Volumetric Capacity: <i>Usable energy density from H₂ (net useful energy/max system volume)</i>	<i>kWh/L</i> <i>(kg H₂/L system)</i>	0.7 (0.02)	1.3 (0.04)
Storage System Cost <i>(based on LHV of delivered H₂):</i>	<i>\$/kWh</i> <i>(\$/kg H₂)</i>	20 667	15 500
Durability/Operability: · <i>Operational cycle life (1/4 tank to full)</i> · <i>Min delivery pressure from storage system;</i>	<i>Cycles</i> <i>bar (abs)</i>	5000 (5 yr) 3	10000 (10 yr) 3
Charging / Discharging Rates: · <i>System fill time</i> · <i>Minimum full flow rate</i>	H ₂ capacity <i>min</i> <i>(kg H₂/min)</i> <i>(g/s)/kW</i>	 5 0.4 0.02	2 kg 3 0.7 0.02
Shock and Vibration	<i>g</i>	3	15

Preliminary H₂ 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: <i>Usable, specific-energy from H₂ (net useful energy/max system mass)</i>	<i>kWh/kg</i> <i>(kg H₂/kg system)</i>	0.3 (0.01)	1.0 (0.03)
System Volumetric Capacity: <i>Usable energy density from H₂ (net useful energy/max system volume)</i>	<i>kWh/L</i> <i>(kg H₂/L system)</i>	1.0 (0.03)	1.7 (0.05)
Storage System Cost <i>(based on LHV of delivered H₂):</i>	<i>\$/Wh</i> <i>(\$/g H₂)</i>	2.0 67	1.0 33
Durability/Operability: <ul style="list-style-type: none"> · <i>Operational cycle life (1/4 tank to full)</i> · <i>Min delivery pressure from storage system;</i> · <i>Max delivery pressure from storage system</i> 	 <i>Cycles</i> <i>bar (abs)</i> <i>bar (abs)</i>	 Single use / Rechargeable NA / 25 1.5 3	 NA / 100 1.5 3
Environmental Health & Safety: <ul style="list-style-type: none"> · <i>Permeation & leakage</i> · <i>Toxicity</i> · <i>Safety</i> 		Meets ISO-16111:2008; IEC 62282; or other applicable standards	

Preliminary H₂ 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)

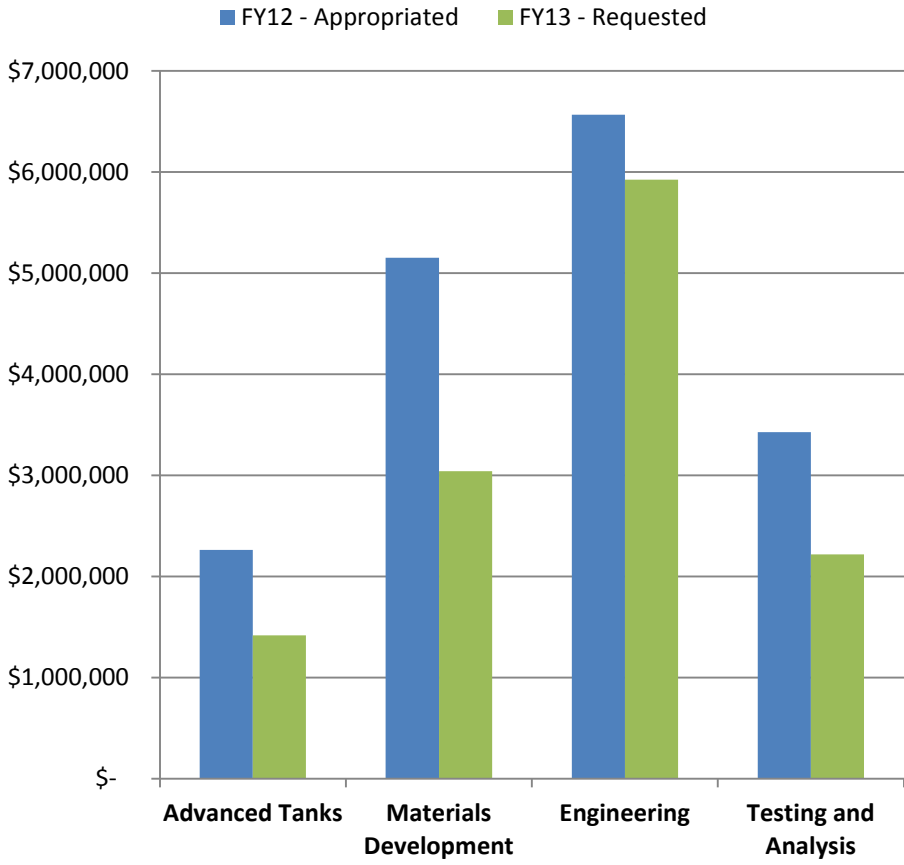
Current Status	Gravimetric (kWh/kg sys)	Volumetric (kWh/L sys)	Costs (\$/kWh)
700 bar compressed (Type IV) ^a	1.7	0.9	18.9
350 bar compressed (Type IV) ^a	1.8	0.6	15.5
Cryo-compressed (276 bar) ^a	1.9	1.4	12.0
Metal Hydride (NaAlH ₄) ^b	0.4	0.4	11.3
Sorbent (MOF-5, 200 bar) ^b	1.7	0.9	18.0
Off-board 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

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

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

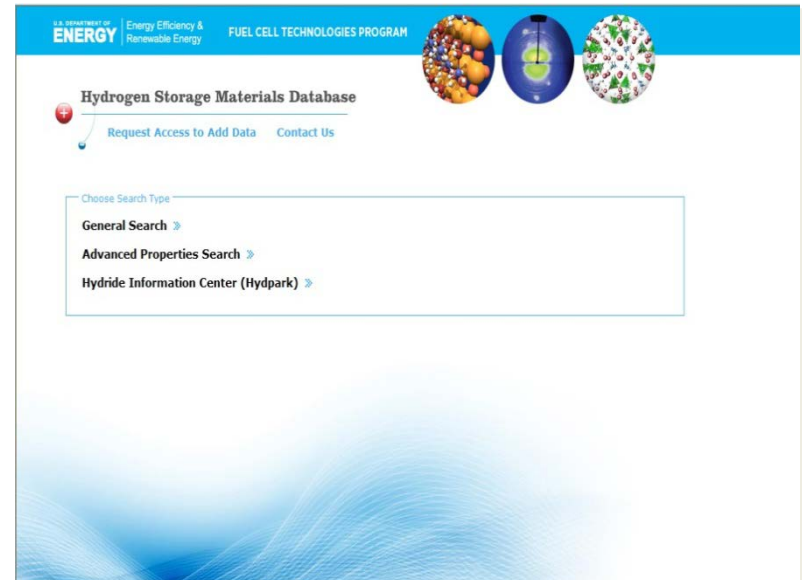


Publicly available, searchable database on Hydrogen Storage Materials Properties launched:
<http://hydrogenmaterialssearch.govtools.us/>

Still looking to populate it with more data!

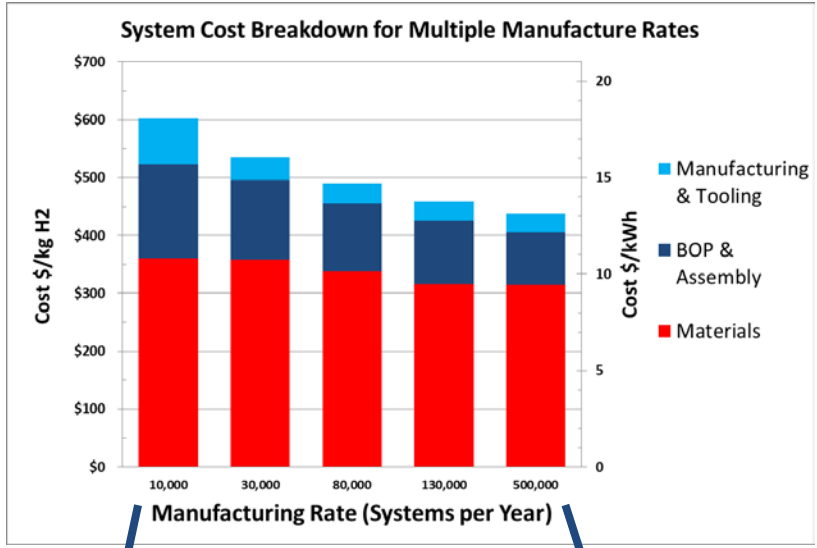
Final reports and executive summaries from the three Hydrogen Storage Materials CoEs available through the DOE website:

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



Current Status: Cost Analysis

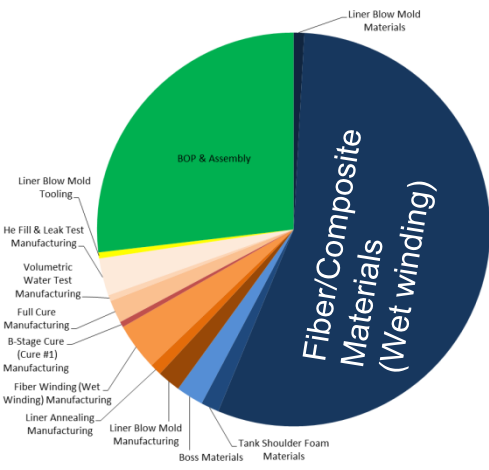
*Tank costs come down with volume manufacture, but they remain too high!
Carbon fiber composite costs dominate even at low-volume manufacture.*



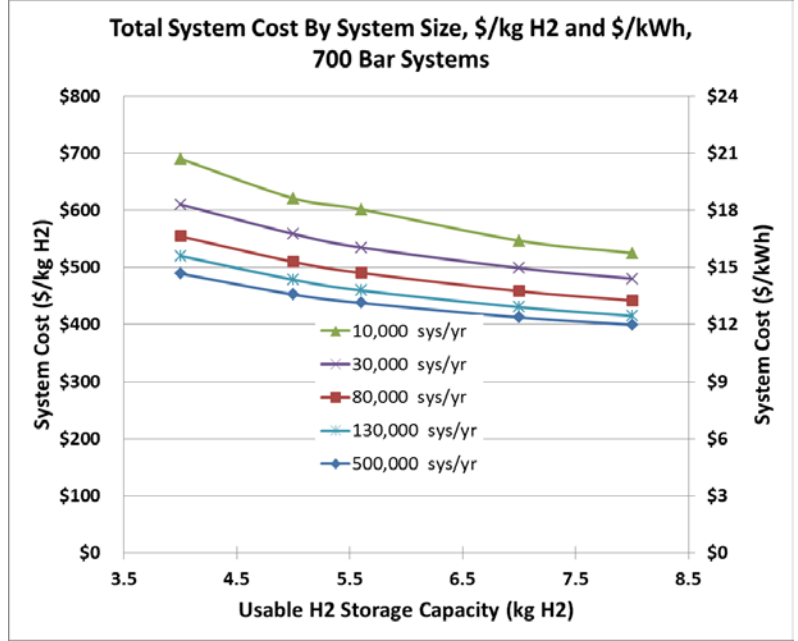
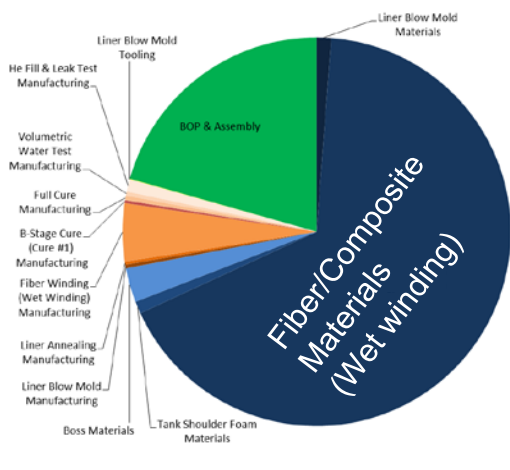
Preliminary analyses show “wet winding” manufacture is lower cost than using “Prepreg” (precombined fiber and resin).

Costs ~ linear with H₂ storage capacity

System Cost @ 10,000 Systems/Year



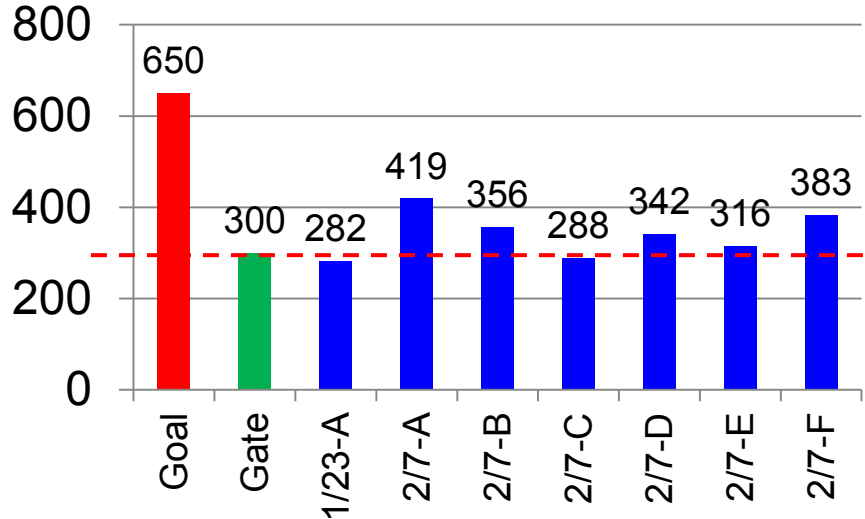
System Cost @ 500,000 Systems/Year



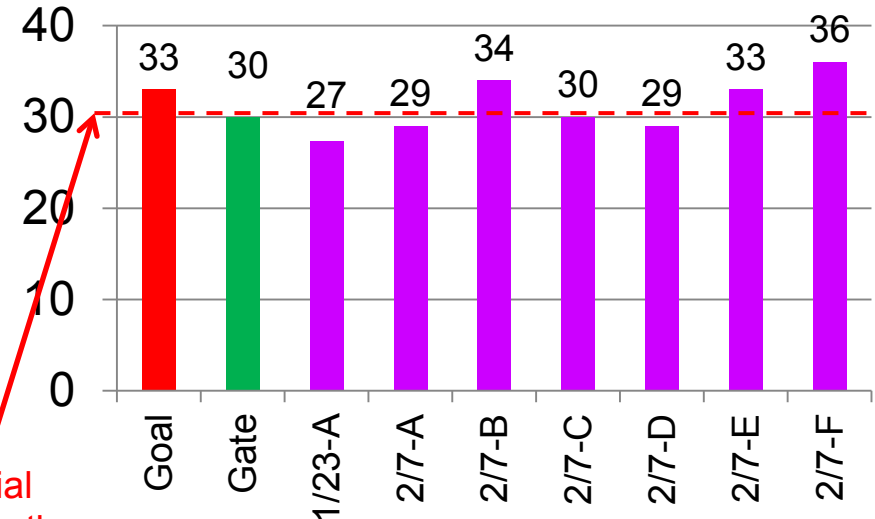
2012 Progress: Reducing CF precursor cost

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

Tensile Strength (KSI)



Tensile Modulus (MSI)



Initial strength targets

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*

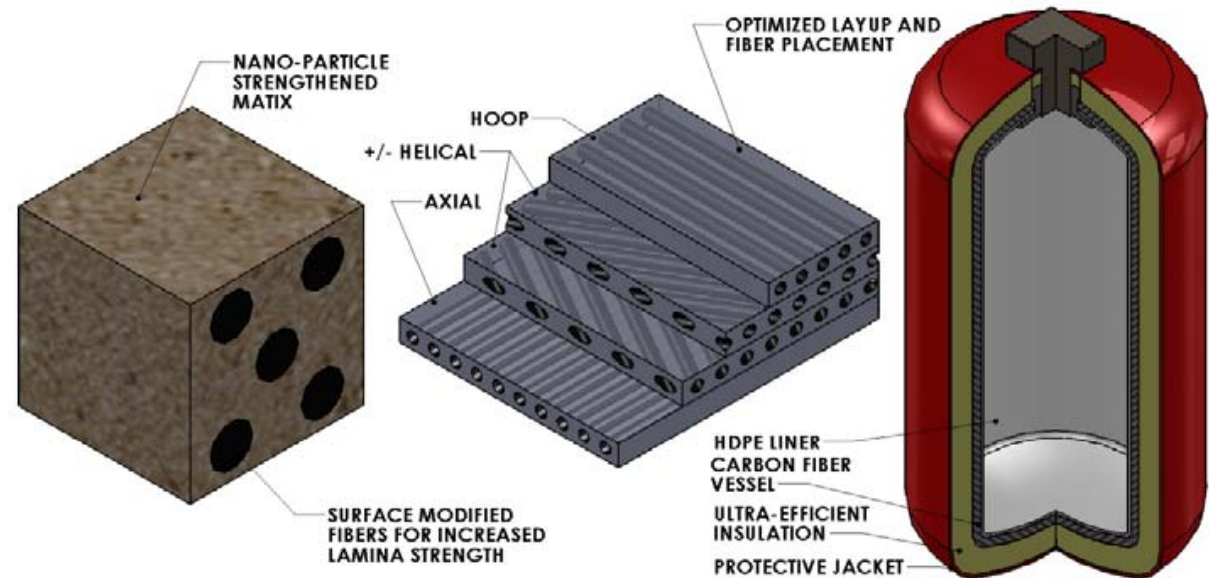
Synergistically enhanced materials and design parameters for reducing the cost of hydrogen storage tanks

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

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

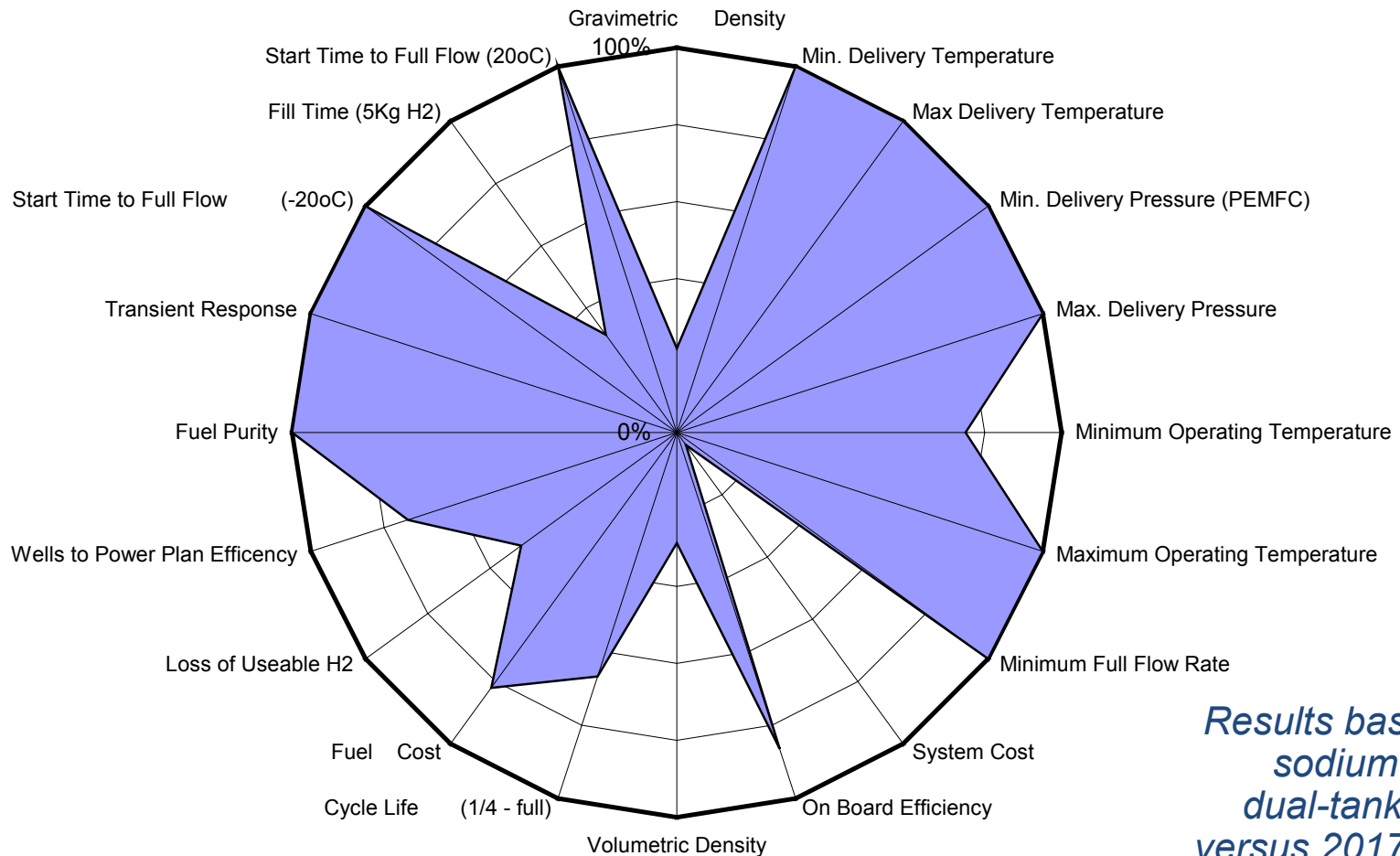
Coordinated approach for compressed H₂ tank cost-reduction focuses on:

- 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

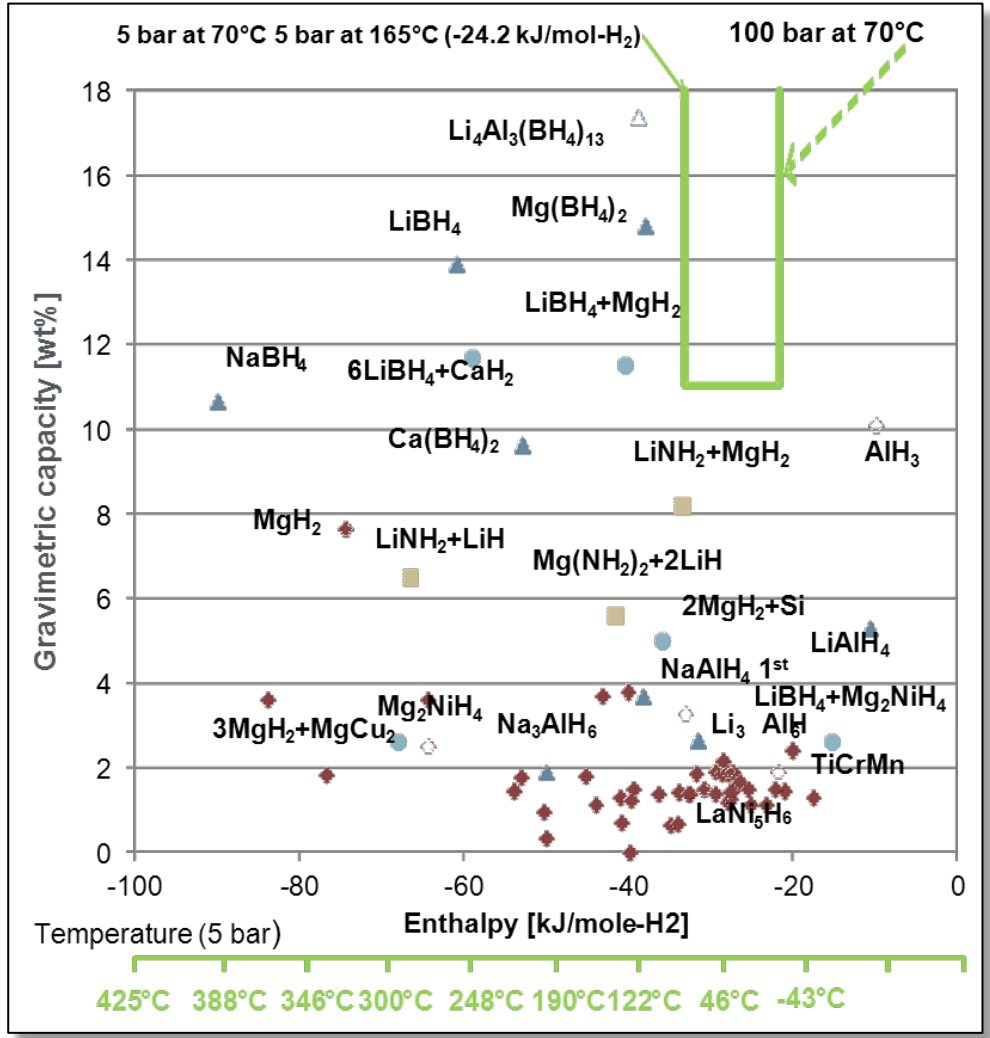
- Very simple system.
- Fuel cell waste heat stream used
- No separate buffer tank: use H₂ in pores.

Media Characteristics

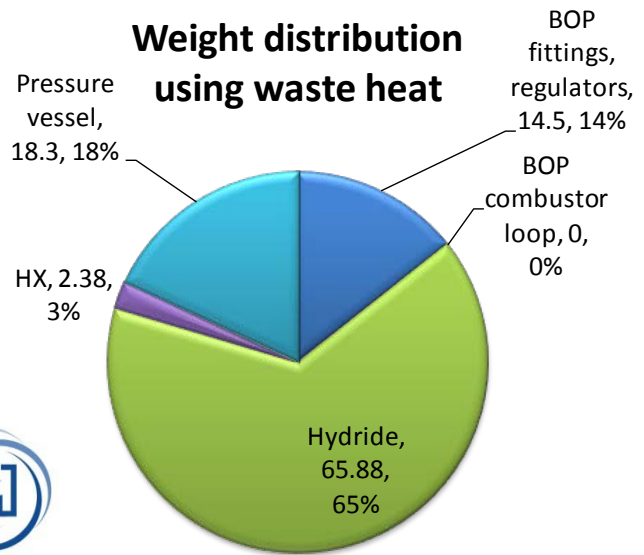
- $\Delta H = 27 \text{ kJ/mol-H}_2$ ($T_{5 \text{ bar}} = 20.7 \text{ }^\circ\text{C}$)
- 11 wt.% material capacity

Results

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



Weight distribution using waste heat

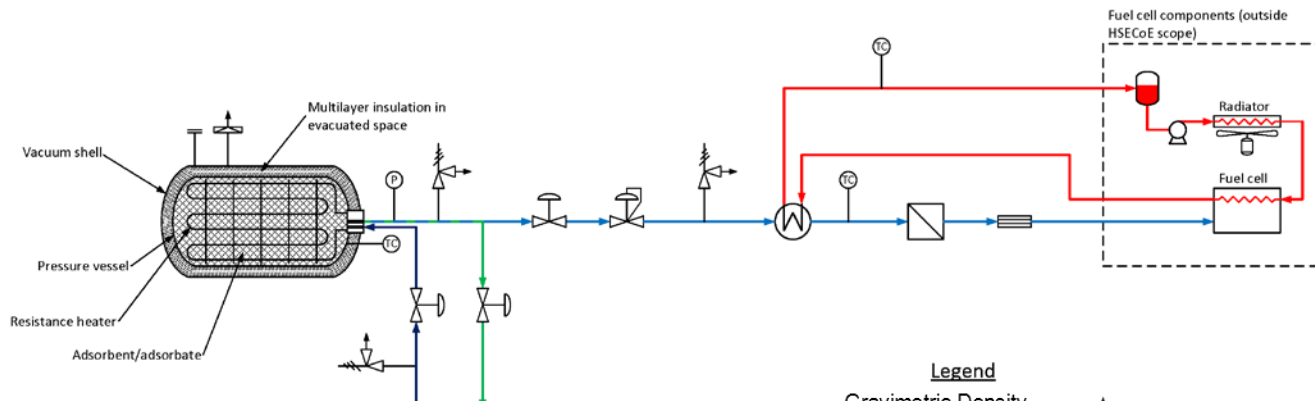


Material property requirements can be determined to focus material discovery efforts

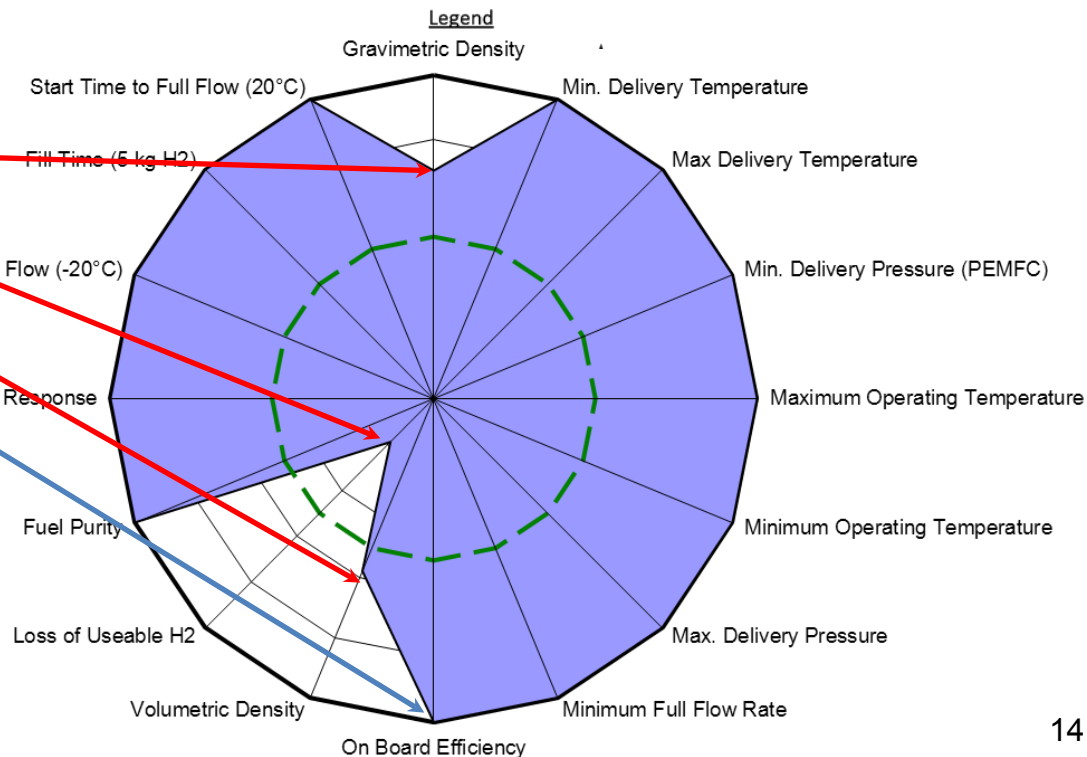


2012 Progress: HSECoE – Cryo-sorbent Systems

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 H₂
3. Volumetric Density
4. On-Board Efficiency
5. System Cost

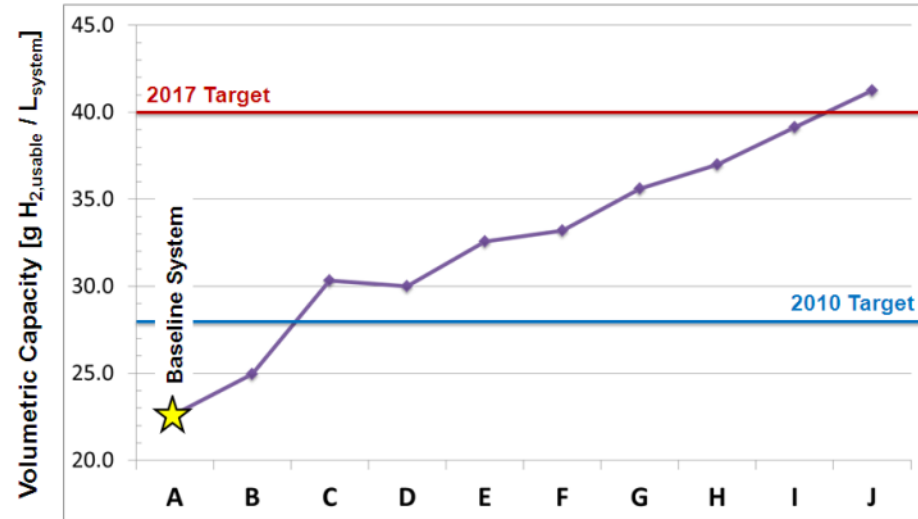
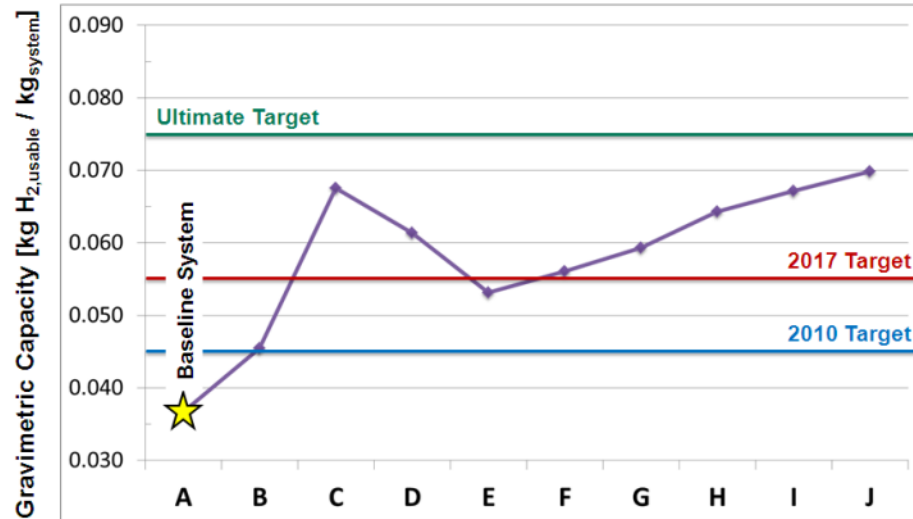


AX-21, 200 bar, flow-through design, 80K fill



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%

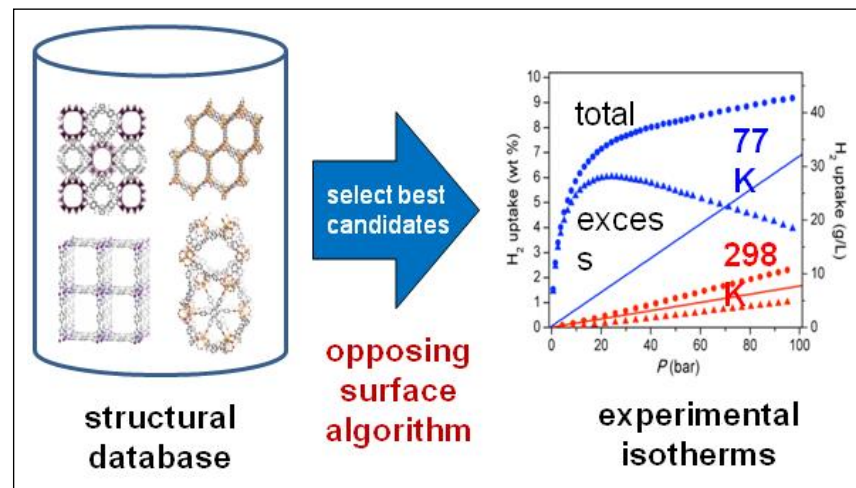


2012 Progress: *Two New Projects – Sorbents*

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

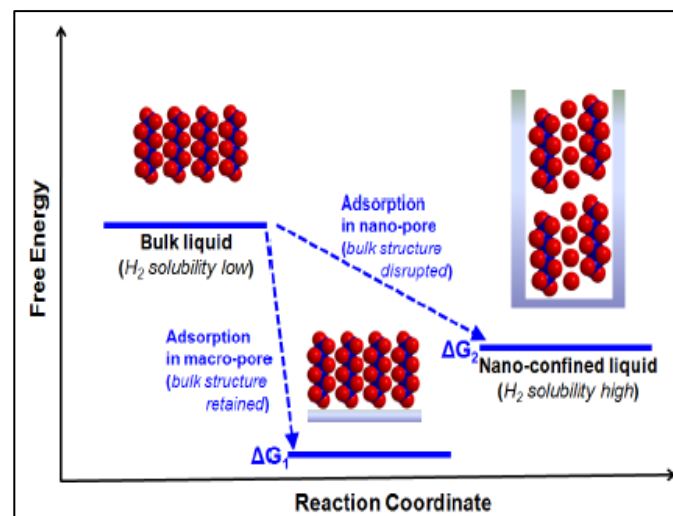
Lawrence Berkeley National Laboratory (PI: Jeffery Long)
Partners: NIST and GM

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



HRL Laboratories, LLC
(PI: John Vajo)

Investigates engineered liquids to efficiently absorb and release hydrogen gas

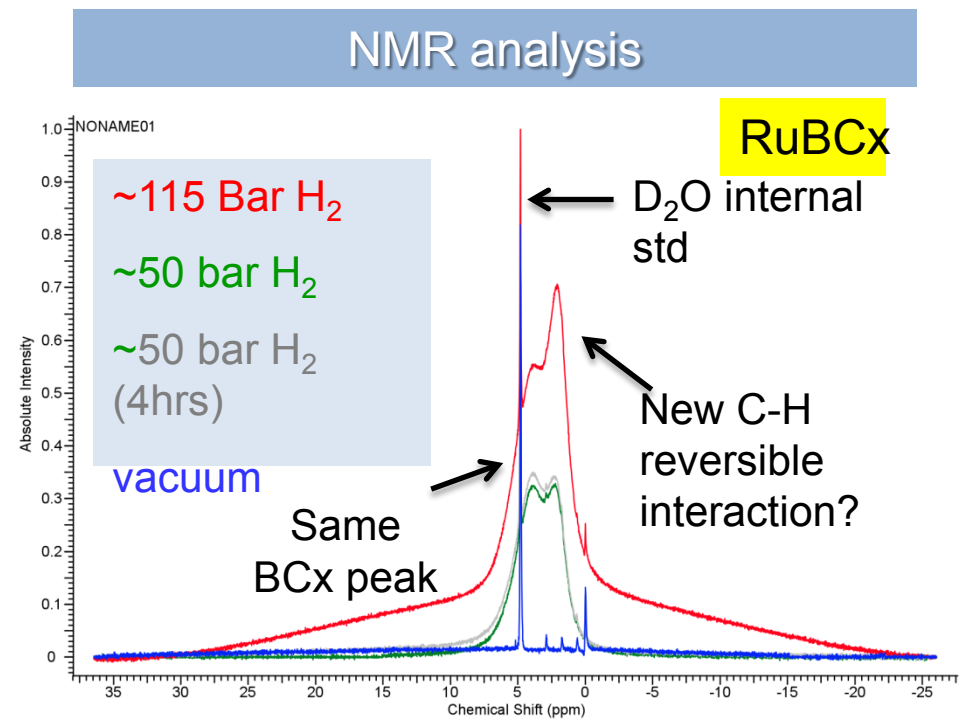
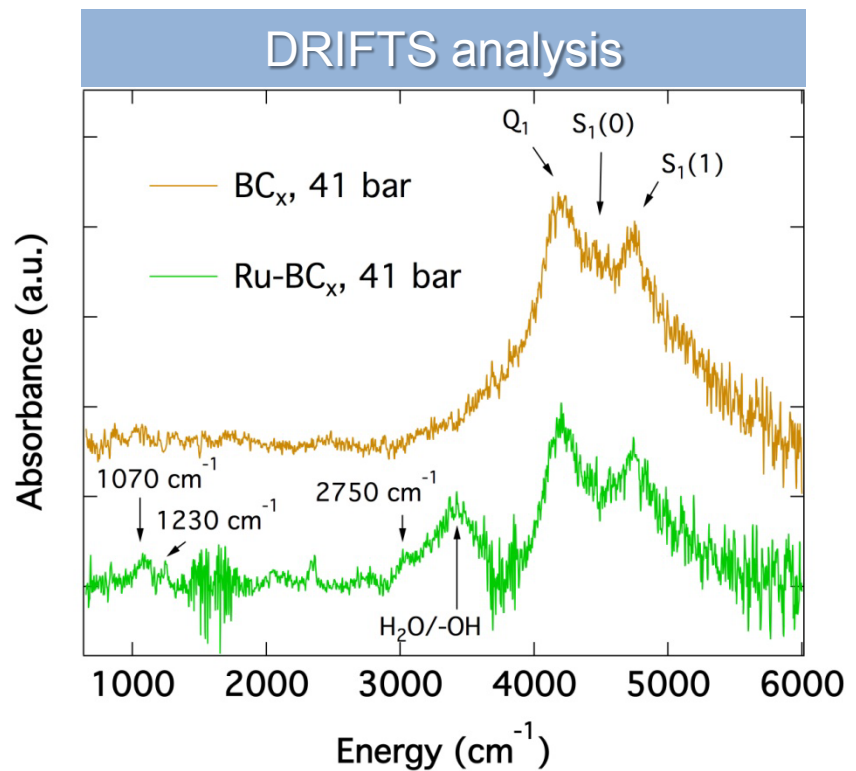


2012 Progress: *Spillover Taskforce Update*

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

Achievements:

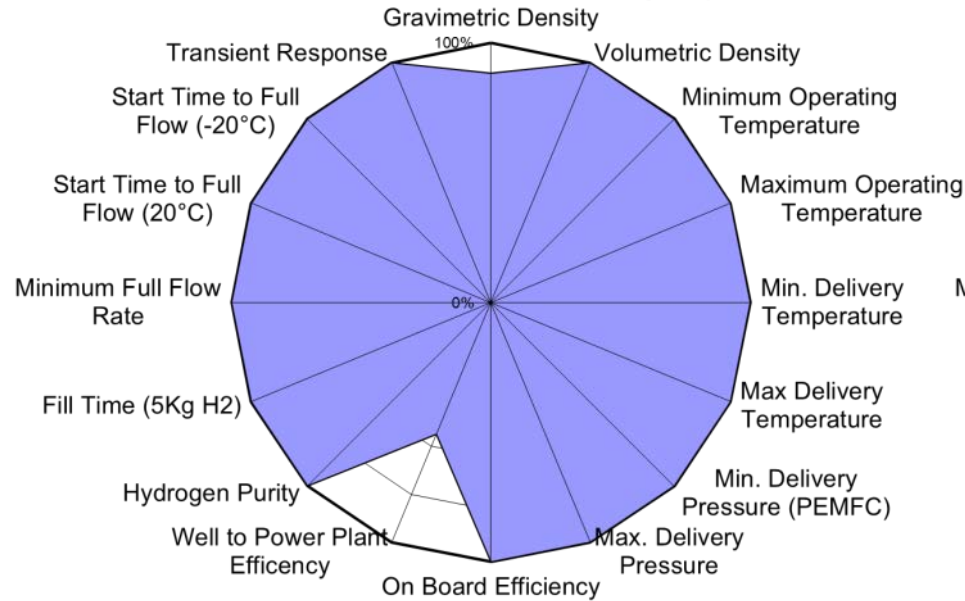
- Demonstrated reproducibility between laboratories – synthesis and measurements
- Demonstrated > 15% enhancement in room-temperature adsorption on metal-doped sorbents – RuBC_x and Pd-TC
- Demonstrated spectroscopic evidence of reversible substrate-hydrogen interactions—DRIFTS, NMR and Inelastic Neutron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



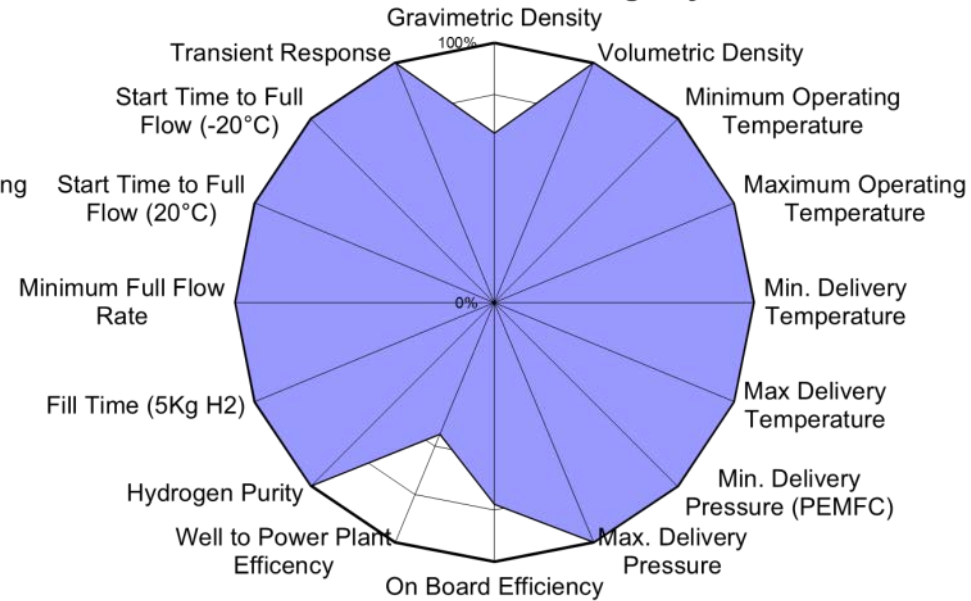
Endo- and exothermic release material systems can meet most key DOE system performance targets for onboard vehicle applications.

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

DOE 2017 Targets for Liquid Ammonia Borane Flow Through System



DOE 2017 Targets for Liquid Alane 50 wt% Flow Through System

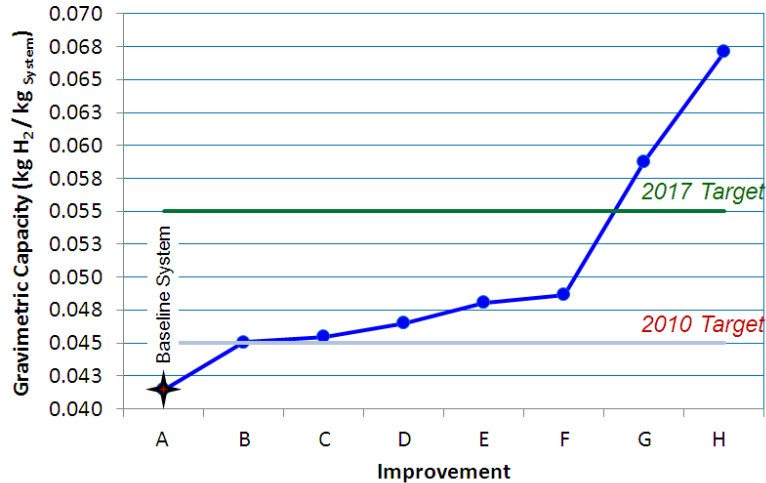


Off-board regeneration efficiency is still an issue.

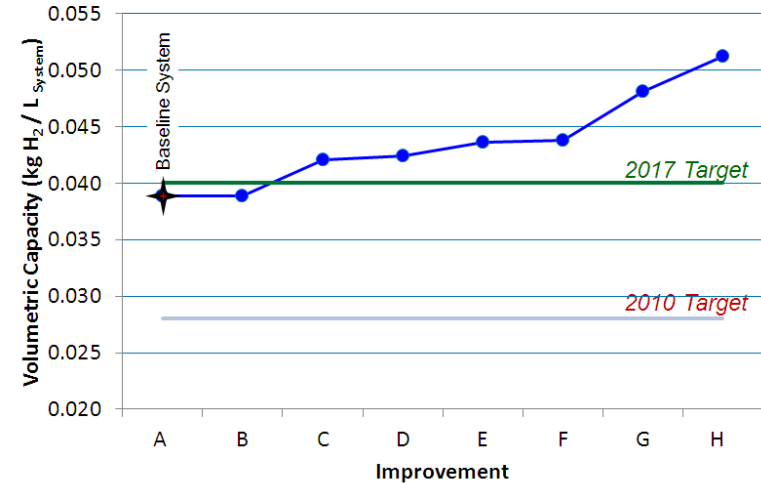
2012 Progress: HSECoE – Chemical Hydrogen System Improvement Pathways

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*

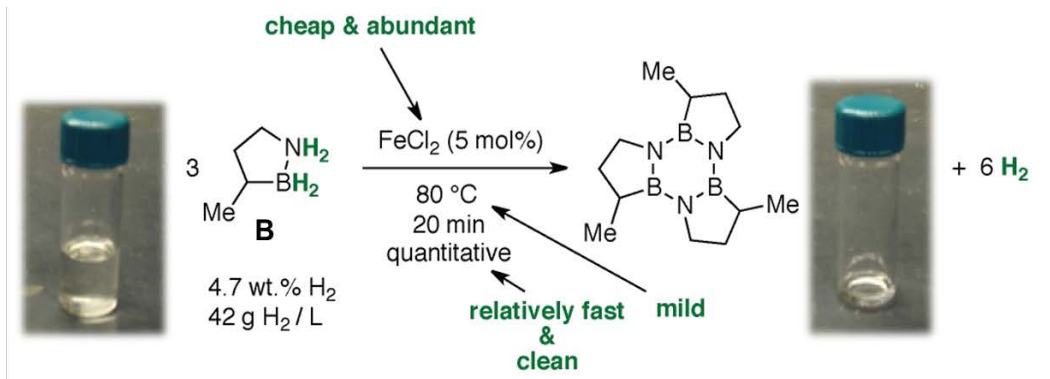
Novel Carbon (C) – Boron (B) – Nitrogen (N) containing hydrogen storage materials as liquid hydrogen carriers

University of Oregon (PI: Shih-Yuan Liu)

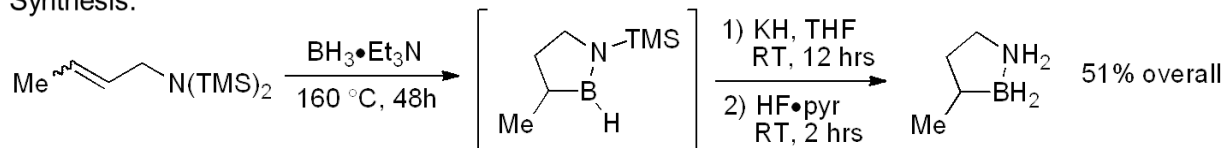
Partners: Pacific Northwest National Laboratory, Univ. of Alabama, Protonex Technology Corp.

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

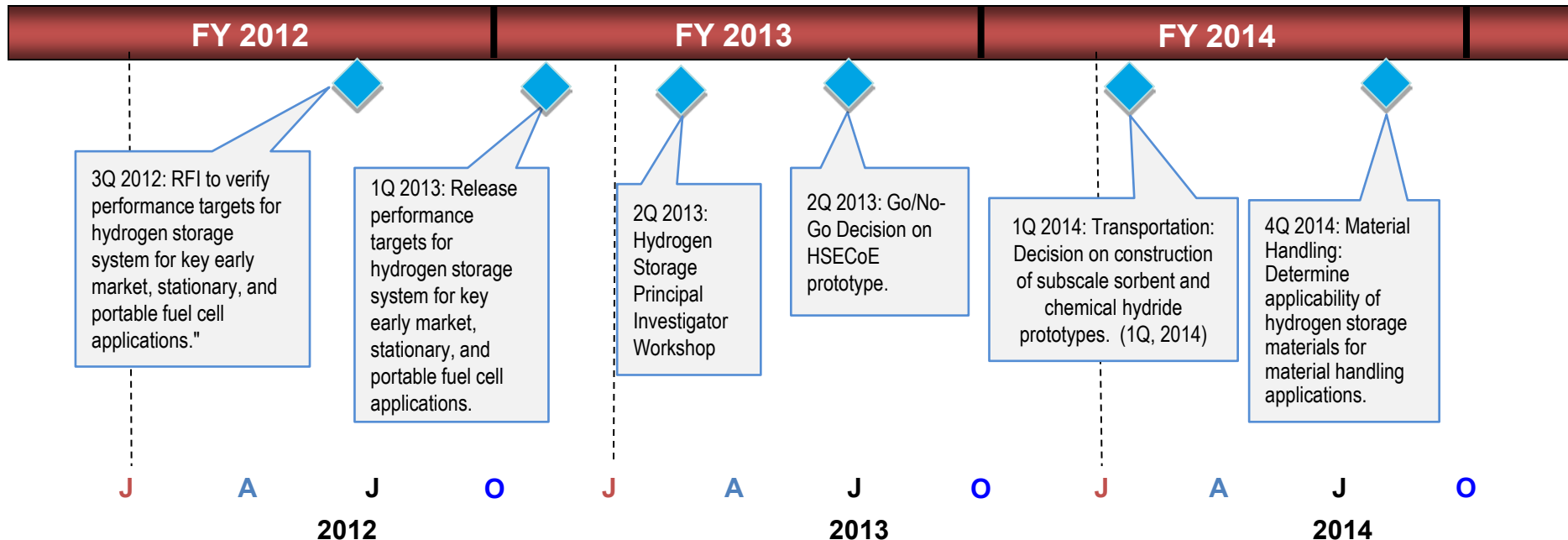
Summary of activities and upcoming milestones

Physical Storage

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

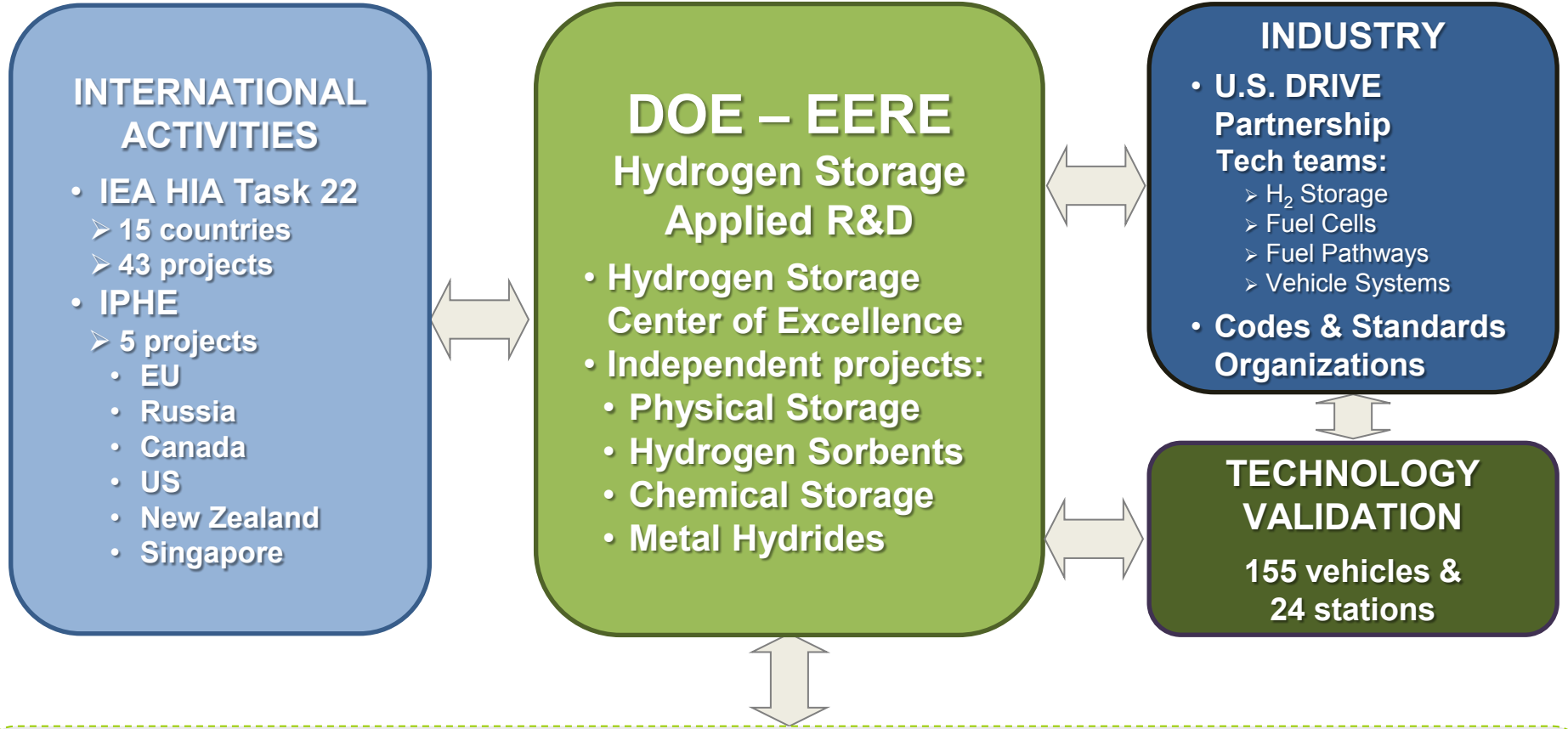
Material-based Storage

- 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..



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:
 - H₂ 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

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Katie Randolph
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Kathleen O'Malley
Support contractor
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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



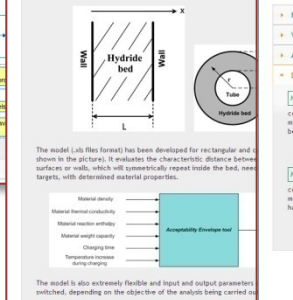
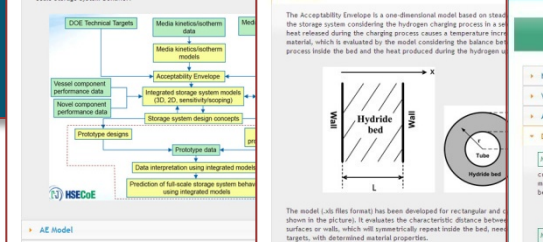
Model Download



Identification of User



www.HSECoE.org



Hydrogen Storage Engineering CENTER OF EXCELLENCE

Home Mission Partners Approach Technology Areas Progress Technical Gap Models Contact

Models

News

- What is the metal hydride AE?
- AE Model
- Downloads

Downloads

Metal hydride AE for rectangular coordinates (IMAREC) The IMAREC 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 achieve determined targets, with selected material properties. The model has been implemented with different boundary conditions.

Download Model

Metal hydride AE for cylindrical coordinates (IMACEC) The IMACEC 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. We will use your information to see the number of users. We do not share any of our user with third parties.

E-mail *

Please Verify *

2012 Progress: Predicting Metal Hydride Requirements

- Enthalpy such that waste heat is not enough

❖ Attributes

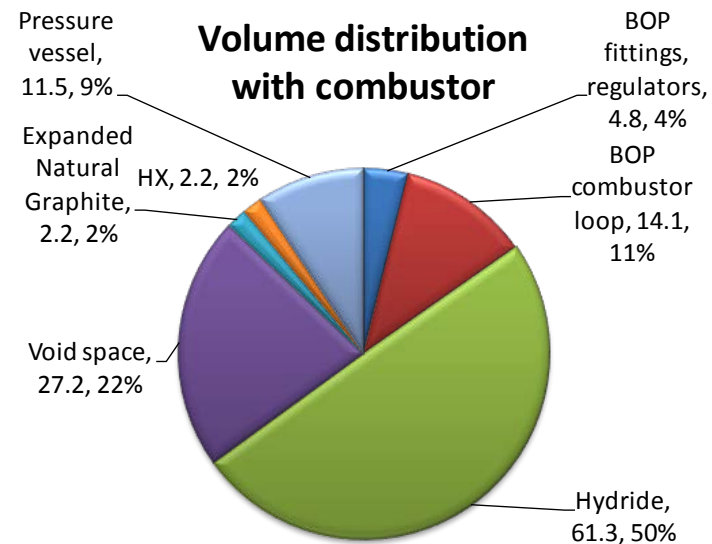
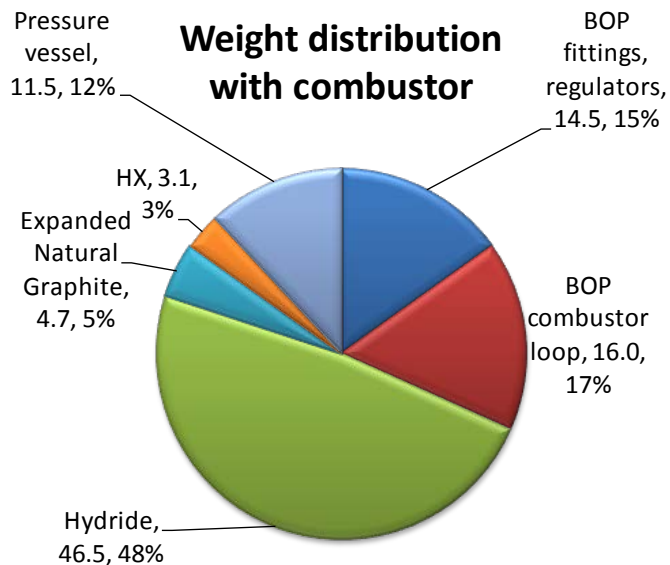
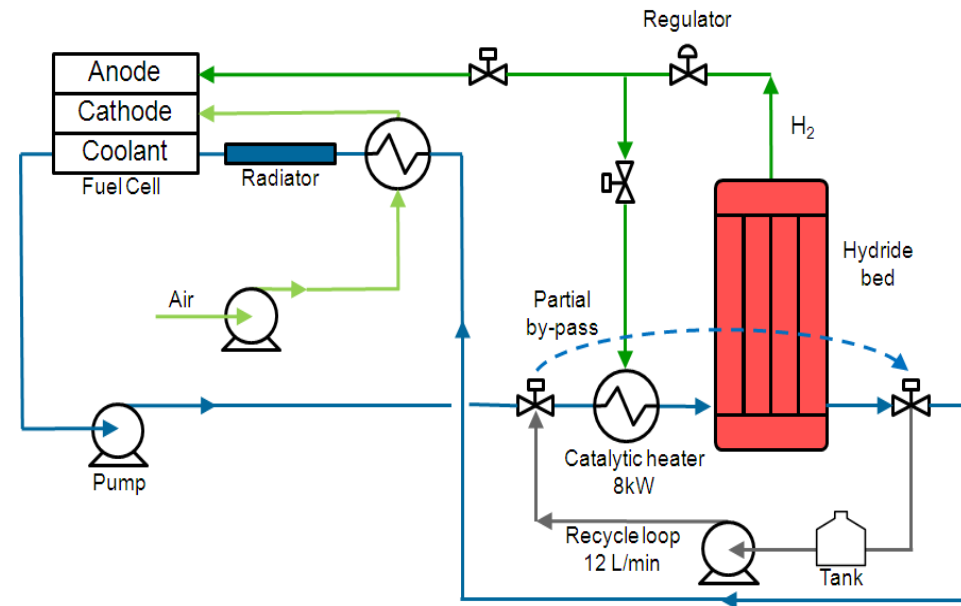
- Mix of fuel cell coolant and recycled fluid used for warm-up and to maintain T_{tank} .
- No separate buffer tank: use H_2 in pores.

❖ Media Characteristics

- $\Delta H = -40 \text{ kJ/mol-}H_2$ ($T_{5 \text{ bar}} = 122.8 \text{ }^\circ\text{C}$)
- 17 wt.% pure material capacity

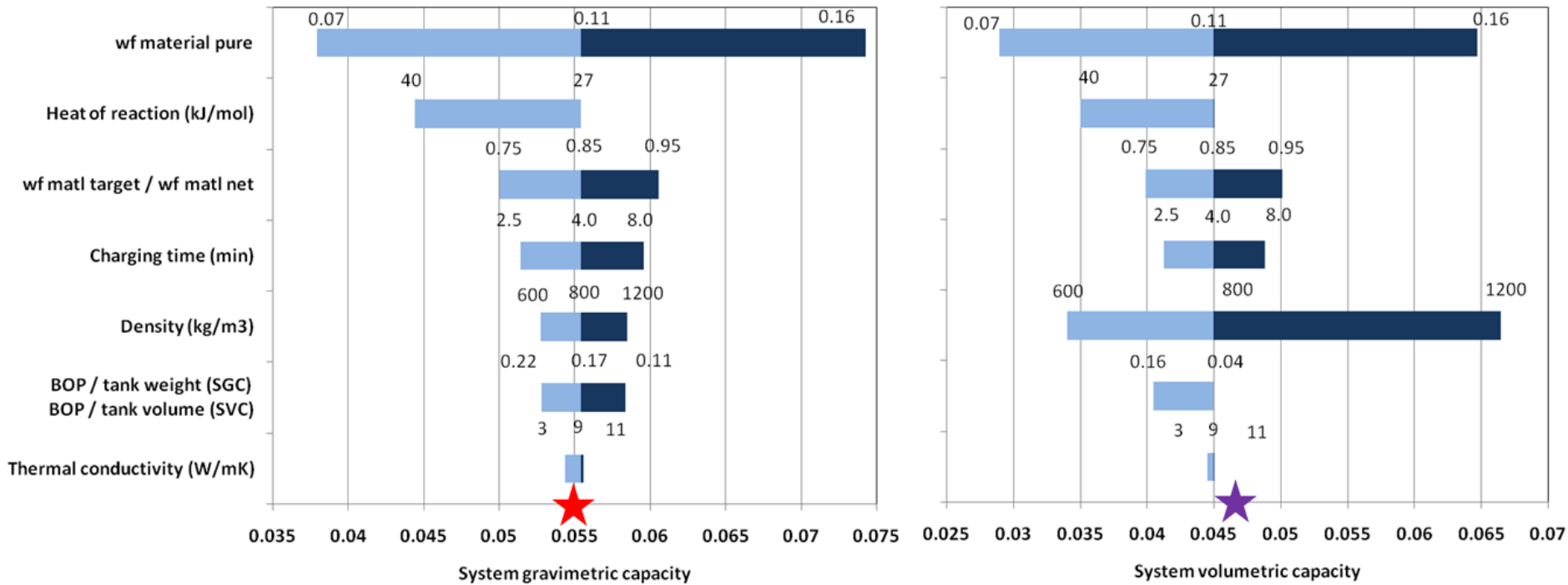
❖ Results

- Satisfies targets except system efficiency.
- On-board efficiency: ~81%
- System: 103 kg, 126 liters
- Operating at 130°C delivers $5.4 \text{ kg-}H_2$
(delivered + combusted: $6.6 \text{ kg-}H_2$)



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/m³
- 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

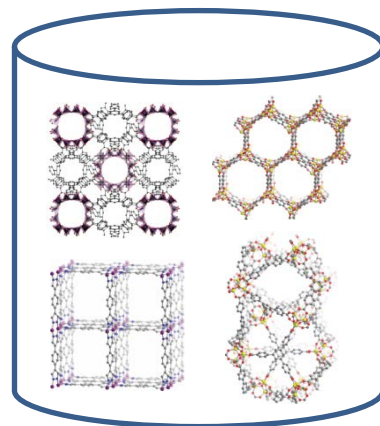
Project Lead: **Lawrence Berkeley National Laboratory** –

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

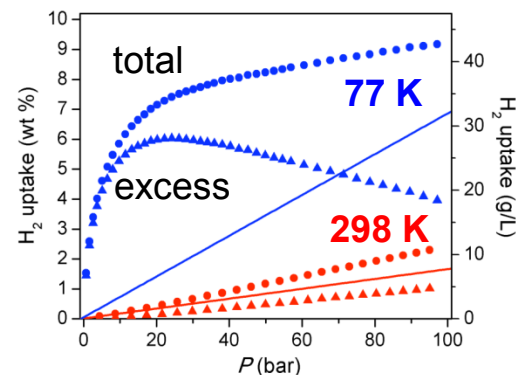
- develop and test “metal-organic framework” materials;
- surfaces allowing high charge density;
- pores engineered to enable hydrogen storage at near-ambient temperatures.



structural database



opposing
surface
algorithm



experimental isotherms

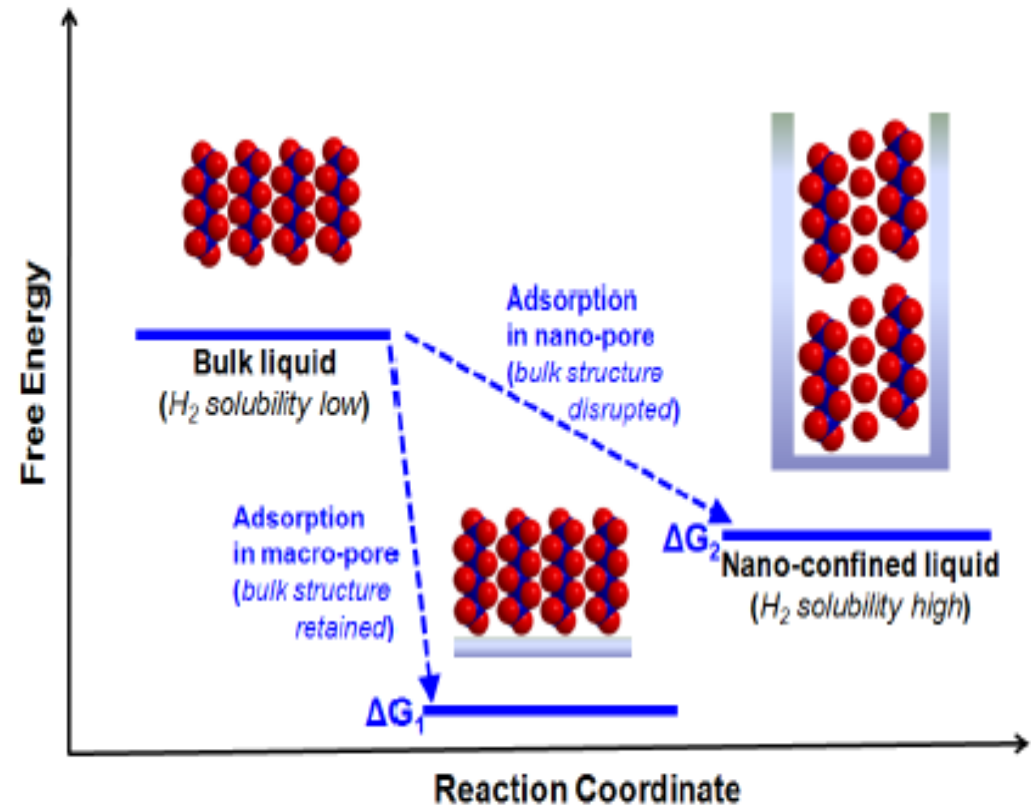
2012 Progress: *New Project – Novel Concept*

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;

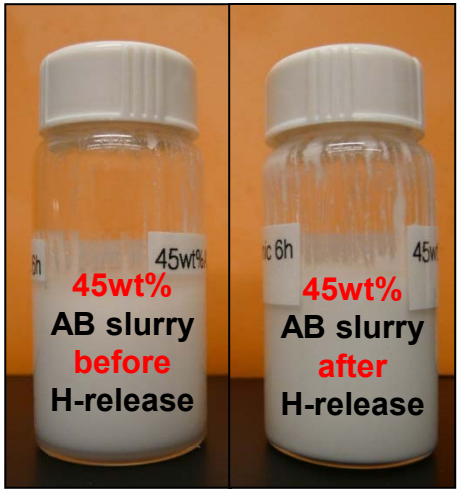
- liquids nano-confined in porous structures absorb significantly more gas;
- develop composite materials capable of dissolving up to **50 times greater** quantities than bulk liquid;
- enable a high density, ambient temperature, compact hydrogen storage.



2012 Progress: Development of fluid AB materials

Liquid-Slurry Chemical Hydrogen Storage Development (AB Slurry)

Down-select to AB silicone oil slurry
45wt% AB slurry: ~7wt% H₂

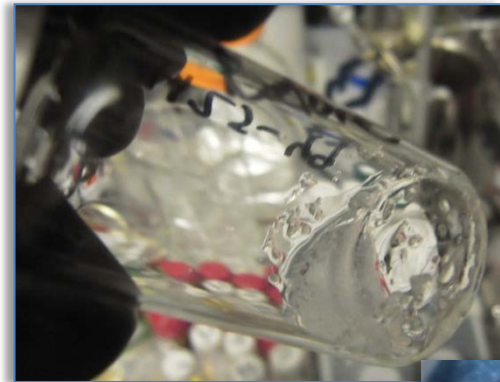


Pacific Northwest
NATIONAL LABORATORY
Source: PNNL

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

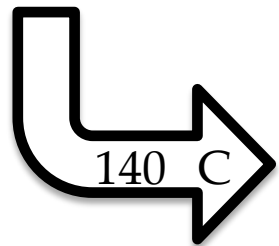
	AB slurry before H-release	AB slurry after H-release	Measured Temp. (°C)
Plastic viscosity (cP)	~ 617	~ 442	25
Yield stress (Pa)	~ 48	~ 3.7	25

Fluid Phase H₂ Storage Material Development (Liquid AB)



New Additives Synthesized

Additive amine-boranes have 3-4 wt. % usable H₂ and maintain fluid phase.



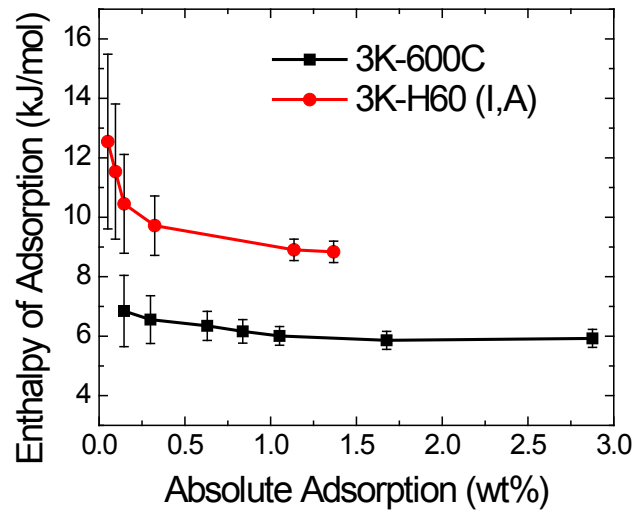
Picture @ Room Temperature

20 wt. %AB in hexylAB (6.0 wt. % H₂) transforms from a slurry to liquid upon dehydrogenation

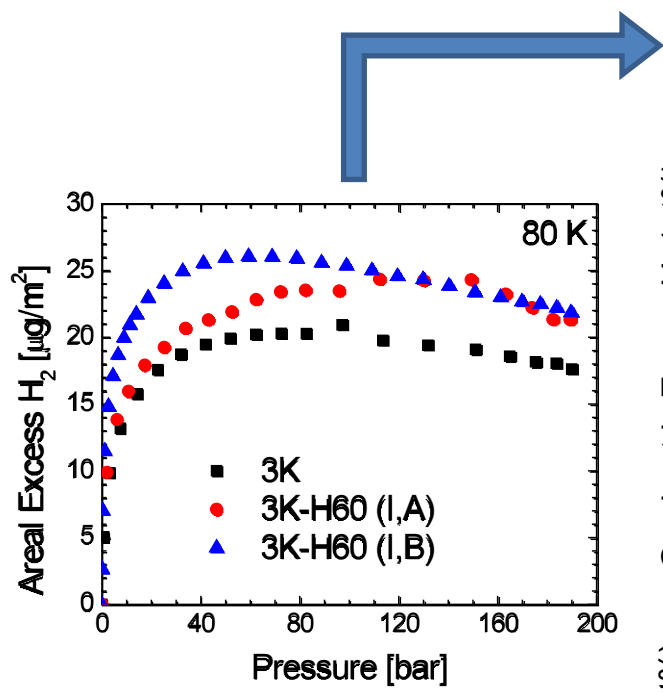
Source: LANL Los Alamos NATIONAL LABORATORY

2012 Progress: Improving Sorbents

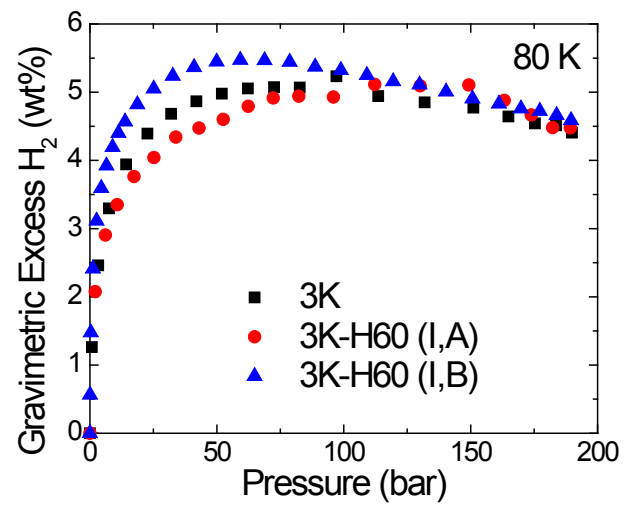
*Achieved ~9% Boron Doping with <15% Reduction in Surface Area
Leading to Higher Binding Energies and Uptake*



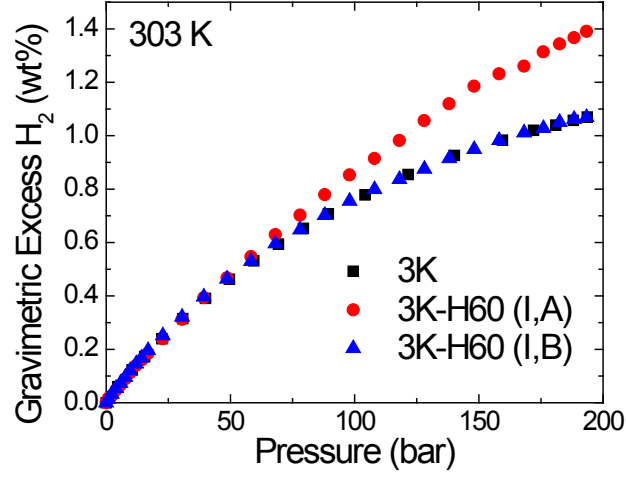
Increases Binding Energy as Predicted by Theory



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



Leads to Increase in Uptake per Unit Surface Area



Sample	B:C %	Σ_{N_2} (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

