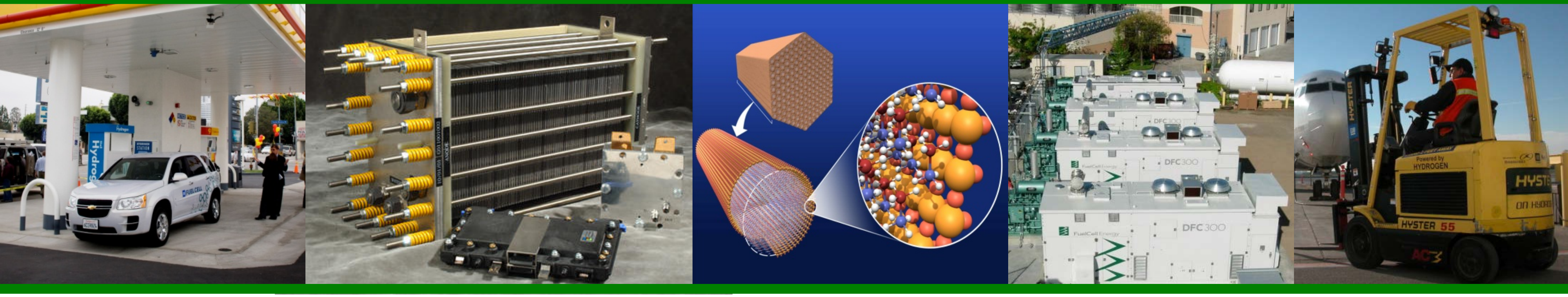
U.S. DEPARTMENT OF
ENERGY



Hydrogen Storage Overview

Ned T. Stetson

2012 Annual Merit Review and Peer Evaluation Meeting
(May 15, 2012)

Goal and Objectives

U.S. DEPARTMENT OF ENERGY

***Goal:* Develop and demonstrate viable hydrogen 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

U.S. DEPARTMENT OF ENERGY

Storage to enable a driving range of greater than 300 miles, while meeting vehicular packaging, cost and performance requirements across all vehicle platforms to achieve significant market penetration

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 CF cost due to the precursor**
- **Other applications are being commercialized now where H_2 storage is a barrier**

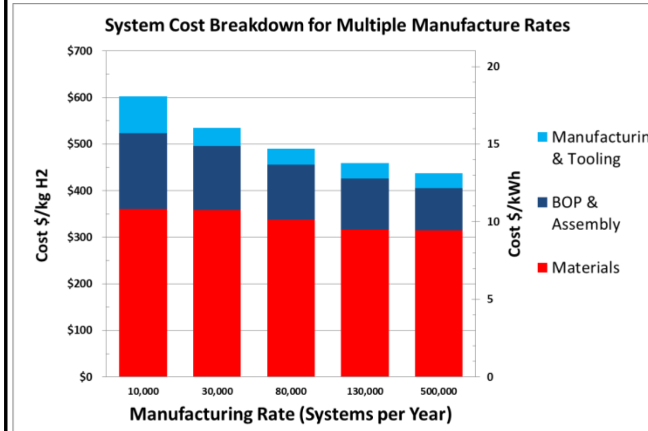
Long-term Options

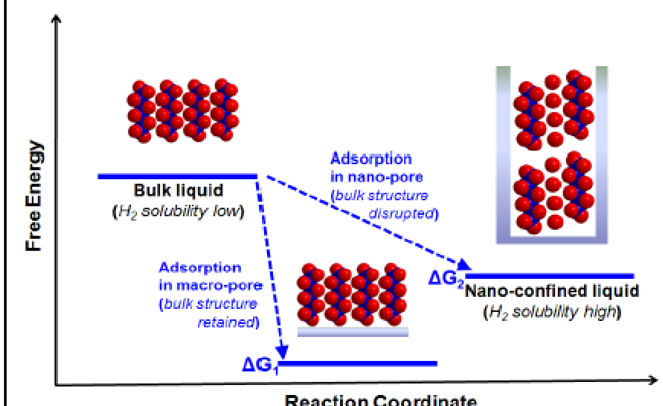
Materials-based solutions targeted to meet all on-board storage targets simultaneously

- **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





*: Greater than a 400 mile driving range 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

Current Status

U.S. DEPARTMENT OF ENERGY

Analyses show 2017 onboard vehicle gravimetric and volumetric targets are within reach of some H_2 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

Challenges: Preliminary Targets for MHE

U.S. DEPARTMENT OF ENERGY

Hydrogen fuel cells are finding acceptance in material handling applications (e.g., forklifts), however 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

U.S. DEPARTMENT OF ENERGY

Portable Hydrogen Fuel Cell appliances are coming to market, hydrogen storage is a key for their successful commercialization

Storage Parameter	***Units***	***2015***	***2020***
System Gravimetric Capacity: *Usable, specific-energy from H_2 (net useful energy/max system mass)*	*kWh/kg* *(kg H_2/kg system)*	0.3 (0.01)	1.0 (0.03)
System Volumetric Capacity: *Usable energy density from H_2 (net useful energy/max system volume)*	*kWh/L* *(kg H_2/L system)*	1.0 (0.03)	1.7 (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	

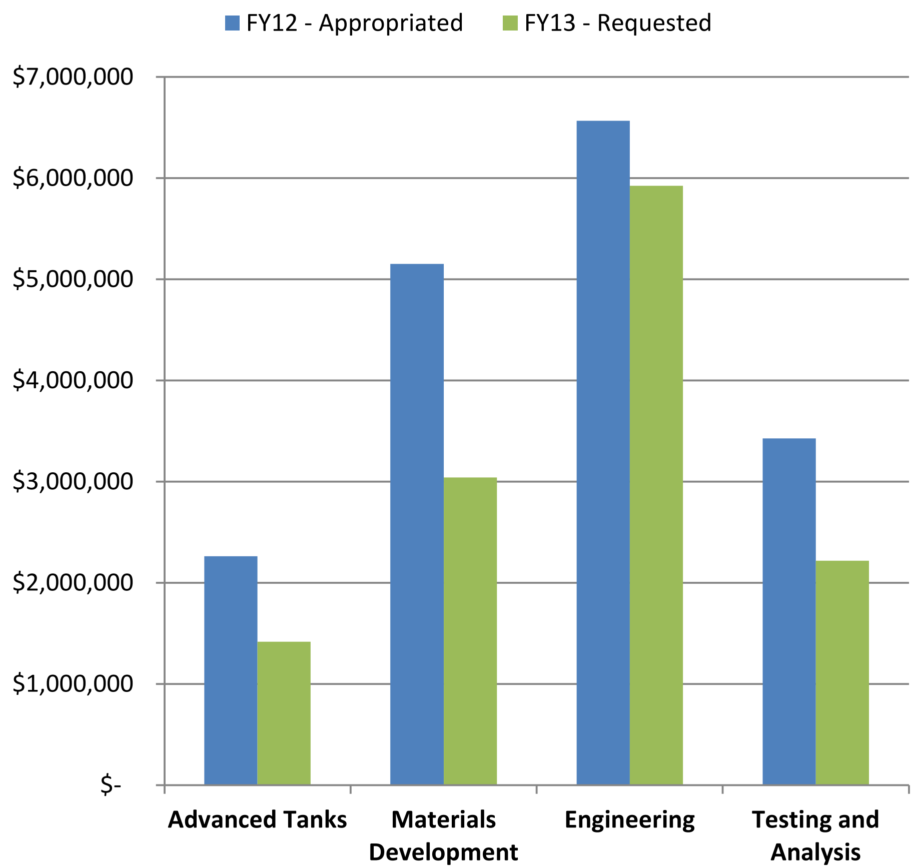
Preliminary H_2 storage targets developed for Portable Power, RFI issued to gather input from stakeholders on appropriateness of targets.

Hydrogen Storage Budget

U.S. DEPARTMENT OF ENERGY

FY 2013 Request = $13M

FY 2012 Appropriation = $17.4M



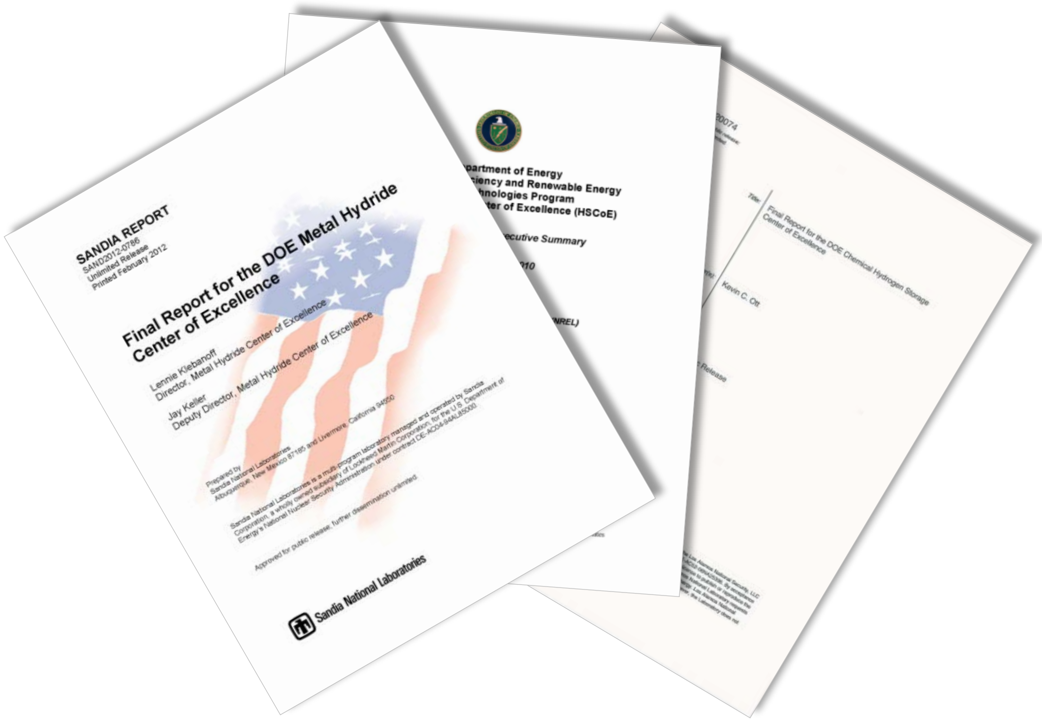
EMPHASIS

- 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

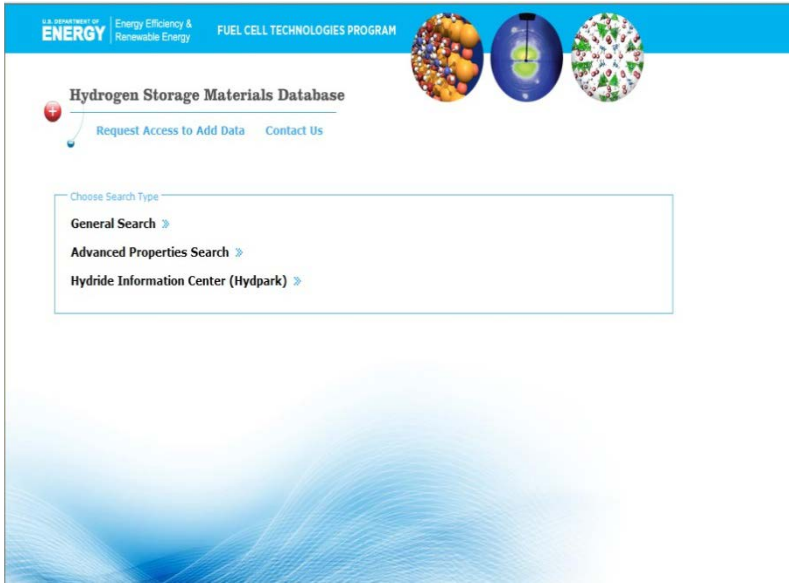
Getting the word out on the progress made in developing and understanding hydrogen storage material properties!



Final reports and Executive Summaries from the 3 Hydrogen Storage Materials CoEs available through the DOE website: http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage

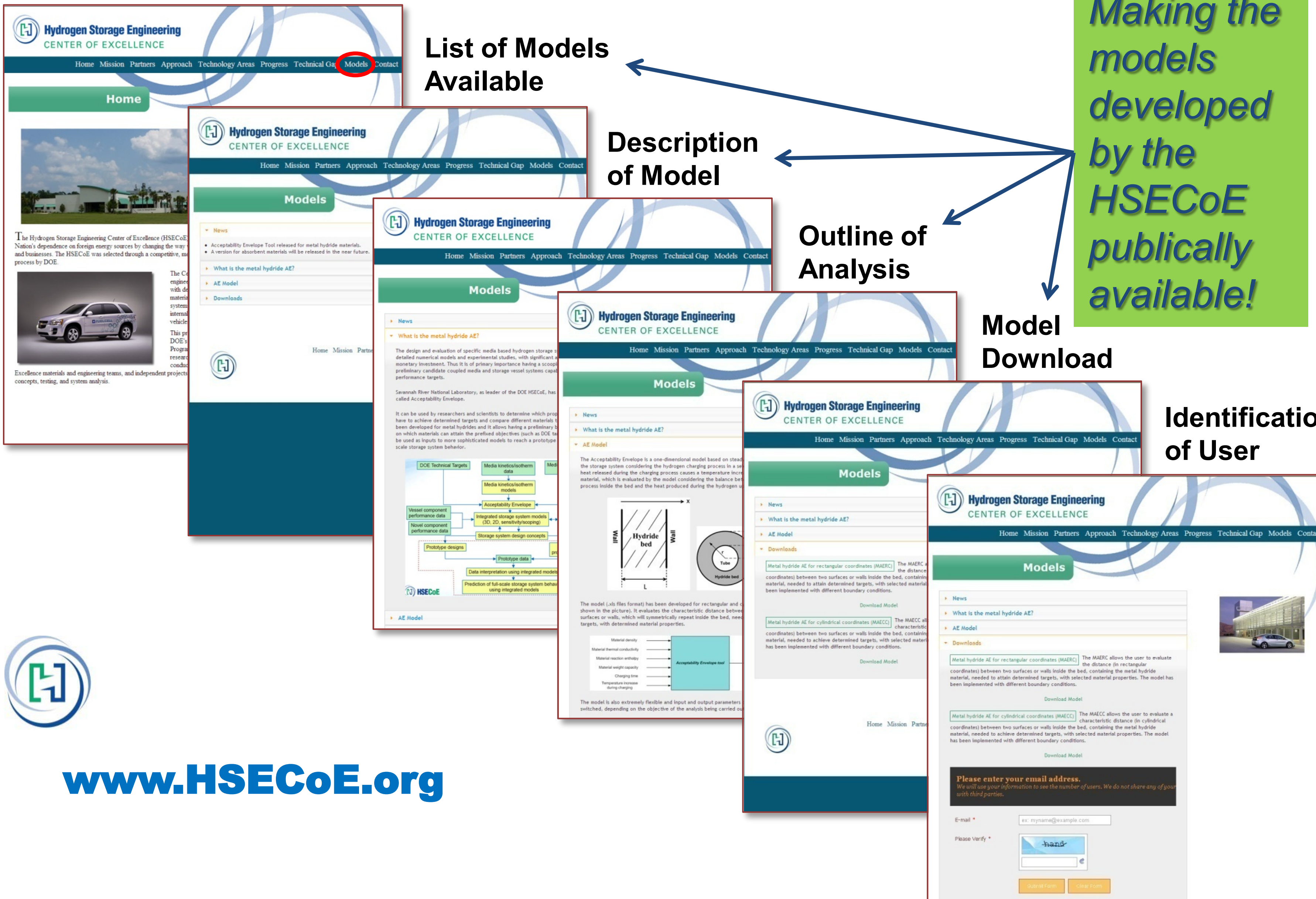
Publically available, searchable database on Hydrogen Storage Materials Properties launched: http://hydrogenmaterialssearch.govtools.us/

Still looking to populate it with more data!



2012 Progress: Getting tools out for public use

U.S. DEPARTMENT OF ENERGY



List of Models Available

Description of Model

Outline of Analysis

Model Download

Identification of User

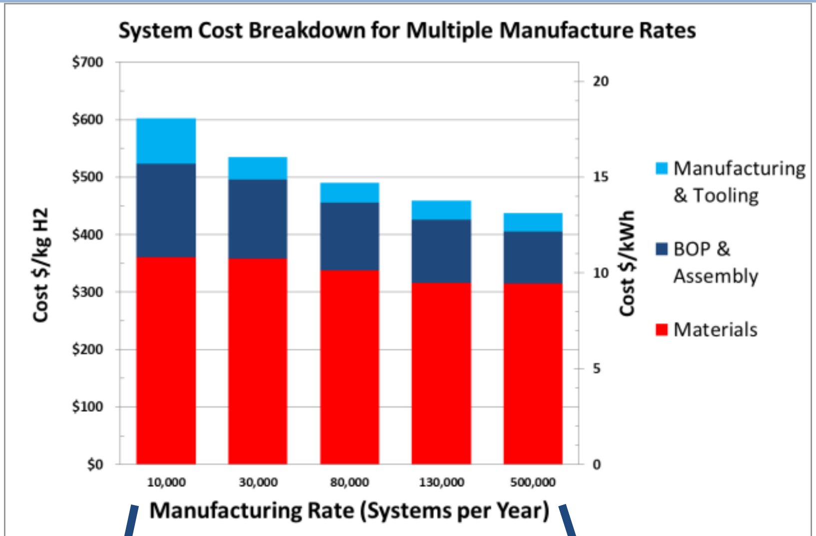
Making the models developed by the HSECoE publically available!

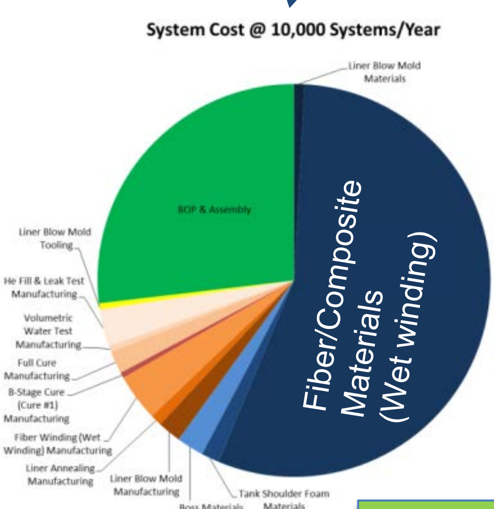
www.HSECoE.org

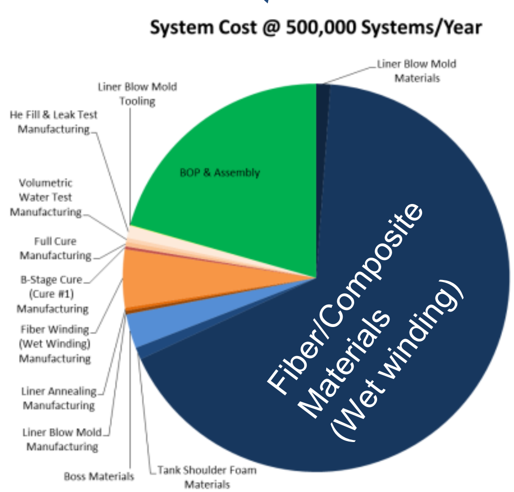
Tanks: Cost Analysis & Progress

U.S. DEPARTMENT OF ENERGY

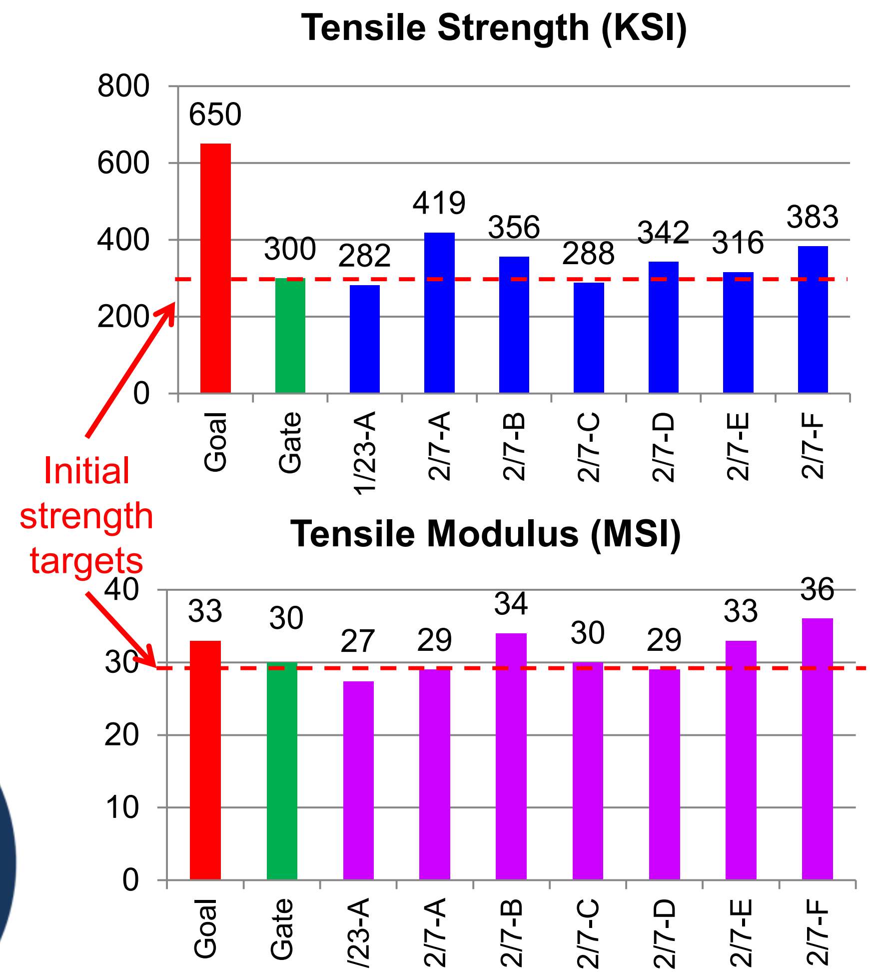
Tank costs come down with high volume manufacturing, but still too high!
Low-cost PAN precursors offer opportunity to reduce CF costs by up to 30%.







Carbon fiber costs dominate!



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

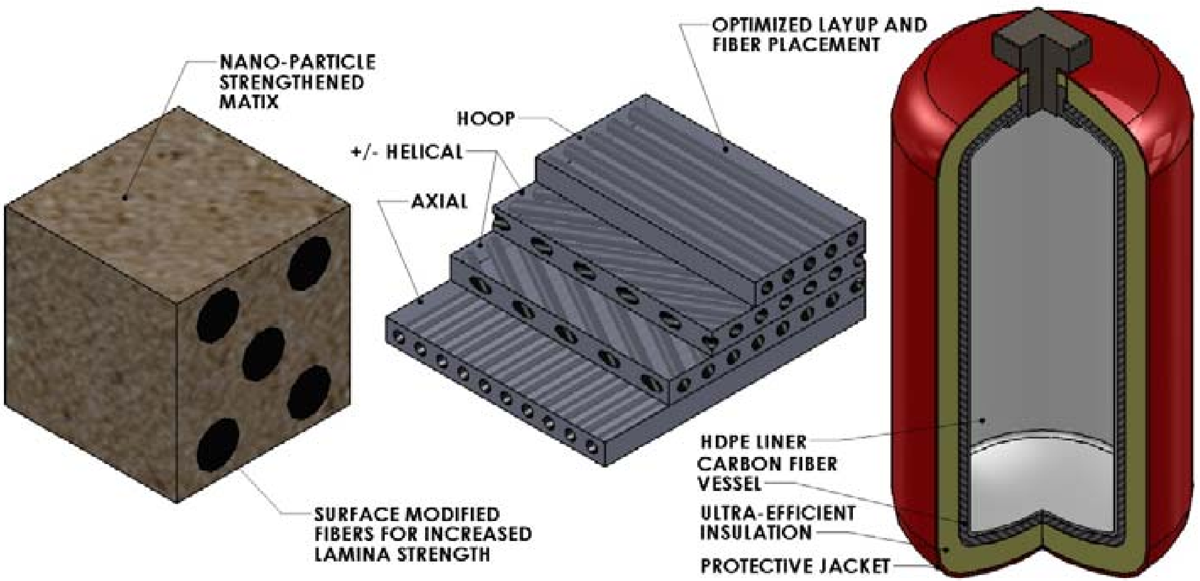
2012 Progress: *New Advanced Tank Project*

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.,

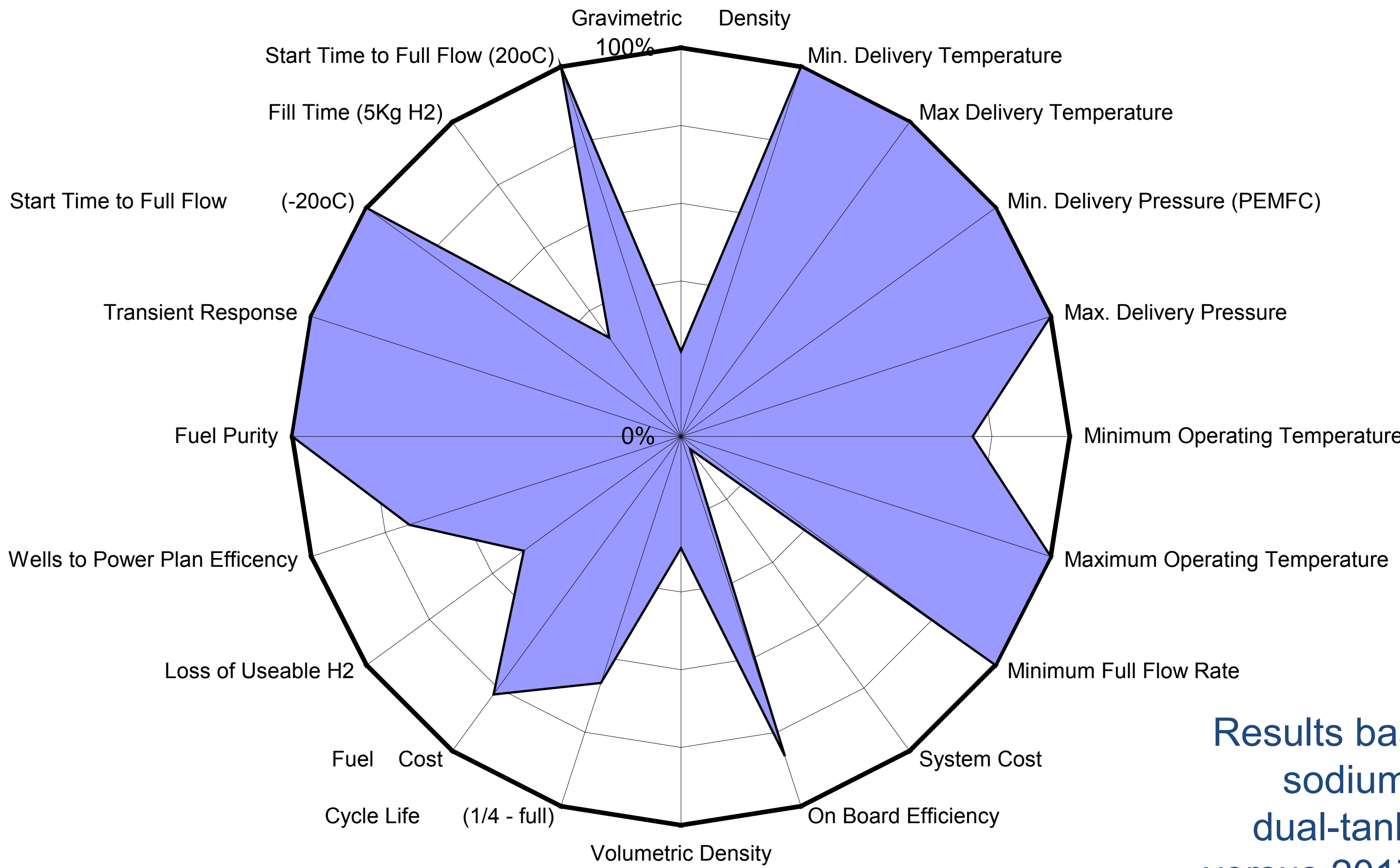
- Coordinated approach for compressed H_2 tank costs reduction focuses on:
  - improved carbon fiber composite materials; design and manufacture of hydrogen storage tanks;
  - investigates use of "cold" hydrogen, including impact on the infrastructure;
  - targets cost reduction by more than 1/3 compared to current projections.



Pacific Northwest NATIONAL LABORATORY

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

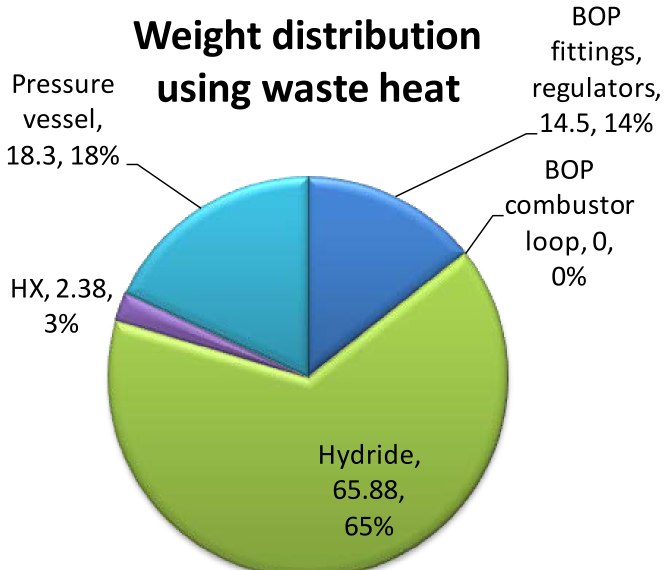


Results based on a sodium alanate dual-tank system versus 2017 targets

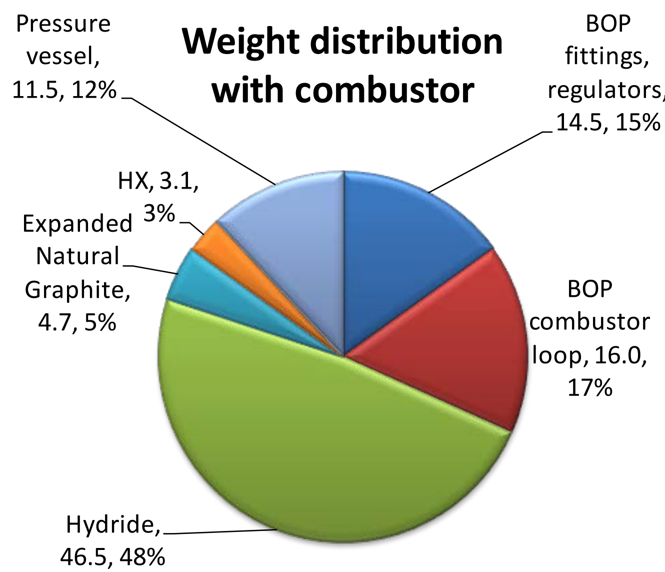
No-Go Decision made for Metal Hydride system within the HSECoE, this does not preclude further metal hydride materials development.

2012 Progress: Predicting Metal Hydride Requirements - effect of reaction enthalpy

- Attributes
  - Very simple system.
  - Fuel cell waste heat stream used
  - No separate buffer tank: use H_2 in pores.
- **Media Characteristics**
  - **ΔH = 27 kJ/mol-H_2 ($T_{5\ bar}$ = 20.7 °C)**
  - **11 wt.% material capacity**
- Results
  - Satisfies all targets.
  - On-board efficiency: ~100%
  - System: 101 kg, 124 liters

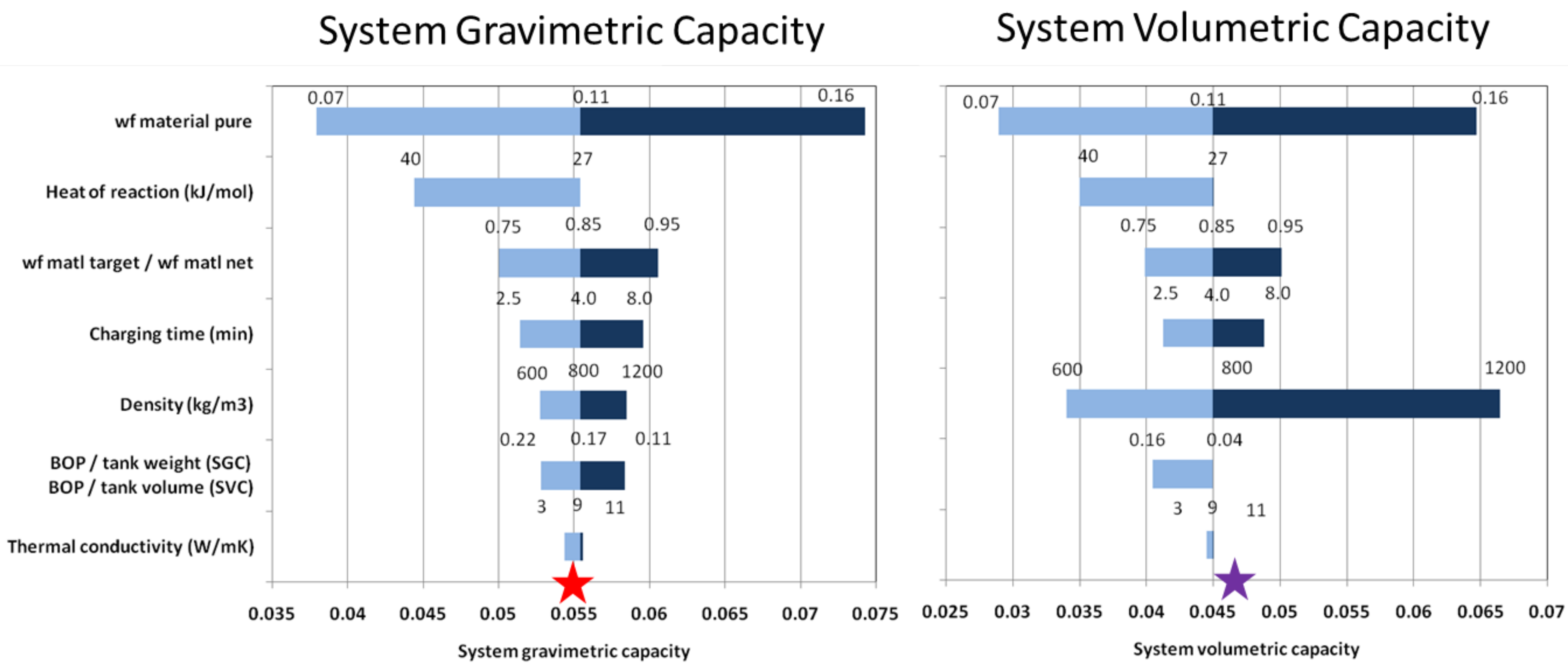


- Attributes
  - Mix of fuel cell coolant and recycled fluid used for warm-up and to maintain T_{tank}.
- **Media Characteristics**
  - **ΔH = -40 kJ/mol-H_2 ($T_{5\ bar}$ = 122.8 °C)**
  - **17 wt.% pure material capacity**
- Results
  - Satisfies targets except system efficiency.
  - On-board efficiency: ~81%
  - System: 103 kg, 126 liters
  - Operating at 130°C delivers 5.4 kg-H_2 (delivered + combusted: 6.6 kg-H_2)



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

U.S. DEPARTMENT OF ENERGY

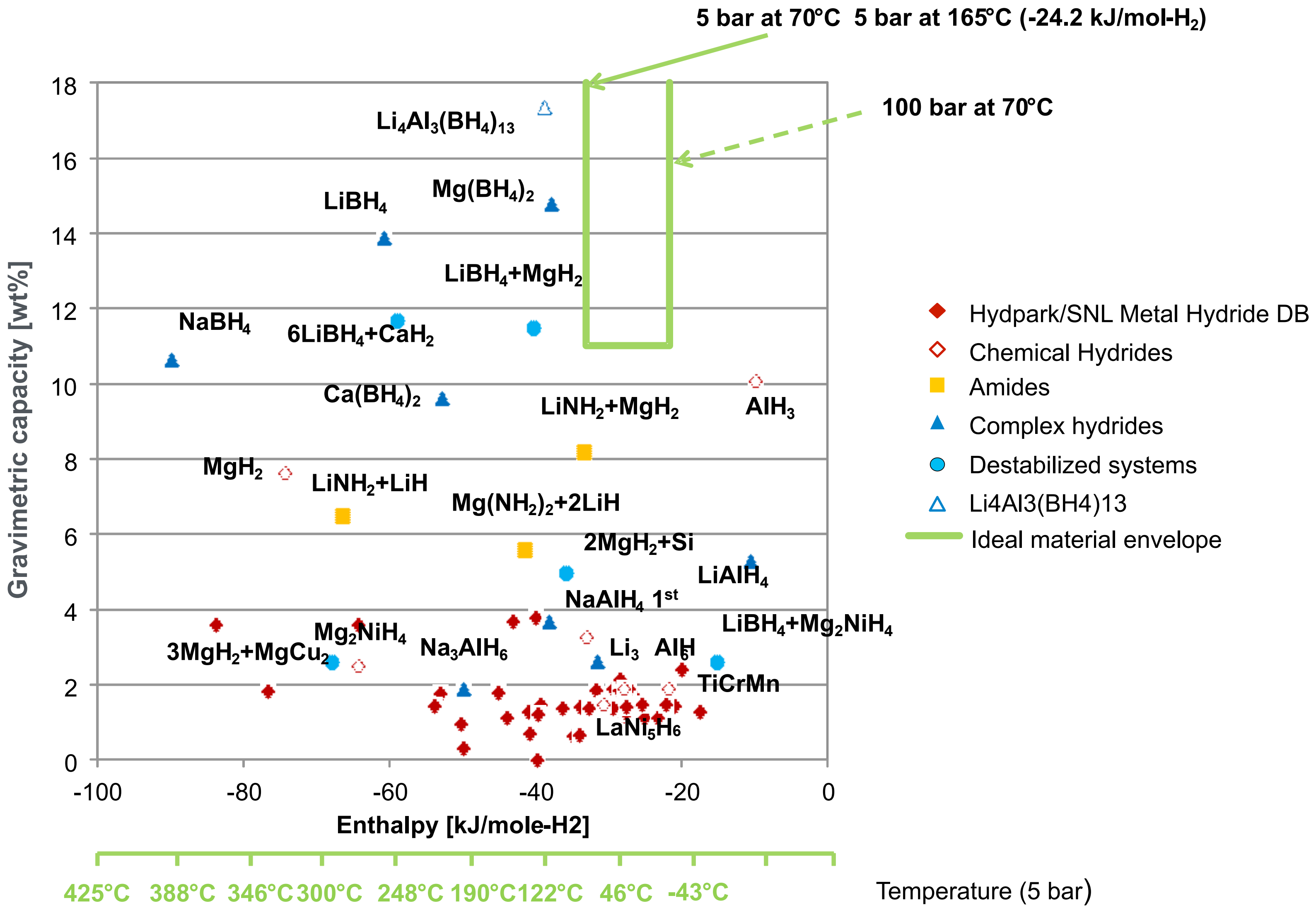


★ ★ **DOE 2017 targets, gravimetric and volumetric capacity, respectively**

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: Status of MH materials to meet onboard storage requirements

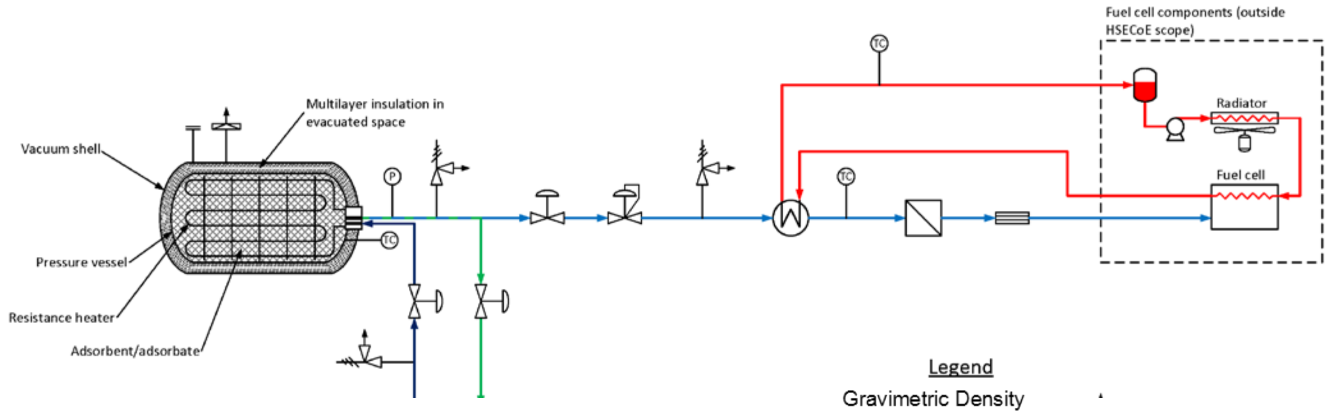


Material property requirements can be determined to focus material discovery efforts

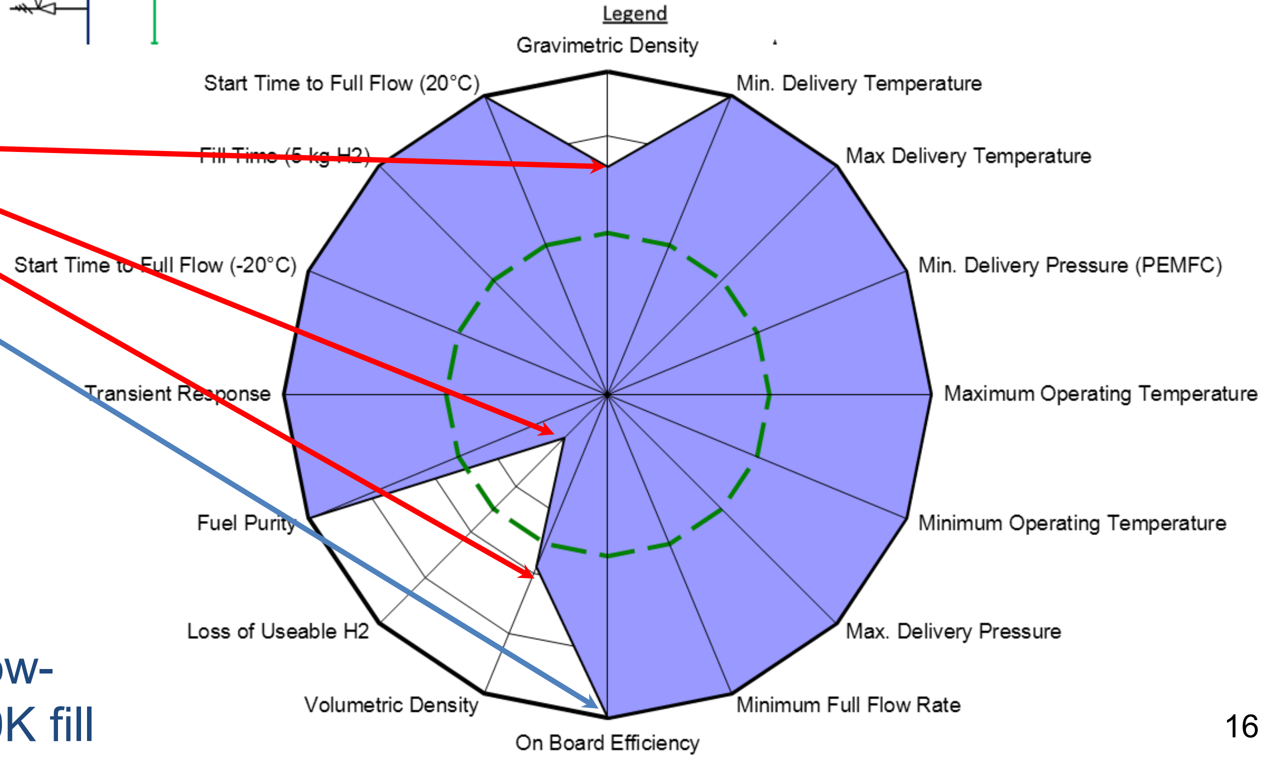
2012 Progress: HSECoE – Cryo-sorbent Systems

U.S. DEPARTMENT OF ENERGY

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

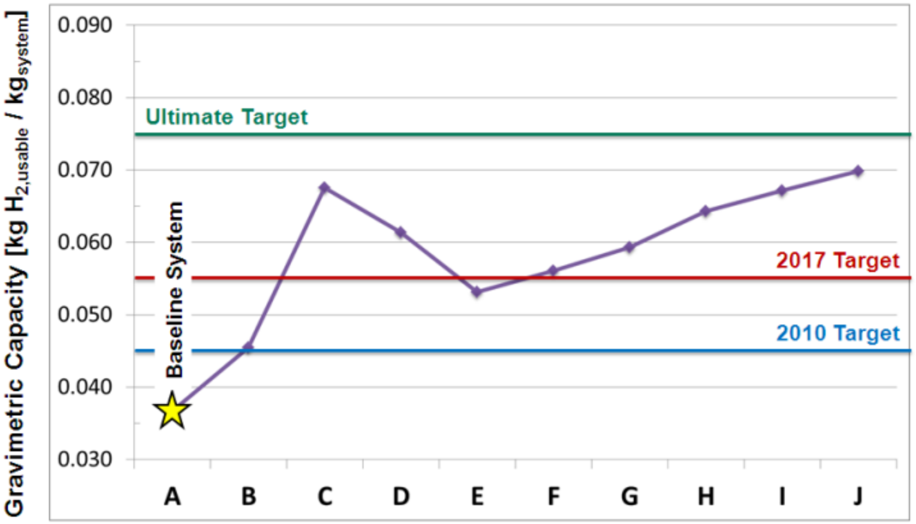


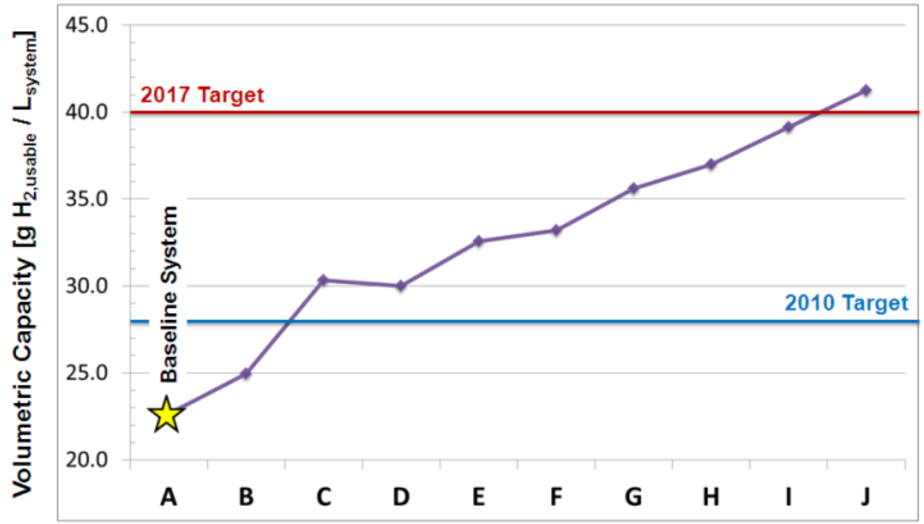
AX-21, 200 bar, flow-through design, 80K fill

2012 Progress: HSECoE – Sorbent System Improvement Pathways

U.S. DEPARTMENT OF ENERGY

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: 2 *New Projects – Sorbents*

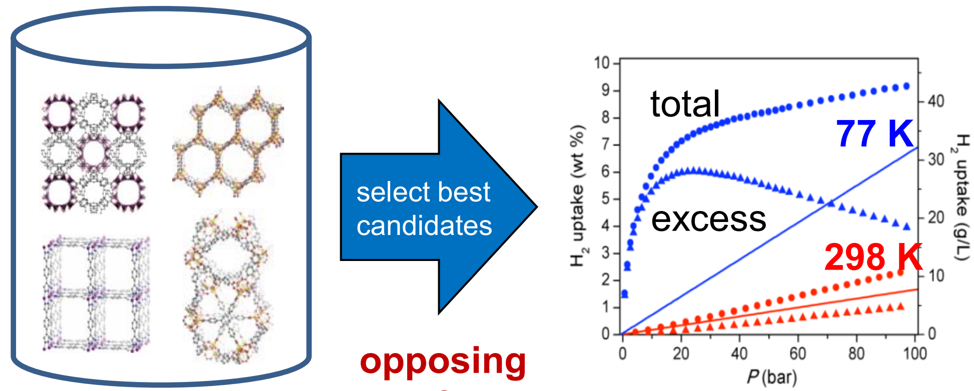
U.S. DEPARTMENT OF ENERGY

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

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

Partners: NIST and GM

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



structural database

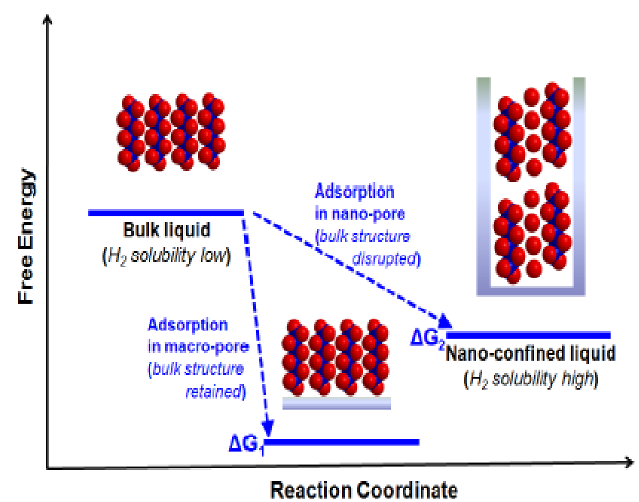
opposing surface algorithm

experimental isotherms

Berkeley Lab

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

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

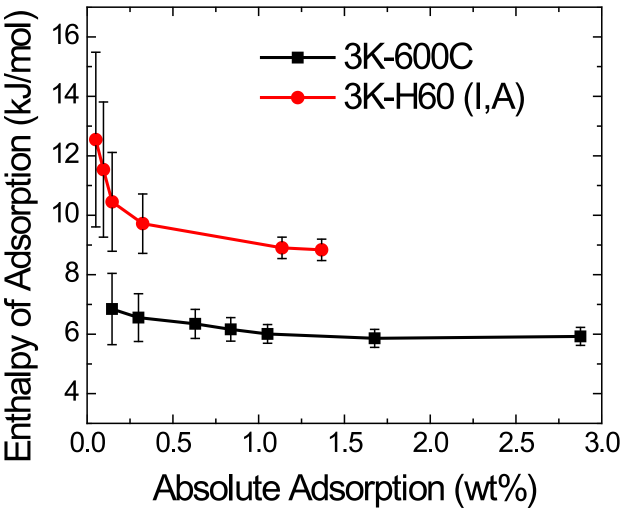


HRL LABORATORIES

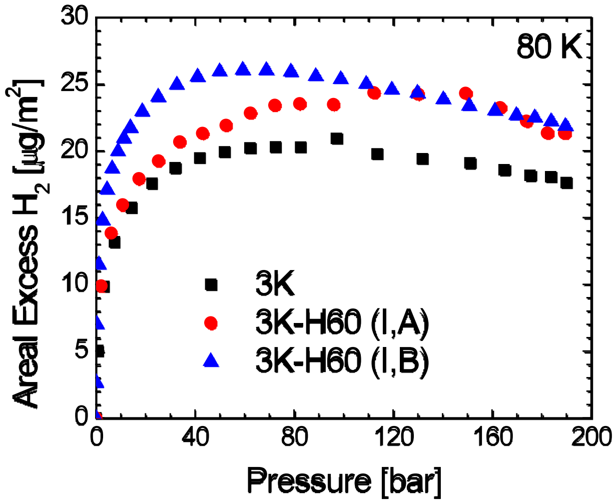
2012 Progress: *Improving Sorbents*

U.S. DEPARTMENT OF ENERGY

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

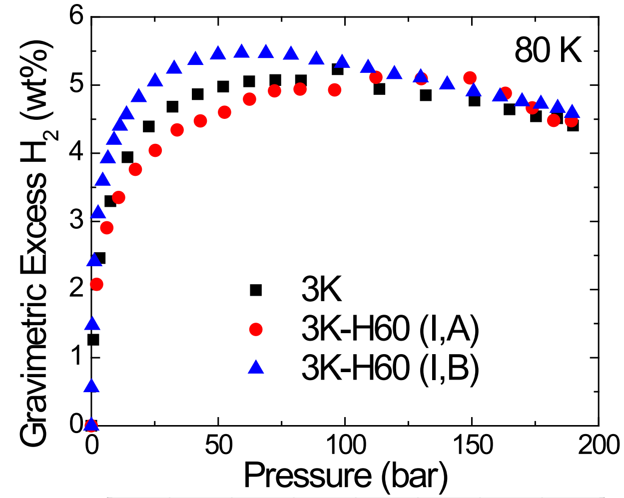


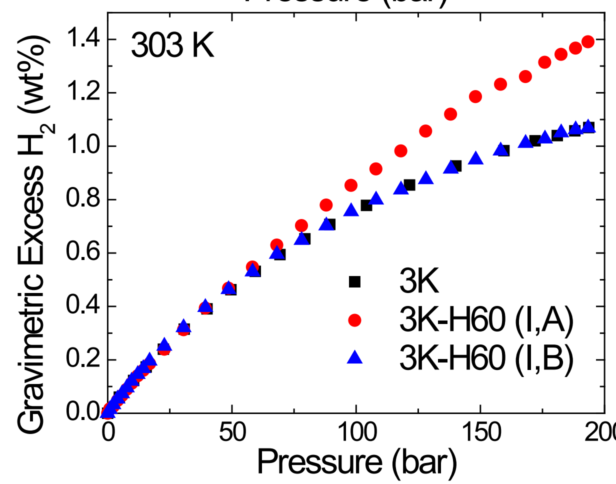
Increases Binding Energy as Predicted by Theory



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

2012 Progress: *Spillover Taskforce Update*

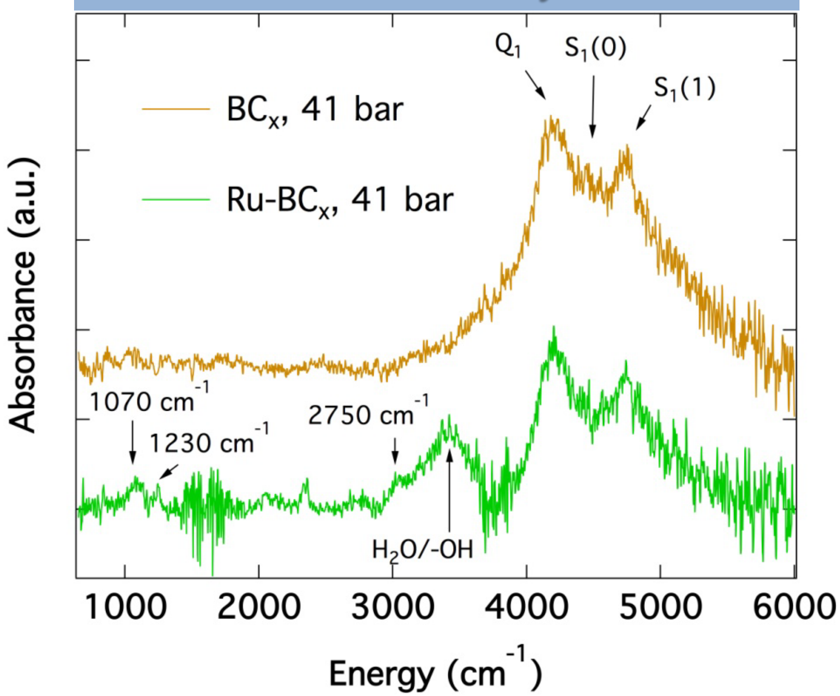
U.S. DEPARTMENT OF ENERGY

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

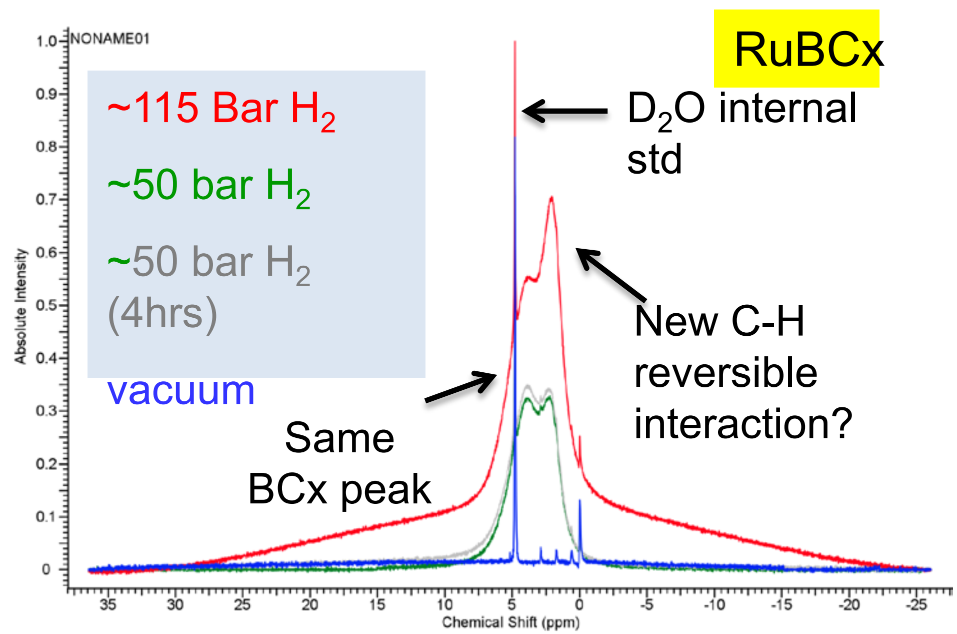
<u>Achievements</u>:

- 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

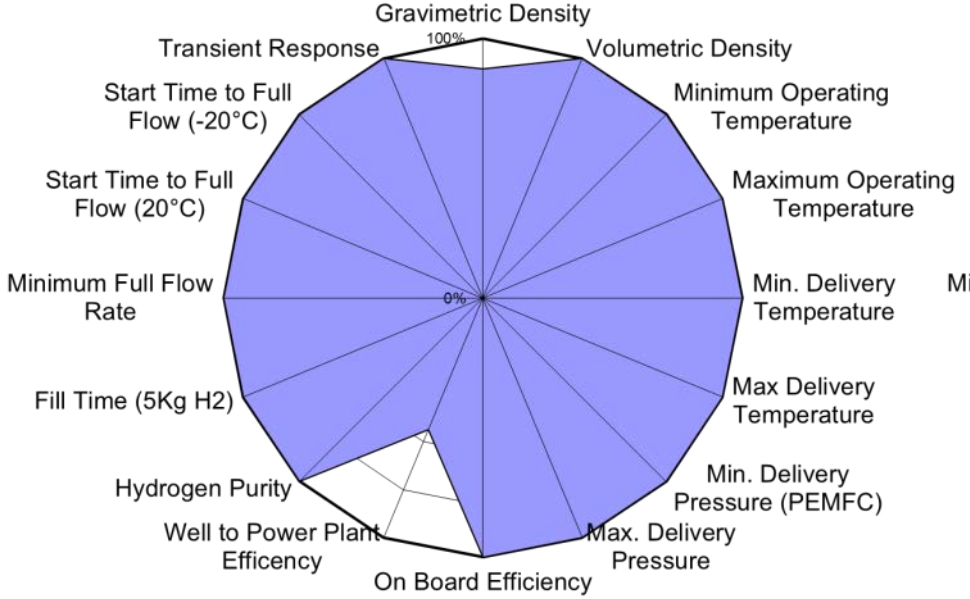


2012 Progress: HSECoE – Status of Chemical Hydrogen Systems

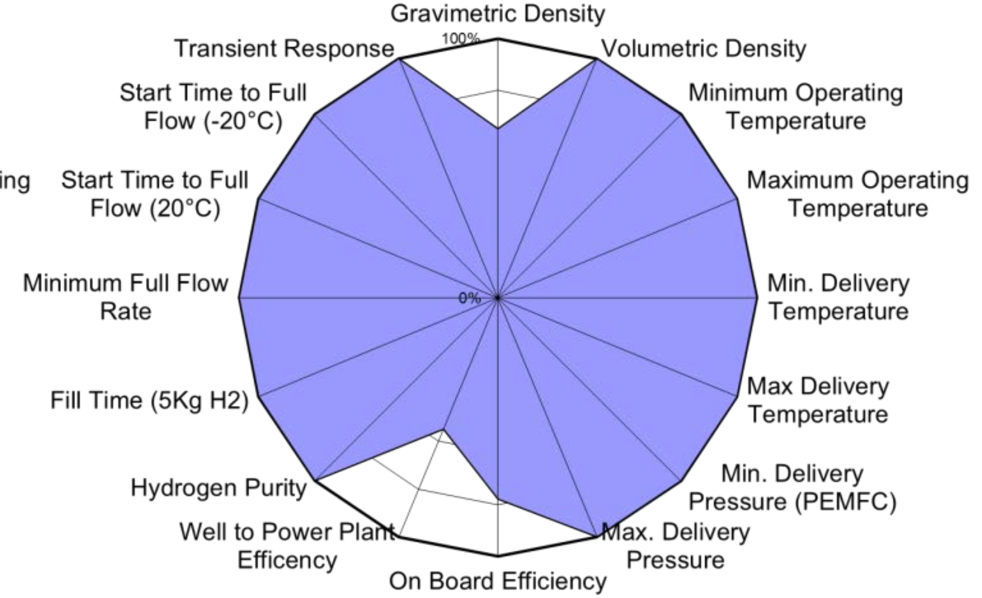
Endo- and Exothermic release material systems can meet most key DOE system performance targets for onboard vehicle applications

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

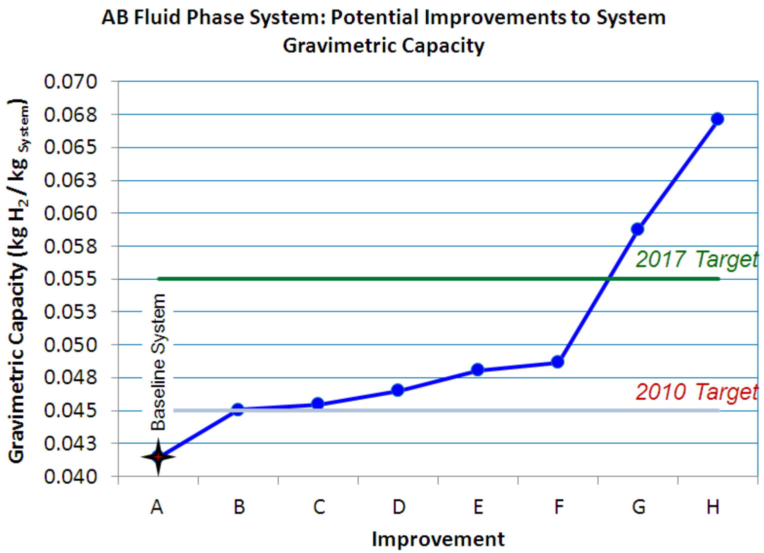


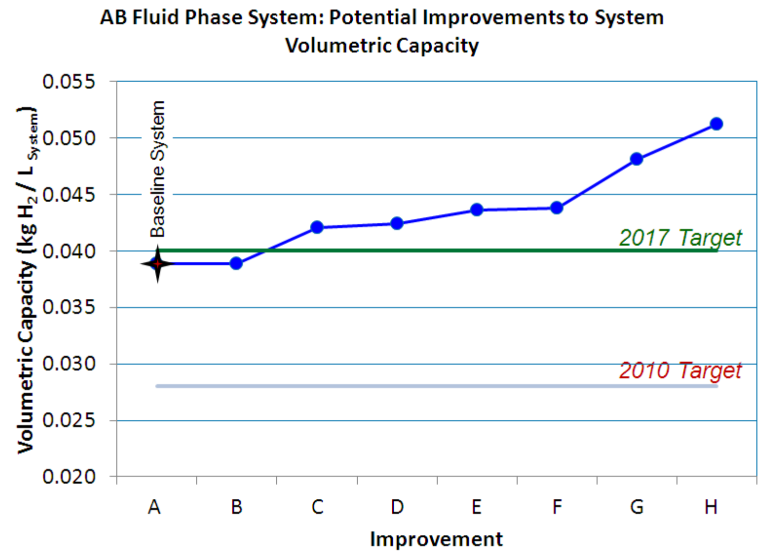
Off-board regeneration efficiency is still an issue

2012 Progress: HSECoE – Chemical Hydrogen System Improvement Pathways

U.S. DEPARTMENT OF ENERGY

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





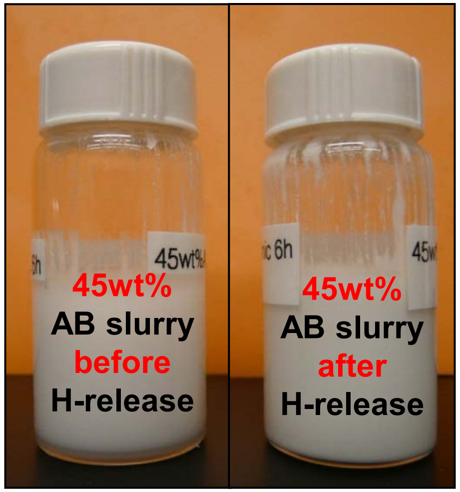
Step	Description
A	Phase 1 Baseline: 50:50 Fluid composition
B	Change from steel shell ballast tank to aluminum
C	Reduce HX from 76 kW to 38 kW
D	Reduce H_2 Wetted Tubing
E	Low Mass Borazine Scrubber
F	Low Mass Ammonia Scrubber
G	Increase AB loading from 50 to 65 wt. %
H	Increase AB loading from 65 to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

2012 Progress: 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

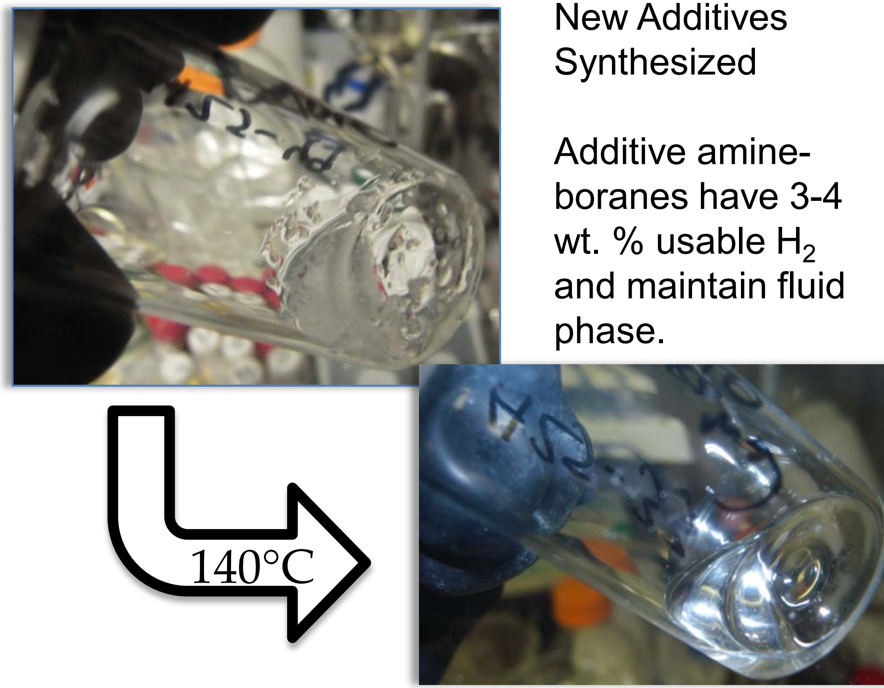
Material remains a liquid-slurry before and after H-release
Fresh slurry no settling/flocculation for 3+ months
Spent slurry settling within several hours

	AB slurry before H-release	AB slurry after H-release	Measured Temp. (°C)
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: *New Project – Liquid Carriers*

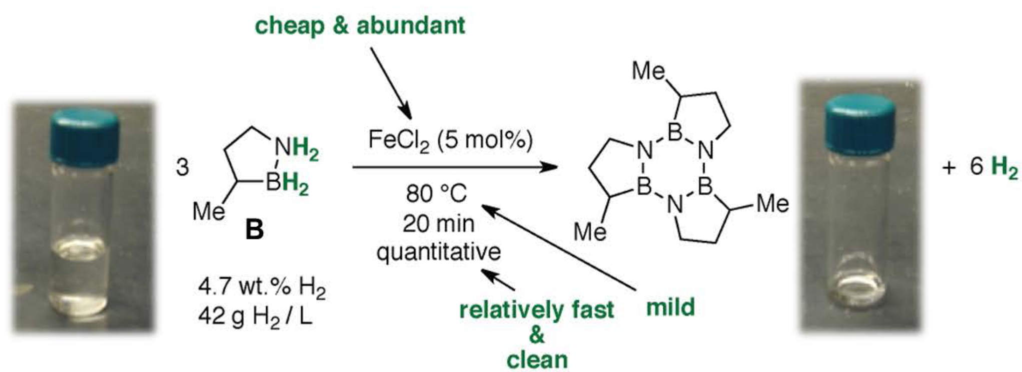
Novel Carbon (C) – Boron (B) – Nitrogen (N) containing hydrogen storage materials as liquid hydrogen carriers

Project Lead: **University of Oregon** – PI: Shih-Yuan Liu

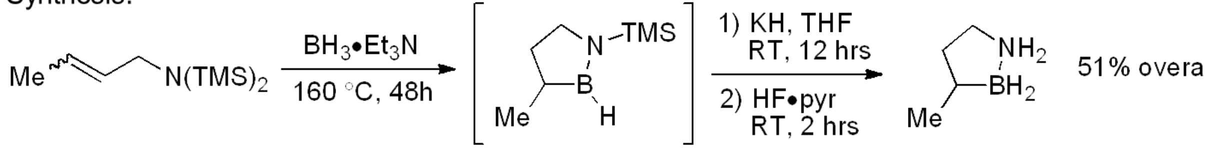
Partners: Pacific Northwest National Laboratory, Univ. of Alabama, Protonex Technology Corp.

Description: 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:



UNIVERSITY OF OREGON

Summary

U.S. DEPARTMENT OF ENERGY

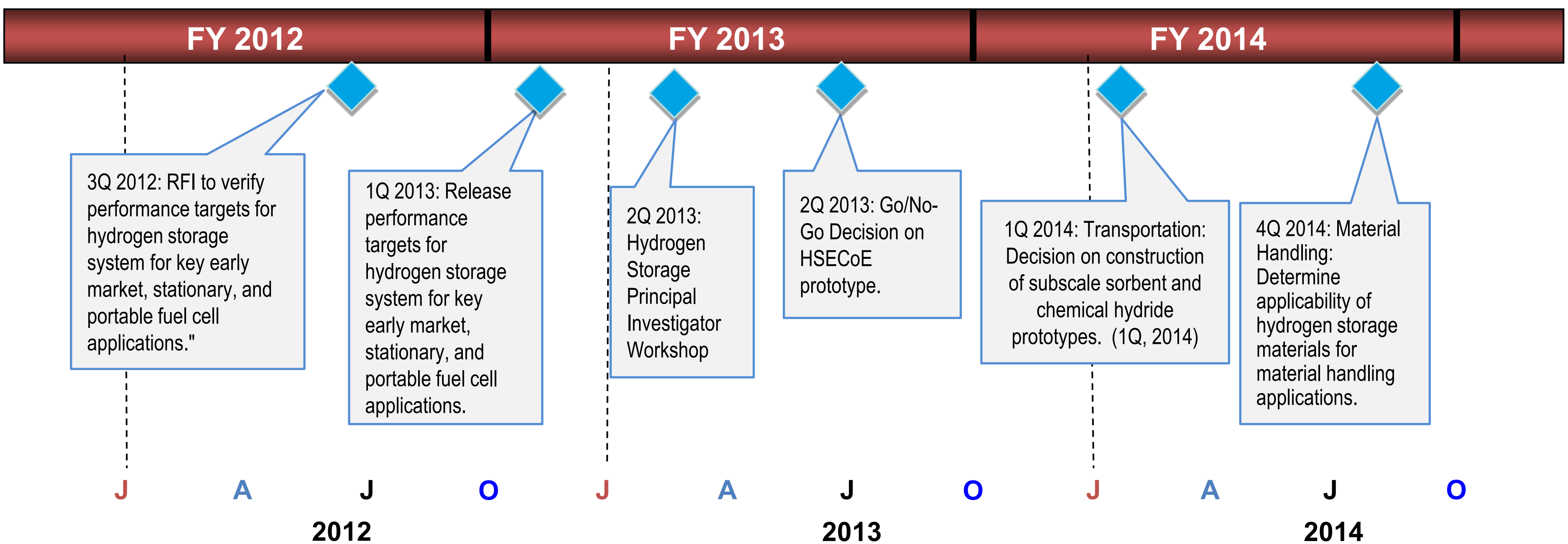
Summary of activities and upcoming milestones

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



The Hydrogen Storage Team

U.S. DEPARTMENT OF ENERGY

For more information contact:

Ned Stetson - Team Lead **202-586-9995** ***ned.stetson@ee.doe.gov***	
Grace Ordaz *202-586-8350* *grace.ordaz@ee.doe.gov*	***Jesse Adams*** *720-356-1421* *jesse.adams@go.doe.gov*
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!***

Session Instructions

U.S. DEPARTMENT OF ENERGY

- This is a review, not a conference.
- Presentations will begin precisely at scheduled times.
- Talks will be 20 minutes and Q&A 10 minutes.
- Reviewers have priority for questions over the general audience.
- Reviewers should be seated in front of the room for convenient access by the microphone attendants during the Q&A.
- Please mute all cell phones and other portable devices.
- Photography and audio and video recording are not permitted.

Reviewer Reminders

U.S. DEPARTMENT OF ENERGY

- Deadline to submit your reviews is **May 25th at 5:00 pm EDT.**

- ORISE personnel are available on-site for assistance.
  - **Reviewer Lab Hours:** Tuesday – Thursday, 7:30 am – 8:30 pm; Friday 7:30 am – 1:00 pm.
  - **Reviewer Lab Locations:**
    - Crystal Gateway Hotel—*Rosslyn Room* (downstairs, on Lobby level)
    - Crystal City Hotel—*Roosevelt Boardroom* (next to Salon A)

- Reviewers are invited to a brief feedback session — at 3:45 pm Thursday (after last storage talk), in this room.