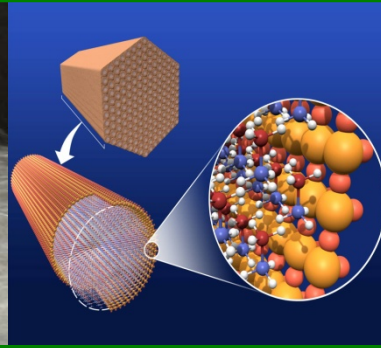
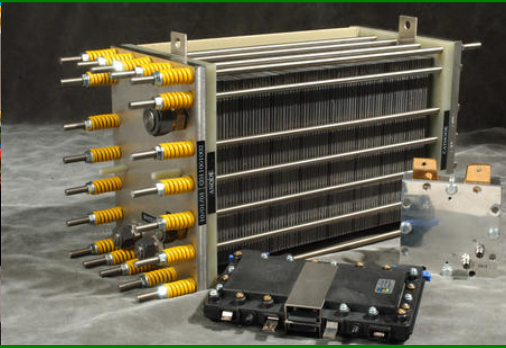




U.S. DEPARTMENT OF  
**ENERGY**



# Hydrogen Storage Program Area -Plenary Presentation-

*Ned T. Stetson*  
*Fuel Cell Technologies Office*

*2017 Annual Merit Review and Peer Evaluation Meeting*  
*June 5 - 9, 2017*

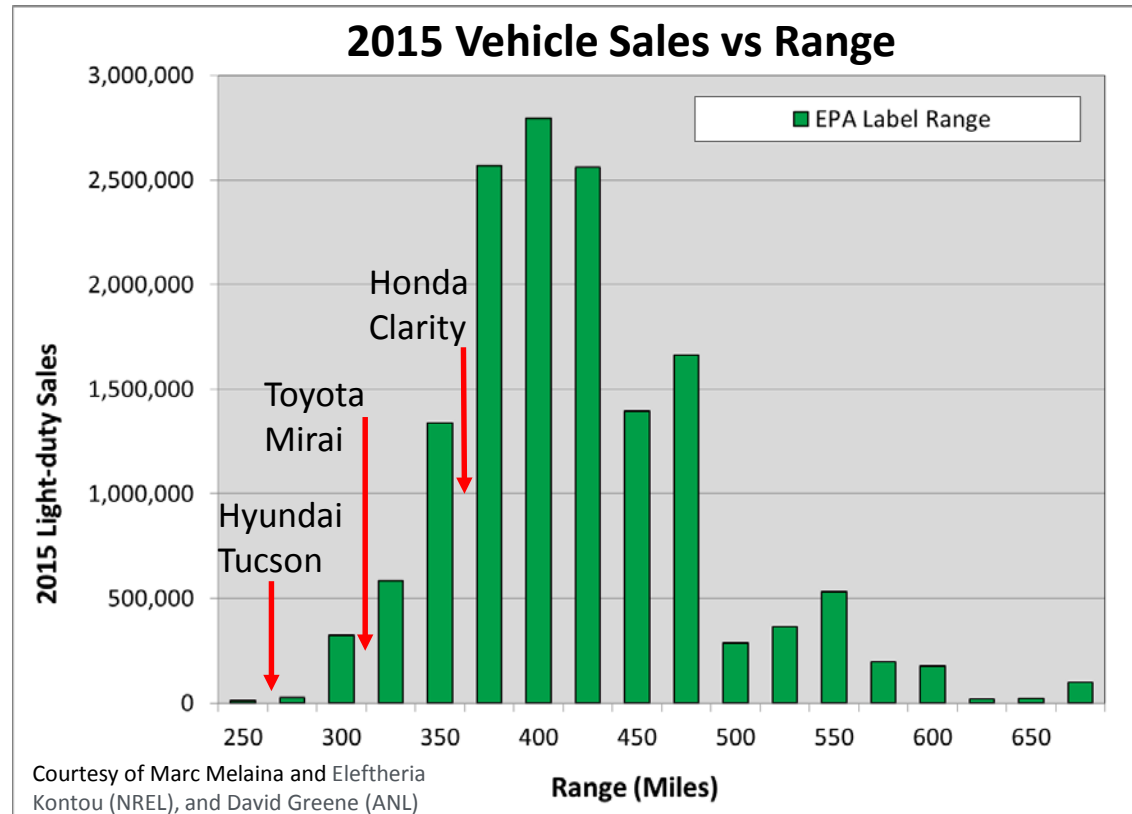
# Goals and Objectives

**Objective:** Develop H<sub>2</sub> storage technologies with performance to enable fuel cell products to be competitive with conventional technologies

For Light-Duty Vehicles:

- Comparable driving range
- Similar refueling time (~3 minutes)
- Comparable passenger and cargo space
- Equivalent level of safety

Onboard H<sub>2</sub> storage targets to be reviewed approximately every five years and revised as appropriate



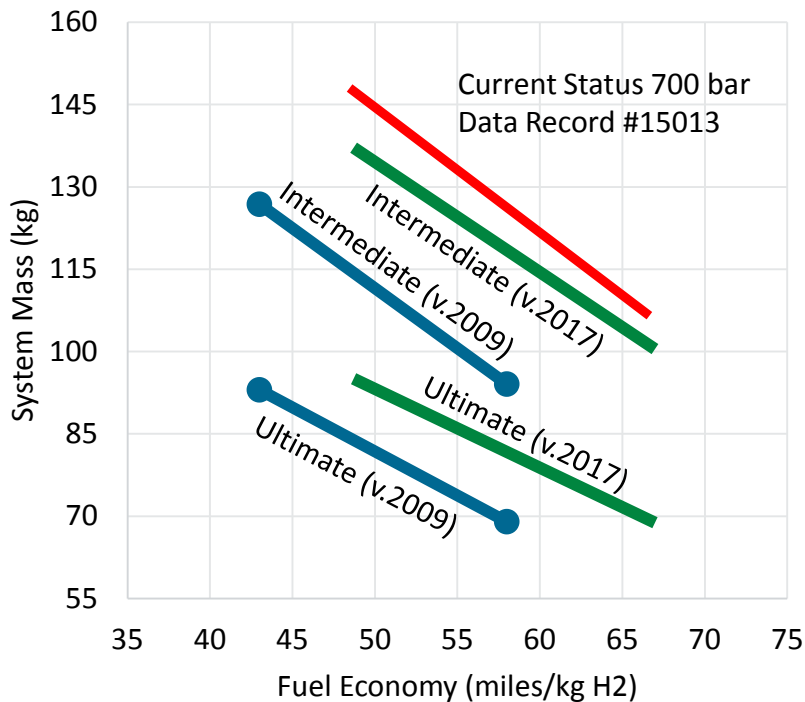
***GOAL: Develop advanced hydrogen storage technologies to enable successful commercialization of hydrogen fuel cell products***

# Onboard Storage Target Revisions

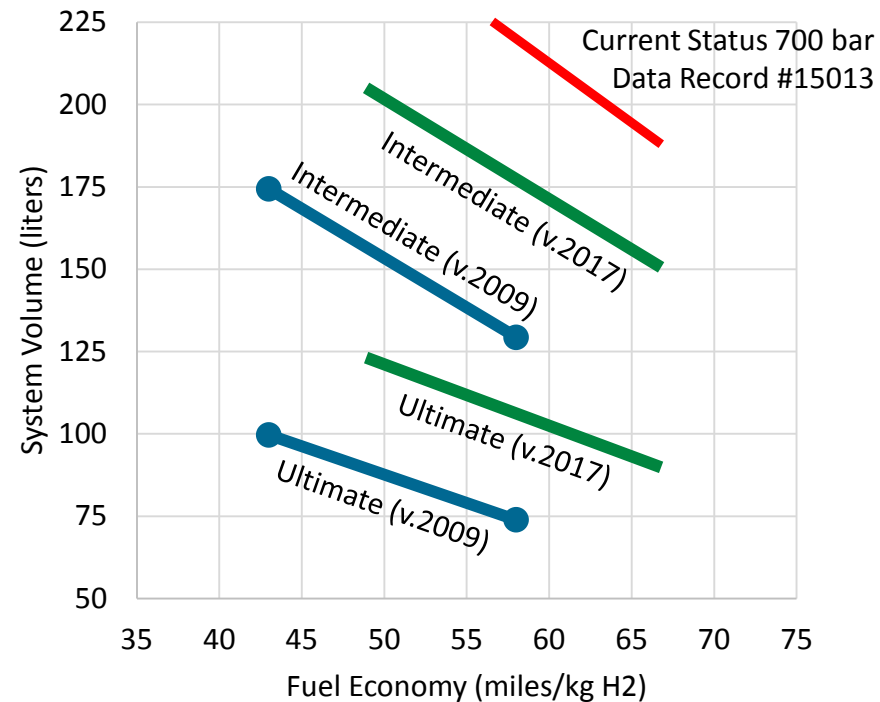
Vehicle performance has improved since the 2008/09 target review

- Fuel economy range increase from 48-53 to 49-67 miles per kg H<sub>2</sub>
- Autonomie (ANL) available for full vehicle performance analysis

Fuel System Mass as a function of Fuel Economy (300 mi range)



System Volume as a function of Fuel Economy (300 mi range)



*Onboard storage targets are periodically reviewed in terms of current vehicle performance data and revised as appropriate*

# Revised Onboard H<sub>2</sub> Storage Targets

Revised System Targets for Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles						
Storage Parameter	Units	2020 (previous)	2020 (new)	2025 (new)	Ultimate (previous)	Ultimate (new)
<b>System Gravimetric Capacity:</b>	kWh/kg (kg H <sub>2</sub> /kg system)	1.8 (0.055)	<b>1.5 (0.045)</b>	<b>1.8 (0.055)</b>	2.5 (0.075)	<b>2.2 (0.065)</b>
<b>System Volumetric Capacity:</b>	kWh/L (kg H <sub>2</sub> /L system)	1.3 (0.040)	<b>1.0 (0.030)</b>	<b>1.3 (0.040)</b>	2.3 (0.070)	<b>1.7 (0.050)</b>
<b>Storage System Cost :</b>	\$/kWh net (\$/kg H <sub>2</sub> )	10 (333)	10 (333)	<b>9 (300)</b>	8 (266)	8 (266)
<b>Charging / Discharging Rates:</b>						
System fill time	min	3.3	<b>3-5</b>	<b>3-5</b>	2.5	<b>3-5</b>

*System target revisions considered vehicle performance*

# New Onboard H<sub>2</sub> Storage Targets

## New System Targets for Onboard H<sub>2</sub> Storage for Light-Duty Fuel Cell Vehicles

Storage Parameter	Units	2020 (new)	2025 (new)	Ultimate (new)	Notes
<b>Charging / Discharging Rates:</b> Average flow rate	(g/s)/ kW	0.004	0.004	0.004	New target to differentiate between Average flow rate & Minimum full flow rate
<b>Dormancy:</b> Dormancy time target (minimum until first release from initial 95% usable capacity)	Days	7	10	14	New targets to address Dormancy (a challenge for systems that operate below ambient temperate)
Boil-off loss target (max reduction from initial 95% usable capacity after 30 days)	%	10	10	10	

*The full set of onboard H<sub>2</sub> storage targets available online at:*  
<https://energy.gov/node/1315186>

# Current Status vs Targets

<b>Storage Targets</b>	<b>Gravimetric kWh/kg (kg H<sub>2</sub>/kg system)</b>	<b>Volumetric kWh/L (kg H<sub>2</sub>/L system)</b>	<b>Costs <sup>1</sup> \$/kWh (\$/kg H<sub>2</sub>)</b>
2020	1.5 (0.045)	1.0 (0.030)	\$10 (\$333)
2025	1.8 (0.055)	1.3 (0.040)	\$9 (\$300)
Ultimate	2.2 (0.065)	1.7 (0.050)	\$8 (\$266)
<b>Current Status <sup>2</sup></b>			
700 bar compressed (5.6 kg H <sub>2</sub> , Type IV, Single Tank)	1.4 (0.042)	0.8 (0.024)	\$15 (\$500)

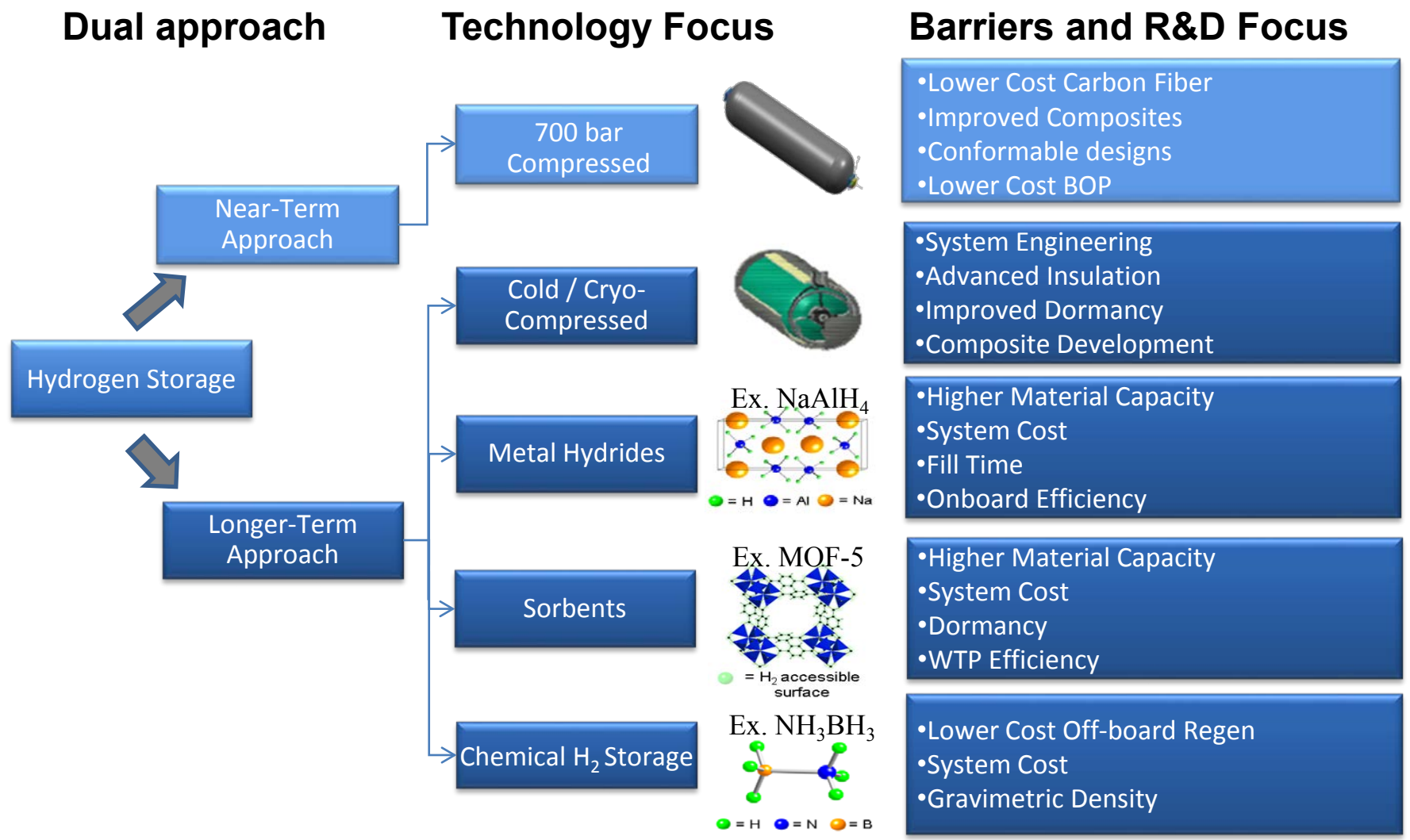
The full set of H<sub>2</sub> storage targets can be found on the Program's website:

<https://energy.gov/eere/fuelcells/downloads/doe-targets-onboard-hydrogen-storage-systems-light-duty-vehicles>

<sup>1</sup> Projected at 500,000 units/year

<sup>2</sup> FCTO Data Record #15013, 11/25/2015: [https://www.hydrogen.energy.gov/pdfs/15013\\_onboard\\_storage\\_performance\\_cost.pdf](https://www.hydrogen.energy.gov/pdfs/15013_onboard_storage_performance_cost.pdf)

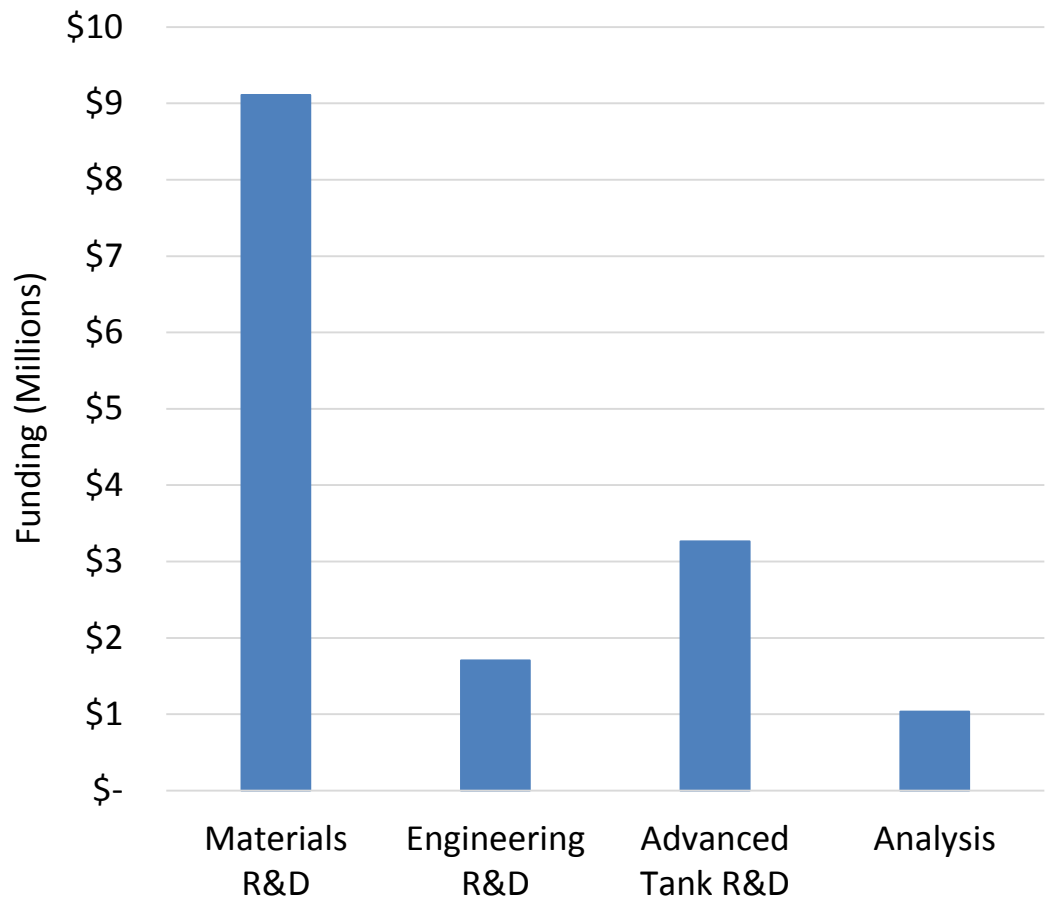
# Hydrogen Storage Team - Strategy and Barriers



**Objective: Achieve a driving range competitive with conventional vehicles for full span of light-duty vehicles, while meeting packaging, cost, safety, & performance requirements**

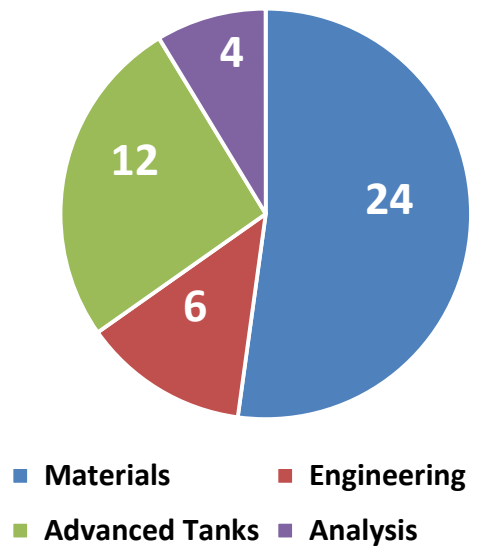
**FY 2017 Appropriation = \$15.6M**

**FY2017 Funding Allocations by Focus Area**



*Emphasis is on early phase R&D for H<sub>2</sub> storage materials and lower cost physical storage*

**Number of Projects in Portfolio by Focus Area**  
(Includes subs directly funded by DOE)

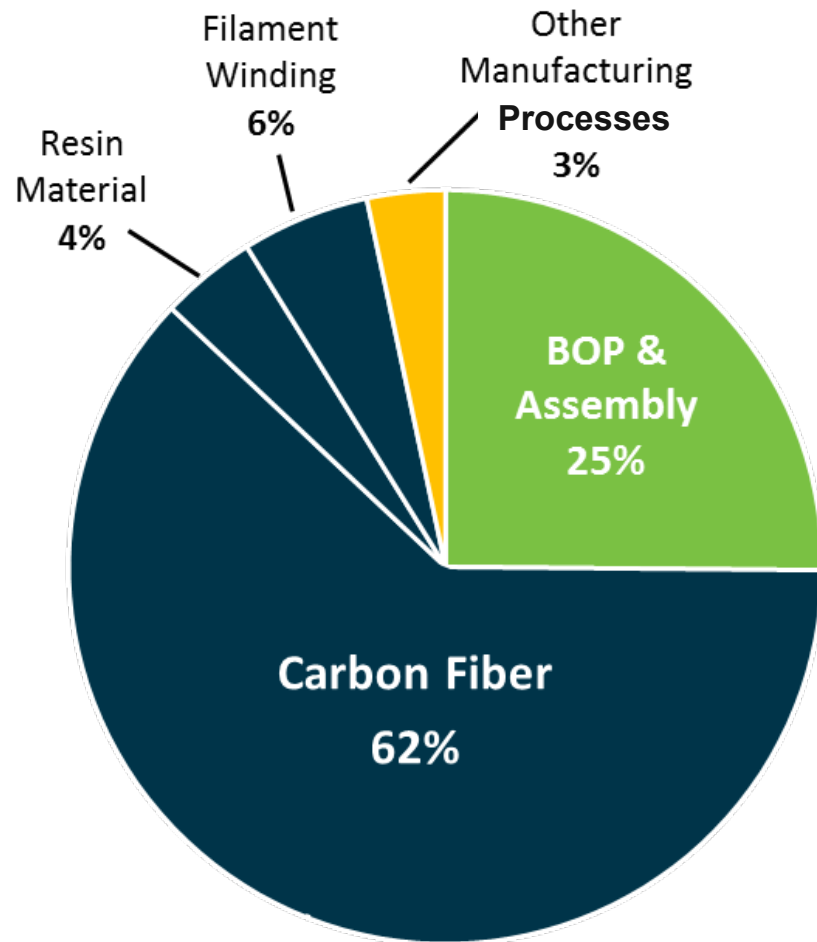




# Physical Storage Activities

# Current Status – 700 Bar System Cost Breakout

- **Cost breakdown at 500k systems/yr.**
- System cost is **dominated, 72%, by composite materials and processing**
- Carbon Fiber composite cost:
  - ~ 50% Carbon fiber precursor
  - ~ 50% Precursor fiber conversion
- BOP costs are a major cost contributor, especially at low annual production volumes

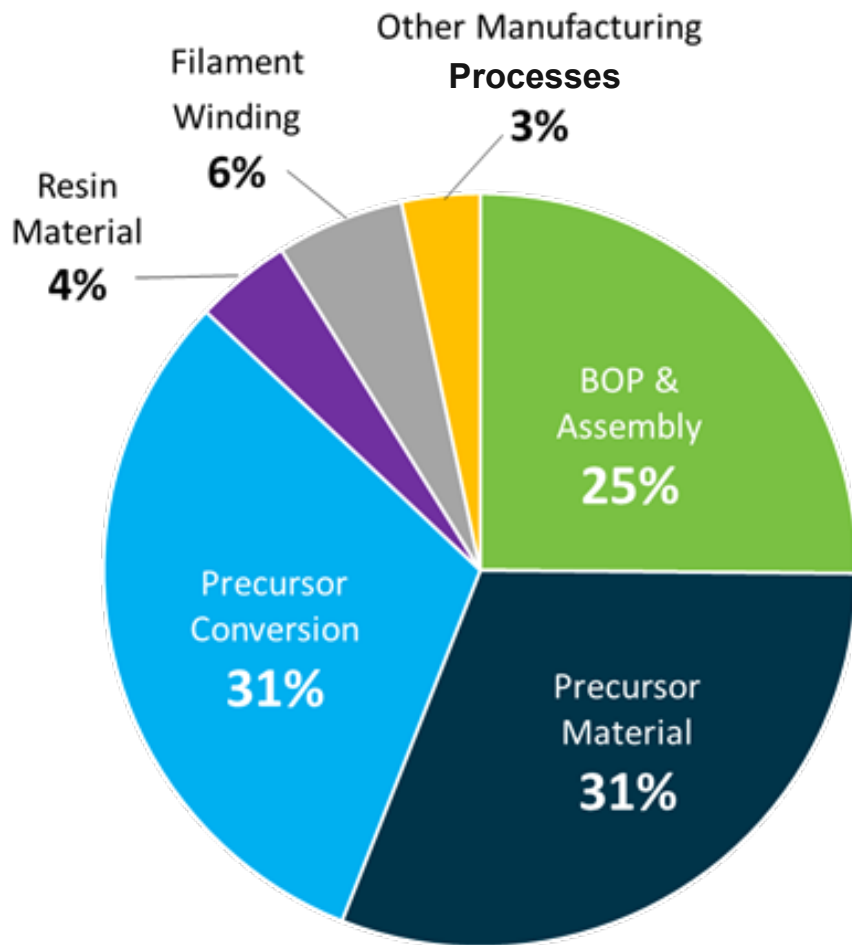


Ordaz, G., C. Houchins, and T. Hua. 2015. "Onboard Type IV Compressed Hydrogen Storage System - Cost and Performance Status 2015," DOE Hydrogen and Fuel Cells Program Record, [https://www.hydrogen.energy.gov/pdfs/15013\\_onboard\\_storage\\_performance\\_cost.pdf](https://www.hydrogen.energy.gov/pdfs/15013_onboard_storage_performance_cost.pdf), accessed 5 July 2016.

*Carbon fiber cost reduction is needed to drive down cost of 700 bar storage systems*

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Ordaz, G., C. Houchins, and T. Hua. 2015. "Onboard Type IV Compressed Hydrogen Storage System - Cost and Performance Status 2015," DOE Hydrogen and Fuel Cells Program Record, [https://www.hydrogen.energy.gov/pdfs/15013\\_onboard\\_storage\\_performance\\_cost.pdf](https://www.hydrogen.energy.gov/pdfs/15013_onboard_storage_performance_cost.pdf), accessed 5 July 2016.

*Carbon fiber cost reduction is needed to drive down cost of 700 bar storage systems*

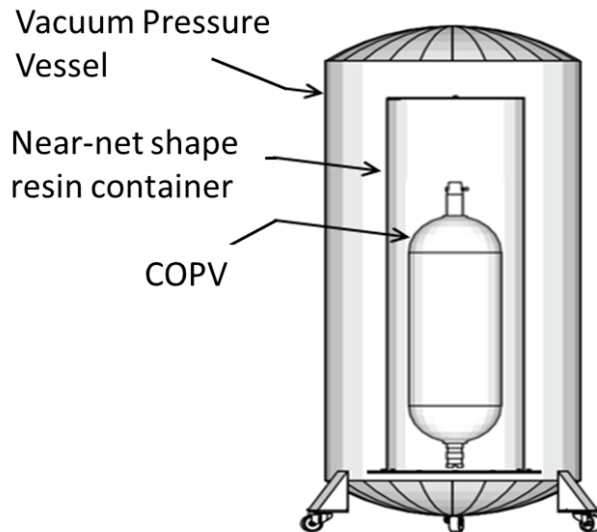
- **Precursor development for low-cost, high-strength carbon fiber (CF) for use in composite overwrapped pressure vessel applications**
  - Resulting CF to have properties similar to Toray T700S
  - Target cost of \$12.60/kg of CF
- **Areas of interest:**
  - PAN-based fibers formulated with co-monomers and additives that permit lower cost processing to produce the PAN fiber than conventional solution spinning processes, and or that reduce the conversion cost of the PAN-fiber to CF;
  - Polyolefin-based fibers capable of being cost effectively converted into high-strength CF;
  - Novel material precursor fibers that can lead to low-cost, high-strength CF production.

# Accomplishments - Project Highlights

## Alternative Resin and Manufacturing [Materia/MSU/Spencer Composites/ Hypercomp Engineering]

- Reducing composite volume/mass through use of alternative resin and manufacturing processes
- **Improved process cut resin infusion time in half for prototype tanks**

### Nested Assembly for New Process



ST114

## Conformable 700 bar H<sub>2</sub> Storage Systems [CTE/HECR/UT/Stan Sanders]

- Developing conformable 700 bar pressure vessels without use of carbon fiber composites
- **Demonstrated vessel with a 34,000 psi burst (2345 bar), exceeding the 2.25 safety margin for 700 bar systems**



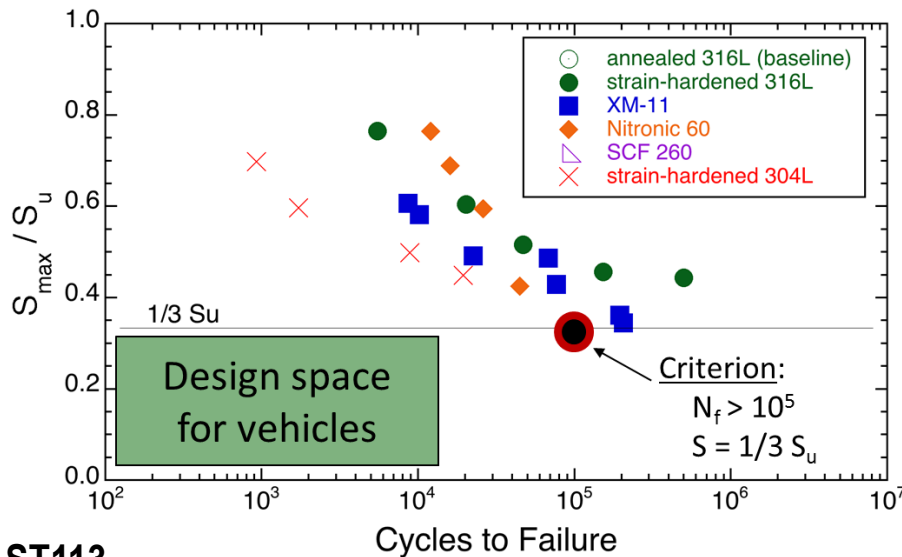
ST126

*Addressing cost through reduced carbon fiber use*

# Accomplishments - Project Highlights

## Alternative Materials for BOP [SNL/Hy-Performance Materials]

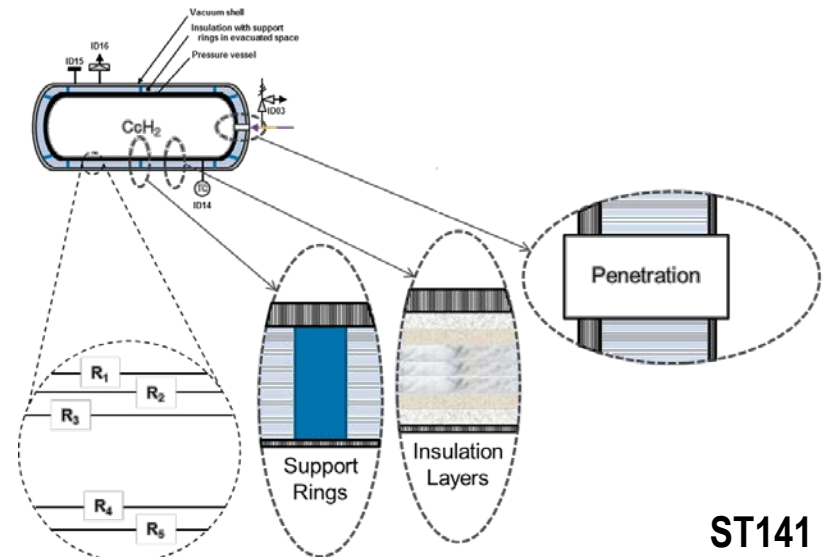
- Identifying alternative alloys to lower BOP cost and weight through testing and computational material screening
- Identified alloys with potential to reduce cost and weight by >50% compared to 316L SS baseline**



## Insulation for Cryogenic Storage Tanks [Vencore/Aspen Aerogels/Energy

Florida/Hexagon Lincoln/IBT/NASA-KSC/SRNL]

- Developing integrated advanced insulation system capable of meeting dormancy requirements for vehicle applications
- Down-selection of concept technologies in-progress**





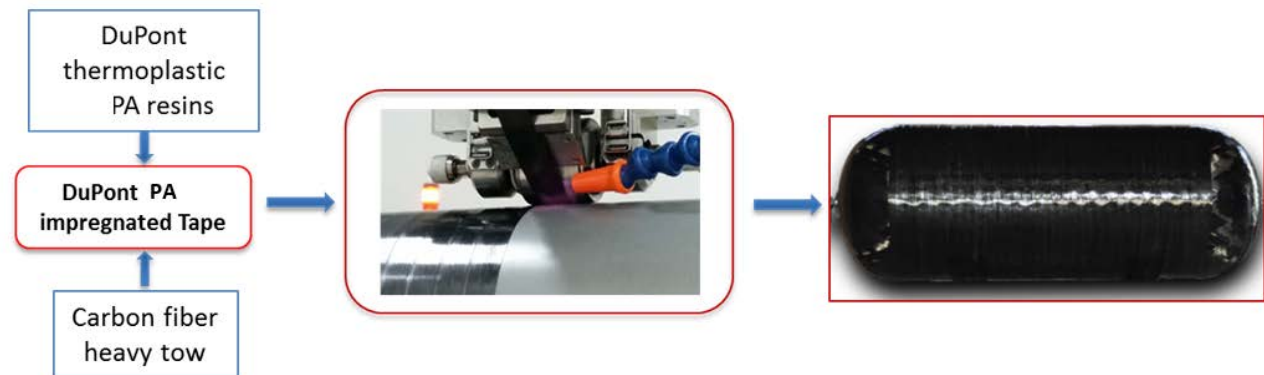
THE  
COMPOSITES  
INSTITUTE

## Institute for Advanced Composites Manufacturing Innovation

- Institute of Manufacturing USA
- Managed by the EERE Advanced Manufacturing Office
- Technology Focus Areas:
  - Vehicles
  - Wind Turbine Blades
  - **Compressed Gas Storage Vessels**
  - Design, Modeling & Simulation
  - **Composite Materials & Processes**

## Leveraged project: Thermoplastic Composite Compressed Gas Storage Tanks

- Project lead: DuPont
- Partners:
  - Composite Prototyping Center (CPC)
  - Steelhead Composites
  - University of Dayton Research Institute (UDRI)
- Kick-off: FY2017, Q1



# Materials-Based Storage Activities



### Individual projects



### National Laboratories

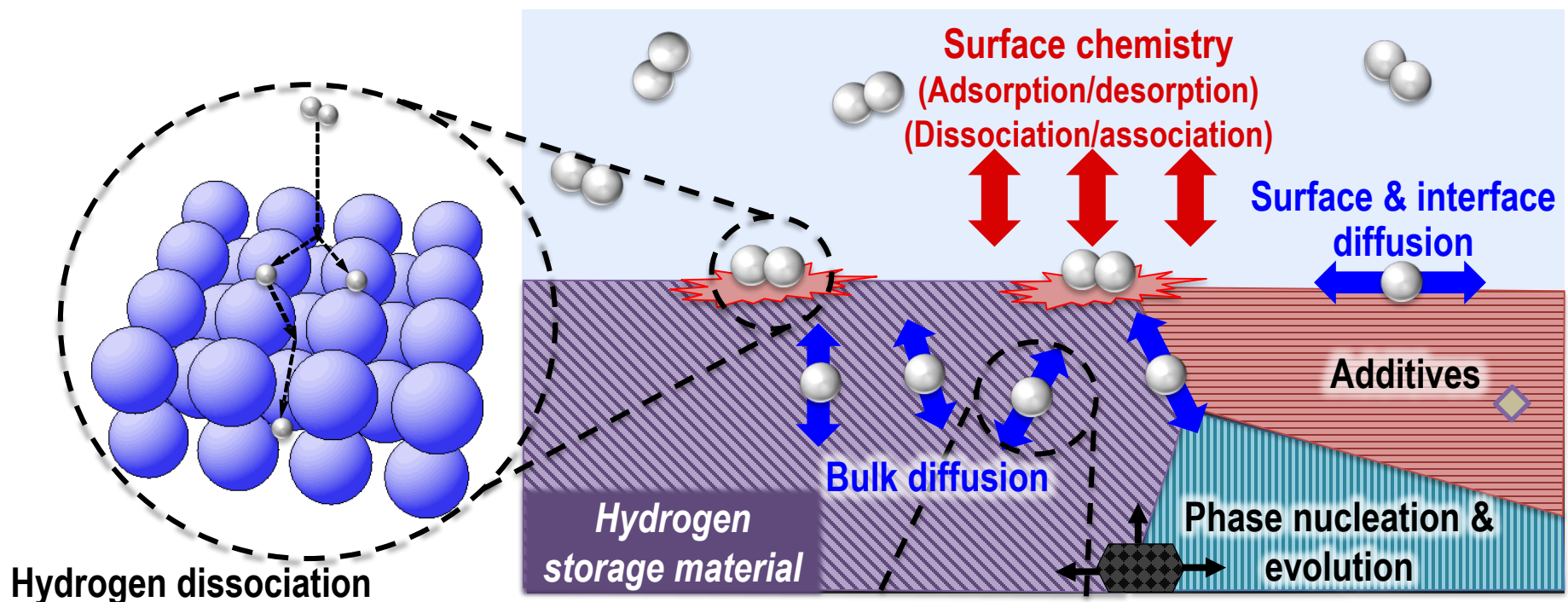
### Core Team

### Characterization and Validation Team



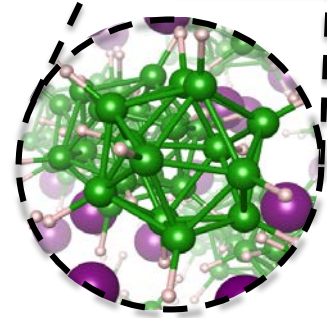
- **Applied materials development**
  - Novel material concepts
  - High-risk, high-reward
- **Concept feasibility demonstration**
- **Advanced development of viable concepts**
  
- **Foundational research**
- **Material development tools**
  - Foundational R&D
  - Computational modeling development
  - Synthetic/characterization protocol development
- **Guidance to individual projects**
- **Database development**
  
- **Characterization resources**
  - “User-facility” for HyMARC projects
- **Characterization method development**
- **Validation activities**
  - Validation of Performance
  - Validation of “Theories”

Effective thermal energy for H<sub>2</sub> release:  $\Delta E(T) = \Delta H^\circ (T) + E_a$

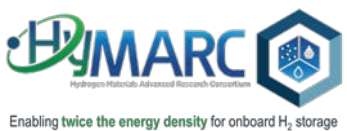


Hydrogen dissociation and absorption

- Task 1: Thermodynamics*
- Task 2: Transport*
- Task 3: Gas-surface interactions*
- Task 4: Solid-solid interfaces*
- Task 5: Additives and dopants*
- Task 6: Materials informatics*



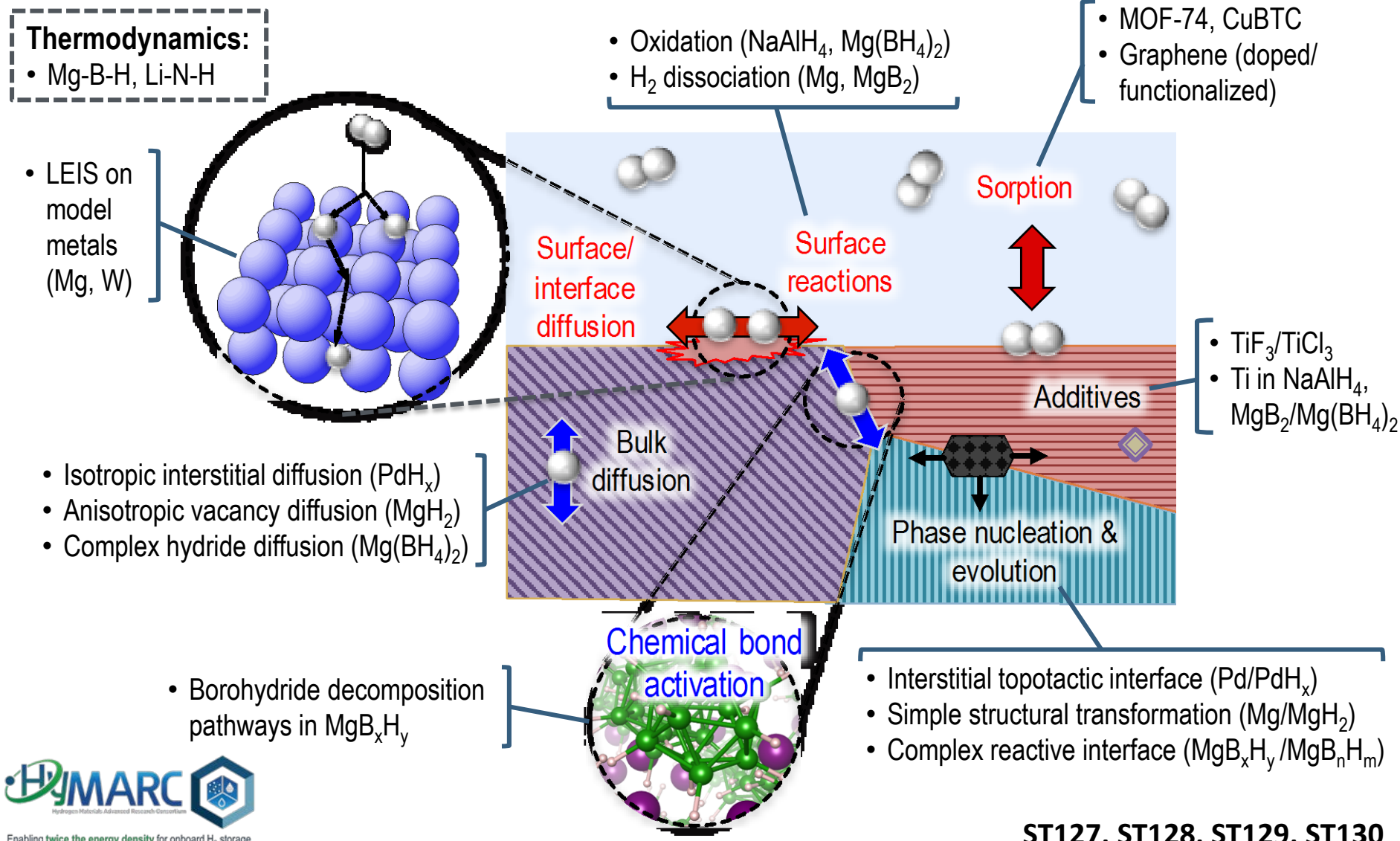
Chemical bonding



ST127, ST128, ST129, ST130

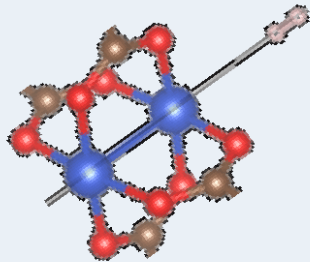
**Focusing on overcoming thermodynamic and kinetic barriers simultaneously**

# HyMARC – Understanding the phenomena of hydrogen interactions with materials



# HyMARC accomplishments – *theory capabilities*

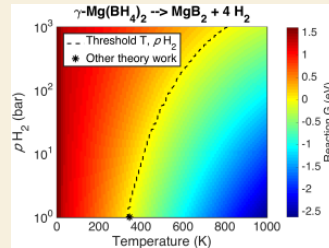
## Improved sorbent isotherms



Recipes for integrating different levels of theory in sorbent isotherm models

Seedling: Chung/PSU

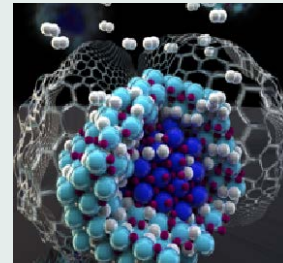
## Accurate hydride thermodynamics



Finite- $T$  free energy, environment- and morphology-dependent thermodynamics

Seedlings: Liu/ANL, Severa/U. Hawaii

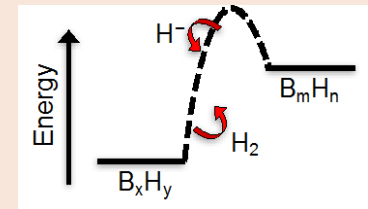
## Solid mechanics & interfaces in hydrides



Internal and confinement stress effects; reactive diffuse interfaces

Seedlings: Liu/ANL, Severa/U. Hawaii

## Kinetic modeling



Semiempirical kinetic modeling and rate analysis; phase evolution kinetics

Seedlings: Liu/ANL, Severa/U. Hawaii

## Additional accomplishments in compiling databases and reference libraries (“Task 6”):

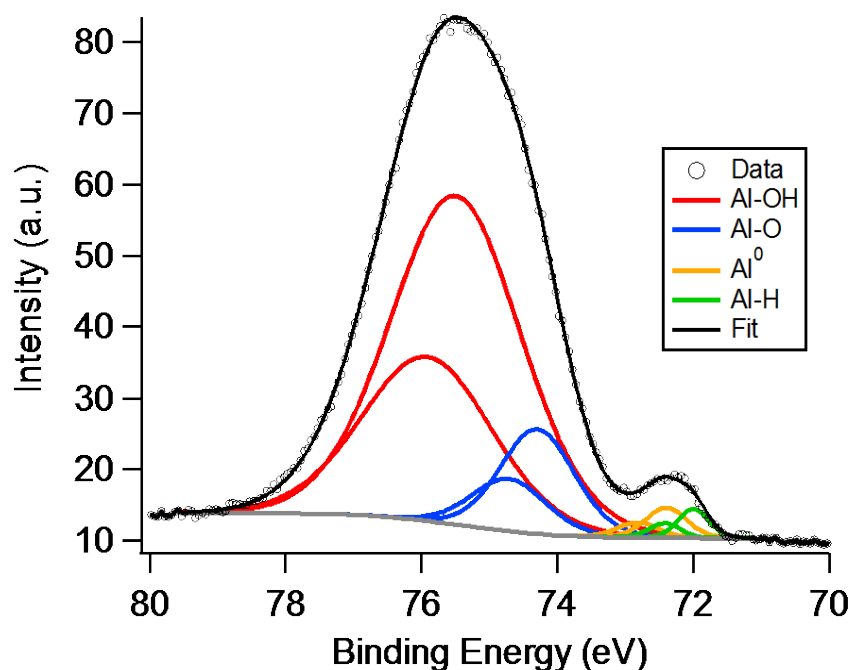
- *Simulated & measured spectroscopy database (NMR, FTIR, XAS/XES) for identifying  $MgB_xH_y$  (preparing manuscript w/LBNL/SNL/HySCORE)*
- *Library of analytical free energies for Li-N-H (published) and Mg-B-H (preparing manuscript), with validation at a range of pressures via NMR (w/SNL/HySCORE)*
- *Database of classical potentials for simulating borohydride mixtures and interfaces (w/SNL)*

ST129

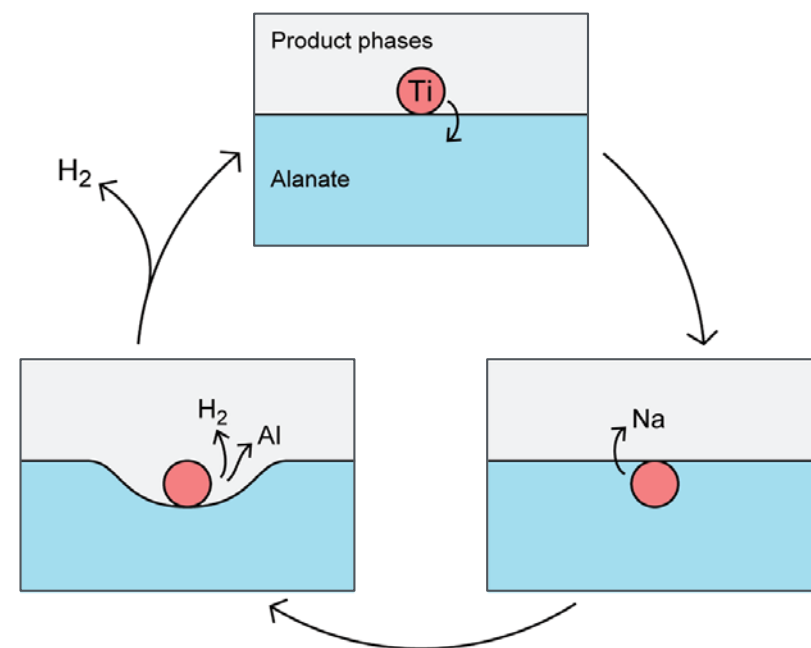
***Seedling projects help focus theory method development prioritization***

- Investigated model system Ti-doped NaAlH<sub>4</sub> via AP-XPS, LEIS and Auger spectroscopy
  - Detected no Ti species on sample surface before or during desorption, reappears during absorption
  - Disproved models invoking surface Ti during dehydrogenation reaction

Four Al species detected by AP-XPS during dehydrogenation



Data supports proposed zipper mechanism

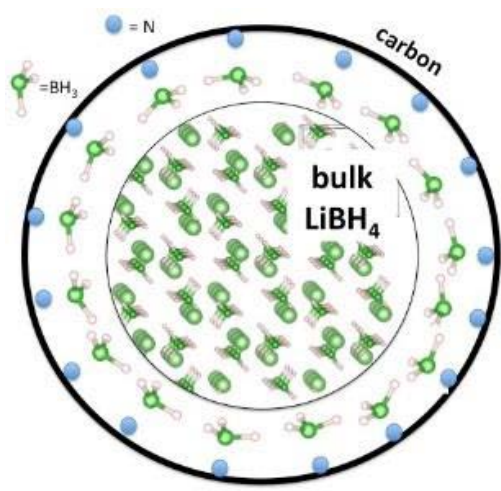


ST128

Chem. Rev. 2012, 112, 2164-2178

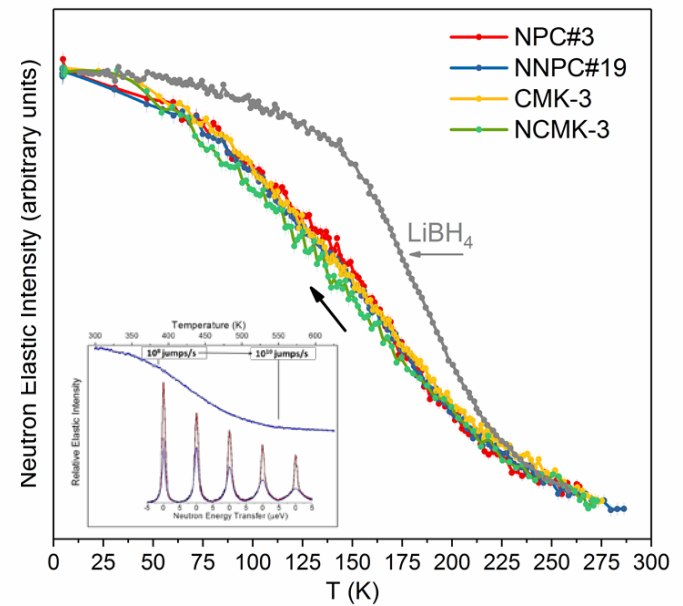
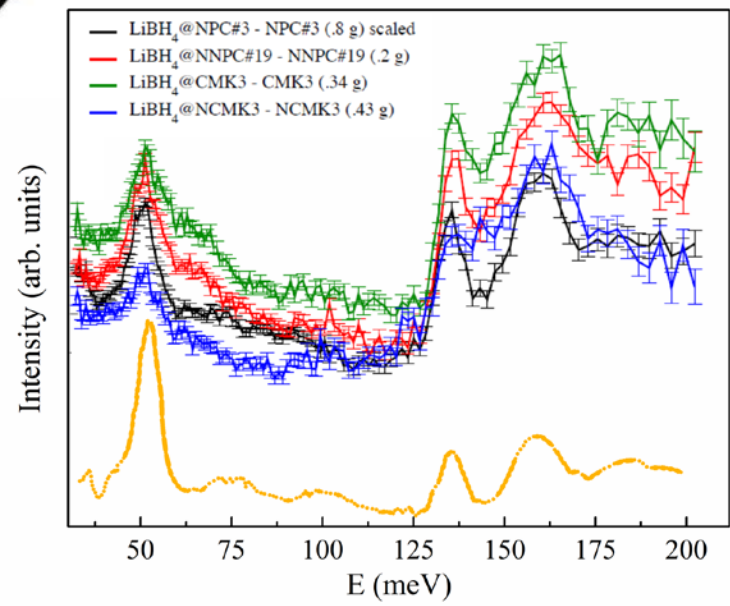
*Proposed mechanisms are evaluated based on experimental data*

## NREL and NCNR carries out neutron vibrational spectroscopy measurements on $\text{LiBH}_4$ infiltrated mesoporous carbon samples from UMSL



Can nanoconfinement in functionalized porous materials facilitate reversible hydrogen storage reactions?

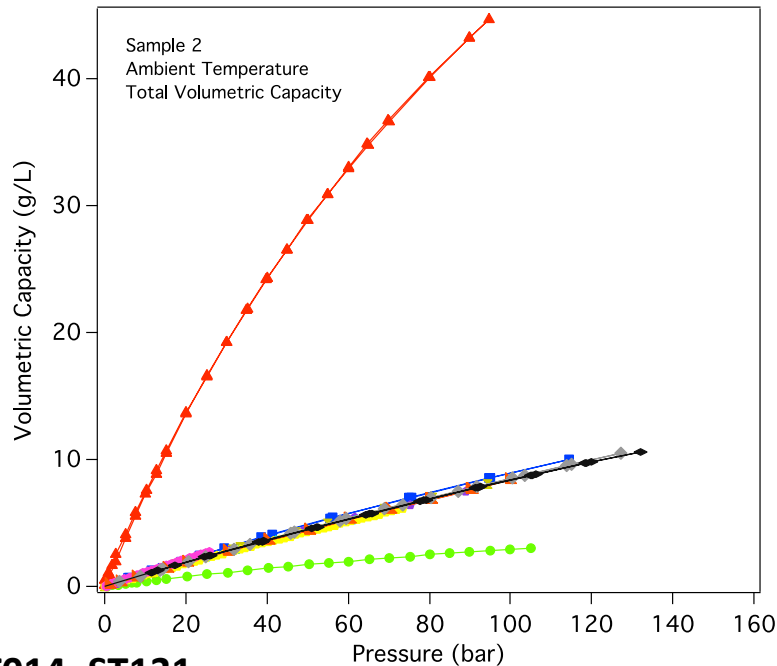
- NVS show  $\text{LiBH}_4$  infiltrated
- Shifting and broadening show there is an effect of confinement
- Degree of N-doping enhances  $\text{BH}_4^-$  orientational mobilities



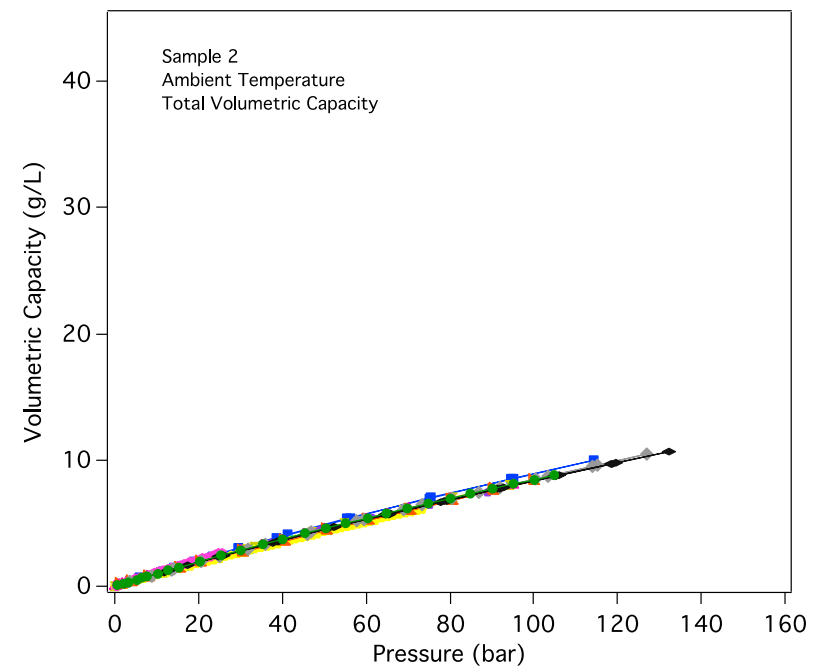
ST135, ST139

## Led an international inter-laboratory volumetric capacity $H_2$ adsorption measurement round-robin study

- Promoted valid comparisons of hydrogen-storage materials
  - necessary to evaluate implementations of protocols
- Decreased irreproducibility due to systematic and “black box” errors
  - NREL gives direct feedback on data
- Determining a “natural” spread of data from instrument and operator variables



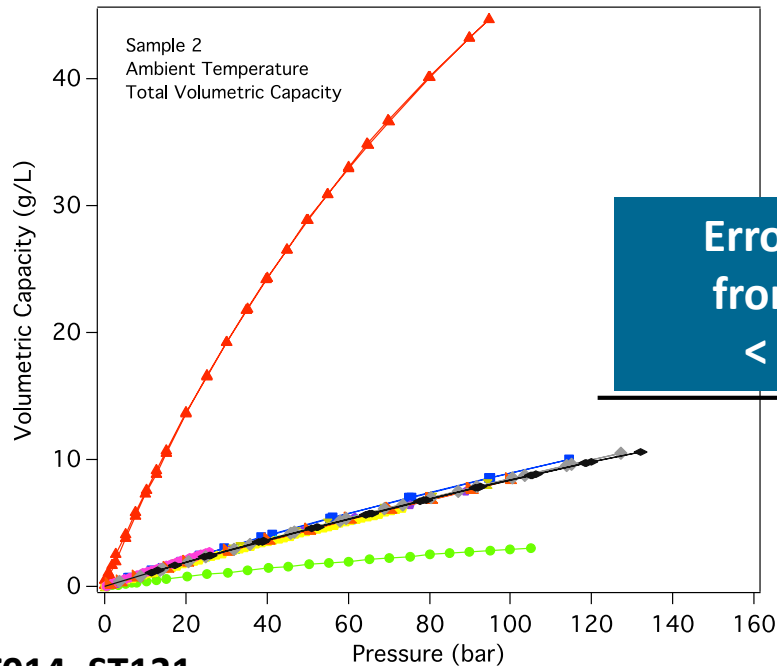
ST014, ST131



*Promoting standard protocols for performing and reporting sorption measurements*

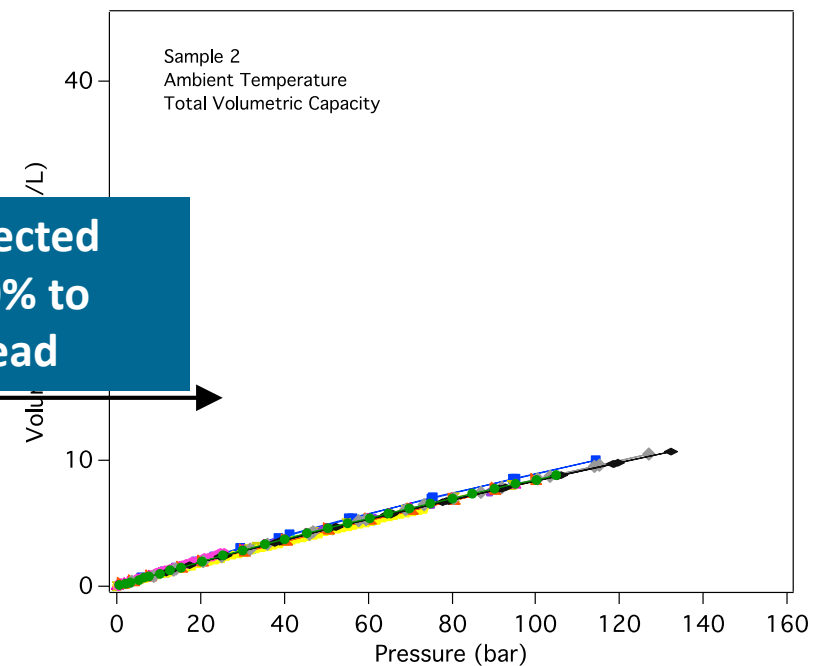
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ST014, ST131

**Errors Corrected  
from > 400% to  
< 5% spread**



*Promoting standard protocols for performing and reporting sorption measurements*

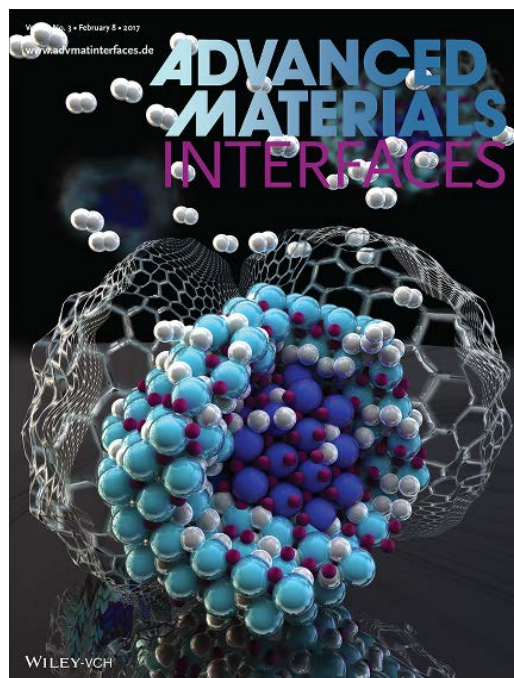


**32: Publications published or submitted for publication**

**4: Patents applications submitted**

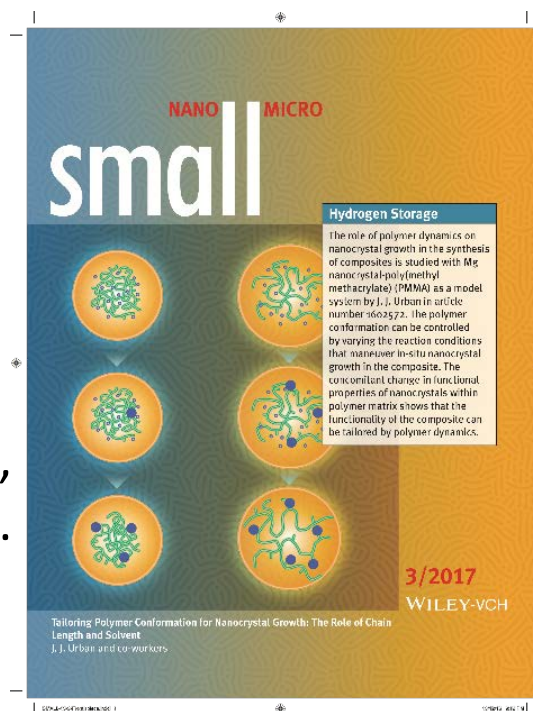
**7: Manuscripts in preparation as of April 2017**

**2: Selected as cover features**



B. C. Wood et al., *Advanced Materials Interfaces*, **2017**, 4, 1600803.

E. S. Cho, J. J. Urban et al., *Small*, in press (2017).

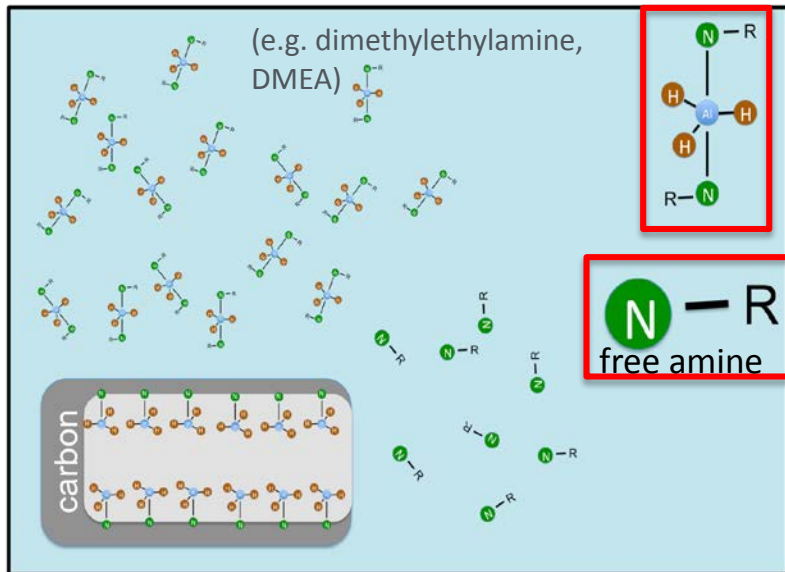


*The lab teams are producing high-value R&D and disseminating it to the R&D community*

# Accomplishments - HyMARC Project Highlights

## Surface functionalized mesoporous carbons [HyMARC seedling—UMSL]

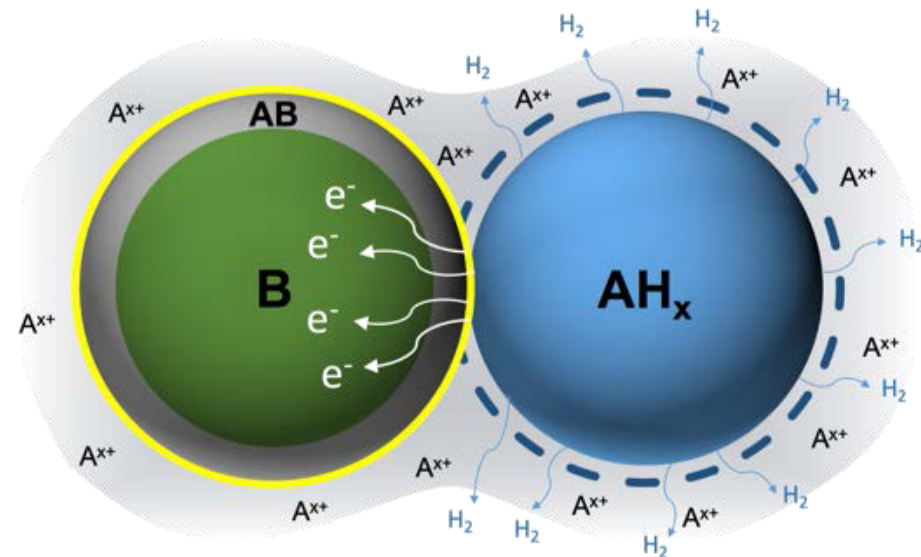
- Demonstrating ability of functionalized mesoporous carbons to facilitate reversible  $H_2$  sorption reactions of hydride materials
- Prepared N-doped carbons and demonstrated infiltration of Al and B-based materials



ST139

## Electrolyte Assisted Storage Reactions [HyMARC seedling—Liox Power]

- Improving reaction kinetics through use of electrolytes to facilitate atomic rearrangement and diffusion
- Have carried out initial screening studies of possible electrolytes



ST137

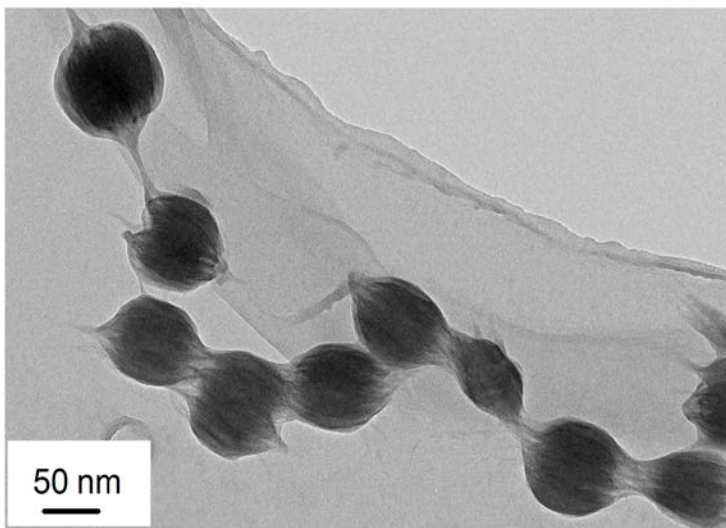
*Accelerating development of improved hydrogen storage materials*

# Accomplishments - HyMARC Project Highlights

## “Graphene-wrapped” hydrides [HyMARC seedling—ANL]

- Encapsulating nanoparticles of complex hydrides with graphene to enhance reversibility and kinetics
- **Demonstrated 9 wt% uptake in NaBH<sub>4</sub> systems with 80% regenerable release over 6 cycles**

SEM of NaBH<sub>4</sub> nanoparticles wrapped in graphene

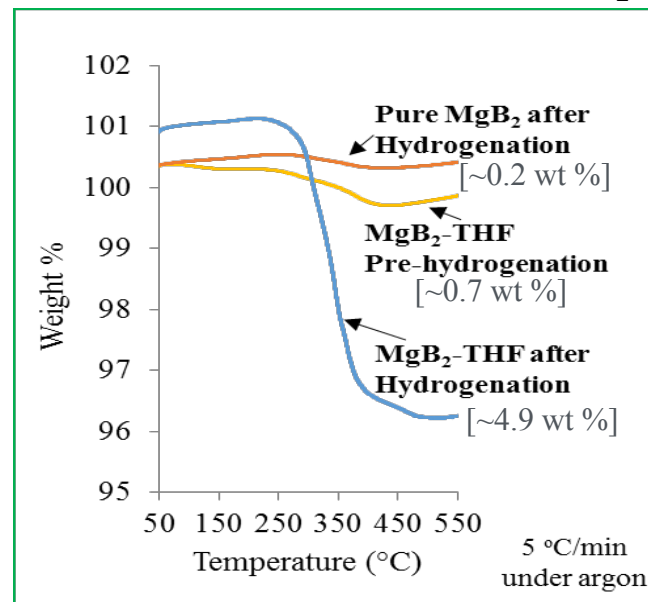


ST136

## Magnesium boride etherates [HyMARC seedling—U. Hawaii]

- Improve reversibility of Mg(BH<sub>4</sub>)<sub>2</sub> through formation of MgB<sub>2</sub>-etherates
- **Demonstrated the formation of significant amounts of β-Mg(BH<sub>4</sub>)<sub>2</sub> at 300 °C**

TGA of hydrogenated ball milled MgB<sub>2</sub>-THF



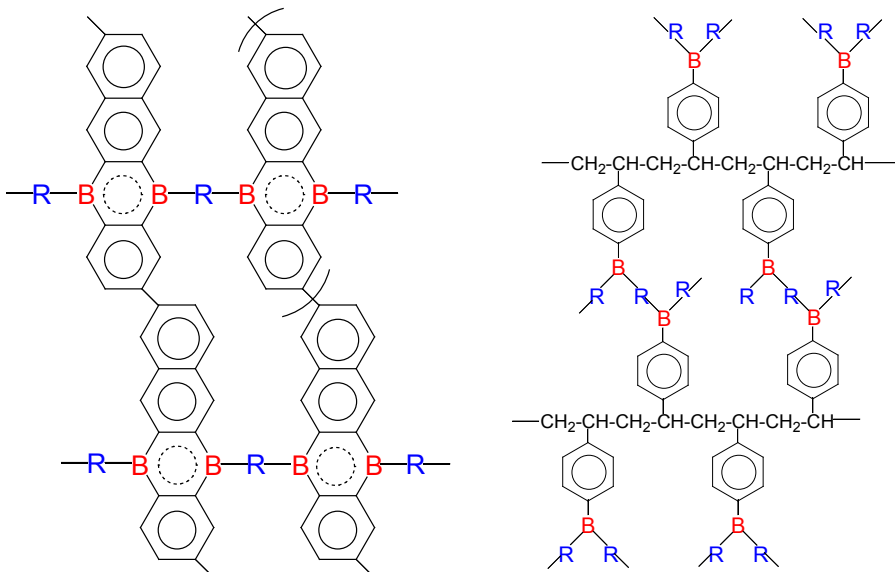
ST138

*Accelerating development of improved hydrogen storage materials*

# Accomplishments - HyMARC Project Highlights

## Novel boron-containing polymers [HyMARC seedling—Penn State]

- Developing novel boron containing porous polymers with higher H<sub>2</sub> binding energy
- **Designed and synthesized two new classes of microporous polymers that contain boron.**

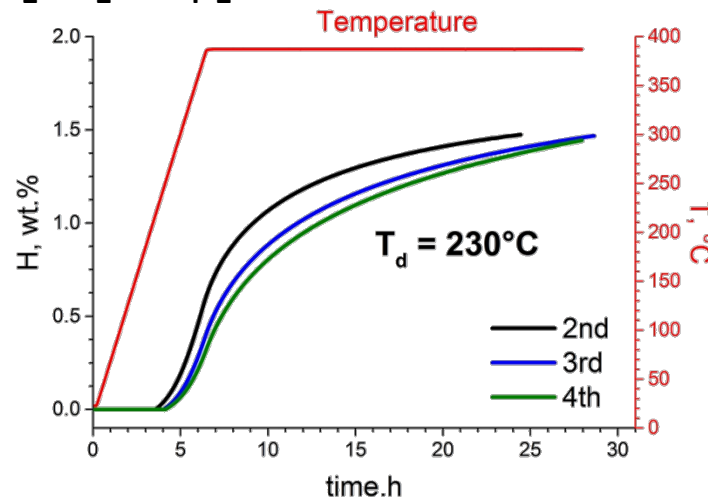


ST140

## High-capacity Hydrogen Storage Materials via Mechanochemistry [Ames Laboratory]

- Prepare high hydrogen capacity silicon-based borohydrides through mechanochemical methods
- **Demonstrated several new materials with reversibility for part of their total capacity**

### “Li<sub>2</sub>SiS<sub>2</sub>(BH<sub>4</sub>)<sub>2</sub>” desorption measurements



ST119

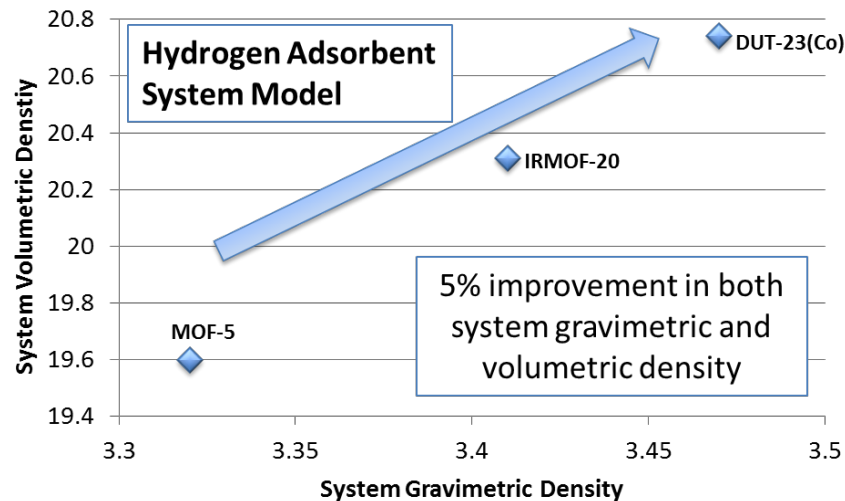
*Accelerating development of improved hydrogen storage materials*

- **Hydrogen Storage Materials Discovery (HyMARC)**
  - innovative, high-risk, high-payoff concepts for hydrogen storage materials
  - project teams will be integrated into HyMARC as individual projects
  - phase I Go/No-Go milestone must provide confidence that the proposed concept has reasonable potential to result in a hydrogen storage material capable of meeting automotive performance requirements
- Areas of interest:
  - novel, advanced onboard-rechargeable hydrogen storage materials
  - physi- and chemisorption materials acceptable
- Only Phase I effort will be supported until Go/No-Go criteria is met, additional support will be contingent on meeting criteria

# Accomplishments - Project Highlights

## Computational Screening of MOFs with High Volumetric Density [U. Michigan]

- Identifying high-performing MOF's through screening of large structure databases
- Synthesized and tested several MOFs for their H<sub>2</sub> adsorption properties; IRMOF-20 and DUT-23(Co) both projected to surpass MOF-5 in system performance**

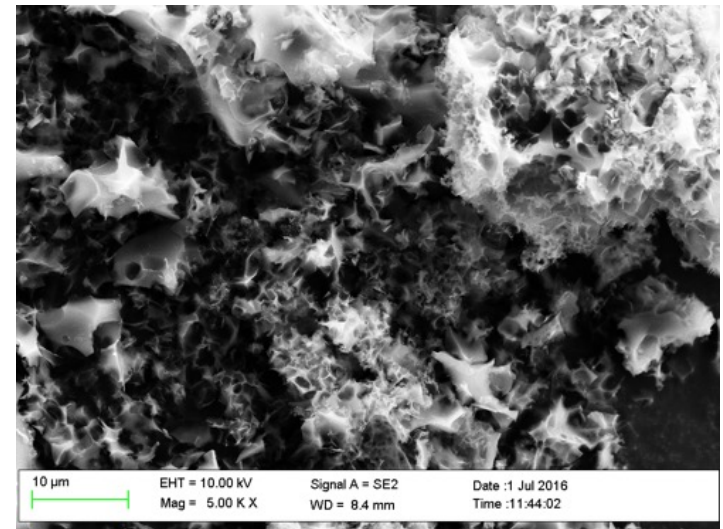


ST122

## Graphene-based carbon sorbents [Caltech]

- Design and synthesize porous graphene materials as high-capacity H<sub>2</sub> sorbents
- Demonstrated progress in preparing high-surface area carbons and inserting metal atoms to achieve higher heats of adsorption**

SEM of high surface area graphene prepared from graphene oxide



ST120

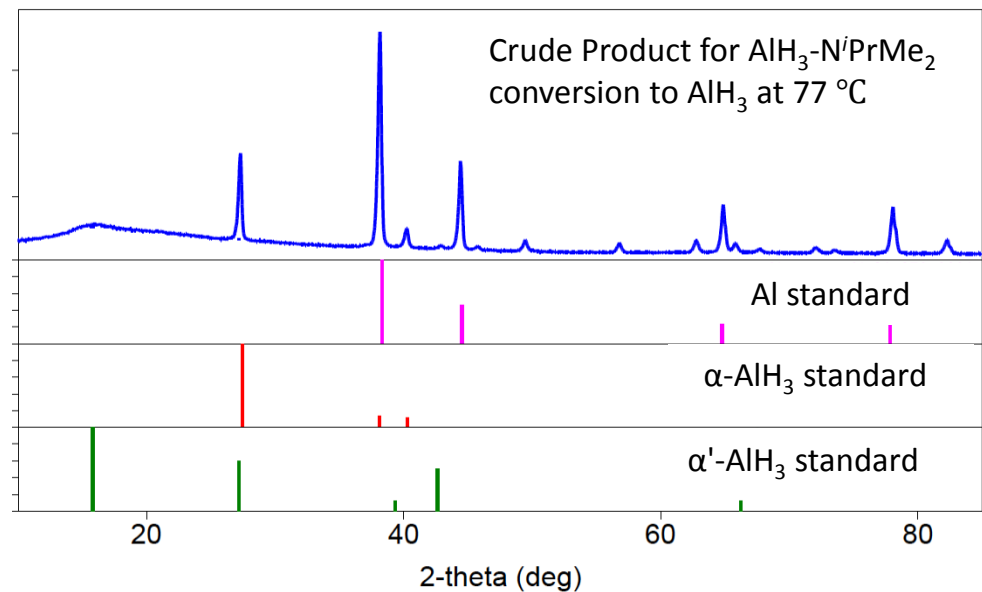
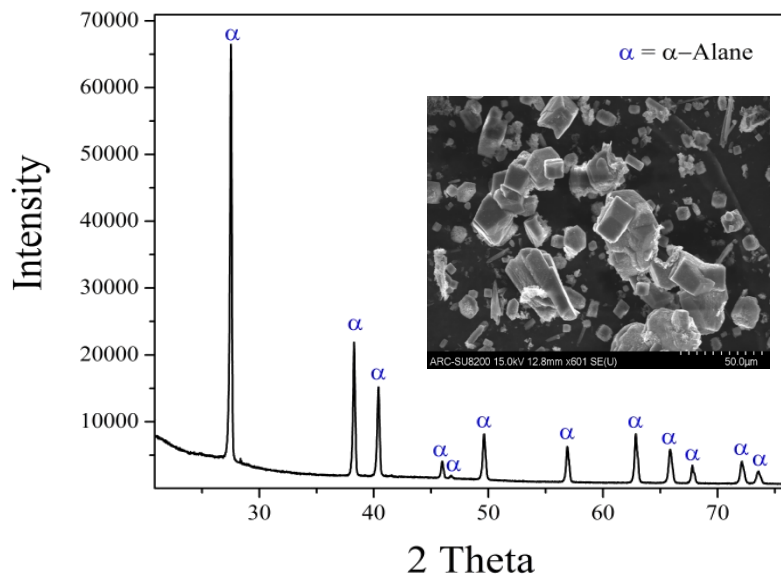
*Developing improved adsorbent storage materials*

# Accomplishments - Project Highlights

## Low-cost methods for $\alpha$ -alane production [SRNL, Greenway; Ardica, SRI]

- Developing and demonstrating low-cost processes for scale-up of alane ( $\text{AlH}_3$ ) preparation
- **Demonstrated improved crystallization and passivation process to produce high-purity, stable  $\alpha$ -alane from chemical synthesis in batches of up to 200 grams (SRNL, Greenway)**
- **Demonstrated ability to yield  $\alpha$ -alane from electrochemical synthesis, however further improvements are needed (Ardica, SRI)**

## XRD of crystallized $\alpha$ -alane from chemical (left) and electrochemical (right) syntheses



ST063

ST116

*Developing low-cost  $\alpha$ -alane ( $\text{AlH}_3$ ) production processes*

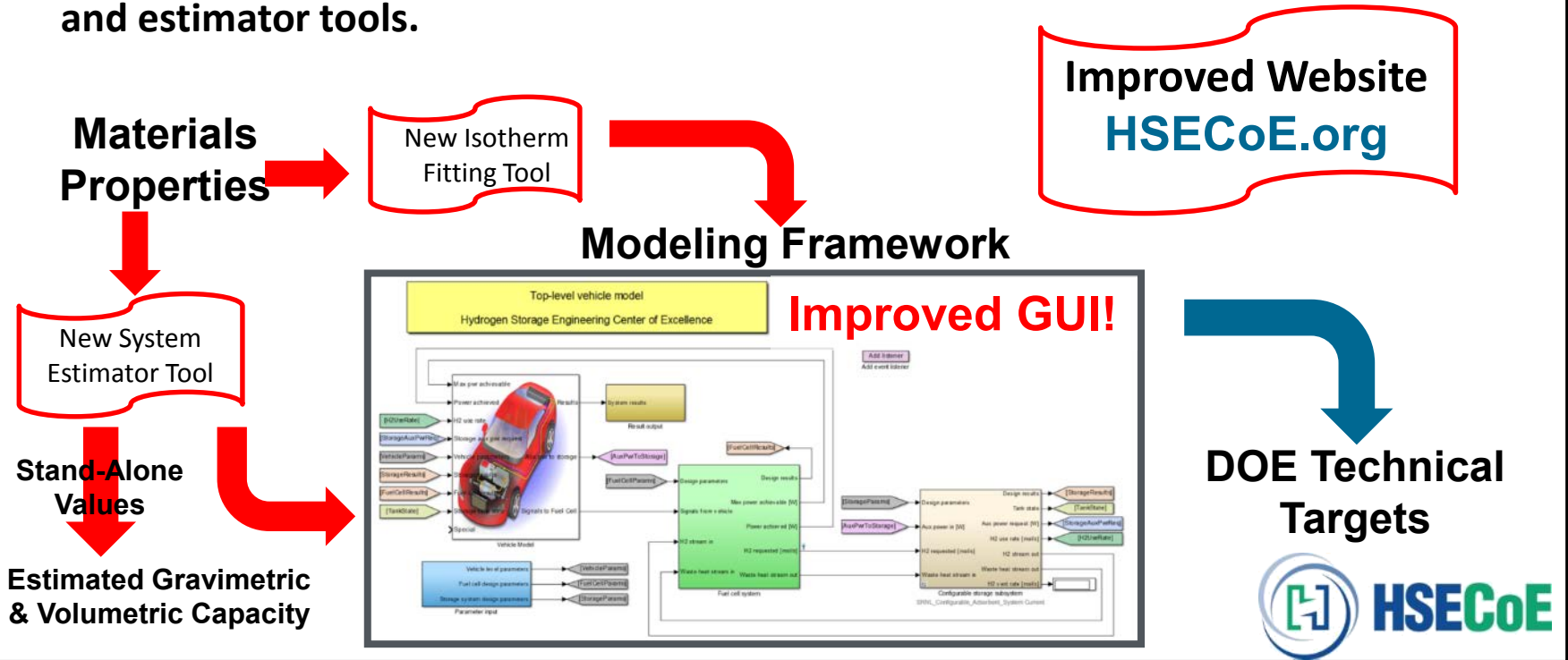
# Engineering



# Accomplishments - Project Highlights

## Maintenance and Enhancements for HSECoE Models [NREL/PNNL/SRNL]

- Collaborative effort to maintain, update and enhance system models developed under HSECoE to provide a resource to hydrogen storage materials developers
- Posted models include metal hydride, chemical, and sorbent H<sub>2</sub> storage systems
- **Improved framework utility for materials researchers through new isotherm fitting and estimator tools.**



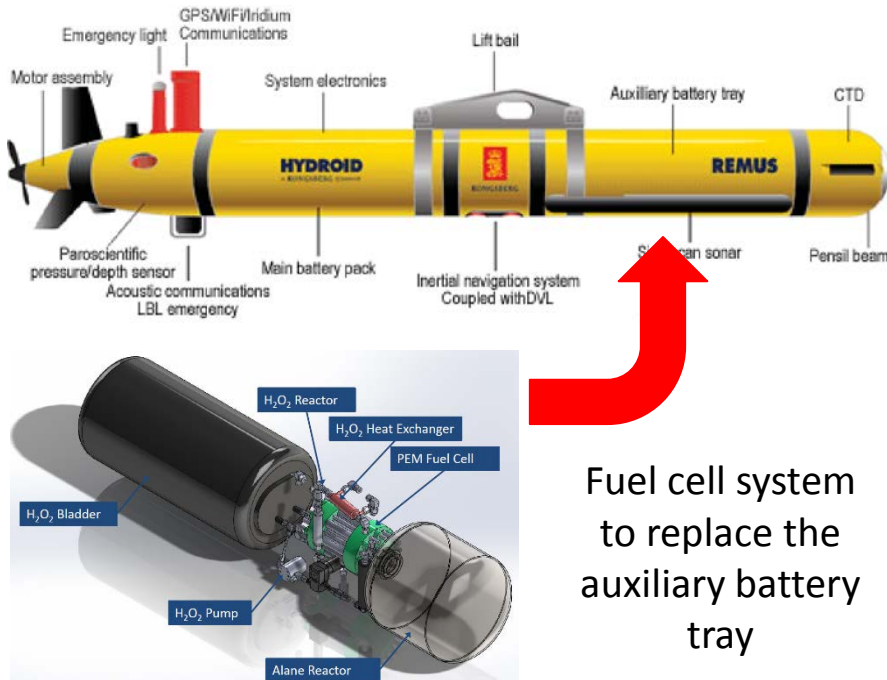
ST008

*Online system models maintained and accessible to the research community*

# Accomplishments - Project Highlights

## Materials-based H<sub>2</sub> Storage for UUV Applications [SRNL/US Navy/Ardica]

- Developing a materials-based H<sub>2</sub> storage system to extend UUV mission duration
- **Preliminary analysis indicate ≥2 times longer mission capability over battery operation**



Fuel cell system to replace the auxiliary battery tray

## Metal Hydride H<sub>2</sub> Storage for Forklift Applications [Hawaii H<sub>2</sub> Carriers/SRNL]

- ***Small Business Voucher*** project to demonstrate MHHS performance on a forklift under realistic conditions and its fast fill capabilities; perform preliminary DFMA analysis
- **System originally designed and built under a SBIR program**



ST134

*Leveraging HSECoE models and capabilities for high-value applications*

# Analysis

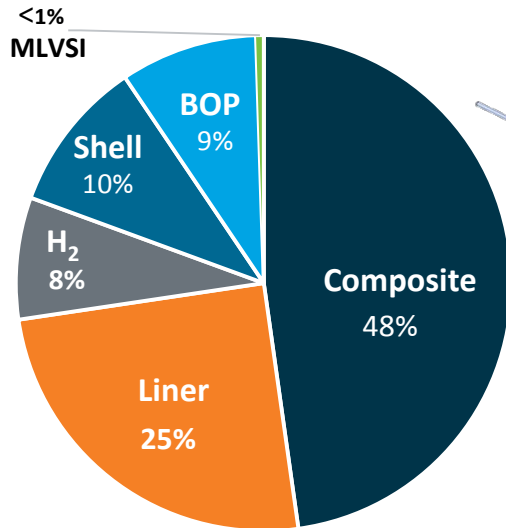
# Accomplishments – Project Highlights

## Hydrogen Storage System Performance [ANL] and Cost Analyses [SA/PNNL/ANL]

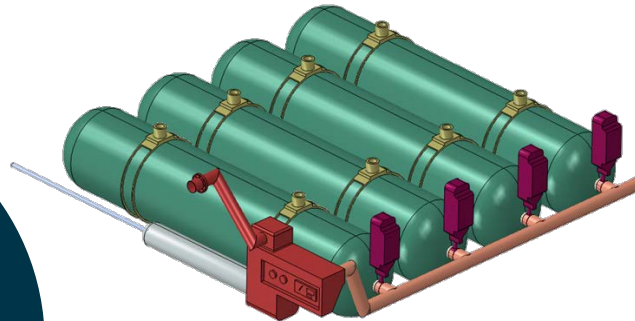
- Analyses are carried out to estimate system performance and cost of various technologies to help identify focus areas for the Program and to gauge technology development progress
- Cryo-compressed H<sub>2</sub> storage systems were evaluated for heavy duty fleet (bus) applications
- 500 bar, 40 kg H<sub>2</sub> capacity systems projected to be able to achieve 7.3 wt.% and 43 g/L storage densities with a cost of \$15/kWh**

### Analysis of a 40 kg H<sub>2</sub> capacity, 500 bar cryo-compressed system for bus applications

Weight breakdown

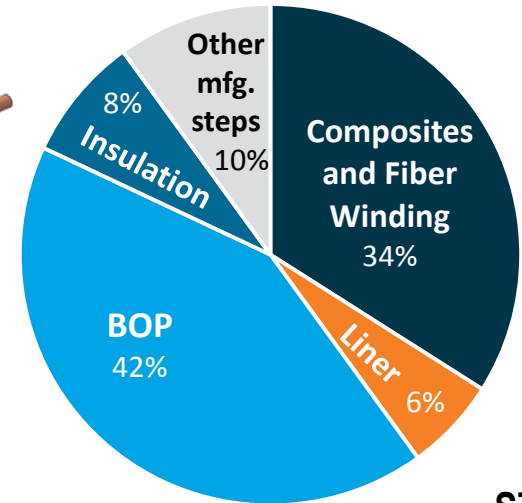


ST001



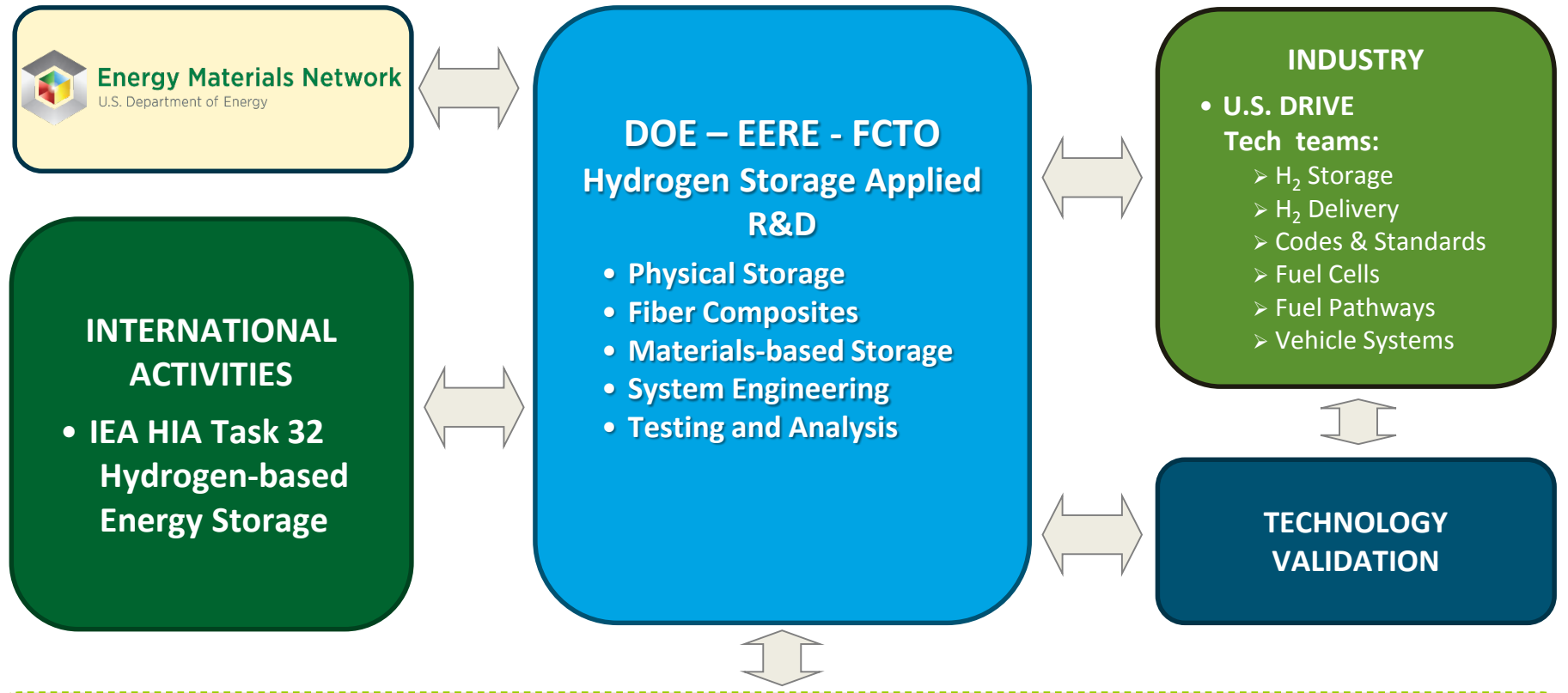
Cost Breakdown @ 5000/yr

\$19,907/System @ \$14.93/kWh

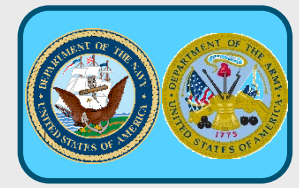
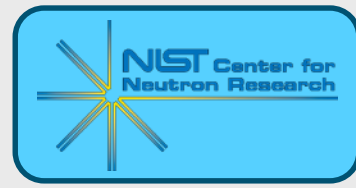
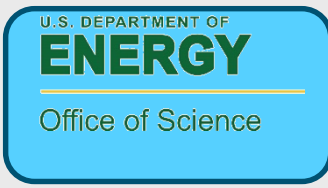
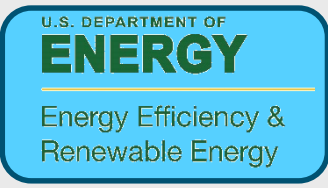


ST100

*Techno-economic and performance analyses used to target key R&D areas*



## National Collaborations (inter- and intra-agency efforts)



- **Physical Storage**
  - Focus is on developing technologies to lower the cost of 700 bar systems
  - On-going projects on alternative materials and manufacturing processes
  - Conformable tank designs may provide improved packaging onboard vehicles
  - FOA topic on low-cost, alternative precursors for high-strength carbon fiber
- **Materials-based Storage**
  - Focus is to accelerate development of H<sub>2</sub> storage materials with targeted properties
  - HyMARC core team performing foundational research to develop computational tools
  - Rechargeable metal hydrides and hydrogen sorbents are primary materials areas
  - First round of seedling projects underway and FOA topic to select second round
  - Engineering activities leverage prior work to meet needs of high-value applications

## FY 2017

- HyMARC team to prepare sorbent strategy prioritization
- First round of seedlings working with HyMARC
- Second round of seedlings to be selected
- Low-cost high-strength CF precursor projects to be selected

## FY 2018

- First round of seedlings have go/no-go decisions
- Second round of seedlings working with HyMARC
- Low-cost high-strength CF precursor projects up and running

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<http://energy.gov/eere/fuelcells/fuel-cell-technologies-office>

**BACK UP**



# HyMARC: Accelerating the discovery of breakthrough H<sub>2</sub> storage materials



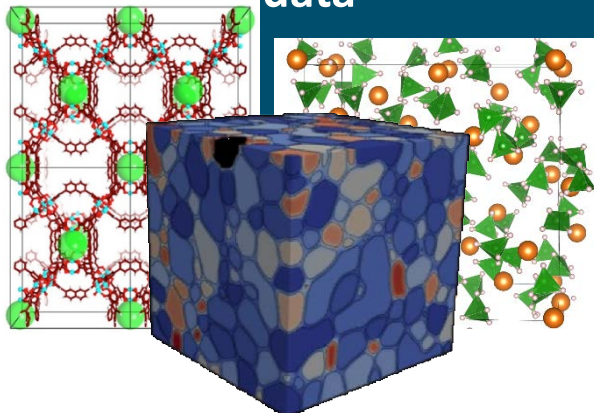
HyMARC provides **capabilities** and **foundational understanding** of phenomena governing thermodynamics and kinetics for the development of solid-state hydrogen storage materials

HyMARC delivers **community tools and capabilities**:

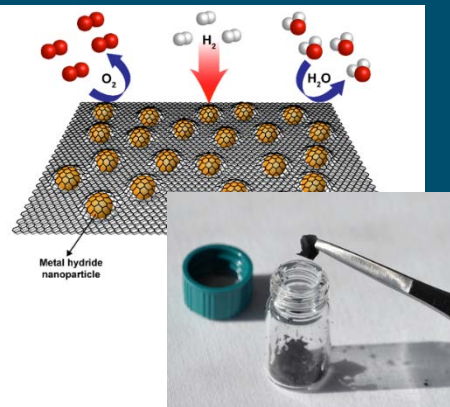
- **Computational models and databases** for high-throughput materials screening
- **New characterization tools and methods** (surface, bulk, soft X-ray, synchrotron)
- **Tailorable synthetic platforms** for probing nanoscale phenomena

Website: [hymarc.org](http://hymarc.org)

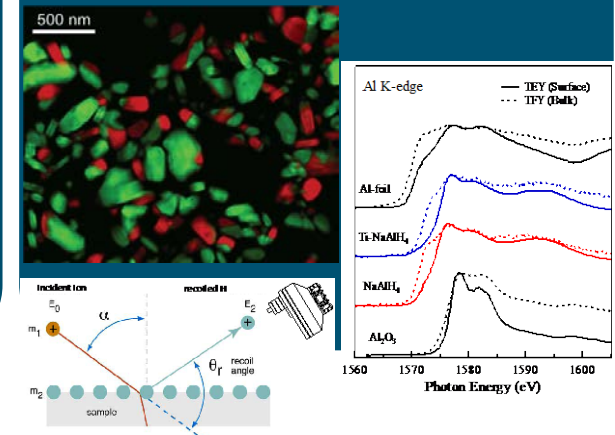
## Theory, simulation, & data



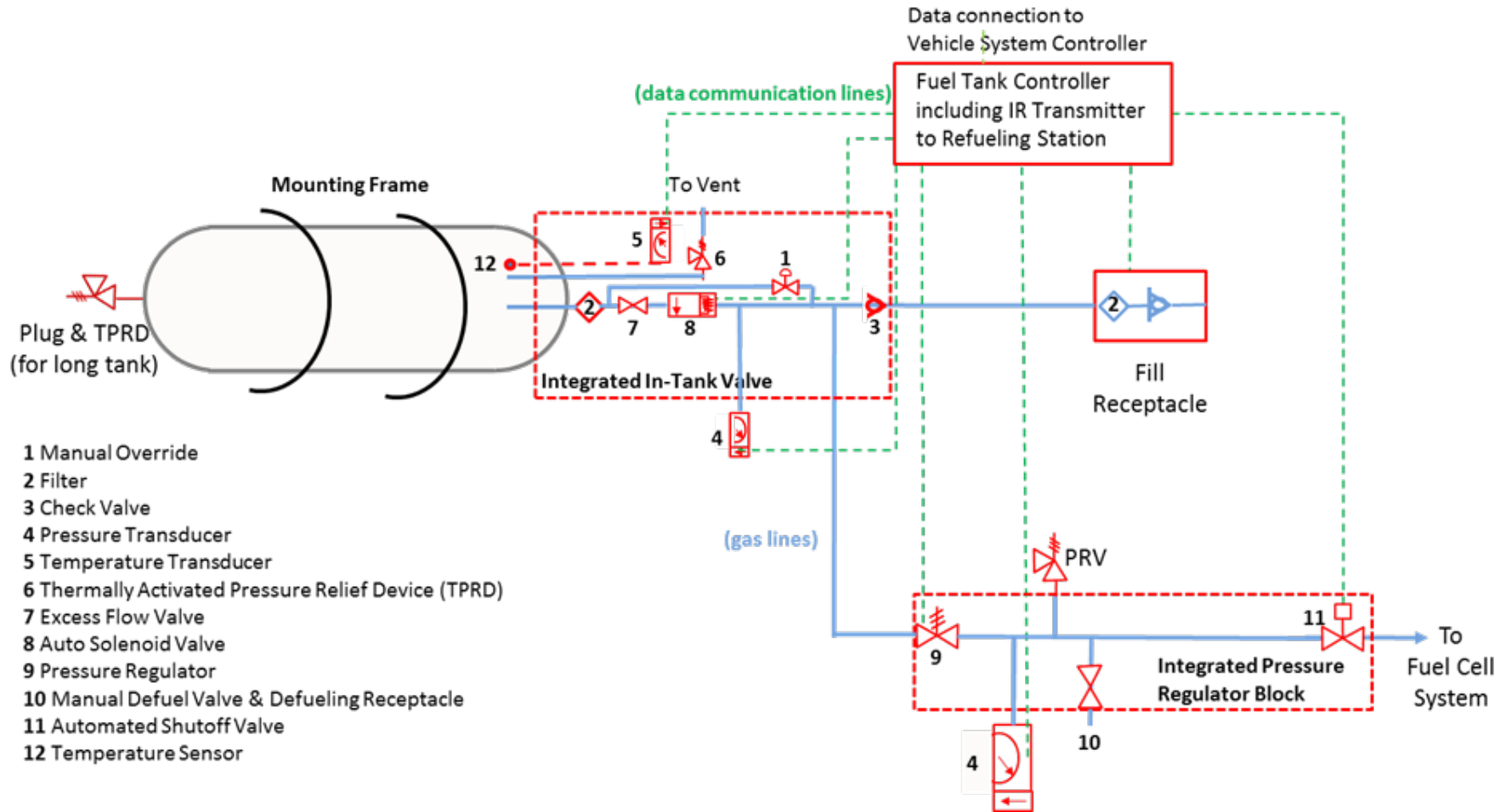
## Controlled synthesis



## In situ characterization



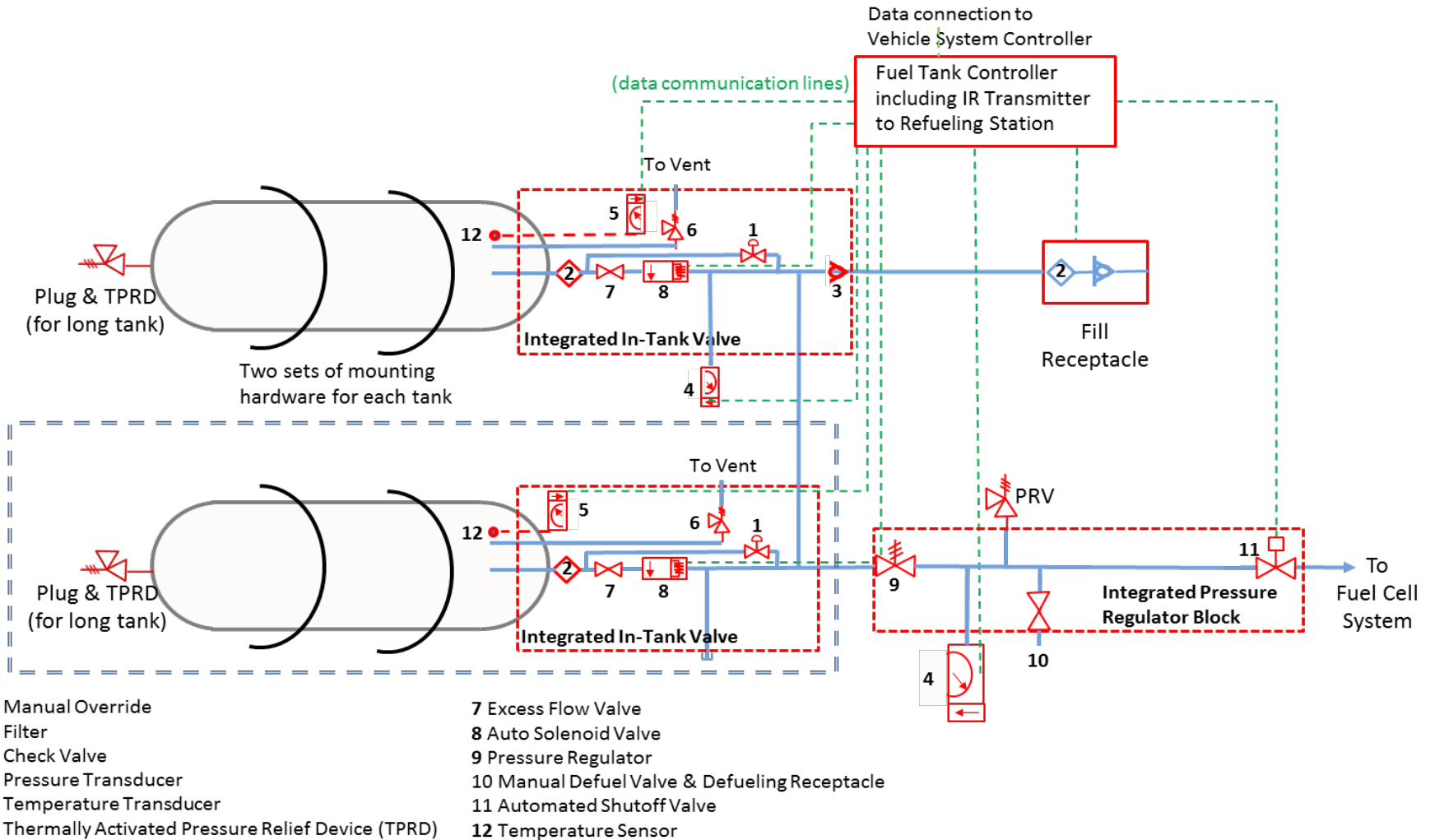
# Single tank system schematic



**Lowest cost, but most difficult to package onboard a vehicle**

*Baseline system projections based on single tank design*

# Dual tank system schematic



**Higher cost, but most easier to package onboard a vehicle**

*All current commercial FCEVs have dual tank designs*