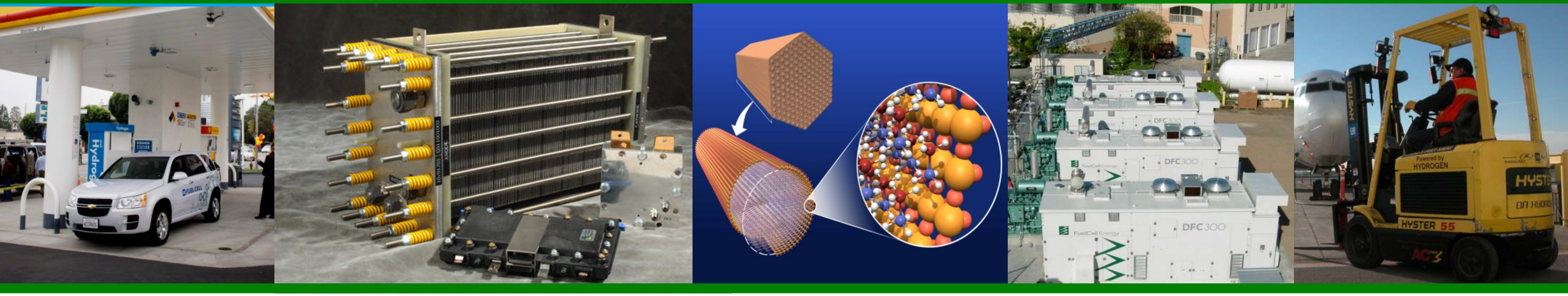
U.S. DEPARTMENT OF ENERGY




# Hydrogen Storage Program Area
# -Plenary Presentation-


*Ned T. Stetson*

*Fuel Cell Technologies Office*



***2016 Annual Merit Review and Peer Evaluation Meeting***

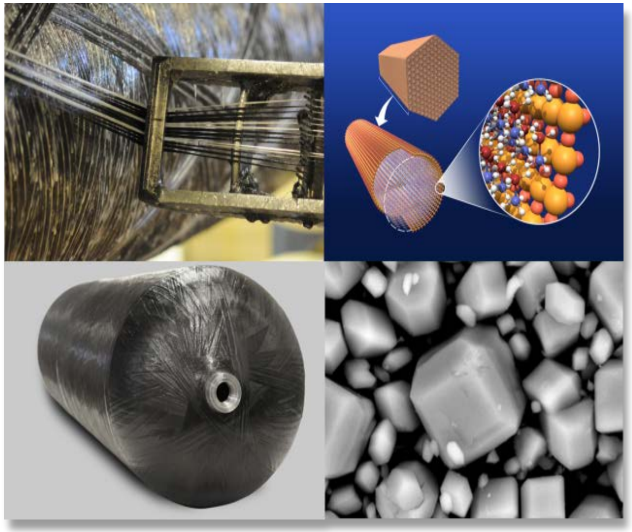
***June 6 - 10, 2016***

# Goals and Objectives



## Objectives

- By 2020, develop onboard vehicle $H_2$ storage systems achieving **1.8 kWh/kg** (5.5 wt% $H_2$) and **1.3 kWh/L** (40 g $H_2$/L) at **$10/kWh** ($333/kg $H_{2\ stored}$) or less.
- By 2020, demonstrate $H_2$ storage systems in MHE applications achieving **1.7 kWh/L** (50 g$H_2$/L); ability to recharge with 2 kg of $H_2$ within 2.8 minutes at **$15/kWh** ($500/kg $H_{2\ stored}$) or less.
- Ultimate targets: to develop onboard $H_2$ storage systems achieving **2.5 kWh/kg** (7.5 wt.% $H_2$) and **2.3 kWh/L** (70 g $H_2$/L) at **$8/kWh** ($266/kg $H_{2\ stored}$) or less.
- Other specific objectives are in the Hydrogen Storage Section of the MYRD&D Plan.



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

# Hydrogen Storage Team - Strategy and Barriers



## Dual approach

- Hydrogen Storage
  - Near-Term Approach
  - Longer-Term Approach

## Technology Focus

**Near-Term Approach:**

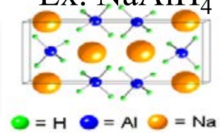
- 700 bar Compressed

**Longer-Term Approach:**

- Cold / Cryo-Compressed

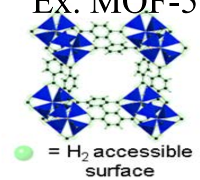
- Metal Hydrides

Ex. $NaAlH_4$



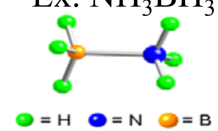

- Sorbents

Ex. MOF-5




- Chemical $H_2$ Storage

Ex. $NH_3BH_3$




## Barriers and R&D Focus

**700 bar Compressed:**
- Lower Cost Carbon Fiber
- Improved Composites
- Conformable designs
- Lower Cost BOP

**Cold / Cryo-Compressed:**
- System Engineering
- Advanced Insulation
- Improved Dormancy
- Composite Development

**Metal Hydrides:**
- Higher Material Capacity
- System Cost
- Fill Time
- Onboard Efficiency

**Sorbents:**
- Higher Material Capacity
- System Cost
- Dormancy
- WTP Efficiency

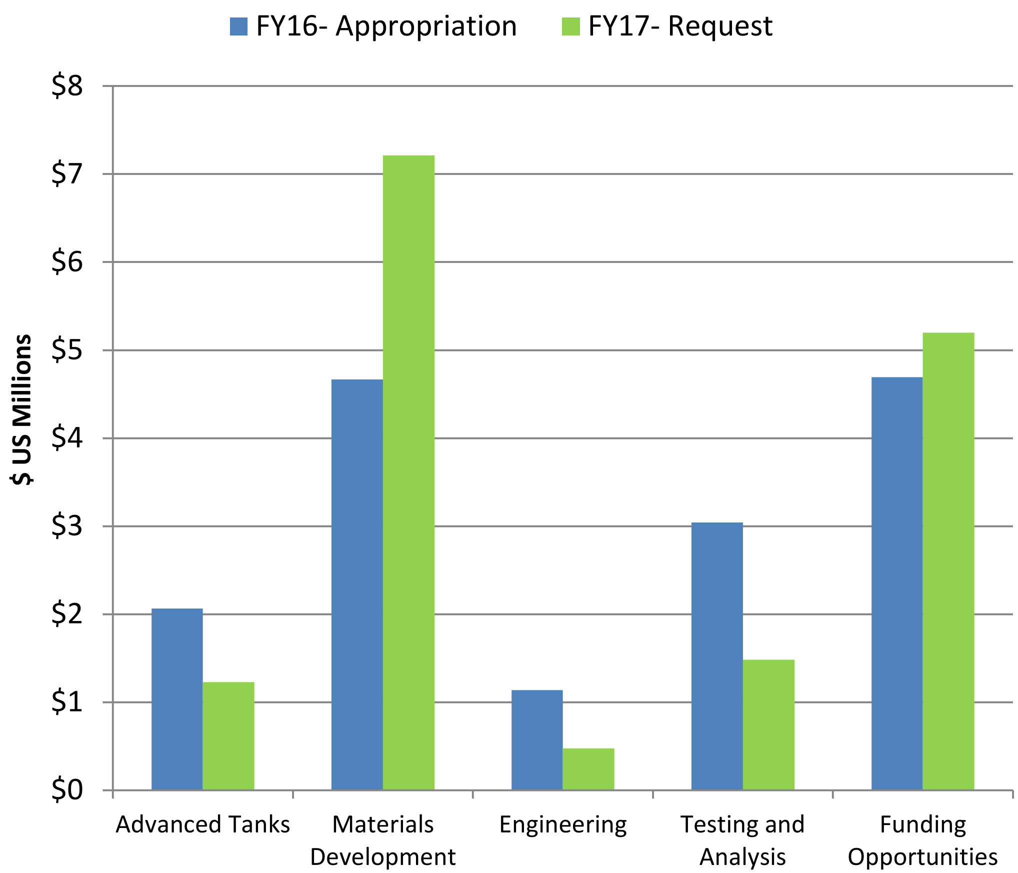
**Chemical $H_2$ Storage:**
- Lower Cost Off-board Regen
- System Cost
- Gravimetric Density

***Objective: Achieve a driving range >300 miles for full span of light-duty vehicles, while meeting packaging, cost, safety, & performance requirements***

# Budget

**FY 2016 Appropriation = $15.6M**

**FY 2017 Request = $15.6M**




## EMPHASIS

- Close coordination with EERE Offices on carbon fiber composites, including AMO, VTO and BETO
- Focus on cost reduction for high pressure tanks
- Increase materials development efforts through national lab-led consortium, HyMARC, and materials characterization and validation capabilities
- Portfolio is balanced between mid- and long term

***Steady budget for several consecutive years, annual FOAs to initiate new projects in target technology areas***

# Current Status of $H_2$ Storage Technologies



| Storage Targets | Gravimetric kWh/kg (kg $H_2$/kg system) | Volumetric kWh/L (kg $H_2$/L system) | Costs \$/kWh (\$/kg $H_2$) |
|---|---|---|---|
| 2020 | 1.8 (0.055) | 1.3 (0.040) | \$10 (\$333) |
| Ultimate | 2.5 (0.075) | 2.3 (0.070) | \$8 (\$266) |

Full set of comprehensive hydrogen storage targets can be found in the Program's Multi-year Research, Development and Demonstration Plan: http://energy.gov/sites/prod/files/2015/05/f22/fcto_myrdd_storage.pdf

| Projected $H_2$ Storage System Performance (5.6 kg $H_2$ usable) | Gravimetric kWh/kg (kg $H_2$/kg system) | Volumetric kWh/L (kg $H_2$/L system) | Costs* \$/kWh (\$/kg $H_2$) |
|---|---|---|---|
| 700 bar compressed (Type IV, Single Tank) | 1.4 (0.044) | 0.8 (0.024) | \$15 (\$500) |
| Metal Hydride ($NaAlH_4$/Ti) | 0.4 (0.012) | 0.4 (0.012) | \$43 (\$1,432) |
| Sorbent (MOF-5, 100 bar, MATI, LN2 cooling) | 1.3 (0.04) | 0.7 (0.020) | \$16 (\$533) |
| Chemical Hydrogen Storage (AB-50 wt.%) | 1.4 (0.043) | 1.3 (0.040) | \$17 (\$566) |

- 700 bar compressed $H_2$ system projections from ANL / SA
- Materials-based system projections from Hydrogen Storage Engineering Center of Excellence (5/2015)

* Projected at 500,000 units / year

# Physical Storage

## Low-cost CF precursors [ORNL/VT]

- Approach: Melt-spinning process to produce PAN/comonomer fiber for use as precursor for high-strength CF production
- Goal: ~30% lower cost CF than with conventional PAN precursor fibers
- **Down-selected water/plasticizer combinations for PAN/VA formulations and demonstrated spinning of >100 filament tows of length >10m**


Modified extruder feed

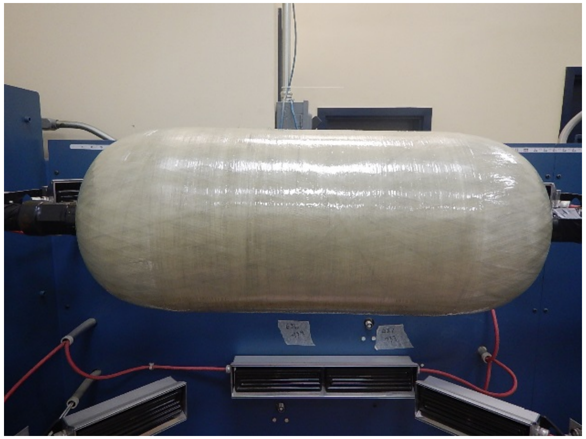

Melt-spun PAN/MA fiber

ST093

## Low-cost alternative fibers to CF [PPG/Hexagon Lincoln/PNNL]

- Approach: Ultra-high strength fiber glass
- Goal: New fiber glass with tensile strength exceeding Toray T700 CF at ~50% of cost
- Demonstrated pilot scale high temperature glass fiber manufacturing process and produced 1200 lb of fiber glass
- High strength fiber tanks outperformed the reference fiber tanks on burst pressure and cyclic pressure tests.
- **One high strength fiber with sizing A significantly outperformed on stress rupture test.**


Batch melting process


Vessel winding

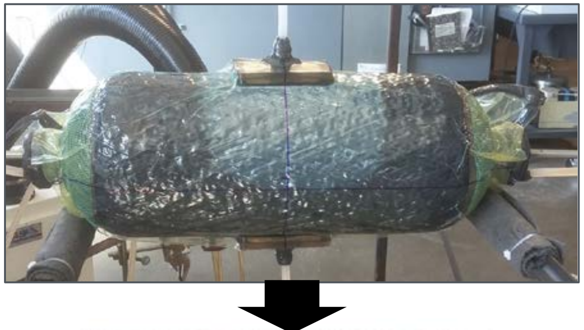
ST115

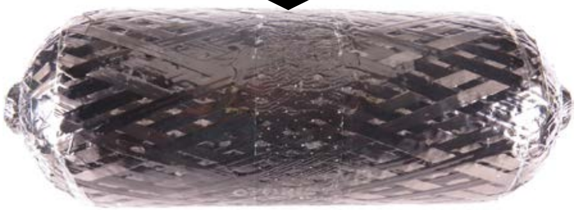
***Reducing cost of composites for use in $H_2$ storage vessels***

# Accomplishments - Project Highlights

## Alternative resin and manufacturing [Materia/MSU/Spencer Composites]

- Approach: low-viscosity, high-toughness resin with VARTM manufacturing process
- Goal: 35% reduction in composite costs
- Optimized vacuum infusion process and winding pattern, achieved infusion of high quality, small COPV
- **Achieved burst pressure of 732 ksi compared to 693 ksi obtained from a wet wound epoxy resin tank.**





**ST114**

## Optimized cost and performance of COPVs [CTD/ORNL/Adherent Tech.]

- Approach: Graded construction utilizing thick wall effect
- Goal: demonstrate potential for 10-25% lower cost through graded-construction approach
- Evaluated Panex 35 ™ as potential lower-cost candidate fiber to replace portion of Toray T700S
- **Updated Analysis: Cost reduction potential of 9-33%**


**ST110**

***Reducing cost of $H_2$ storage vessels through alternative manufacturing***

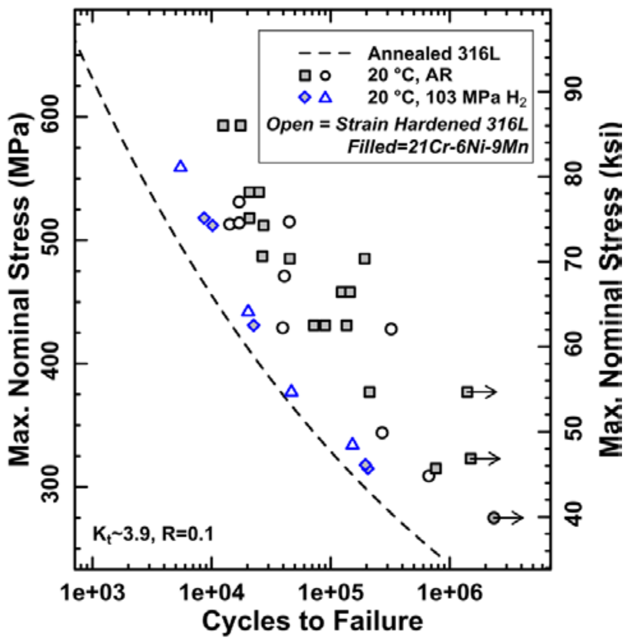
# Accomplishments - Project Highlights



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

- Approach: Screening based on fatigue stress and computational material design
- Goal: Reductions in BOP of up to 50% in weight and 35% in cost
- **Fatigue performance quantified for low-Ni austenitic stainless steel: 21Cr-6Ni-9Mn (XM-11).**

Fatigue life for both XM-11 and strain-hardened 316L exceeded annealed 316L baseline material's fatigue life.

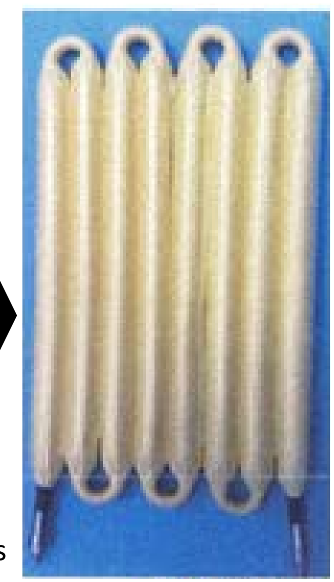



ST113

## Conformable 700 bar $H_2$ Storage Systems [CTE/HECR/UT]

- Approach: Develop a light weight, low cost over-braided, coiled pressure vessel for 700 bar $H_2$ storage
- Goal: Surpass DOE system targets for specific energy (3.7 kWh/kg) and cost (< $10/kWh)
- Achieves efficient onboard vehicle packaging through use of a shaped corrugated core over-braided with aramid fiber for strength
- **Selected resin for prototype vessel permeability testing**

Kevlar Overbraiding



Over-braided coiled vessels

ST126

***Alternative materials for BOP and conformable designs***

# Accomplishments - Project Highlights

## Cold-compressed $H_2$ storage [PNNL/Ford/Hexagon Lincoln/AOC/Toray]

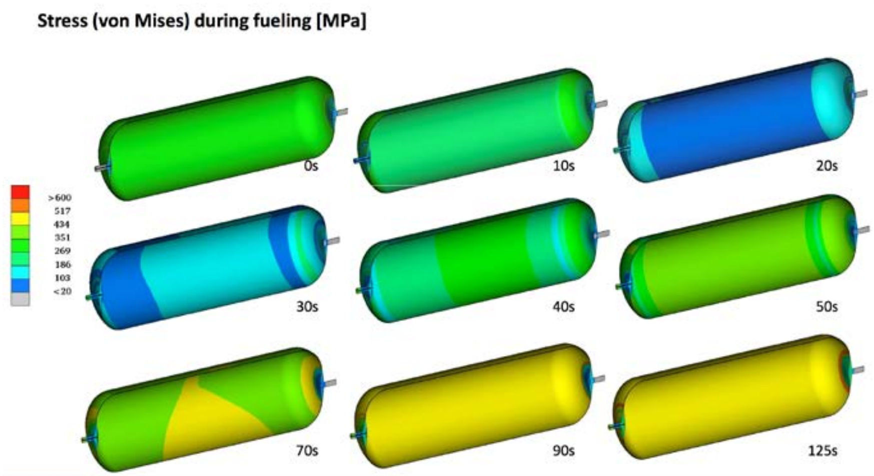
- Approach: Synergistically consider pressure vessel and operating conditions (500 bar, 200 K)
- Goal: 30% reduction in system cost over 2013 baseline cost for 700 bar system
- Vinyl Ester and epoxy resin composites both show improved strength at 200 K
- **Lower-cost vinyl ester resin (XR-4079) able to match epoxy performance with 5-7% weight**

| | | Epoxy | Vinyl Ester |
|---|---|---|---|
| | Test Type | Relative Burst | Relative Burst |
| No Impact | Burst | 105% | 111% |
| | Cycle A | 100% | 103% |
| | Cycle B | 99% | 95% |
| | | | |
| Impact test round 1 | Burst | 57% | 55% |
| | Cycle A | 67% | DNF |
| | Cycle B | 58% | 63% |
| | | | |
| Impact test round 2 | Burst | 70% | 82% |
| | Cycle A | 55% | 74% |
| | Cycle B | 62% | 67% |

ST101

## Cryo-compressed $H_2$ storage [LLNL/BMW/Linde/Spencer]

- Approach: Develop a thin-lined, high fiber fraction composite pressure capable, cryogenic vessel
- Goal: Demonstrate 3 kWh/kg and 1.7 kWh/L system capacities at 700 bar
- Installed new test facility for vessel cryo-compress cycle testing
- **Fluid and structural computational modeling of wall stress during refueling performed**



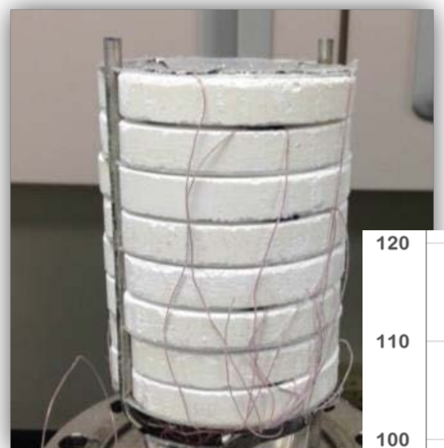

ST111

***Cold and cryo-compressed $H_2$ storage for improved performance***

# Materials Based

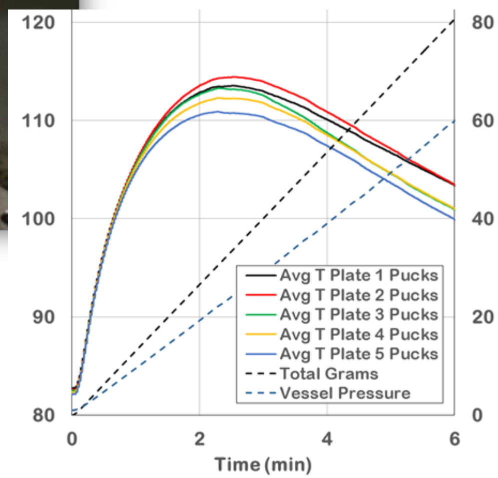
# Accomplishments – $H_2$ Storage Engineering CoE

## Evaluated two sorbent prototype systems for model validation:



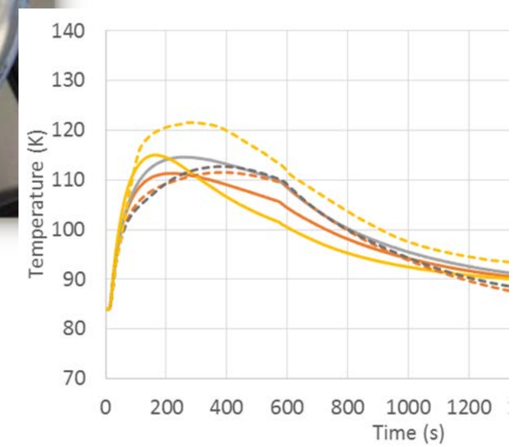
MATI

$H_2$ Charging @ 150 SLPM




Hexcell

$H_2$ Charging @ 100 SLPM, 80 Bar




## Posted system models online for research community use: *http://HSECoE.org*

- MH acceptability envelope
- MH finite element model
- MH framework model
- Physical $H_2$ framework models
- Chemical hydrogen framework model
- Adsorption framework model
- Adsorption finite element model (coming)
- Tank volume/cost model

**ST004 & ST008**

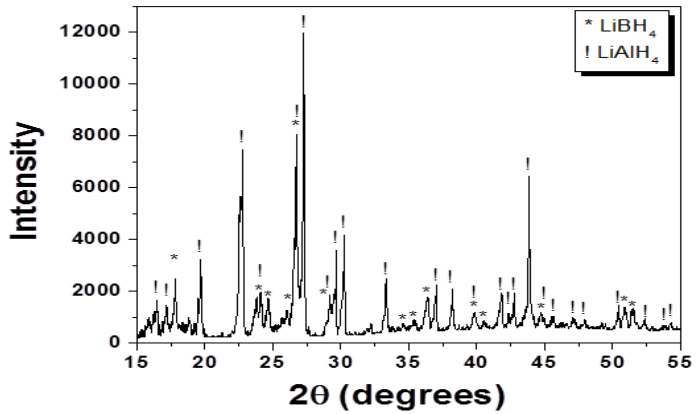
***Online system models maintained and accessible to the research community***

# Accomplishments - Project Highlights

## Low-cost methods for α-alane production [SRNL]

- Approach: Develop low-cost, efficient processes for alane synthesis
- Focused on improving electrochemical process for efficient α-alane production, coupled with
- Improving the recrystallization process of high-capacity α-alane
- **Achieved >99% recovery of electrolyte and additive materials**

Reagent recovery after α-alane recrystallization

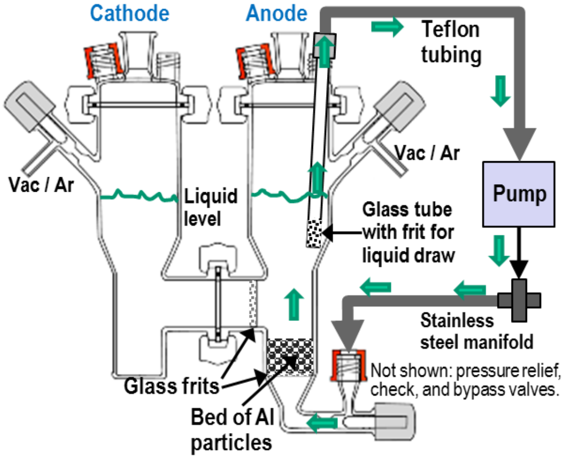



ST063

## Low-cost methods for α-alane production [Ardica/SRI]

- Approach: Develop fluidized electrochemical process for low-cost commerical α-alane production
- Goal: Reduce alane production costs to less than $10/kg
- **Demonstrated successful isolation of an alane adduct from highly conducting $NaAlH_4$/THF electrolyte**

Schematic of particle bed electrochemical cell



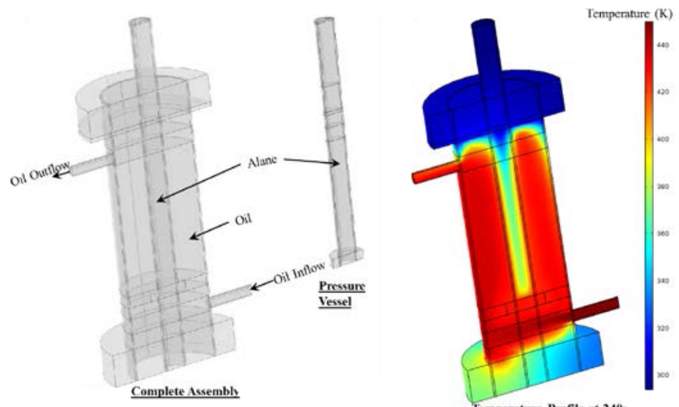

ST116

***Low-cost α-alane production for commercial applications***

# Accomplishments - Project Highlights

## Materials-based $H_2$ Storage for UUV Applications [SRNL/US Navy/Ardica]

- Objective: Screen $H_2$ storage systems to meet DoD targets and requirements for UUV applications.
- Goal: Develop complete system designs that meet Gen 1 and 2 requirements.
- Identified reversible (Gen 1) and non-reversible (Gen 2 ) materials that meet UUV targets
- Completed preliminary engineering analysis and proof-of-concept testing for an $AlH_3$ system
- **Preliminary analysis indicate 2-3 times energy storage compared to battery systems**

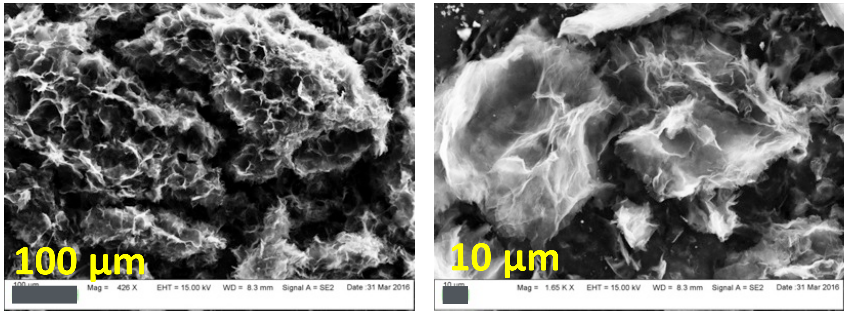



ST134

## Design and Synthesis of Materials with High-Capacities for Hydrogen Physisorption [California Institute of Technology]

- Objective: Develop high performing $H_2$ adsorbents prepared from either graphene or exfoliated graphite.
- Goal: A hydrogen storage capacity of ≥ 11 wt.%, and near-constant isosteric heat of adsorption.
- Prepared activated graphene oxide material with 2336 $m^2/g$
- **Demonstrated metal functionalization of graphene via plasma deposition and chemical routes**

KOH activation of microwaved GO




ST120

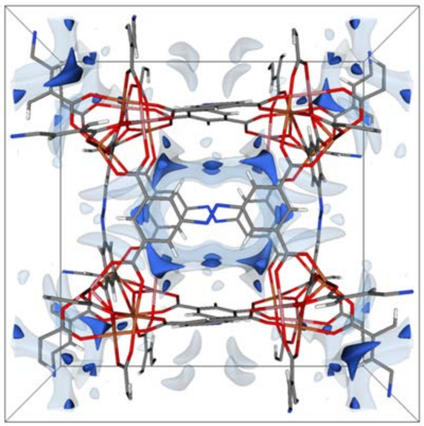
***Leveraging HSECoE models and developing improved $H_2$ sorbents***

# Accomplishments - Project Highlights

## High-Capacity & Low-Cost Hydrogen-Storage Sorbents for Automotive Applications [Texas A&M University]

- Objective: Develop metal-organic framework (MOF) sorbents with capacities exceeding the conventional storage limit per unit surface area
- Approach: Design MOF materials with high-valent metals to increase $H_2$ affinity relative to surface area to exceed the Chahine rule
- Performed detailed characterization, including activation and densification studies, of PCN-250
- **Measured 1.5x Chahine rule prediction for excess $H_2$ adsorption**

Potential energy contours for $H_2$ absorbed in PCN-250.

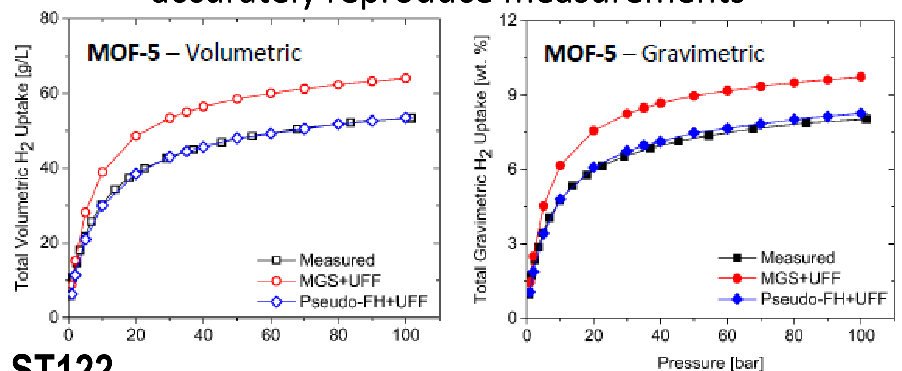


ST121

## Hydrogen Adsorbents with High Volumetric Density: New Materials and System Projections [University of Michigan]

- Objective: Develop high volumetric adsorbents that also have high gravimetric capacities
- Approach: Investigate "best-in-class" sorbents identified through screening of reported structures in the Cambridge Structure Database
- Computationally screened over 2000 MOFs for adsorption capacity – identifying several promising candidates
- **IRMOF-20 synthesized and shown to have higher usable capacity than MOF-5**

Pseudo-FH force field appears to more accurately reproduce measurements




ST122

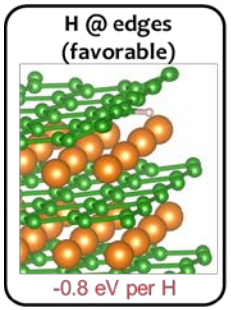
**_New MOF development targeting high volumetric capacities_**

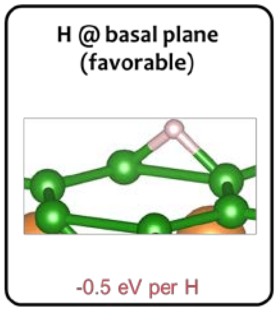
# Accomplishments - Project Highlights

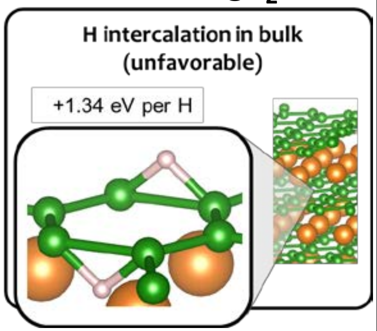
## Improved performance for $Mg(BH_4)_2$ [LLNL/SNL]

- Approach: Combined computational and empirical effort to identify ways to improve performance
- Goal: Develop flexible, validated, multi-scale model and use to develop practical material that satisfies DOE 2020 targets.
- Computed energetics of hydrogen in $MgB_2$
- **Experimental evidence supports proposed mechanism of selective hydrogenation of B atoms concentrated at interfaces in $MgB_2$, forming $BH_4$-like species**

**Thermodynamic computations suggest hydrogen migrates to surfaces and interfaces of $MgB_2$**



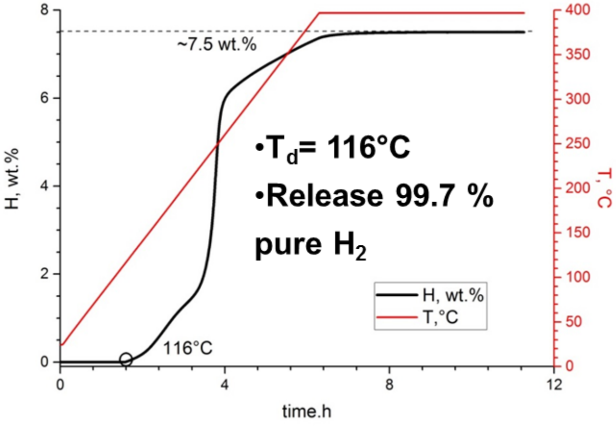




ST118

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

- Objective: Develop low-cost, reversible, high-performance $H_2$ storage materials
- Approach: Computational modeling to guide mechanochemical processing synthetic methods to produce hypersalts of silicon borohydrides
- Computational screening identified several metastable candidates to investigate
- **Investigated several novel systems with potential of over 17 wt.% theoretical $H_2$ capacity**

**Desorption isotherm for "$LiSi(BH_4)_5$"**




ST119

***Boron-based, high-capacity $H_2$ storage materials***

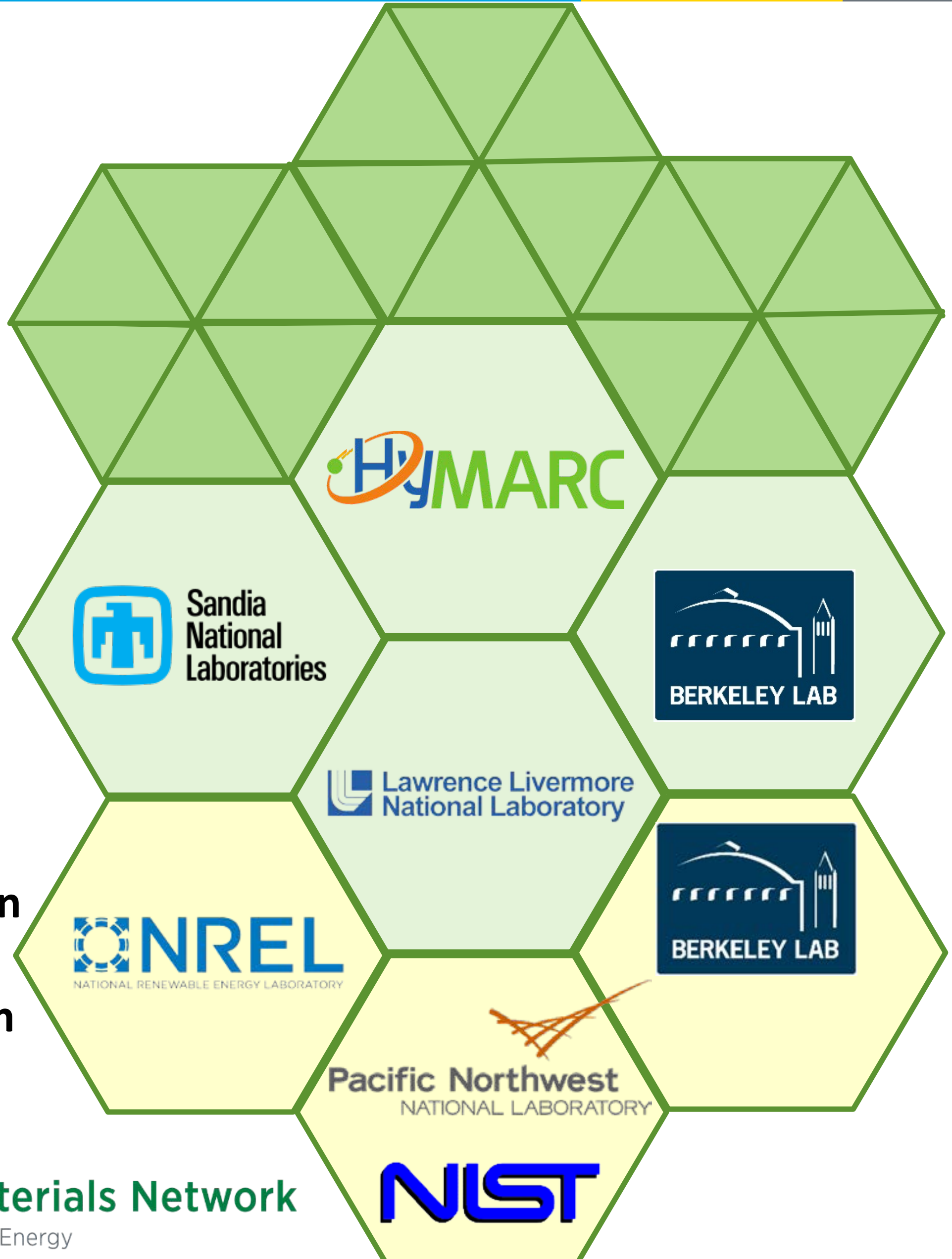
# New Effort: HyMARC
## *Hydrogen Materials – Advanced Research Consortium*



**Individual projects**

**Core National Laboratory Team**

**Characterization and Validation Team**




- **Applied material development**
  - Novel material concepts
  - High-risk, high-reward
- **Concept feasibility demonstration**
- **Advanced development of viable concepts**

- **Material development tools**
  - Foundational R&D
  - Computational modeling development
  - Synthetic/characterization protocol development
- **Guidance to FOA projects**
- **Database development**

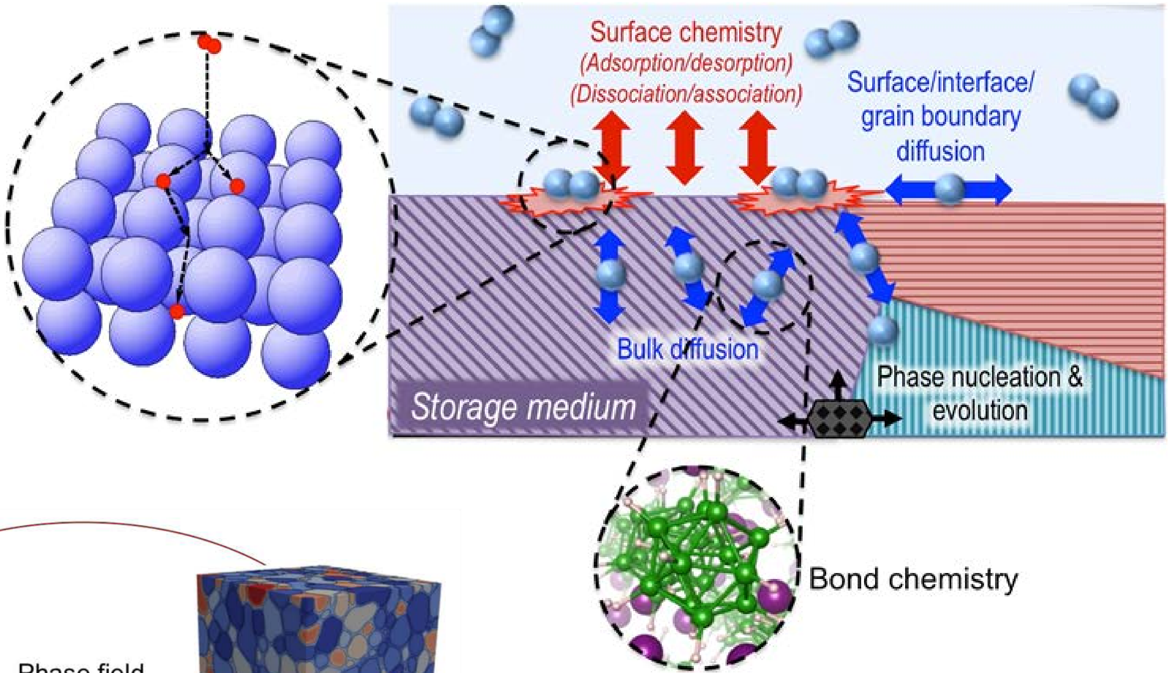
- **Characterization Resources**
  - Validation of Performance
  - Validation of “Theories”
- **“User-facility” for FOA projects/HyMARC**
- **Characterization Method Development**

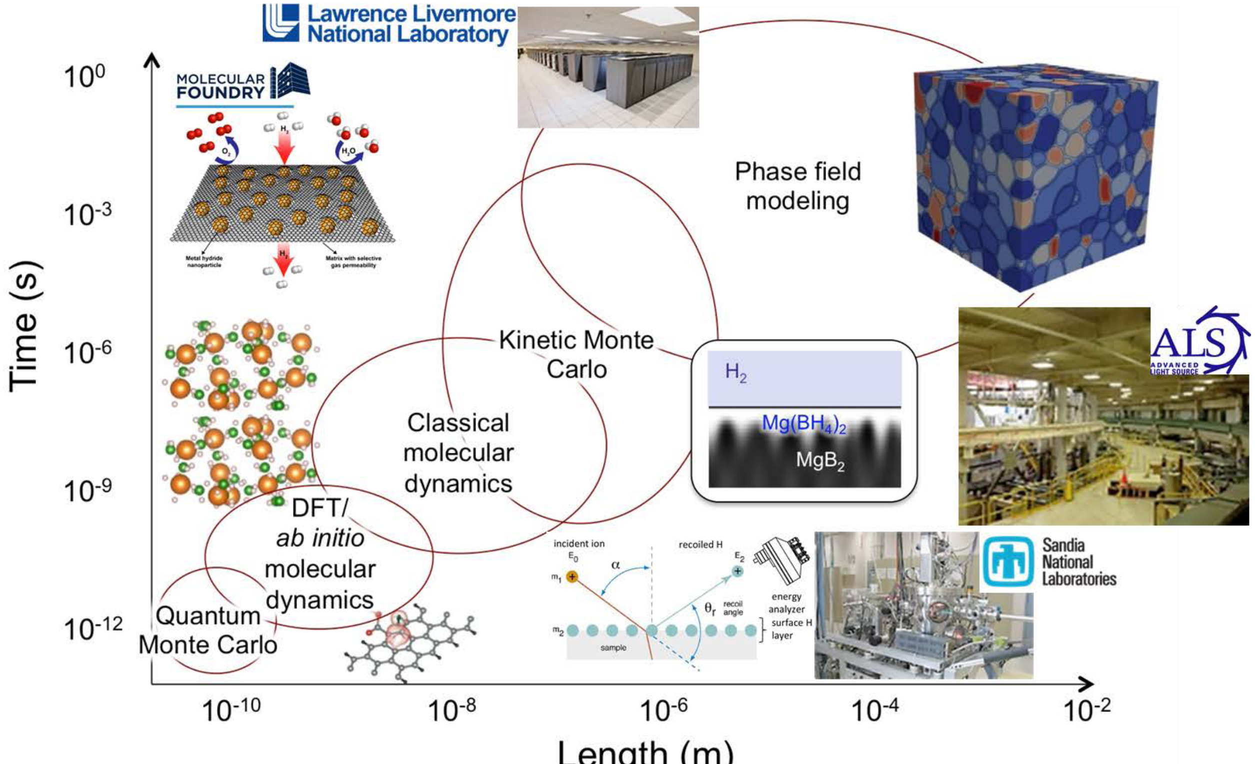
Part of the
Energy Materials Network
U.S. Department of Energy

# New Effort: HyMARC
# The Core National Laboratory Team (SNL/LLNL/LBNL)

***Address large gaps in the foundational science of hydrogen storage materials:***

- Reaction thermodynamics
- Solid-state diffusion
- Surface chemistry
- Phase nucleation and microstructure
- Catalysis and additive behavior




***Development of tools to accelerate development of hydrogen storage materials:***

- Multi-scale, multi-physics computational materials design tools
- Advance materials characterization tools
- Synthetic protocols
- Database development

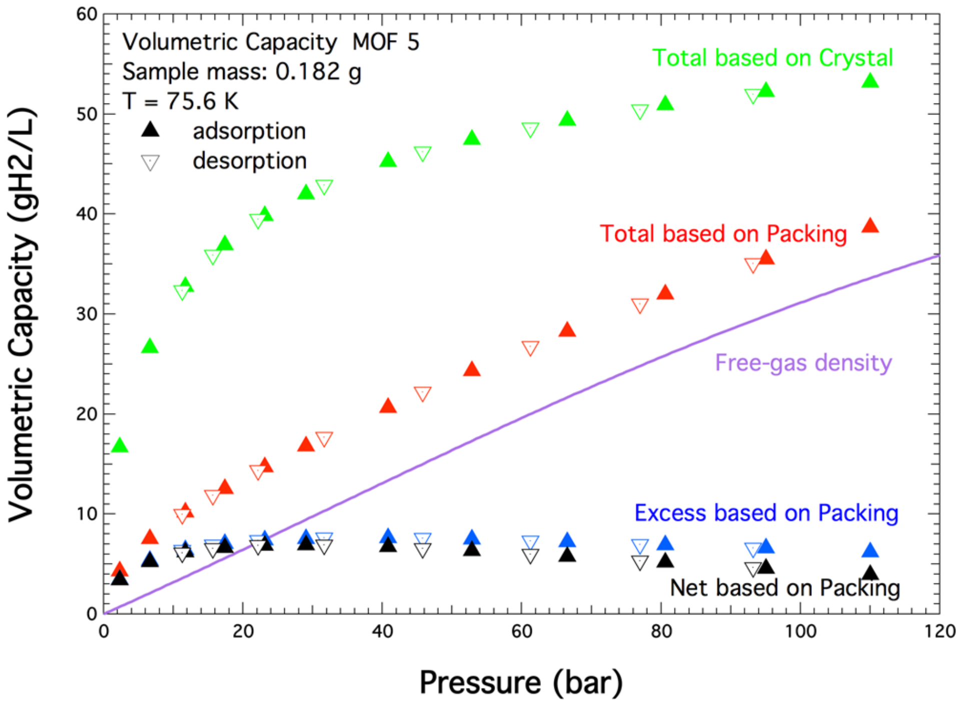
**ST127; ST128; ST129; ST130**

# New Effort: The Hydrogen Storage Characterization and Validation Research Team (NREL/PNNL/LBNL/NIST)

***Previously supported core characterization and validation capabilities combined into a coordinated effort:***

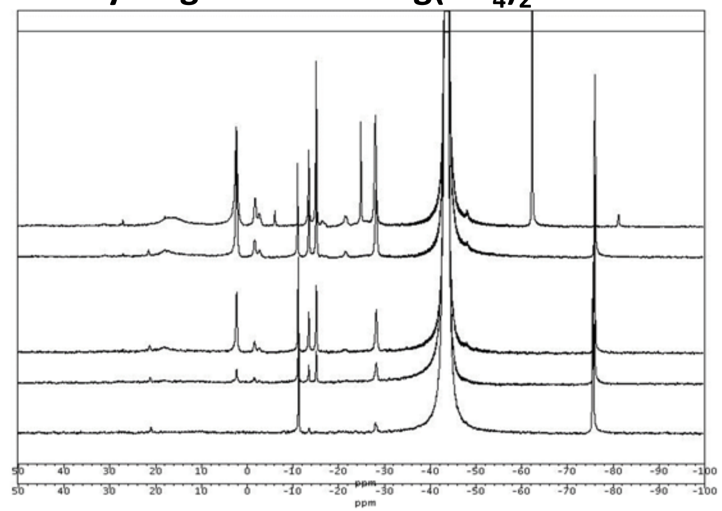
- To *Develop* and *Enhance* Core Characterization Techniques and Capabilities
- To *Validate* claims, concepts, and theories of hydrogen storage materials

**Normalization of reporting of capacity volumetric data**




**ST014; ST131; ST132; ST133; ST135**

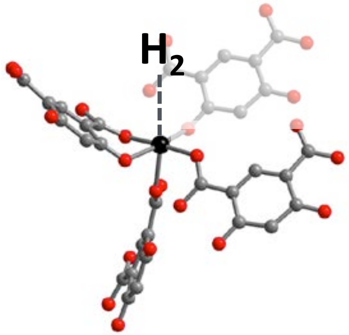
***In-situ* solid-state MAS [11]B NMR of the dehydrogenation of $Mg(BH_4)_2$ at 200 °C**



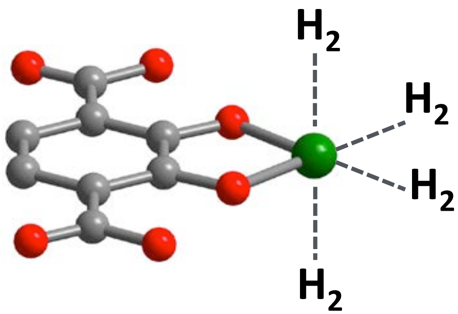

***Suite of characterization capabilities available include:***

- Variable temperature (cryogenic to high) $H_2$ adsorption measurements
- Variable temperature thermal conductivity
- Extensive NMR (liquid and solid-state)
- Microscopy
- Reaction calorimetry
- IR spectroscopy (DRIFTS)
- Various neutron methods:
  - Diffraction
  - Inelastic neutron scattering
  - Plus others

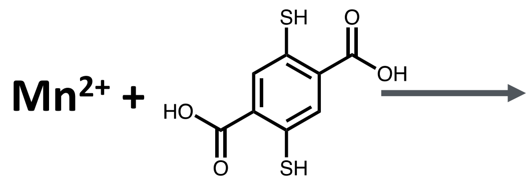
# Major Achievement: *First example of multiple $H_2$ molecules adsorbed at a single metal center*

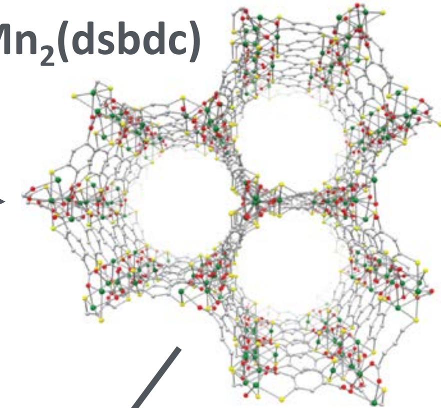



**Traditional Materials:**
**1 $H_2$ per metal cation**



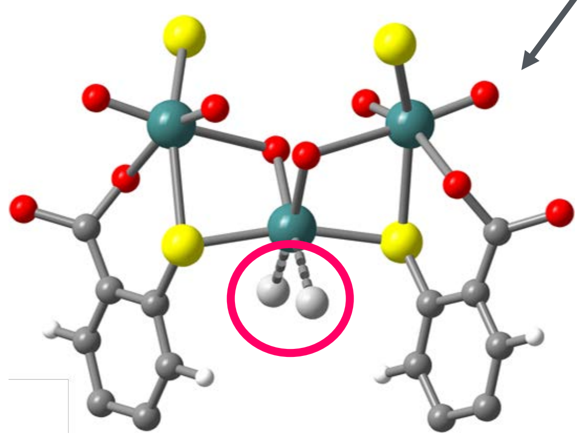

**Target Materials:**
**4 or more $H_2$ per metal cation??**




After desolvation the structure contains 4-coordinate **$Mn^{2+}$** atoms, which can adsorb 2 $H_2$ molecules

**+ $H_2$**



- Can we synthesize materials with under-coordinated metal sites?
- Materials with > 1 $H_2$ molecule adsorbed per site could display substantially increased volumetric capacities
- $Mn_2$(dsbdc) synthesized by **Jeff Long (UC-Berkeley/LBNL)**; neutron diffraction by **Craig Brown (NIST)**
- Meets FY16 GNG for NREL-led characterization team

**First example of multiple $H_2$ molecules adsorbed at a single metal site**

Runčevski, T.; Kapelewski, M. T.; Torres-Gavosto, R. M.; Tarver, J. D.; Brown, C. M.; Long, J. R. *Chem. Commun.*, submitted.

**ST133; ST135**

***Demonstrates a synthetic path to materials with higher densities of adsorbed $H_2$***

# Analysis

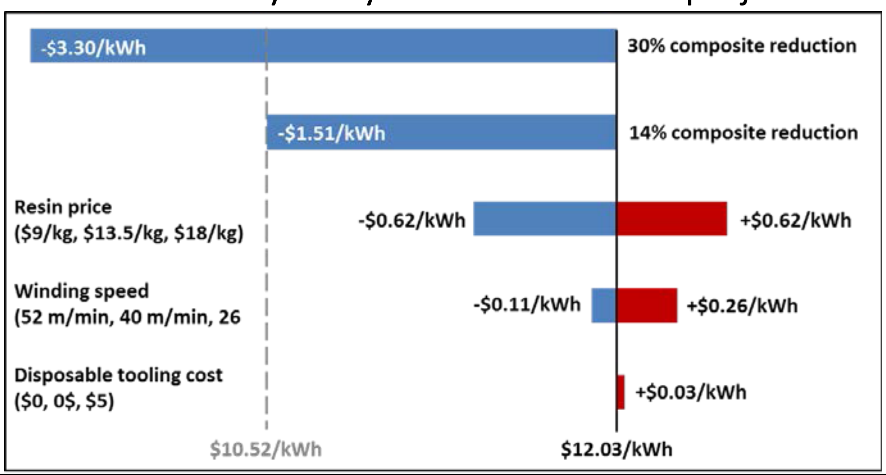
# Accomplishments- Highlights



## Hydrogen Storage Cost Analysis [SA/ANL/NREL]

- Approach- Conduct "Design For Manufacture and Assembly" analyses of $H_2$ storage technologies
- Goal - To identify key R&D areas for Program to focus on to reduce system costs
- Performed trade-off analyses on COPV manufacturing processes
- **Completed preliminary analysis for the Materia project, indicating potential cost reduction**

Preliminary analysis for the Materia project

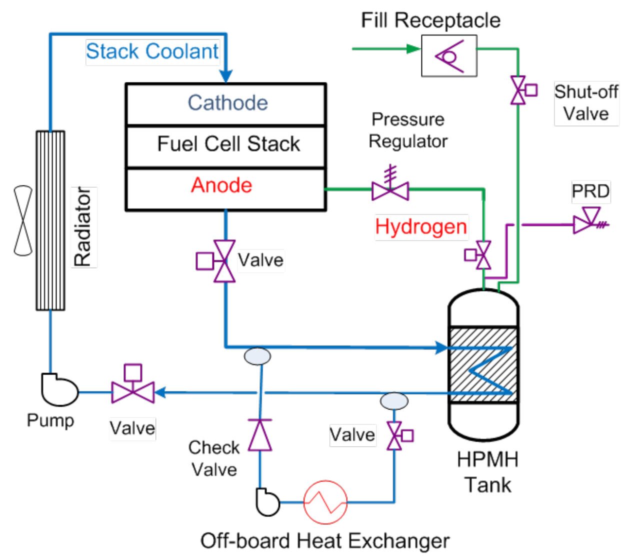



ST100

## $H_2$ Storage System Performance Analysis [ANL]

- Approach- Conduct compete system analyses of $H_2$ storage technologies
- Goal - To identify key R&D areas for Program to focus on to meet performance targets
- Analyzed publically available information on Toyota Mirai $H_2$ COPV design for comparison with DOE baseline system
- **Determined properties for MH/350-bar hybrid systems to match/exceed performance of 700-bar systems**

350-bar Hybrid Storage System Schematic




ST001

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

# New Efforts

- FY16 Office-wide FOA Topics:
  - Techno-economic analysis of onboard $H_2$ storage systems (1 selection announced – *Strategic Analysis Inc. with ANL & PNNL*)
  - Advanced insulation concepts for sub-ambient onboard $H_2$ storage systems (1-2 awards expected)
  - $H_2$ Storage Materials Discovery – HyMARC (multiple awards expected)
- Request For Information – *Cost Reduction and Performance Improvements of Composite Overwrapped Pressure Vessel Systems for Compressed $H_2$ for Onboard Vehicle Applications* (DE-FOA-0001596 – accessable through EERE eXCHANGE)
  - Open until June 30th
  - Responses are to be submitted to H2storage@ee.doe.gov
- Workshop on COPV system cost reduction strategies
  - To be held fall 2016
  - Dates and location still to be determined

***RFIs and workshops used to identify annual FOA topics***

# Collaborations



**INTERNATIONAL ACTIVITIES**

- IEA HIA Task 32 Hydrogen-based Energy Storage

**DOE – EERE - FCTO**
**Hydrogen Storage Applied R&D**

- Physical Storage
- Fiber Composites
- Materials-based Storage
- System Engineering
- Testing and Analysis

**INDUSTRY**

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

**TECHNOLOGY VALIDATION**

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

**DOE - EERE**
VTO; BETO; AMO (i.e. IACMI) ; SETO

**DOE – Office of Science**
BES; ASCR

**DOE – ARPA-E**

**DOC - NIST**
- Neutron scattering
- Measurements

**DOD**
DOD/DOE MOU



***Applied R&D is coordinated among national and international organizations***

# Recent and Upcoming Activities



**Low-cost Compressed $H_2$ Storage Systems:**

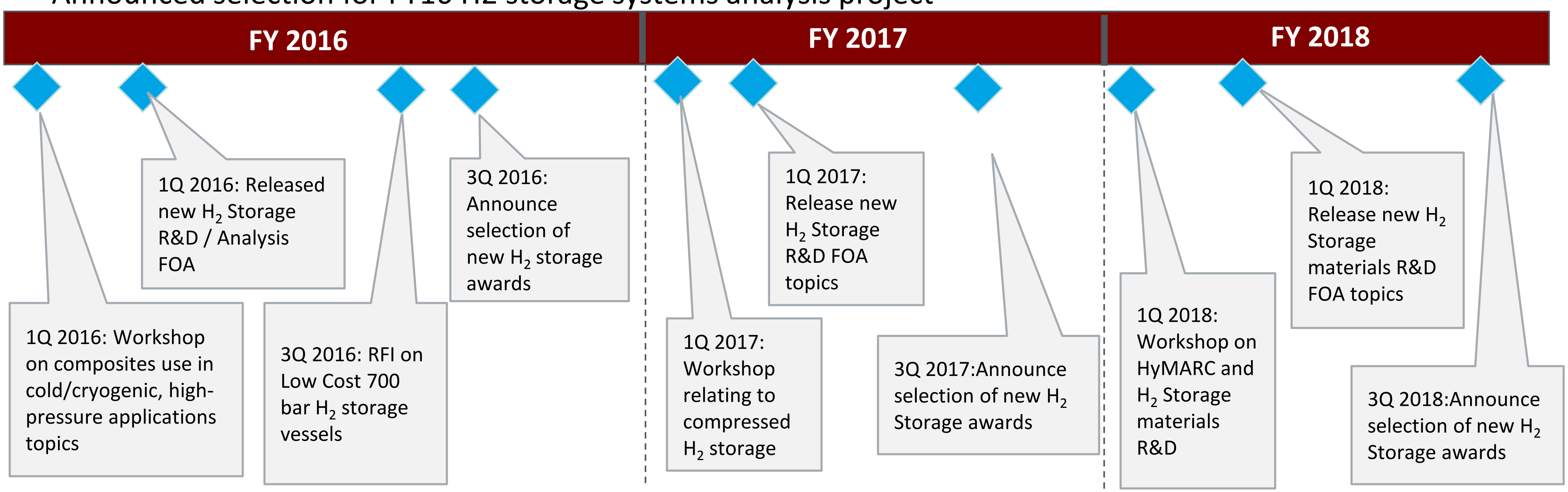
- Updated 700 bar compressed hydrogen system cost record to $15/kWh
- Announced selections for FY16 project(s) on advanced insulation for cold/cryogenic compressed $H_2$ storage
- Released RFI on strategies for improved performance, low-cost compressed hydrogen systems
- Engage with IACMI through AMO on compressed gas storage activities

**Materials-Based Hydrogen Storage:**

- Launched a revamped, coordinated hydrogen storage materials development effort:
  - HyMARC consortium (led by SNL)
  - Hydrogen Storage Characterization and Validation Research Team (led by NREL)
- HSECoE completed construction, testing and evaluation of two sorbent system prototypes and posted systems models for use by R&D community
- Announce selections FY16 projects to support HyMARC effort

**Analysis**

- Announced selection for FY16 H2 storage systems analysis project



# Contacts



| Ned Stetson – Program Manager<br>202-586-9995<br>ned.stetson@ee.doe.gov | |
|---|---|
| Grace Ordaz<br>202-586-8350<br>grace.ordaz@ee.doe.gov | Jesse Adams<br>720-356-1421<br>jesse.adams@ee.doe.gov |
| Katie Randolph<br>720-356-1759<br>katie.randolph@ee.doe.gov | Zeric Hulvey<br>ORISE Fellow<br>202-586-1570<br>Zeric.Hulvey@hq.doe.gov |
| Vanessa Trejos<br>Support contractor<br>202-586-5153<br>vanessa.trejos@ee.doe.gov | John Gangloff<br>ORISE Fellow<br>202-586-7009<br>john.gangloff@ee.doe.gov |

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