

HyMARC: A Consortium for Advancing Hydrogen Storage Materials

Thomas Gennett, Mark Allendorf (SNL)
National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

ST127

Timeline*

Project Start: 10/1/2015

End: Project continuation determined by DOE. Currently scheduled through 9/30/18 (*previously a component of NREL's materials development program and supported annually since 2006)

Budget

HySCORE:

FY15-17 = \$3.764M

FY 18 = \$1.750M

Total = \$8.944M

HyMARC all:

FY15-17: \$6.498M

FY18: \$4.775M

Total Effort: \$18.383M

Barriers addressed

General:

A. Cost, B. Weight and Volume, C. Efficiency, E. Refueling Time

Reversible Solid-State Material:

M. Hydrogen Capacity and Reversibility
N. Understanding of Hydrogen Physi- and Chemisorption
O. Test Protocols and Evaluation Facilities

Partners/Collaborators

NIST – Craig Brown, Terry Udovic

PNNL – Tom Autrey, Mark Bowden

LBNL – Jeff Long, Martin Head-Gordon

HyMARC – Core Team – SNL, LLNL, LBNL

LANL, USA – Troy Semelsberger

H2Technology Consulting, USA – Karl Gross

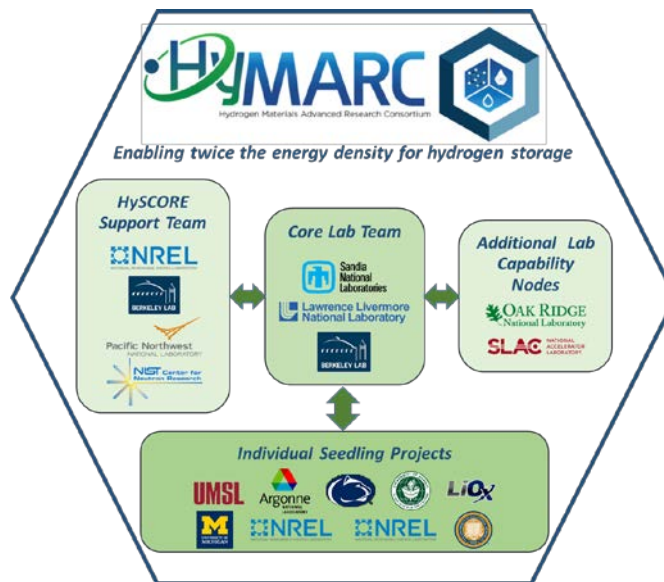
H₂ST², USA – Hydrogen Storage Tech Team

University of Delaware – Eric Bloch

Thesis Corporation – Justin Lee

Univ. Wyoming – Bruce Parkinson

Ford – Justin Purewal, Mike Veenstra



Hydrogen Storage Characterization and Optimization Research Effort

“Enabling twice the energy density for onboard H₂ storage”

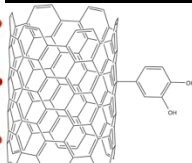
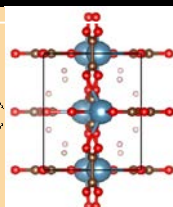
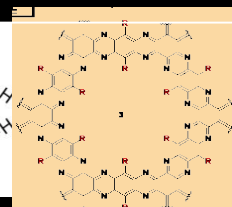
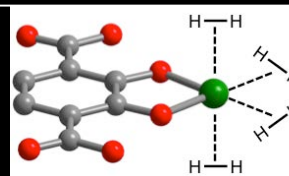
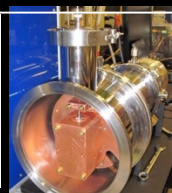
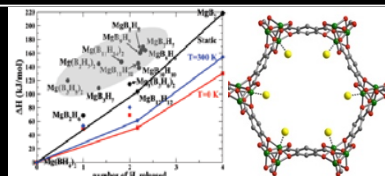
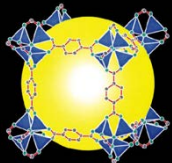
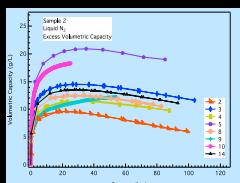
Collaboration and synergistic research effort NREL, LBNL, PNNL, NIST

- To **Develop** and **Enhance** Hydrogen Storage Core Capabilities, i.e. Characterization Techniques
 - NMR, DRIFTS, PCT, TC, TPD, Calorimetry, Neutron. X-Ray
- To **Validate** claims, concepts and theories of hydrogen storage materials
 - Properties of gas-solid interactions in high surface area materials
 - Benchmarking theory
- To **Accelerate** the path forward to development of hydrogen storage materials for transportation
 - Provide insight into the kinetic and thermodynamic bottlenecks
 - Rational design of new materials
 - Unravel complex phenomena

Tom Gennett, Phil Parilla Jeff Long, Martin Head-Gordon, Tom Autrey, Mark Bowden, Craig Brown Terry Udovic

**Tom Gennett, Phil Parilla, Katie Hurst, Sarah Shulda,
Robert Bell, Noemi Leick, Madison Martinez, Jeff
Blackburn, Wade Braunecker**

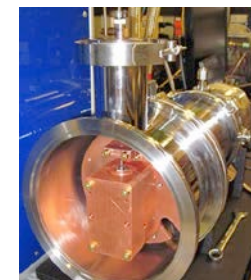
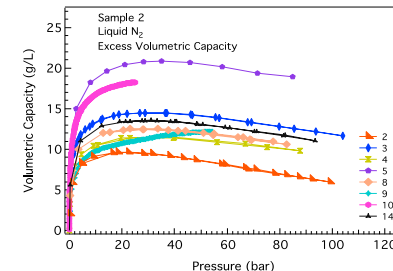
(ST014, ST131)



Approach: Validation measurements and protocols

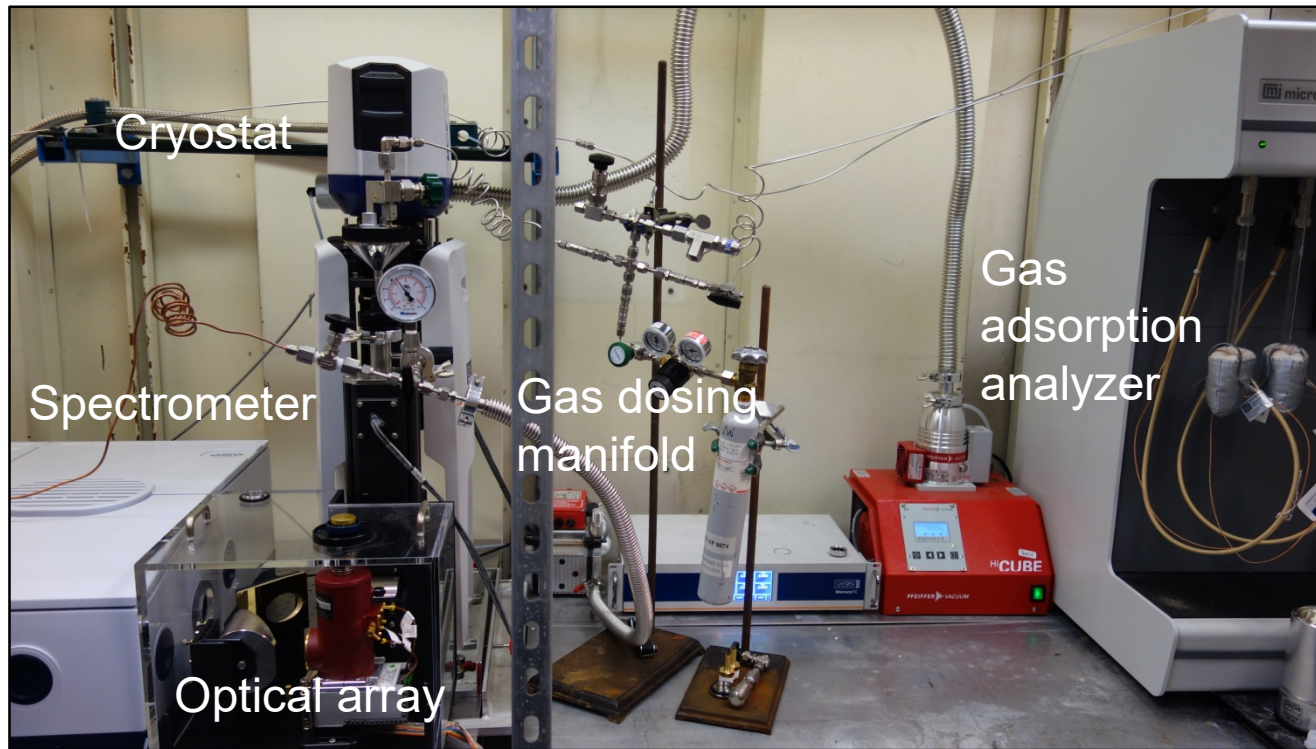


- **Perform validation measurements for DOE**
300K, 75.6K, other bath temperatures.
up to 200 bar volumetric adsorption
- **Collaborate by measuring other groups samples**
BET, TPD, PCT, DRIFTS, TC measurements.
- **Promote hydrogen adsorption measurement accuracy**
Round Robin Experiments
Measurement/Reporting Protocols
- **Develop new advanced characterization techniques**
Cryo-PCT system, Cryo-TC system
New SLAC collaboration
- **Support Seeding projects**



“Recommended Volumetric Capacity Definitions and Protocols for Accurate, Standardized and Unambiguous Metrics for Hydrogen Storage Materials”, P. A. Parilla, K. Gross, K. Hurst, T. Gennett” Appl. Phys. A. 122; 201, 2016

- **Can we alter desorption temperatures with bound metal centers in model systems?**
- **Can we modify carbon based sorbents to enhance their binding energies and desorption temperatures?**
 - Boron and Nitrogen Doping (NREL, PNNL, SNL)
 - Catechol or other chelating sites (LBNL, NREL, LLNL)
 - C₂N Framework materials
 - Control, optimize and maximize small pores (all labs)
 - Modify materials chemistry
 - Mass transport manipulation



- Diffuse reflectance system coupled to cryostat and gas adsorption analyzer
- Improved: sample cell, gas dosing manifold, purge of IR beam path
- Can collect data at 15-373 K and 0-100 bar (controlled dosing up to 1.2 bar)

- PCT data analysis of HKUST and NOTT 100 at 77K and room temperature (SNL)
- Collaborated on experimental planning for MgB_2 and $\text{Mg}(\text{BH}_4)_2$ on the Transmission x-ray microscope (TXM) at SLAC (SNL)
- Diffraction experiments at SLAC with $\text{Mg}_x\text{Mn}_{(1-x)}\text{B}_2$ materials (SNL)
- Characterize initial H_2 sorption properties of Cu(I)-MFU-4l with TPD (LBNL)
- Establish Joint postdoc position (LBNL/LLNL)
- Developing together Phase 2 initiatives (SNL, NREL, LLNL, LBNL, NIST, PNNL)
- Steering Committee, Joint calls, joint papers (SNL, NREL, LLNL, LBNL, NIST, PNNL)
- Joint Perspective article submitted for publication

Hydrogen Storage Characterization and Optimization Research Effort

Martin Head-Gordon and Jeffrey R. Long

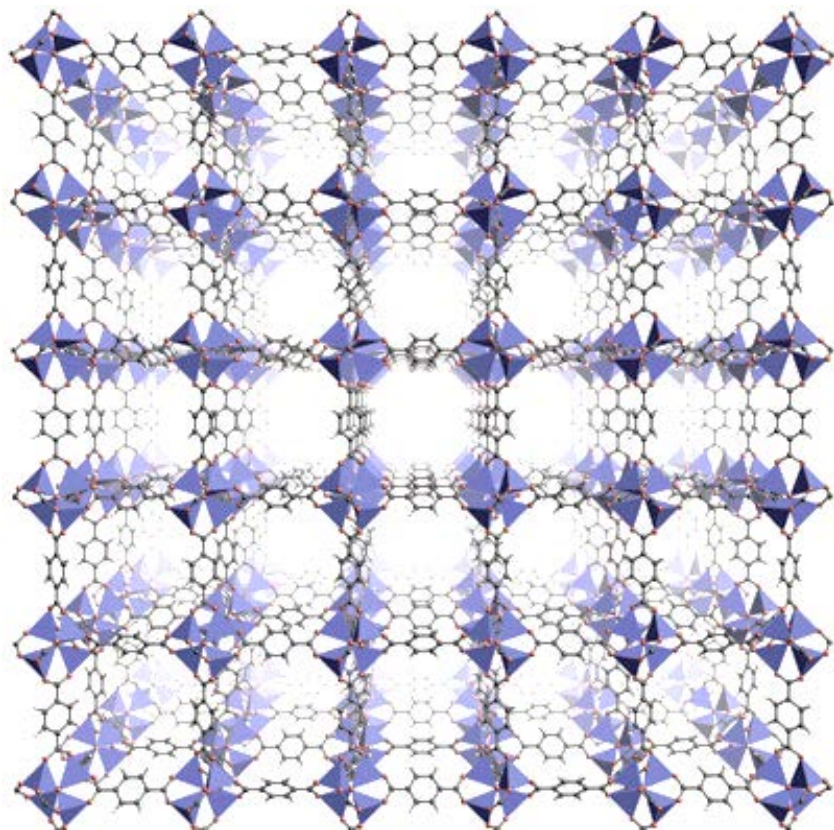


Materials Sciences Division

Lawrence Berkeley National Laboratory

(ST133)

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$\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})_3$
MOF-5

BET surface areas up to 7100 m²/g

Densities as low as 0.13 g/cm³

Tunable pore sizes up to 10 nm

Channels connected in 1-, 2-, or 3-D

Internal surface can be functionalized

Can these high-surface area materials be used for hydrogen storage at ambient temperatures?

Is it possible to have a binding energy -15 to -25 kJ/mole?

Are assumptions about correlation between enthalpy and entropy valid?

Yaghi et al. *Nature* **2003**, 423, 705, Kitagawa et al. *Angew. Chem., Int. Ed.* **2004**, 43, 2334, Férey *Chem. Soc. Rev.* **2008**, 37, 191

- **Density Functional Theory calculations**
 - Can calculate interaction energy and other properties for around 200 density functionals
 - Computations are very cheap and functional deficiencies are well-known
- **Post Hartree-Fock methodologies**
 - Accurate but expensive evaluation of interaction energies taking electron correlation into consideration
- **Energy Decomposition Analysis**
 - Decomposition of interaction energy into chemically meaningful terms like dispersion, electrostatics, polarization and charge transfer energy
 - Analysis is based on Absolutely Localized Molecular Orbitals (ALMOs)



Pacific Northwest
NATIONAL LABORATORY



HySCORE

Tom Autrey, Mark Bowden, Abhi Karkamkar, Bojana Ginovska,
Marina Chong, Adrian Houghton, Iffat Nayyar, Gary Edverson

Pacific Northwest National Laboratory

(ST132)

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Approach: Unique capabilities to assist material development



- Solid-state in-situ high-pressure variable-temperature ^{11}B , ^{13}C , ^{15}N NMR (to identify key intermediates involved in the release and uptake of H_2),
- Solid-state low temperature ^1H and ^2H NMR (5 – 300 K) to investigate physi-sorption of H_2 , ultimate goal to validate $> 2\text{H}_2/\text{metal site}$.
- Variable pressure reaction calorimetry to experimentally determine enthalpy of H_2 addition in solid and liquid hydrogen stores (high pressure cells unique to PNNL)
- XRD and TEM for new materials characterization

Approach: Dynamic connection between theory and experiment

- Use theory to guide experiment and interpret complex results
 - Predict key intermediates and products based on thermodynamics (E_{static} , ΔH° and ΔG°)
 - Binding energies of H₂ to B-doped carbon

- Use experiment to benchmark and validate theory
 - NMR to follow evolution of H₂ release pathways (key intermediates and products)
 - Calorimetry to measure enthalpies of H₂ uptake and release



Accomplishments: Collaborations

providing access to instrumentation and sample preparation



- Argonne - ^{11}B NMR NaBH_4 @graphene
- NREL - ^{11}B NMR MgB_2 and MgBH_4 @ Al_2O_3
- NREL – ^{11}B NMR of B-doped carbons
- NIST – $\text{THF}_x^*\text{Mg}(\text{}^{11}\text{BD}_4)_2$ for neutron studies
- LBNL – Low temperature ^2H NMR Mg-dobdc
- SRNL – High pressure XRD
- Geneva - ^{11}B NMR and calorimetry unsolvated $\text{Mg}(\text{B}_3\text{H}_8)_2$.
- DICP - Reaction calorimetry ΔH_{H_2} and validation of claims.
- AIST – High pressure NMR *in-situ* solution phase ^{13}C NMR – (EXSY) key intermediate for release and uptake of H_2 in Hydrogen Carriers. Catalysts characterization *in-situ* solid state NMR



NIST Center for Neutron Research

Efforts within HySCORE



Craig Brown (NIST)

Terry Udovic (NIST)

Mira Dimitrievska (NIST/NREL)

Jacob Tarver (NIST/NREL)

(ST135)

- **Neutron Powder Diffraction (NPD):** Determine where the atoms are located
- **Quasielastic Neutron Scattering (QENS):** Diffusional and reorientational dynamics
- **Inelastic Neutron Scattering (INS)** as a sensitive probe of local structure/potential

Isotopes have different scattering powers



Incoherent

- Does not 'see' neighbor atoms

SPECTROSCOPY



Coherent

- 'Sees' neighbor atoms

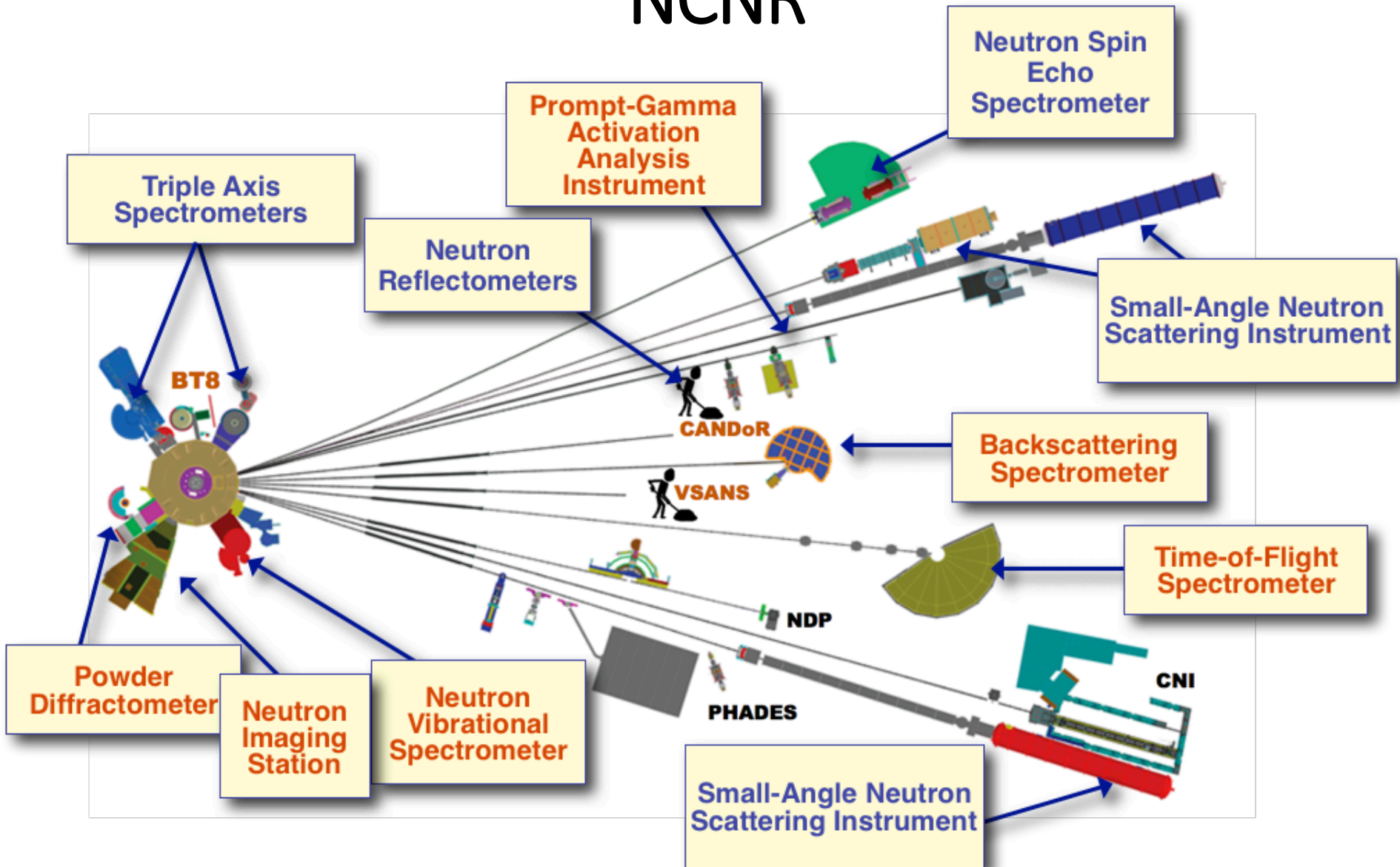
STRUCTURE

Accomplishment: Collaborations



- **NREL/NIST collaboration**
 - Characterizing ultra-microporous materials using neutron diffraction and neutron spectroscopy
- **NREL/NIST collaboration with LBNL**
 - Characterizing hydrogen adsorption in metal organic framework materials using neutron diffraction and neutron spectroscopy
 - Characterizing various hydrogen storage materials at the Advanced Photon Source
- **NREL/NIST collaboration with PNNL**
 - Developing spectroscopic signatures for $\text{Mg}(\text{BH}_4)_2 \cdot x\text{THF}$
- **NREL/NIST collaboration with LLNL and SNL**
 - $\text{MgB}_2/\text{MgBH}_4$ hydrogenations/dehydrogenations
 - Catalytic dissociation of H_2/D_2
- **NREL/NIST collaboration with EPFL**
 - Characterizing new open-metal MOFS based on benzenetristriazolate and triazine-derivative ligands
 - Characterizing effect of induced framework polarization on hydrogen adsorption in zeolitic imidazolate frameworks

NCNR



Accomplishments

- **> 15 National Laboratory Scientists and 2 technicians involved.**
- **34 publications**
- **4 more papers recently submitted**
- **>300 presentations, mostly invited talks, several plenary**
- **8 Ph.D. thesis projects**
- **Project awards (5)**
- **Organized 3 separate Hydrogen storage symposia.**
- **At least 9 postdocs hired with support NREL/NIST (5), LBNL (2), PNNL (2)**



HySCORE

How have we moved the bar?



2 hydrogens per metal center (ST133 and ST135)

Highest capacity room temperature material to date (ST133)

Improved reversibility of $\text{Mg}(\text{BH}_4)_2$ below 200 °C (ST132, ST131)

Benchmark theory for predicting isotherms (ST133)

Benchmark theory for determining binding energies (ST133, ST131)

Developed model compounds to establish desorption temperature control with chelated metals in a sorbent (ST133, ST131)

Established that desorption temperatures can be kinetically controlled (ST131, ST132)

Established ability to alter hydrogen binding energies approaching 15 kJ/mole (ST133, ST131)

Established protocol for gravimetric capacity determination (ST014)

Established new protocol for volumetric capacity determination (ST014)

Determination of entropy and enthalpy of hydrogen sorption (ST133, ST132, ST135)

Developed new cryo-PCT system (ST014, ST131)

Developed new NMR methodologies for investigating hydrogen sorption (ST132)

Developed new “one off” DRIFTS apparatus (ST133)

Developed a new “one off” of Thermal Conductivity apparatus (ST014)

Established the effectiveness of a vibrant EMN collaboration (All)

Proposed Future Work: Subject to change based on funding levels



Further integration of various PI's across all of HyMARC:

Modelling (As we move to better predict materials behavior)

Seedling support, hydrides, sorbents

Thermodynamics of on/off boarding processes (Determination, characterization, model system testing)

binding energies, entropy effects, phase change, phase diagrams

Kinetics

pore size and chemistry, mass transport (microstructures, oxide layers, pores, phase), interfacial barriers

Characterization

new materials, new processes/mechanisms and real system-like analysis

Data Management

EMN requirement

Hydrogen Carriers (New H₂@SCALE)

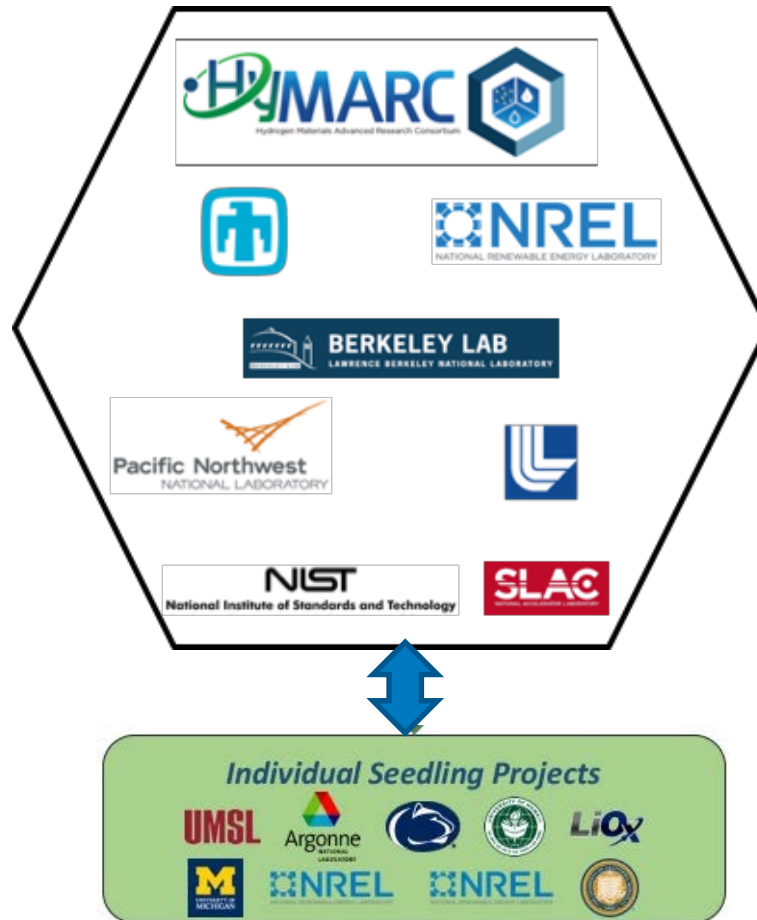
TEA, materials sets, forecourt/delivery requirements, solids, liquids.

Joint HySCORE Milestones

Q3	VI. Demonstrate computational accuracy by showing that the calculated capacity for a MOF, PAF, or carbon-based material with multiple H ₂ molecules bound per metal is within 15% of the experimental capacity.	100% Complete	FY18/Q1	Synthesize three low-valent metal precursors and develop a methodology to use these precursors to metalate the cat-UiO-68 metal-organic framework.	Regular Completed
Q4	<p>VIII. Go/No-Gos:</p> <p>1. Triazine-based hydrogen carriers: Solid phase organic carrier: if > 50g H₂/L uptake is observed in solid phase triazine at T < 100 C and P < 100 bar, then go. If <50 g H₂/L then no-go on solid phase organic carriers: Liquid phase organic carriers: if blend of perhydrotriazines are liquid at room temperature and remain liquid after H₂ release and release > 48g H₂/L at T < 100 C and P < 100 bar, then go, otherwise no-go. If carriers or spent fuel are solid then no go on liquid carriers.</p> <p>2. <i>Determine the viability of Boron and nitrogen doped materials for increased binding energy and capacities that could approach 2020 goal</i></p> <p><i>a. Demonstrate reversible hydrogen uptake within a molecular solid-FLPs, sorption <30 minutes at 25 °C and desorption <60 minutes at 120 °C.</i></p> <p><i>b. Synthesize a boron or nitrogen or co-doped sorbent with >8 atomic percent dopant incorporated into the backbone, with 2000 m²/gram surface area and a hydrogen binding energy >12 kj/mole.</i></p>	95% Complete Report due at end of FY 18 Q1 (Report delayed)	FY18/Q2	Submit a paper to a peer reviewed journal that has Authors from at least three of the four participating laboratories. (LBNL, NIST, PNNL, NREL)	Regular Completed
			FY18/Q3	XI. Demonstrate that Mg(BH ₄) ₂ can be regenerated from Mg(B ₁₀ H ₁₀) at T < 150 C and P < 150 bar	Regular In progress
			FY18/Q4	Synthesize a framework, aerogel or polymeric material exhibiting a total H₂ storage capacity of at least 40 g/L at temperatures above 150 K and < 150 bar.	Final FY18 Stretch Deliverable

Acknowledgements

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Technical back up slides

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Mike Toney

Small Angle X-Ray Scattering (SAXS) – Beam lines 1-4 and 1-5: 100 bar 200 °C

- Pore sizes
- Changes in pore sizes as a function of hydrogen pressure

Diffraction – Beam lines 7-2 and 2-1: 100 bar 900°C

- Crystal structure determination
- Changes in d-spacing as a function of hydrogen pressure

Hard X-Ray Adsorption Spectroscopy (XAFS) Beam line 4-1: 100 bar 200 °C

- Binding environment and oxidation states of high Z elements
- Binding environment of metals on hydrogen storage materials

Soft X-Ray Absorption (XANES) – Beam line 10-1: UHV, 500 °C

- Oxidation state of low z elements
- Ex-situ only - soft x-rays cannot penetrate the pressure chamber

X-ray Raman Scattering – Beam line 6-2: 100 bar 200 °C

- Oxidation state of low Z elements (XANES spectra is obtained)
- Analyzes energy loss of scattered hard x-rays –in-situ XANES experiments with the pressure chamber

Ambient Pressure X-Ray Photoelectron Spec. (AP-XPS) – Beam line 13 - 2: 10 torr 600 °C

- XPS studies to determine surface species and oxidation states under hydrogen pressure